

# Prospective of Upfront Nitrogen (N<sub>2</sub>) Removal in LNG Plants: Technical Communication

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**Citation:** Almomani, F.; Othman, A.; Pal, A.; Al-Musleh, E.I.; Karimi, I.A. Prospective of Upfront Nitrogen (N<sub>2</sub>) Removal in LNG Plants: Technical Communication. *Energies* **2021**, *14*, 3616. <https://doi.org/10.3390/en14123616>

Academic Editor: Lorenzo Ferrari and Andrea Baccioli

Received: 18 May 2021

Accepted: 15 June 2021

Published: 17 June 2021

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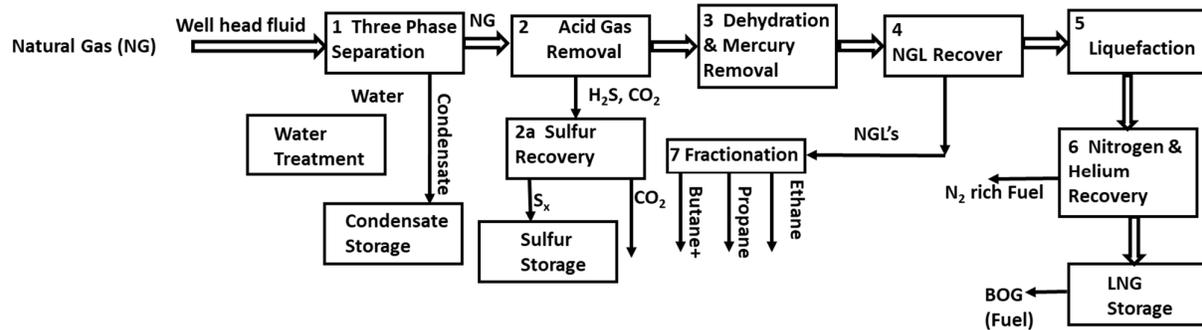
**Abstract:** Conventional natural gas (NG) liquefaction processes remove N<sub>2</sub> near the tail of the plant, which limits production capacity and decreases energy efficiency and profit. Engineering calculations suggest that upfront N<sub>2</sub> removal could have substantial economic benefits on large-scale liquefied natural gas (LNG) processes. This article provides an overview of the most promising technologies that can be employed for upfront N<sub>2</sub> removal in the LNG process, focusing on the process selection and design considerations of all currently available upfront N<sub>2</sub> removal technologies. The literature review revealed that although adsorption has proven to be a huge success in gas separation processes (efficiency ≥ 90%), most of the available adsorbents are CH<sub>4</sub>-selective at typical NG conditions. It would be more encouraging to find N<sub>2</sub>-selective adsorbents to apply in upfront N<sub>2</sub> removal technology. Membrane gas separation has shown growing performance due to its flexible operation, small footprint, and reduced investment cost and energy consumption. However, the use of such technology as upfront N<sub>2</sub> removal requires multi-stage membranes to reduce the nitrogen content and satisfy LNG specifications. The efficiency of such technology should be correlated with the cost of gas re-compression, product quality, and pressure. A hybrid system of adsorption/membrane processes was proposed to eliminate the disadvantages of both technologies and enhance productivity that required further investigation. Upfront N<sub>2</sub> removal technology based on sequential high and low-pressure distillation was presented and showed interesting results. The distillation process, operated with at least 17.6% upfront N<sub>2</sub> removal, reduced specific power requirements by 5% and increased the plant capacity by 16% in a 530 MMSCFD LNG plant. Lithium-cycle showed promising results as an upfront N<sub>2</sub> chemical removal technology. Recent studies showed that this process could reduce the NG N<sub>2</sub> content at ambient temperature and 80 bar from 10% to 0.5% N<sub>2</sub>, achieving the required LNG specifications. Gas hydrate could have the potential as upfront N<sub>2</sub> removal technology if the is process modified to guarantee significant removals of low N<sub>2</sub> concentration from a mixture of hydrocarbons. Retrofitting the proposed technologies into LNG plants, design alterations, removal limits, and cost analysis are challenges that are open for further exploration in the near future. The present review offers directions for different researchers to explore different alternatives for upfront N<sub>2</sub> removal from NG.

**Keywords:** natural gas; nitrogen removal; process optimization; energy recovery

## 1. Introduction

Natural gas (NG) in its liquefied form is undoubtedly the lifeline of different exporters (e.g., Qatar, Australia and the USA). The NG industry has been growing rapidly worldwide since it is the cleanest fossil fuel energy resource. For the effective utilization of NG, the industrial sector has been leaning on the liquefaction of NG, as it reduces its volume by approximately 600 times compared to its gaseous state [1]. As a result, lique-

fied natural gas (LNG) transportation has become easier, and the associated cost is significantly reduced. The LNG can be transported in tanks globally instead of the huge network of pipelines used for gas transportation locally. NG processing (Figure 1) and liquefaction are very complex as they require the removal of multiple impurities such as carbon dioxide ( $\text{CO}_2$ ), hydrogen sulfide ( $\text{H}_2\text{S}$ ), helium (He), nitrogen ( $\text{N}_2$ ), water ( $\text{H}_2\text{O}$ ), and mercury (Hg), in addition to the separation of heavy hydrocarbons ( $\text{C}_{3+}$ ) to achieve the required commercial heating value [2].



**Figure 1.** Block diagram showing conventional LNG plant.

The preliminary calculations show that the presence of  $\text{N}_2$  in NG limits the production capacity, reduces the caloric value, and decreases energy efficiency, thus decreasing the expected profit. Conventional LNG plants (see Figure 1) remove  $\text{N}_2$  near the tail of the plant (unit #6). In other words, the  $\text{N}_2$  passes through the entire system as an inert, whose removal would increase the plant capacity right away.  $\text{N}_2$  is also a very light component (normal boiling point near  $-196\text{ }^\circ\text{C}$ ) that lowers the liquefaction temperature of NG and increases the refrigeration load and the fuel consumption in the liquefaction block (unit #5) of Figure 1. Despite the very low  $\text{N}_2$  composition ( $\sim 5\%$ ) in NG, engineering calculations showed that upfront  $\text{N}_2$  removal of even 70% could have substantial economic benefits on a large scale. The dead volume occupied by  $\text{N}_2$  could be replaced by extra LNG capacity and reduce the power needed to liquefy NG. Our preliminary calculations show that the energy requirements of the propane/mixed refrigerant ( $\text{C}_3/\text{MR}$ ) liquefaction cycle can be reduced from 33 to 31 MW/MTA LNG if 70% upfront  $\text{N}_2$  removal is applied. Other benefits include lower boil-off gas (BOG) generation during LNG storage and ship loading, which is usually more than the plant fuel requirement [3]. Our thermodynamic analysis shows that  $\text{N}_2$  removal requires minimal energy compared to the above benefits. For example, thermodynamic calculations show that no more than 17 MW of thermodynamic work is required to remove all of the 5 vol%  $\text{N}_2$  in a 78 MTA LNG plant. With a 30% efficiency, this translates to about 57 MW of actual compression work, which is nearly 55% of the energy savings in the  $\text{C}_3/\text{MR}$  cycle liquefying  $\text{N}_2$  free NG.

Previous studies have focused on the removal of  $\text{N}_2$  after the liquefaction stage. Kuo et al. [4] evaluated eight technologies for an optimum nitrogen removal unit (NRU): cryogenic distillation, membrane separation, molecular gate adsorption, solvent absorption,  $\text{N}_2$  sponge, pressure-swing adsorption on carbon molecular sieve, lean-oil absorption, and the use of a chelating chemical. These technologies focus on optimizing the existing NRU rather than developing upfront  $\text{N}_2$  removal technology. Several other works have also studied various non-cryogenic methods [5–8]. Gabrielli et al. [5] developed a comprehensive method that includes criteria for the optimal design and operation of the membrane for  $\text{CO}_2$  and  $\text{N}_2$  separation processes. The study described the influence of diverse design and operating variables on the optimal energy demand; however, this study did not provide a clear conclusion about how this technology can be retrofitted within the LNG plant. Ohs et al. [6] presented an optimized membrane cascade process that can selectively remove  $\text{N}_2$  and save up to 40% of the total process cost. However, this study focused on

membrane process optimization and material preparation rather than upfront technology itself. Other studies [7,8] focused on processes that worked on capturing methane from N<sub>2</sub> gas. Rufford et al. [9] presented a review that includes all the conventional technologies (distillation, adsorption, membrane separation, and hydrates) for the N<sub>2</sub> removal from NG. The study showed that although technologies based on absorption and adsorption are commercially available for smaller scales, cryogenic distillation is the leading NRU technology for large-scale operation. The general conclusion is that the approaches require development for higher efficiency and optimal operation. No previous research deals with upfront N<sub>2</sub> removal technology; hence, there is a need for a lot of research.

Given the clear benefits of upfront N<sub>2</sub> removal, the key questions that need to be answered are: (1) What are the available technologies that can be used? (2) What is the suitable location to carry out the upfront N<sub>2</sub> removal? (3) How much to remove? (4) At what purity? To the best of our knowledge, these questions have not been addressed in the open literature, and a systematic approach is needed to clarify the perspective of such a process. As the upfront N<sub>2</sub> removal topic is concerned with the application at a large scale, the technology readiness levels (TRL) of any proposed technology should be identified. Therefore, the primary objective of this review is to present a detailed and systematic analysis of the available technologies for upfront N<sub>2</sub> removal and to identify the best option. This review also aims to conclude and advise on the best strategy for either retrofitting the selected technology to the existing LNG plants or synthesizing new systems as required. The TRL of each technology was briefly discussed.

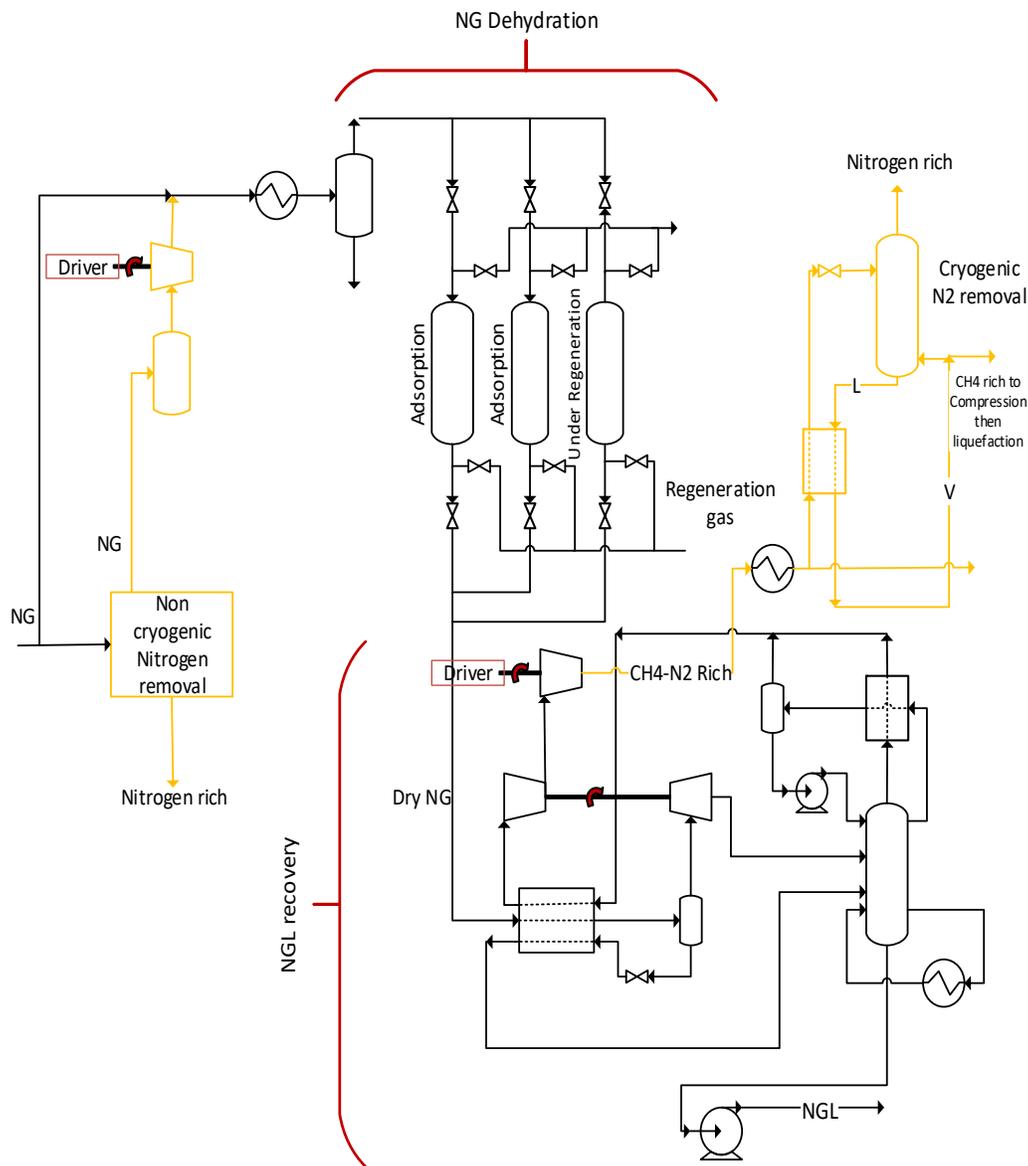
## 2. Advances on State-of-the-Art

The state-of-the-art in LNG plants is to remove N<sub>2</sub> towards the end of the plant after liquefaction. The idea of removing N<sub>2</sub> upfront is novel and creative. It is not practiced by the LNG industry today. Once the N<sub>2</sub> is removed, even partially, the NG stream (temperature, composition, pressure) that enters the downstream units will be changed. Since each unit has a certain operating window, a change in its feed may demand significant retrofitting. To put this into perspective, consider the following example. Removing the N<sub>2</sub> after the slug catcher (block 1 of Figure 1) by using a membrane or adsorption system may result in an NG feed pressure lower than the allowable pressure range of the acid gas removal (AGR). While one can use a compressor to increase the pressure downstream of the N<sub>2</sub> removal, it may both generate capital and energy expenses, and as such, a better solution is needed. Another major challenge is the aggressive environment of the process before the AGR. Raw NG may contain corrosive components such as water, hydrogen sulfide, and carbon dioxide, and it is fed to the slug catcher at very high pressure (above 70 bar). These may constrain the use of available techniques, thus necessitating the need for unconventional solutions. The fact that the N<sub>2</sub> content of NG is very small will pose many challenges for the proposed technology and evaluation of innovative alternatives.

Therefore, the first key challenge of the proposed upfront N<sub>2</sub> removal practice is to identify an adequate N<sub>2</sub> removal technology. Other key challenges are identifying the best location for N<sub>2</sub> removal, targeting purity of the removed nitrogen, and N<sub>2</sub> removal rate. The sooner the N<sub>2</sub> is removed, the more volume for NG processing, which requires further work in redesigning the whole LNG plant. Late removal, however, should require less separation energy as the NG will be more concentrated in N<sub>2</sub> (more separation driving force). As discussed above, the removal location will also be affected by the removal technology. It should be noted that the more N<sub>2</sub> is removed, the greater the separation energy and equipment sizes; thus, higher energy and implementation costs. High N<sub>2</sub> purity will typically be easier to achieve at a lower removal rate. The plant itself will be impacted, as after N<sub>2</sub> removal, each subsequent unit will be processing a different NG stream than the one they are designed to process (i.e., pressure, composition, and perhaps temperature).

One configuration that could be proposed is shown in Figure 2. Here, a portion of NG is processed in an adsorption system to remove some nitrogen. The nitrogen-lean NG stream is then compressed to be mixed with the parent nitrogen-rich NG. With this

scheme, compression energy can be reduced compared to the case where the full N<sub>2</sub> rich NG feed is processed through the adsorbers and subsequent compression step. At the cold end of the plant, a part of the entire rich methane-N<sub>2</sub> stream leaving the NGL recovery is totally or partially condensed in a stripping column reboiler. The high-pressure condensed NG is then flashed and fed to the stripping column. All liquid leaving the bottom of the column will be evaporated into the reboiler to supply the refrigeration needed to condense the feed in the reboiler. A part of the evaporated liquid will be fed back to the column to provide a boil up to the column to strip N<sub>2</sub> from the liquid hydrocarbons, while the remaining NG, which will typically be lean in nitrogen, will be compressed and liquefied in the conventional liquefaction scheme. The adsorption step can offer additional volume to process more NG before liquefaction. On the other hand, the cryogenic step can offer additional volume at the conventional liquefaction step. It is to be noted that this is a new configuration that does not exist in the open and patent literature to our knowledge.



**Figure 2.** Hybrid upfront N<sub>2</sub> removal making use of cryogenic and non-cryogenic processes. The orange lines represent upfront N<sub>2</sub> removal before dehydration and liquefaction.

### 3. Upfront N<sub>2</sub> Removal Methodology

The first stage of implementing upfront N<sub>2</sub> removal methodologies includes shortlisting the available N<sub>2</sub> removal technologies. The selected technologies can be thoroughly modeled and optimized in standalone modes. The models can be constructed to capture material/energy balances, rigorous vapor–liquid equilibrium, and essential hydraulics, including pressure drops. Commercially available simulation packages, such as Aspen Plus™, Promax™, Aspen Adsorbers™, and MATLAB™, can be used to model these technologies. This task should include a detailed parametric analysis to identify the operating windows of the shortlisted schemes. Key variables, such as separation rate, kinetics, and capacity, which impact the removal performance, should be investigated to identify the degree of improvement and enhancement in the removal efficiency. This could be followed by standalone mathematical optimization to maximize N<sub>2</sub> removal while minimizing capital and energy costs.

Considering all of these variables plus the fact that a baseload LNG plant is very complex, thoroughly studying each option will require a significant amount of time, if not be completely impossible. What is proposed instead is to rapidly evaluate plant performance with different N<sub>2</sub> removal technologies, locations, purities, and recoveries using exergy analysis. Here, the full LNG process along with the shortlisted removal configurations will be represented by reversible processing steps (i.e., zero driving forces such as temperature difference and concentration gradient). Using the efficiencies derived from standalone N<sub>2</sub> removal technologies and the optimized LNG models [10,11], exergy losses can be calculated for each unit with different N<sub>2</sub> removal variables (i.e., technology, purity, recovery) installed at different locations. A trade-off study between NG throughput gain and exergy losses shall be identified for the complete plant. Studying the key operating variables, such as temperatures, pressures and efficiencies of each proposed process, will allow rapid identification of their impact on the LNG process. These should give the different optimistic performances that may serve as targets (or benchmarks) for optimizing and retrofitting the LNG plant with the top identified candidates for the upfront N<sub>2</sub> removal technology. With this approach, it is believed that the promising candidates for the subsequent detailed and full-scale plant optimization/retrofitting can be filtered out.

### 4. Literature Analysis of the Upfront N<sub>2</sub> Removal Technologies

This section presents the most promising and technically available upfront N<sub>2</sub> removal technologies. Based on our literature review the available upfront N<sub>2</sub> removal technologies can be classified as (1) Physical Separation, (2) Chemical Separation and Gas Hydrate.

#### 4.1. Physical Separation Technologies

The physical separation technologies have been studied extensively in the literature for multiple applications such as pipeline-quality natural gas, coal-bed methane (CBM), flue gas management, and LNG. In this section, the main goal is to explore and discuss the potential physical separation means for possible implementation as an upfront N<sub>2</sub> removal process in the LNG supply chain. The main physical processes that were investigated broadly are adsorption, membranes, and cryogenic distillation, the current technology, implemented in LNG trains.

##### 4.1.1. Adsorption

Adsorption has proven to be a huge success in gas separation processes. This technology has a high TRL that ranges from 9 for the pressure swinging/vacuum to 5–7 for temperature swinging adsorption. It has been established commercially for N<sub>2</sub> removal from NG [12]. Adsorption is considered advantageous over cryogenic distillation in terms of process economics and could be a promising technology; however, the key operational parameter to this process is to find the ideal adsorbent in terms of selectivity and capacity.

The literature review showed that most of the published works focus on identifying adsorbents for the separation of N<sub>2</sub> from CH<sub>4</sub> as a model of NG. The most promising adsorbents are summarized as follows:

1. Metal-organic frameworks (MOFs): Synthetic nano-porous materials made up of a network of metal ions and organic ligands characterized by high selectivity, adjustable pore size, and pore volumes [13,14]. The MOFs technology is assessed as being at TRL-5 to 6 presuming a favorable testing result.
2. Zeolites: Microporous aluminosilicates characterized by low cost, robustness, and high pore volume. Some examples of zeolites used in CH<sub>4</sub>/N<sub>2</sub> separation are 5A, BETA, and clinoptilolite (CLINO) [12,15]. Zeolite adsorption was set at TRL 5–7.
3. Porous-aromatic frameworks (PAFs): Open-structure aromatic frameworks that are superior over MOFs and zeolites in terms of ultrahigh surface area and high stability [16].
4. Activated carbon (AC): A well-established commercial adsorbent (RTL 7–9) that is cheap, thermally stable, can be easily modified, and has a well-developed structure [17,18].
5. Carbon molecular sieves (CMS): Solid adsorbents manufactured from organic sources such as coconut shell and coal, differing from AC in having a narrower range of pore size [19,20]. It has been stated that they possess a kinetic selectivity for N<sub>2</sub> over methane [21]. The TRL of the CMS is ranged from 6–9.
6. Titanosilicates: Molecular sieves that have been established commercially for N<sub>2</sub> adsorption from natural gas for Molecular Gate™ [22]. They have proven advantageous in energy consumption, operational costs, flexibility, and product purity [23].

Table 1 presents a highlight of the most recent and most important adsorption studies conducted for possible N<sub>2</sub> separation by adsorption. Both experimental and simulation methodologies were used to investigate the separation performance. As it can be noted, the separation of methane and nitrogen is achievable through adsorption, and multiple adsorbents have proven considerable selectivity indicating excellent separation. However, most well-established adsorbents such as MOFs or zeolites favor methane over N<sub>2</sub>, indicating that if these adsorbents were to be used in NG processing plants, a huge amount would be required since methane is the majority component. Furthermore, desorption steps would be required, ensuring that the quality of the gas obtained has not been affected. For the aforementioned reasons, it is more attractive and practical to have an adsorbent with high selectivity to N<sub>2</sub>, as it is a minority component and inert that would not be as useful compared to methane. It is worth highlighting that although the percentage recovery in all the studies presented in Table 1 is higher than 90%, the composition of N<sub>2</sub> in the mixture (CH<sub>4</sub>/N<sub>2</sub>) was higher than 10%, which is considered very high compared with the composition of N<sub>2</sub> in NG. Therefore, further investigation on comparable a composition is required to draw conclusions.

**Table 1.** Summary of the CH<sub>4</sub>/N<sub>2</sub> separation by adsorption.

| Adsorbent Type | Adsorbent Name | Feed (by mol)                             | Operating Conditions | Favored Component | Best Selectivity | Type of Work           | Reference |
|----------------|----------------|---|----------------------|-------------------|------------------|------------------------|-----------|
| AC             | ----           | 50% CH <sub>4</sub><br>50% N <sub>2</sub> | 1 bar<br>30 °C       | CH <sub>4</sub>   | 5.5              | Experimental           | [24]      |
|                | SMAC           | ----                                      | 1 bar<br>25 °C       | CH <sub>4</sub>   | 3.644            | Experimental           | [17]      |
|                | ----           | ----                                      | 3 bar<br>25 °C       | N <sub>2</sub>    | 7.64             | GCMC and MD simulation | [25]      |
| CMS            | ----           | ----                                      | 40 bar<br>25 °C      | N <sub>2</sub>    | 2.1              | Experimental           | [19]      |

|                            |                               |  |                              |  |   |                                       |        |
|----------------------------|-------------------------------|--|------------------------------|--|---|---------------------------------------|--------|
|                            | Takeda CMS                    | 90% CH <sub>4</sub><br>10% N <sub>2</sub>  | 3–16 bar                     | N <sub>2</sub>   | * 97.9% CH <sub>4</sub> for 10% N <sub>2</sub> in the feed                  | simulation                            | [21] † |
| Graphite nanofibers        | ----                          | 50% CH <sub>4</sub><br>50% N <sub>2</sub>  | 0–15 bar<br>25 °C            | N <sub>2</sub>   | 5 to 8  | GCMC simulation                       | [26]   |
| MOF                        | Ni-HKUST-1                    | 50% CH <sub>4</sub><br>50% N <sub>2</sub>  | 1 bar<br>0 °C                | CH <sub>4</sub>  | 5.36  | Experimental                          | [27]   |
|                            | SBMOF-1                       | 50% CH <sub>4</sub><br>50% N <sub>2</sub>  | 1 bar<br>25 °C               | CH <sub>4</sub>  | 11.5  | Experimental                          | [28]   |
|                            | ----                          | 90% CH <sub>4</sub><br>10% N <sub>2</sub>  | 1 bar<br>0 °C and 25 °C      | CH <sub>4</sub>  | 28 @ 0 °C and<br>16 @ 25 °C   | Experimental                          | [29]   |
|                            | Zr-based MOF                  | 50% CH <sub>4</sub><br>50% N <sub>2</sub>  | 1–15 bar<br>25 °C            | CH <sub>4</sub>  | 5.06 @ 1 bar and<br>5.63 @ 15 bar   | Experimental and Molecular simulation | [14]   |
|                            | MIL-101(Cr)                   | 90% CH <sub>4</sub> /10% N <sub>2</sub><br>80% CH <sub>4</sub> /20% N <sub>2</sub> | 0.1–10 bar                   | N <sub>2</sub>   | 5–10 @ 20% N <sub>2</sub> and 10 °C<br>1.32 @ 10% N <sub>2</sub> and 250 °C | Experimental and GCMC simulation      | [30]   |
| PAF                        | PAF-302<br>PAF-303<br>PAF-304 | 10–90% N <sub>2</sub><br>and CH <sub>4</sub>                                       | 1 bar<br>25 °C               | N <sub>2</sub>   | 18.3 to 118.2<br>from 90% N <sub>2</sub> to 10% N <sub>2</sub>              | GCMC simulation                       | [31]   |
| Titanosilicate             | ETS-10                        | 70% CH <sub>4</sub><br>15% CO <sub>2</sub><br>10% N <sub>2</sub><br>5% He          | 10 bar<br>4 °C               | CO <sub>2</sub> then N <sub>2</sub><br>over CH <sub>4</sub>    | 8.35 for CO <sub>2</sub> and<br>1.24 for N <sub>2</sub>                     | Experimental                          | [23]   |
|                            | ETS-4                         | 85% CH <sub>4</sub><br>15% N <sub>2</sub>  | 1 bar and 20<br>bar<br>20 °C | N <sub>2</sub>   | * 95.7% CH <sub>4</sub><br>99% CH <sub>4</sub> recovery                     | Numerical simulation                  | [32]   |
|                            | ----                          | 85% CH <sub>4</sub><br>15% N <sub>2</sub>  | 7 bar                        | CO <sub>2</sub> then N <sub>2</sub>                            | * 90–93% CH <sub>4</sub> recovery<br>4% N <sub>2</sub> in sales gas         | ----                                  | [22]   |
| Zeolite                    | BETA                          | ----   | 40 °C, 100 °C,<br>150 °C     | CH <sub>4</sub>  | 1.27–2.05   | Experimental                          | [33]   |
|                            | CLINO                         | ----   | 0–10 bar<br>30 °C            | CH <sub>4</sub> -Cs <sup>+</sup> ex-<br>changed clinoptilolite | 20.6 in vacuum and<br>5.7 @ 10 bar  | Experimental                          | [34]   |
|                            | CLINO                         | ----   | 0–10 bar<br>0 °C and 100 °C  | CH <sub>4</sub> -Cs <sup>+</sup> ex-<br>changed clinoptilolite | 1 @ 0 °C and 10 bar<br>10 @ 100 °C and 0.001 bar                            | Experimental                          | [35]   |
|                            | CLINO                         | ----   | 1 bar<br>0 °C and 25 °C      | CH <sub>4</sub>  | 1.2–2.6   | Experimental                          | [36]   |
| zeolite framework          | AIPO                          | 85% CH <sub>4</sub><br>15% N <sub>2</sub>  | 10 bar<br>25 °C              | CH <sub>4</sub>  | 3.8   | GCMC simulation                       | [37]   |
| Zeolites with MOF subunits | ZIF                           | 50% CH <sub>4</sub><br>50% N <sub>2</sub>  | 1 bar<br>25 °C               | CH <sub>4</sub>  | 8.44  | molecular simulation and experimental | [13]   |

\* reported CH<sub>4</sub> recovery/purity instead of adsorbent selectivity. † conducted techno-economic analysis in their work.

It can also be understood that numerous works have studied adsorption on an equimolar binary methane–nitrogen mixture, which does not simulate typical natural gas content. These kinds of studies are more useful when discussing the purification of coal-bed methane (CBM), low-grade natural gas, or flue gases. They would not reflect upon sales of natural gas or LNG [26,38–40]. This is considered a huge drawback in the literature

as the N<sub>2</sub> content in NG is usually below 10% and is required to be reduced up to 1–4%, as with the case in cryogenic distillation to meet the sales gas specifications [9,41]. Aside from that, some studies tested some adsorbents for a gas mixture having 10–20% mol N<sub>2</sub>, out of which there would be some potential for upfront N<sub>2</sub> removal. Furthermore, most of the research done was carried out on the basis of low pressure (i.e., 1–3 bar). It would have been more useful to study at high pressures since NG is typically obtained at high pressure [42], and in that case, unnecessary additional costs would be needed to expand and re-compress that gas for N<sub>2</sub> removal. Another drawback in the literature is that most of the research done on adsorption has focused on studying the selectivity of the adsorbent used without discussing the recovery/purity or heating value of the gas obtained, which is a necessity for the field of NG studies.

Emphasis should be placed on the studies that have a potential for upfront N<sub>2</sub> removal, use mixtures that mimic real NG, and highlight the specifications for the product obtained. MOFs and PAFs were tested for gas mixtures having 10% N<sub>2</sub> on both an experimental basis and a simulation basis. For similar feed specifications and operating conditions, Hu et al. [31] obtained a significant selectivity for N<sub>2</sub> using PAFs (i.e., 118 for 10% N<sub>2</sub> content in the feed) in their GCMC simulation study. Li et al. [29] obtained a CH<sub>4</sub> selectivity of 16 using MOF in their experimental study. This could indicate the superiority of PAFs over MOFs and their potential over MOFs to be used for N<sub>2</sub> removal since most MOFs are CH<sub>4</sub>-selective.

Other than MOFs and PAFs, CMS was tested by Effendy et al. [21], who optimized the pressure-swing adsorption (PSA) process using CMS to treat a binary CH<sub>4</sub>-N<sub>2</sub> mixture having 10 mol% N<sub>2</sub>. Using their simulation model and varying the operating pressure between 3–16 bar, 97.9% pure methane was obtained, reducing the N<sub>2</sub> content from 10% to about 2%, matching the pipeline's gas specification (i.e., below 4% of N<sub>2</sub>) [43]. They have included a techno-economic analysis for this process, concluding that the net revenue expected is around USD 4.7–5.5 million/scfd for a feed throughput between 2 and 10 MMscfd where the cost was dominated by the initial and maintenance costs for the adsorption column (40%) in addition to methane loss (40%). This latter cost might make implementing this process questionable.

Another potential adsorbent for upfront N<sub>2</sub> removal is titanosilicate. Weh et al. [32] have obtained 95.7% pure methane from a binary methane-N<sub>2</sub> mixture (85 mol% CH<sub>4</sub> and 15 mol% N<sub>2</sub>) with an overall recovery of 99% using a titanosilicate named ETS-4. This adsorbent was tested under high pressure of 20 bar, indicating its prospective use in the LNG train. In addition, titanosilicates have proven successful for CO<sub>2</sub> removal as well as N<sub>2</sub> in multiple works [22,23]. Therefore, they may eliminate the need for an amine absorption column for CO<sub>2</sub> removal. Finally, titanosilicates are well-established commercially for Molecular Gate™ adsorption having an overall CH<sub>4</sub> recovery of 90–93% producing gas within the pipeline specification [22,43]. The associated cost of using titanosilicates in the industry was estimated to be around 0.4 to 1.2 USD/MCF feed for a feed flow of 0.5–10 MMSCFD.

After an extensive survey of the literature, it was found that most adsorbents, if not all, are CH<sub>4</sub>-selective at typical NG conditions. The CH<sub>4</sub>-selective adsorbents could be used effectively for CH<sub>4</sub>/N<sub>2</sub> separation, but it would be more encouraging to find N<sub>2</sub>-selective adsorbents, as with the case of CMS and titanosilicates, which showed huge potential in the field.

#### 4.1.2. Membranes

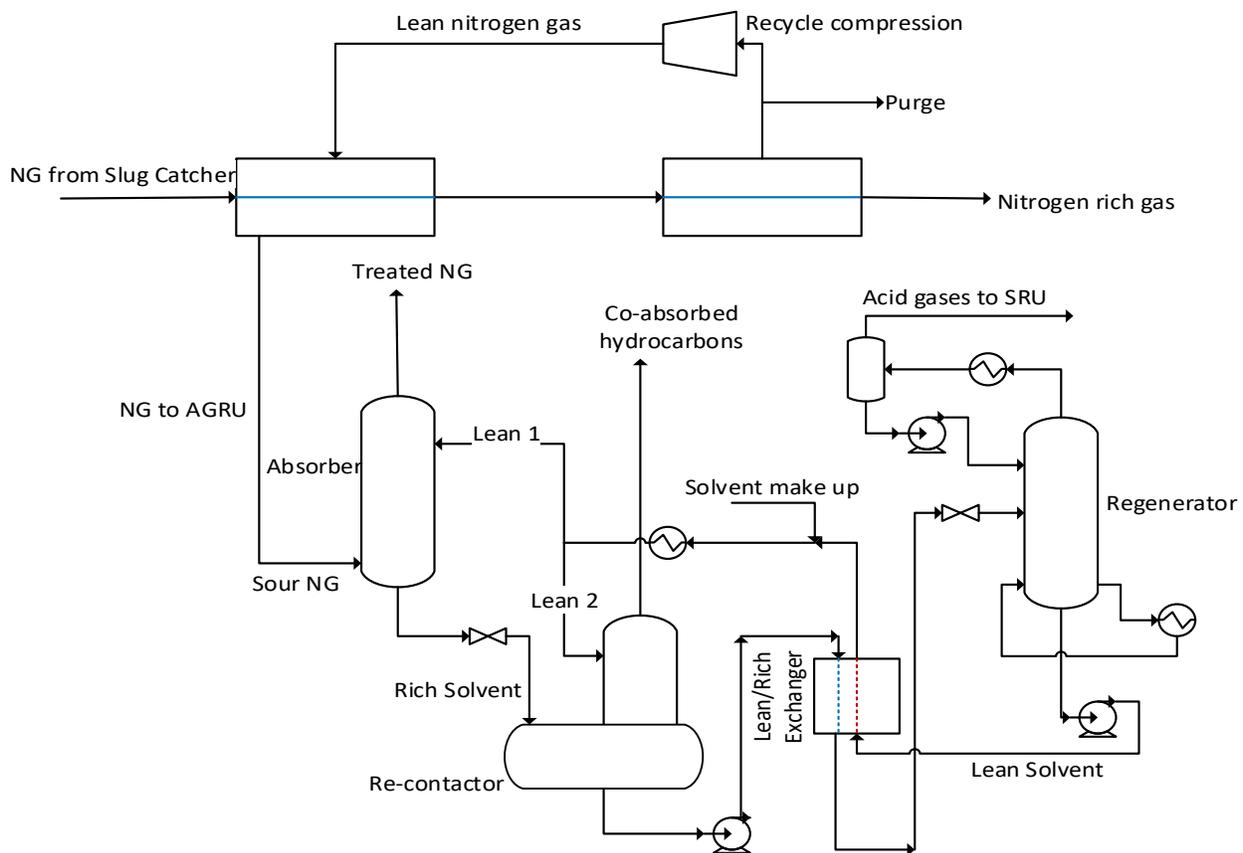
The use of membranes (TRL 9) in gas separation has been growing recently due to their flexible operation, small footprint, reduced investment cost, and energy consumption [44–46]. Membrane separation is a pressure-driven process where a gas permeates through a membrane from a high-pressure zone to a lower pressure zone.

The progress of membrane technology for gas separation advanced with the manufacturing of different types of membranes, including mixed matrix membranes (MMMs) [47]. This type of membrane, which is an alternative to polymer-based membranes, was

developed to improve the separation performance. The MMMs are based on separation properties of the porous materials that are used as fillers with excellent economical value and stable mechanical properties. The MMMs can be tailor-made to have excellent permeability and selectivity to specific compounds (e.g., CO<sub>2</sub> and O<sub>2</sub>). The MMMs have been successfully used for the separation of CO<sub>2</sub> from CH<sub>4</sub> [48] as well as CO<sub>2</sub> from N<sub>2</sub> [49,50]. A combination of MOFs and zeolites with MMMs was used for the separation of CO<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/CH<sub>4</sub>, O<sub>2</sub>/N<sub>2</sub>, and H<sub>2</sub>/CH<sub>4</sub> mixtures [51]. For N<sub>2</sub>/CH<sub>4</sub> separation, various types of membranes were used:

1. Polymeric membranes: The most commercial membranes, which can be rubbery like poly-siloxanes [52] or glassy like polyimides [53].
2. Zeolite membranes: Inorganic membranes where microporous zeolite crystals are grown as a layer supported by a flat or tubular surface, such as silicoaluminophosphate (SAPO) [54] and SSZ-13 [55] membranes.
3. Mixed-matrix membranes (MMMs): Membranes fabricated from organic polymers and inorganic materials to increase the permselectivity of the membrane where inorganic materials could be zeolites, MOFs, or CMS [44].

To appreciate this technology as an upfront N<sub>2</sub> methodology, consider the process shown in Figure 3. Here, the membrane technology is installed to remove all N<sub>2</sub> before the AGR step, assuming it is a viable option. The membrane will selectively permeate NG and reject N<sub>2</sub> by applying a pressure difference across the membrane [4]. The permeated NG will thus be available at a lower pressure. This can have a severe impact on the acid gas removal rate in the absorber, which can result in producing off-spec sweet gas. More circulation at lower temperatures can remove more acid gases even at lower pressures; however, this may increase the regenerator reboiler load beyond its design limit.



**Figure 3.** Proposed upfront N<sub>2</sub> removal upstream of the AGR using membrane technology.

The direction of membrane research for CH<sub>4</sub>/N<sub>2</sub> separation in the literature is similar to that of adsorption: the majority is focused on the design of the membrane and testing its permeance and selectivity without considering real-life scenarios or discussing the product purity and recovery obtained, as can be seen in Table 2 [44,45,54–58]. All types of membranes formerly described have been tested for CH<sub>4</sub>/N<sub>2</sub> separation. As with adsorption, some membranes favor the permeation of N<sub>2</sub>, and others favor the permeation of methane. In an early simulation study, Baker and Lokhandwala [53] reported that to reduce the N<sub>2</sub> content in a gas stream from 10% to 4% using membrane separation, either a CH<sub>4</sub>-permeable membrane with a selectivity of 6 or an N<sub>2</sub>-permeable membrane with a selectivity of 17 is required. However, as the gas is coming at high pressure and it being necessary to conserve this pressure to eliminate the costs of downstream compressors, it is essential to have the membrane N<sub>2</sub>-permeable and keep methane on the retentate side to conserve its pressure. Some commercial membrane units in Kentucky and California use a CH<sub>4</sub>-permeable membrane and re-compress the gas after N<sub>2</sub> removal either using the residual gas or through external power compression [52].

**Table 2.** Summary of the CH<sub>4</sub>/N<sub>2</sub> separation using membranes.

| Membrane Type           | Membrane Name                                      | Feed (by mol)  | Feed Pressure and Temperature          | Favored Component                   | Permselectivity   | Type of Work                                 | Reference |
|-------------------------|--|--|--|-------------------------------------|---|--|-----------|
| Fluorinated polyimides  | 6FDA-durene  | 66% CH <sub>4</sub><br>34% N <sub>2</sub>  | up to 60 bar<br>65 °C                  | N <sub>2</sub>                      | 1   | Molecular dynamics simulations               | [45]      |
| MMM                     | [Ni <sub>3</sub> (HCOO) <sub>6</sub> ]/SBS-5 MMM   | 50% CH <sub>4</sub><br>50% N <sub>2</sub>  | 1 bar<br>25 °C                         | CH <sub>4</sub>                     | 2.9   | Experimental                                 | [44]      |
|                         | Amide and CLINO                                    | 85% CH <sub>4</sub><br>10% CO <sub>2</sub><br>5% N <sub>2</sub>  | 10 bar<br>35 °C                        | CO <sub>2</sub> then N <sub>2</sub> | 31.77 for CO <sub>2</sub><br>and 1.87 for N <sub>2</sub>  | Experimental                                 | [56]      |
|                         | polybenzimidazole (PBI)-based with natural zeolite | binary (10% N <sub>2</sub><br>90% CH <sub>4</sub> ) and ternary (5% CO <sub>2</sub><br>10% N <sub>2</sub><br>85% CH <sub>4</sub> ) | 3.5 bar,<br>10 bar,<br>20 bar<br>35 °C | CO <sub>2</sub> then N <sub>2</sub> | 22.38 for N <sub>2</sub> in the binary mixture @ 3.5 bar and 12.82 for N <sub>2</sub> in the ternary mixture @ 20 bar | Experimental                                 | [57]      |
| perfluorinated polymers | Hyflon® AD 60                                      | 20% N <sub>2</sub><br>20% CO <sub>2</sub><br>60% CH <sub>4</sub>   | 14 bar<br>22 °C                        | CO <sub>2</sub> then N <sub>2</sub> | 2.3 for N <sub>2</sub>  | Experimental                                 | [52]      |
| polymer membrane        | PDMS   | 3% C <sub>3</sub> H <sub>8</sub><br>87% CH <sub>4</sub><br>10% N <sub>2</sub>  | 14 bar<br>23 °C                        | CH <sub>4</sub>                     | 3–3.5   | Experimental                                 | [52]      |
|                         | ----   | 10% N <sub>2</sub><br>90% CH <sub>4</sub><br>10 MMscfd   | 32 bar<br>30 °C                        | CH <sub>4</sub>                     | 3 for CH <sub>4</sub><br>* ≤4% N <sub>2</sub>   | Commercial simulation package (Chem-Cad 5.5) | [52] †    |
|                         | ----   | 0.2 MMscfd gas having 7% N <sub>2</sub>  | ----                                   | HCs                                 | * <3.8% N <sub>2</sub><br>80% HC recovery   | Field (Southern Kentucky)                    | [52]      |
|                         | ----   | 12 MMscfd<br>16% N <sub>2</sub><br>900 Btu/scf   | 67.5 bar                               | CH <sub>4</sub> and heavier HCs     | * 9% N <sub>2</sub><br>990 Btu/scf<br>95% HC recovery   | Field (Rio Bista, California)                | [52]      |

|                       |         |   |                     |                |                             |              |      |
|-----------------------|---------|---|---------------------|----------------|-----------------------------|--------------|------|
| Zeolite mem-<br>brane | SAPO-34 | ----                                      | 3 bar<br>40 °C      | N <sub>2</sub> | 4.38                        | Experimental | [54] |
|                       | SSZ-13  | 90% CH <sub>4</sub><br>10% N <sub>2</sub> | ΔP = 2 bar<br>25 °C | N <sub>2</sub> | 11.8 and 5 @ ΔP<br>= 25 bar | Experimental | [55] |
|                       | SSZ-13  | 50% CH <sub>4</sub><br>50% N <sub>2</sub> | 7 bar<br>25 °C      | N <sub>2</sub> | 13                          | Experimental | [58] |

\* reported CH<sub>4</sub> recovery/purity instead of membrane permselectivity. † Conducted techno-economic analysis in their work.

As shown in Table 2, both types of membranes are widely available and were tested in earlier research work with moderate permselectivities for both types. For N<sub>2</sub>-permeable membranes, it was determined that most of them are highly permeable to CO<sub>2</sub> as well. It can separate CO<sub>2</sub> and N<sub>2</sub> from methane, making it advantageous as the CO<sub>2</sub> removal step would be eliminated from NG processing. Nevertheless, a general trend was observed where higher pressures reduced the permselectivity of the membranes; thus there were fewer separation efficiencies [45,55–57]. This indicates that there might be a need to reduce the pressure of the gas and re-compress it again, as is the case in CH<sub>4</sub>-permeable membranes. Yet, PBI mixed-matrix membrane and SSZ-13 zeolite membrane have shown considerable performance over other membranes as they have an order of magnitude higher permselectivities compared to other membranes [55,57,58].

The CH<sub>4</sub>-permeable membranes were tested and developed commercially in multiple fields. Lokhandwala et al. [52] tested a membrane using the ChemCad 5.5 commercial simulation package, assuming a 10 MMscfd feed gas coming at a pressure of 32 bar where the N<sub>2</sub> content was reduced from 10% to less than 4%. In their study, they estimated the installation cost of these membranes to be USD 4–8 million, with annual revenue of USD 3.5–7 million [52]. In addition, they reported two field membrane units working successfully: one reducing the N<sub>2</sub> content from 7% to 3.8% with an overall hydrocarbon (HC) recovery of 80%, and the other reducing the N<sub>2</sub> content from 16% to 9%, increasing the heating value of the gas from 900 BTU/scf to 990 BTU/scf. Although the latter provides an overall 95% hydrocarbon recovery, the former provides better N<sub>2</sub> removal despite its lower recovery. Nonetheless, both units would require an additional upgrade for better gas conservation and more N<sub>2</sub> removal.

The literature review on the use of membrane technology for upfront N<sub>2</sub> removal suggests that an effective process requires multi-stage membranes to reduce the N<sub>2</sub> content and satisfy LNG specifications. The efficacy of such technology must be proven to explain the significant costs required for gas re-compression in the case of CH<sub>4</sub>-permeable membranes, as there might be a trade-off between product quality and product pressure [46].

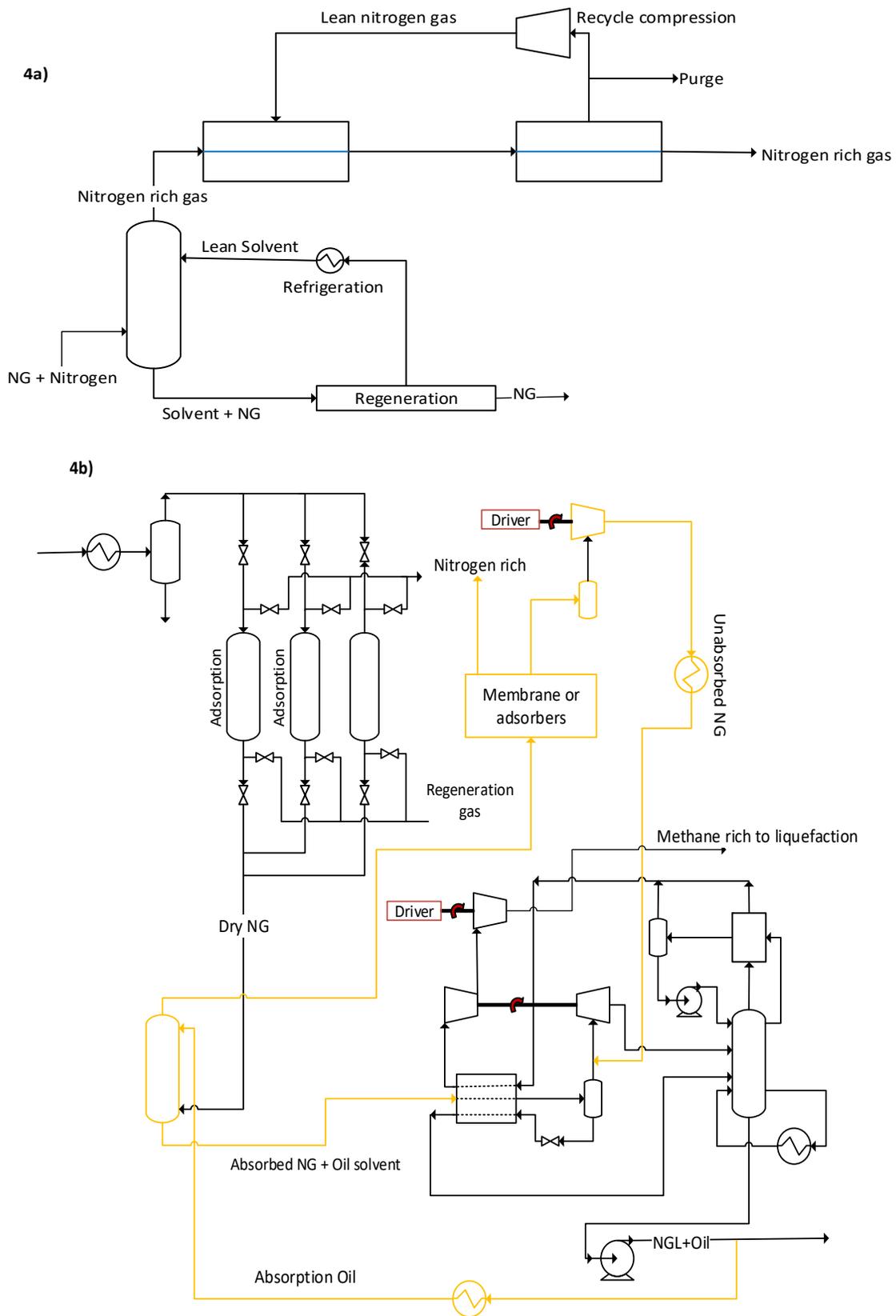
#### 4.1.3. Hybrid Upfront N<sub>2</sub> Removal Technologies

Instead of using adsorption or membrane N<sub>2</sub> removal processes, which are expensive to operate and implement and may result in poor performance, synthesizing a new hybrid system of these current technologies could have significant potential. A scheme of the proposed hybrid systems is shown in Figure 4a. The system uses both absorption and membranes to purify NG from nitrogen. The membrane step may also be replaced by adsorption or another viable option. NG is first fed to a high-pressure absorption column to remove as much NG as possible, using a suitable solvent such as low-temperature oil (i.e., heavy hydrocarbons) [4]. The N<sub>2</sub> rich gas leaving the absorber column is further purified in a membrane system to recover as much of the unabsorbed NG as possible. On the other hand, the solvent plus NG leaving the absorber bottom will need to be regenerated for solvent reuse and NG recovery. One of the motivations of this scheme can be to remove as much N<sub>2</sub> as possible while minimizing the loss of the NG pressure (as in the case of processing all the NG into a membrane or adsorber system). Consequently, it may be beneficial to minimize NG carryover from the top of the absorber such that it minimizes

the load on the membrane, which can result in excessive pressure drop hence, reducing NG re-compression. This would also mean a need for high-pressure solvent regeneration. If the solvent is made of heavy hydrocarbons (e.g., NGLs) then the solvent regeneration may be carried out in the existing NGL recovery step of the plant, see Figure 4b. While this may increase the NGL column reboiler rate, the K-1 compressor will process a stream without (or with lower) nitrogen, reducing its power. Pinch analysis may also be needed to exploit any available wasted refrigeration in the plant for lean solvent chilling before the absorber. The plant-wide degrees of freedom will also need to be optimized to determine the overall benefits without violating the process constraints, in this case, the NGL recovery heat exchangers, compressors surge/stonewall, columns hydraulics, etc. This newly developed N<sub>2</sub> removal scheme needs additional plant retrofitting. For example, the C-1 column in the NGL recovery step may require replacing the existing internals with high-capacity trays or packing, as it will be processing NG plus the oil solvent.

#### 4.1.4. Distillation

Figure 5a illustrates the potential of using the distillation process (TRL 9) as an up-front N<sub>2</sub> removal technology. This can be achieved by integrating the N<sub>2</sub> removal process with an NGL recovery column (C-201), one high-pressure nitrogen removal column (C-202), and one low-pressure nitrogen removal column (C-203). The cold section of the NG upgrading process comprises a natural gas liquid (NGL) recovery unit, liquefaction, and N<sub>2</sub> removal unit (NRU). The energy required to achieve the cold temperature is provided by an external refrigeration cycle in a multi-stream heat exchanger (MSHE). Figure 5b describes the cold section of a conventional large-scale LNG plant. The sweet natural gas (NG) from AGRU is liquefied in the cold section after the separation of the heavy hydrocarbons in the NGL recovery column (C-101). The lean NG from the NGL recovery unit undergoes further sub-cooling and is sent to single-column NRU(C-102). The LNG is then flashed to near atmospheric pressure to be stored in atmospheric storage tanks. The waste hydrocarbon-rich stream is used as fuel gas to generate power in a gas turbine to meet the plant's power requirements. Specialized heat transfer equipment such as MSHE allows multiple streams to exchange heat simultaneously and achieve the operating conditions. The MSHE has a quite complex and compact design with complex flow channels for reliable heat transfer over a wide pressure range [59]. The capacity of the MSHE is the bottleneck of the process, and removal of inert gases from the feed stream before it enters the MSHE will create volume for processing more hydrocarbon and increase the capacity of the plant. The introduction of an N<sub>2</sub> removal unit upfront of existing MSHE in the LNG plant, with the cold section operating at maximum capacity, generates room for more hydrocarbon to be liquefied and reduces the cold energy requirement from the MR cycle.



**Figure 4.** (a) Hybrid absorption and membrane upfront N<sub>2</sub> removal unit, and (b) integration of hybrid the upfront N<sub>2</sub> removal unit in the existing NGL recovery process (Orange lines).



The model of the proposed upfront N<sub>2</sub> removal via double-column distillation was developed using Aspen HYSYS V.10 and PSO algorithm coded in MATLAB. For a process with a feed flow rate of 530 MMSCFD, a minimum of 17.6% upfront N<sub>2</sub> removal before the MSHE-201 process resulted in more than 5% of the specific power requirement (from 33.13 MW/MTA to 31.4 MW/MTA) and a 16% increase in the plant capacity (from 530 to 619 MMSCFD).

#### 4.2. Chemical Separation Technologies

In chemical separation, the reagent to be used must be reactive with one component and non-reactive with the other component for an ideal separation. In the case of N<sub>2</sub> removal, an N<sub>2</sub>-reactive reagent that is simultaneously non-reactive with CH<sub>4</sub> is needed to preserve the BTU content of the gas. Table 3 lists all studies covering the chemical separation of N<sub>2</sub> from NG. Throughout the literature, surveying for potential chemical separation processes, two main processes were found: absorption through complexation and adsorption using lithium (Li) metal.

As stated earlier, all chemical separation processes target the N<sub>2</sub> instead of methane in the gas. It would not be reasonable to consume the gas needed and have an alternative to producing it back. The absorption process mainly employs a solvent that dissolves N<sub>2</sub>, not methane. Solvents that have proven successful are transition metal complex (TMC) solutions. In an experimental study, Friesen et al. [64] had a patent for using the combination of ligands and TMC solution to treat a gas feed with 15% N<sub>2</sub> content coming at typical NG conditions. The utilized solutions managed to have around 5.75 N<sub>2</sub> selectivity over methane. Li et al. [65] achieved a N<sub>2</sub> selectivity over methane of around 2 using ruthenium-based TMC at ambient temperature and a pressure of 30 bar. However, Li stated that a ruthenium-based TMC absorption process would be hindered in industrial-scale applications due to its limited availability and its low concentration in an aqueous solution [66]. Furthermore, Gilbertson et al. [67] established using iron-phosphine complexes for the separation of N<sub>2</sub> from NG at low temperatures and pressures, but they did not state the change in the N<sub>2</sub> content using these absorbents. Although all the aforementioned studies did not report any information about the purity of the gas obtained, other studies obtained NG at pipeline specifications as well as LNG specifications.

**Table 3.** Summary of N<sub>2</sub> removal from NG through chemical processes.

| Separation Method | Feed   | Operating Conditions                   | Solvent/Media                              | Favored Content | Selectivity/Product Purity /HHV            | Type of Work         | Ref    |
|-------------------|--|--|--|-----------------|--|----------------------|--------|
| Absorption        | ----   | 3–30 bar<br>30 °C                      | TMC Solution (K-[Ru <sup>II</sup> (EDTA)]) | N <sub>2</sub>  | 1.7–2.4                                    | Experimental         | [65]   |
|                   | ----   | Low T and P                            | Fe <sup>II</sup> phosphine complexes       | N <sub>2</sub>  | ----                                       | Experimental         | [67]   |
|                   | 15% N <sub>2</sub><br>85% CH <sub>4</sub>  | 69 bar<br>20 °C                        | Ligands and TMCs solution                  | N <sub>2</sub>  | 5.75                                       | Experimental         | [64]   |
|                   | 1 MM SCFD<br>20% N <sub>2</sub><br>80% CH <sub>4</sub>   | 69 bar<br>20 °C                        | Organometallic complex solution (Mo)       | N <sub>2</sub>  | * 4% N <sub>2</sub><br>96% CH <sub>4</sub> | Experimental         | [68]†  |
| Adsorption        | 20 SCCM<br>10% N <sub>2</sub><br>90% CH <sub>4</sub>   | 8.8 bar<br>60 °C                       | Lithium                                    | N <sub>2</sub>  | * 2% N <sub>2</sub>                        | Experimental         | [66] † |
|                   | (i) 10% N <sub>2</sub><br>90% CH <sub>4</sub><br>(ii) pretreated NG (4% N <sub>2</sub> , 95.9% CH <sub>4</sub> , CO <sub>2</sub> and H <sub>2</sub> O) | (i) 25 °C, 80 bar<br>(ii) 25 °C, 1 bar | Moisture-pretreated lithium                | N <sub>2</sub>  | * <0.5% N <sub>2</sub>                     | Numerical simulation | [69]   |

\* reported CH<sub>4</sub> recovery/purity instead of absorbent/adsorbent selectivity. † conducted techno-economic analysis in their work.

Using a molybdenum-based organometallic complex solution, Bomberger et al. [68] treated NG coming at typical well-head conditions reducing the N<sub>2</sub> content from 20% to less than 4%, where the complex bound more readily at a higher pressure and was not affected by the presence of methane. The operating cost associated with this absorption process was estimated to be around USD 1–3 million/SCF for small-scale process (i.e., 1–2 MMSCFD) and USD 0.3 million/SCF for large-scale process (i.e., 75 MMSCFD) [68].

Aside from the former absorption process, lithium-based adsorption was found to be promising, reducing the N<sub>2</sub> content in the gas to low levels, less than 2% [66,69]. This process consists of different steps (Figure 6), including the electrolysis of lithium chloride to obtain lithium. In a commercially established process, the lithium reacts with N<sub>2</sub> in natural gas, producing Li<sub>3</sub>N (Reaction 1). A reaction of lithium nitride hydrolysis can be applied as a part of the proposed cycle (Reaction 2) and an additional step of treating lithium hydroxide with hydrochloric acid to obtain lithium (Reaction 3).



In a numerical simulation analysis, Gu et al. [69] concluded that the N<sub>2</sub> content of the gas could be reduced at ambient temperature and 1–80 bar pressure from 10% or 4% to 0.5% N<sub>2</sub>, achieving LNG specifications where moisture-pretreated lithium is used as an adsorbent, not dry. The advantage of using moisture-pretreated lithium instead of dry lithium was emphasized by Li [66] as water produces active edge sites on lithium and initiates the reactions with nitrogen. In an experimental study, Li [61] used the moisture-pretreated lithium to reduce the N<sub>2</sub> content for a 20-SCCM-NG from 10% down to 2% at a pressure of 8.8 bar. An economic analysis for this adsorption process was conducted where the N<sub>2</sub> removal process was estimated to be profitable with a revenue of USD 88 per ton N<sub>2</sub> removed from a 5 MMTA LNG plant. This process reduced the N<sub>2</sub> content from 10% to 1%. The process is considered profitable as lithium can be easily regenerated, producing ammonia (reaction 2) that can be sold as a byproduct covering the cost of the N<sub>2</sub> removal process [61].

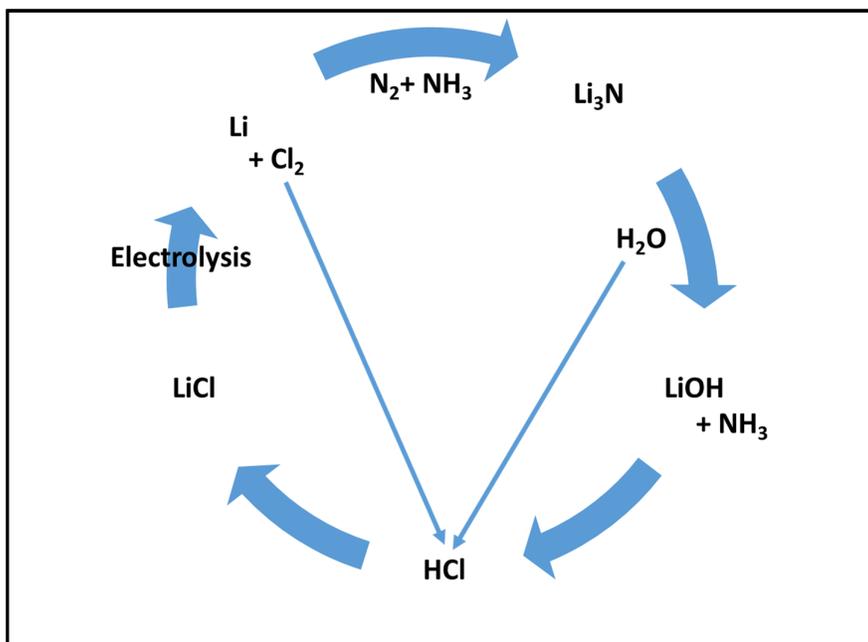


Figure 6. Lithium-based cycle for upfront N<sub>2</sub> removal.

### 4.3. Gas Hydrate Technology

Different research works have investigated gas hydrate production (TRL 4) in aqueous solutions and have proposed possible ways of gas-separation methods using the variations between equilibrium mole fractions in vapor and hydrate phase [70]. Gas hydrates are non-stoichiometric compounds that are combined between the water and the light gas molecules by Van der Waals forces. The host lattice gas molecules that are composed of hydrogen-bonded water molecules stabilize the well-defined cages with variable equilibrium pressures. Different studies showed that the hydrate-formation pressures of  $N_2$  and hydrocarbon (e.g.,  $CH_4$ ) are 14.3 and  $\sim 2.56$  MPa, respectively [71]. Therefore, the hydrocarbon can go through a phase change from gas to solid at low to moderate pressures, while  $N_2$  does not. Consequently, the hydrocarbon can be enriched while  $N_2$  is rejected [72].

The hydrate-based technology has been extensively studied for seawater desalination, marine carbon dioxide sequestration, gas separation processes, natural gas storage and transportation, and cold energy storage applications in the past decades [73]. Recently, numerous patented unit operations were proposed on the use of the gas hydrate for the separation of  $CO_2$  or  $N_2$  from the gas stream. However, none of these technologies are in operation at a commercial scale and, in most cases, still in the developing or pilot testing phase. The gas separation processes using hydrate formation can be implemented by exploiting the difference in the formation conditions (pressure and temperature) for different gas hydrates. Although the hydrate separation method is carried out in the presence of water, hydrate promoters, such as tetra-*n*-butylammonium bromide (TBAB), tetrahydrofuran (THF), sodium dodecyl sulfate (SDS), are generally added to reduce the energy consumption, decrease the equilibrium pressures of hydrate formation, and increase the hydrate formation rate.

Most of the proposed hydrate-based technologies are based on a stirred tank reactor that involves the use of promoter molecules to decrease the required operating pressure or the use of a bubble-column to promote high contact time between the gas and liquid, which was often highlighted as a limiting factor in the formation of gas hydrates. The separation of  $CO_2$  and/or  $N_2$  from a gas mixture using hydrate required a multi-step process to accomplish an adequate separation due to the difficulties in enclathrate the gas stream into the hydrate phase. The process includes passing the NG through hydrate forming reactor where the  $N_2$ -rich stream is released from the reactor, while the NG passes through the hydrate filter and settler to be separated as an NG free of nitrogen [74]. The regenerated hydrate can be recycled back to the reactor for further use. It was reported that the off-gas from the hydrate forming reactor is lean in hydrocarbons due to the preferential occupancy of hydrocarbon over  $N_2$  in the hydrate cages [9].

As the hydrate formation is exothermic, the removal of heat and control of operating temperature is crucial. Therefore, a fluidized-bed heat exchanger was used in all the applications that involve hydrate formation [75]. A continuous-flow gas-hydrate reactor was recently developed by Marathon Oil Company, tested on a pilot scale, and showed the capacity of generating a 410 wt% hydrate slurry at a production rate of 4750 kg/day. The process includes beads of solid media fluidized in the heat exchanger tubes and gently flow upward to reduce the chance for solid deposition and enhance the heat transfer coefficients [75].

Dong et al. [72] investigated the purification of the  $CH_4$  stream from  $N_2$  using a mesoporous carbon material (CMK-3) in the presence of tetrahydrofuran that lowers the hydrate formation pressure. The test successfully improved the composition of  $CH_4$  in the gas stream from 50 mol% to 70 mol% under optimal operating conditions of 1.0–1.4 MPa and 275.15 K. The study concluded that this hydrate can be easily regenerated and reused for the separation of  $N_2$  from hydrocarbons. Cai et al. [76] showed that the gas hydrate formed by using sodium dodecyl sulfate (SDS) and tetrahydrofuran (THF) as chemical promoters is effective in recovering  $CH_4$  from  $CH_4/N_2$  gas generated from coal-bed methane (CBM). The test, which was carried out at 1.50–4.50 MPa and 279.15 K, increased the methane composition from 50 mol% in the feed to 70% in the hydrate slurry. Although these promoters (THF and SDS) were effective and increased the hydrate formation and

separation efficiencies, the irritation, volatility, and corrosivity are challenges to be resolved before large-scale application. Sun et al. [77] used bio-additives such as tea polyphenol and catechin to enhance and promote hydrate formation. The bio-clathrates formed at 5.5–9 MPa and 274.15 K were used to recover CH<sub>4</sub> from CBM containing 34 mol% CH<sub>4</sub> and the balance N<sub>2</sub>. The bio-additives had a significant effect on the hydrate formation rate and storage capacities and consequently the separation efficiency. The gas hydrate developed by adding 1.0 wt% of catechin was selective to CH<sub>4</sub> with a separation factor of 5.31. This hydrate increased the composition of CH<sub>4</sub> from 34% to 61%. Another hydrate prepared using 1.0 wt% of tea polyphenol as a promoter resulted in CH<sub>4</sub> recovery and separation factor of 57.9% and 4.28, respectively.

Zhang et al. [78] examined the role of amino acids (L-tryptophan and L-leucine) in the presence of THF on hydrate formation and the efficiency for CH<sub>4</sub> gas recovery from CBM with a composition of 30 mol% CH<sub>4</sub> and 70 mol% N<sub>2</sub>. The results showed that the addition of 5000 ppm of L-tryptophan at 3.0 MPa and 283.2 K increased the hydrate growth rate by 130% and enhanced the CH<sub>4</sub> recovery from 58.3% to 71.4%. Although the addition of L-leucine did not impact the kinetics, it resulted in the highest CH<sub>4</sub> enrichment in the hydrate phase.

Sun et al. [79] explored the possibility of deploying alkyl polyglucosides (n-hexyl polyglucosides, C6 APG, and octyl-decyl polyglucosides, C8–C10 APG) as promoters for CH<sub>4</sub> hydrate formation and the separation from a stream containing 34.65 mol% CH<sub>4</sub> and the balance N<sub>2</sub>. The polyglucosides showed no effect on the process thermodynamics but act as a kinetic promoter and increased the hydrate formation rate and storage capacity. The C8–C10 APG exhibited a separation factor and percentage CH<sub>4</sub> recovery of 4.14 and 51.33%, respectively.

The aforementioned literature suggests a promising potential of gas hydrate for the separation of CH<sub>4</sub> from and N<sub>2</sub>. All the studies showed that CH<sub>4</sub> has a higher hydrate formation rate than N<sub>2</sub>. However, applying this technology as upfront N<sub>2</sub> removal in the LNG process required further investigation due to the following reasons: (1) The studied N<sub>2</sub> composition in different studies was high ( $\geq 30\%$ ) compared to the content in NG, (2) Most of the studies focused on a gas stream consisting of CH<sub>4</sub>/N<sub>2</sub>, which is different from the composition of the LNG, (3) to be economically feasible, any proposed upfront N<sub>2</sub> technology must have acceptable efficiency to remove very low concentrations of N<sub>2</sub> from LNG stream, and (4) It is not clear if using hydrate formation as upfront N<sub>2</sub> removal technology will be feasible for low-quality feed consisting of N<sub>2</sub> content. Therefore, further investigation is required to investigate the feasibility of a hydrate formation-based separation process as upfront nitrogen removal in a baseload LNG plant with low nitrogen content in feed (5–10 mol%).

## 5. Conclusions

The characteristics, design considerations, and efficiencies of the currently available upfront N<sub>2</sub> removal technologies from NG were covered in this review. Replacing the current industry dominance of the NRU at the tail of the process could substantially enhance the economics of large-scale LNG processes. The objective is to identify the best nitrogen removal process and its proper integration upfront of the liquefaction step. Cryogenic distillation is likely to remain the main N<sub>2</sub> removal technology in the near future due to high separation efficiency. The use of N<sub>2</sub> selective membrane technologies in removing N<sub>2</sub> from NG has significantly increased, though the need for multi-stage membranes is still considered a technical obstacle. There remains significant scope for the development of better performing N<sub>2</sub> selective membranes. Technologies based on N<sub>2</sub>-selective absorption and adsorption are promising commercial technologies for small-scale processes that require further inspections. Gas hydrate still required further investigation to accommodate the low concentration of N<sub>2</sub> in NG. There is future potential for efficient upfront N<sub>2</sub> removals, such as hybrid adsorption/membrane and chemical technologies. Synthesis of stable and selective N<sub>2</sub> solvents and/or adsorbents would improve the emergence of these processes

as upfront N<sub>2</sub> technologies. Challenges such as suitable location, retrofitting the proposed technologies, degree of removal, and cost require further investigation.

### Abbreviations

|       |                           |
|-------|---------------------------|
| AC    | Activated carbon          |
| CBM   | Coal-bed methane          |
| CMS   | Carbon molecular sieves   |
| HCS   | Hydrocarbons              |
| LNG   | Liquefied natural gas     |
| NG    | Natural gas               |
| PSA   | Pressure swing adsorption |
| C3/MR | Propane/mixed refrigerant |
| BOG   | Boil-off gas              |
| AGR   | Acid gas removal          |
| MOFs  | Metal-organic frameworks  |
| CBM   | Coal-bed methane          |
| SAPO  | Silicoaluminophosphate    |
| NRU   | Nitrogen removal unit     |

**Author Contributions:** Literature and Data curation, A.O.; Formal analysis, F.A.; Investigation, E.I.A.-M., Methodology, A.P., A.O., F.A.; Project administration, F.A., I.A.K. All authors have read and agreed to the published version of the manuscript.

**Funding:** National priority research fund No. NPRP11S-1231-170152, Qatar National Research Fund, a member of the Qatar Foundation.

**Acknowledgments:** The authors acknowledge the financial support through from Qatar National Research Fund grant No. NPRP11S-1231-170152. The statements made herein are solely the responsibility of the authors.

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

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