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A critical review on the practical use of lithium cycle as an upfront nitrogen removal technology from natural gas

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Abstract

The increase in energy demand as the world population grows, as well as the competition in the liquefied natural gas (LNG) market, force producers to work hard on developing cost-effective production technologies. Upfront nitrogen removal (UNR) before the LNG plant's cold section is considered a promising option to save energy that would otherwise be wasted to cool down a large volume of unused nitrogen in the gas stream. In this study, the use of the lithium cycle (Li-Cy) as a cost-effective method for UNR is investigated. The Li-Cy is compromised of three stages: lithium chemisorption of nitrogen ($Chem_{N_2}$), hydrolysis of lithium nitride (Hyd_{Li_3N}), and electrowinning (Elec.-w) of the final product to precipitate lithium metal for further reuse. The relevant chemistry, applicability, economic, and future challenges of Li-Cy as a UNR technology from natural gas (NG) were explored and discussed. The main challenges that required further investigation to apply Li-Cy to large-scale applications were highlighted for future works. The literature review revealed that Li-Cy can spontaneously remove nitrogen from NG even at low temperatures and produces ammonia as a valuable hydrogen storage material. The used lithium can be regenerated via Hyd_{Li_3N} and Elec.-w and reused again many times. The cost of the Li-Cy can be compensated by energy savings, the increase in production rate, and by selling the generated ammonia. Calculations showed that selling the produced ammonia from LNG plants with capacity in the range of 1–5 MTPA would not only offset the costs of Li-Cy but would generate a net profit of $21MM to $103MM, respectively.

KEYWORDS
energy-saving, hydrogen storage, lithium cycle, net profit, reaction kinetic

1 | INTRODUCTION

Liquefied natural gas (LNG) has quickly matured and is now an important component of the global energy market.[1] Reports showed that the LNG trade has quadrupled in the last two decades. Even as it grows, the LNG industry faces numerous challenges and threats that must be addressed for the industry to grow not only in volume but also in value.[2]

Figure 1 summarizes the unit operation within the conventional LNG plant. In general, natural gas (NG) processing and liquefaction include complicated unit
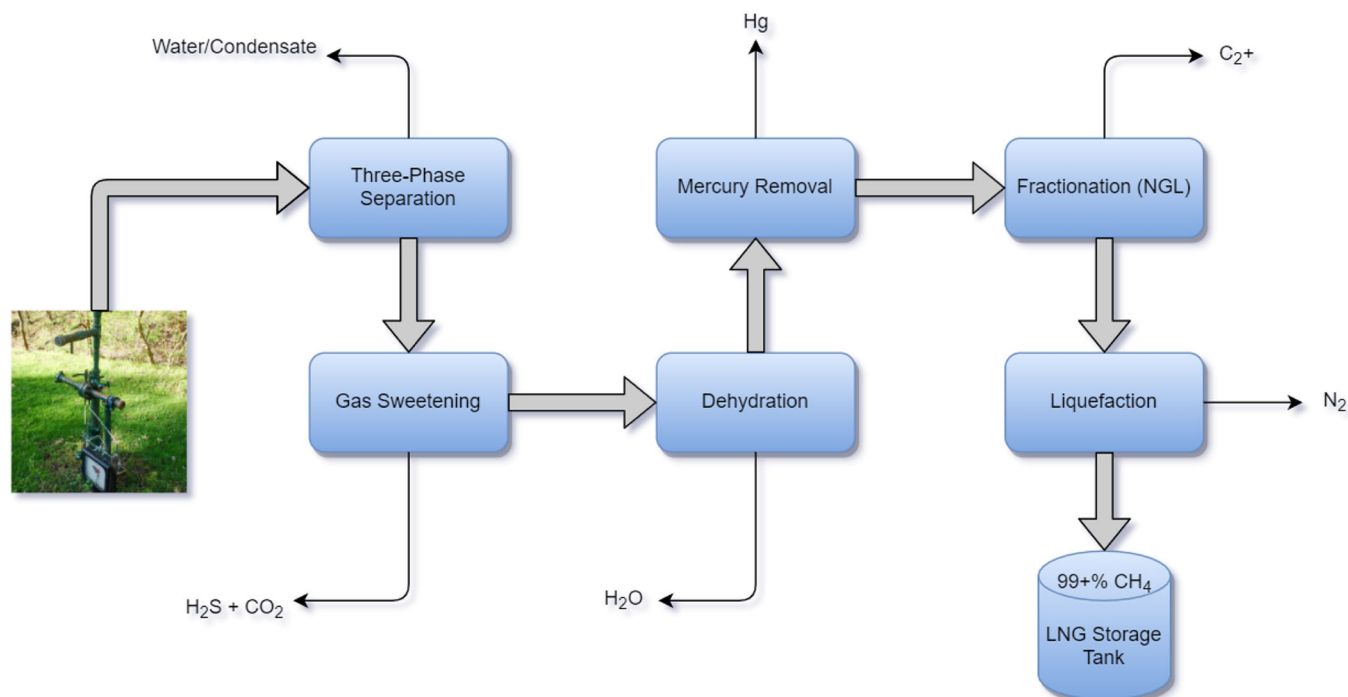
FIGURE 1 Conventional liquefied natural gas (LNG) plant.

operations, including phase separation, impurities removal (e.g., CO_2 and H_2S), dehydration, mercury removal, separation of heavy hydrocarbons (C^{3+}), and liquefaction. The cold section is the pillar of the liquefaction process and consumes roughly 60% of the total energy demand. This section is comprised of the refrigeration cycles (C_3MR or SMR, etc.), fractionation unit, nitrogen removal unit (NRU), and helium extraction unit. Shaft's work used to operate compressors accounts for the majority of the total energy demand in this section. Although the NG liquefaction process is well-established, there is much innovation to be added that could further optimize the production process and increase the profit. Therefore, heat integration and process optimization are commonly used to reduce energy demand in the LNG process.

One particular area of research that could be optimized within an LNG production plant is the NRU, which is usually placed at the tail end of the plant to remove nitrogen impurities from the LNG.[3] The LNG standards call for stringent and lower nitrogen specifications as nitrogen content >1 mol% in LNG tanks can cause safety hazards and risk of rollover. The removal of nitrogen from NG in the cold section is usually implemented via separation processes based on molecular, thermodynamic, and/or transport properties between nitrogen and the hydrocarbons (mostly methane). Cryogenic distillation process, which relies on the difference between the boiling points (BP) of NG

(BP ~ 111.7 K) and nitrogen (BP ~ 77.3 K), is the most commonly used NRU in commercial LNG plants. This process is reliable and consistently exhibits superior performance in achieving hydrocarbon recovery up to 99%. The high expenses of the chilling equipment, the need for shaft work to operate gas compressors and the regular maintenance requirements make this process challenging and complicated and the process.[4] In addition, removing nitrogen after liquefaction generally increases the energy requirements and reduces the production capacity.

Recently, UNR was proposed as a promising alternative to NRU. The fundamental of UNR is based on separating nitrogen from NG at the hot section, which operates at temperature ranges of 0°C to 100°C. This would save energy, increase the production capacity, and reduce the costs associated with the cooling process. According to Almomani et al.,[5] the UNR in the LNG plants can lead to significant energy cost savings due to the removal of nitrogen, which moves as an inert gas through the plant. This occupies volume in the plant that could be used for increasing the NG capacity to subsequently increase the energy load on the plant.

The literature review outlines numerous processes for UNR, including (1) physical separation technologies, such as adsorption,[6–8] membrane separation,[9–11] hybrid processes, and distillations[12]; (2) chemical separation technologies,[13–15] including absorption[15] and lithium-based adsorption[14,16]; and (3) gas hydrate technology.[17–20] A

detailed discussion of all these processes can be seen in our previous publication.[5]

The lithium-based adsorption process was found to be a promising technology for reducing the N_2 content from NG to less than 2%. Figure 2 illustrates the steps included in the lithium cycle (Li-Cy), which consist of the chemisorption of nitrogen ($Chem_{N_2}$),[14,16] hydrolysis of lithium nitride (Hyd_{Li_3N}),[21-24] and electrowinning (Elec.-w) of the final product to precipitate lithium metal for further reuse.[25-27] In such a process, lithium reacts with N_2 in NG producing Li_3N. The generated Li_3N undergoes a hydrolysis process to generate Li(OH), which can be further reacted to recover and recycle the lithium. Although lithium is the least reactive metal in the alkali group, extensive experimental works have been done since mid of the 20th century elucidating the feasibility of reacting lithium with gases through varying degrees. Water vapor was found to prompt these reactions by reacting with lithium to form a dark layer of Li(OH) and generate hydrogen as a side product.[28,29] It was observed that the reaction rate of lithium with other gaseous, such as O_2, $C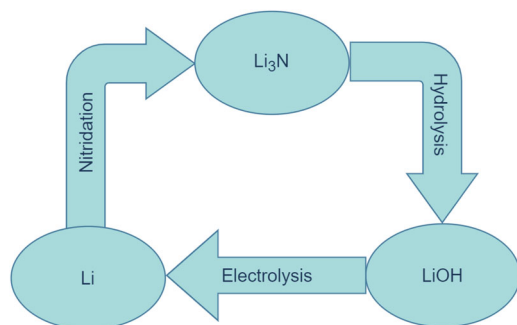O_2$, and N_2 was enhanced in the presence of water vapor.[30,31] According to Shang et al.,[32] the dissociation of water aids in the formation of a LiOH layer on the lithium surface, which provides more active edge sites for approaching gas molecules attachment. While the results of the previously mentioned research may be prone to inaccuracies due to outdated methodologies and less sophisticated equipment, they still prove the existence of the interaction between the lithium metal and gas molecules, which was theoretically established by chemists.

In the context of modern applications of lithium solid for gas chemisorption, lithium was found to be a good medium for hydrogen gas storage through lithium hydride species, which can undergo reverse reactions to produce hydrogen.[33-35] Lithium solid was also used for CO_2 capture, integrated with power generation as in Li–CO_2 batteries[36,37] and for the production of lithium oxide, which can be used as a flux in ceramic glazes. Figure 3 shows the trend of the publications in the last century on the use of lithium for the chemisorption of nitrogen gas in ambient conditions to produce lithium nitride (Li–N_2) and the chemisorption of nitrogen gas from a mixture with methane (Li–N_2–CH_4) to improve the NG quality. It was noted that while the nitridation reaction is well-documented in the literature, particularly in the presence of moisture, and is mostly performed by chemists, its use to remove nitrogen from NG streams is less common. The feasibility of this process was recently highlighted through both experimental and theoretical testing.[16] The thermodynamic favorability of the reaction was also confirmed by Gu et al.[14] Moreover, patents for the usage of lithium for the chemical sorption of nitrogen from NG were issued.[38,39]

Nitrogen removal from NG using lithium solid chemisorption is a promising and novel process. The theoretical nitrogen uptake can reach up to 24 mmol/g Li, which is higher than any other reported method. According to Li,[16]
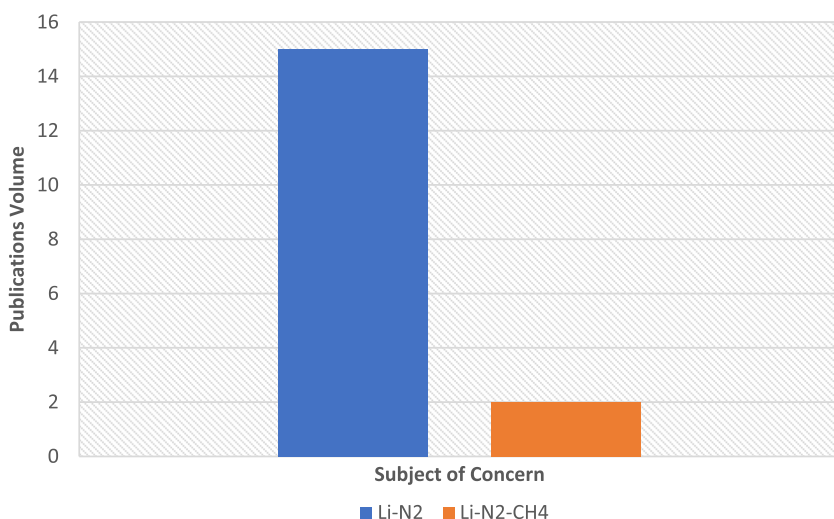

FIGURE 2 Proposed lithium cycle for upfront nitrogen removal.

FIGURE 3 Publications volume of existing literature regarding lithium chemisorption

lithium solid chemisorption can achieve a 100% conversion of lithium to lithium nitride in a mixture of N_2/CH_4. In addition, the regeneration of the lithium occurs by reacting the lithium nitride with water, which produces ammonia as a side product.[22] This increases the economic attractiveness of this method. The aforementioned literature review suggests that Li-Cy is a promising technology for URN from NG. While the use of lithium metal to adsorb nitrogen was conducted in previous research for chemistry studies,[30] safety hazard studies,[40] as a medium to store renewable energy[41] and even as an intermediate in ammonia production,[42] little to no research investigates lithium chemisorption applicability and economic feasibility with NG under real operation conditions. Therefore, this paper will focus on the use of Li-Cy for nitrogen removal from a mixture of gases in general and NG in specific. It was aimed to evaluate the literature research work on the aforementioned Li-Cy steps, including the process chemistry, applicability, economic feasibility, and the challenges and limitations that may be faced during the integration with a real LNG plant. The findings of this study will pave the way for the development of a well-defined Li-Cy, which has the potential to be a viable option among the many options for UNR from NG.

2 | GENERAL CHEMISTRY

This section briefly summarizes the relevant reactions expected to occur in the proposed Li-Cy. It is important to highlight that many more reactions than noted can realistically occur but will not be competitive. Due to differences in free energy reactions, a hierarchy is established, which prioritizes competitive reactions. Given the novelty of the subject, there is minimal literature that investigates these reactions within the context of NG treatments. That being said, Table 1 contains the extracted thermochemistry data for the relevant species in the cycle, and Table 2 provides a summary of the Li-Cy and the expected reactions.

2.1 | Nitridation of lithium

In the first step of the cycle, lithium metal is exposed to nitrogen gas at low temperature, below the melting point, to yield lithium nitride as expressed by Reaction (1). The enthalpy of formation, entropy change, and Gibbs free energy change at 25°C for a single mol of lithium nitride are 164.6 kJ/mol, −121.1 J/mol K, and −128.5 kJ/mol, respectively. These values are extracted/calculated from the NIST Chemistry WebBook.[43]
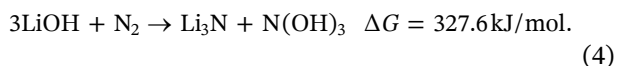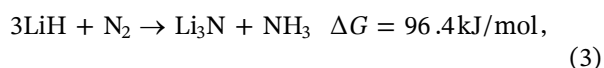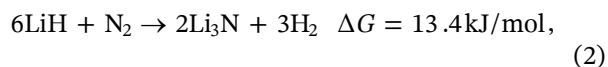
$$6Li_{(s)} + N_{2(g)} \rightarrow 2Li_3N_{(s)}. \qquad (1)$$

This reaction is exothermic and spontaneous. However, according to Jeppson et al.,[44] it does not occur with dry nitrogen and required the presence of water moisture (≥10 ppm). The water moisture activates the surface of lithium and produces the reddish-brown to black lithium hydroxide and lithium hydride, or hydrogen.[32] The reaction with moisture has two benefits: the creation of a lithium hydroxide layer that promotes a more active edge site for the nitridation reaction to occur,[16] and the release of energy (375 kJ/mol) that is used as the activation energy for the nitridation reaction.[14] Based on the existing research literature, there is conflictual evidence on the likelihood of lithium reacting to nitrogen in dry conditions. For instance, Mcfarlane and Tompkins[31] argues that it is possible for the reaction to occur, while Markowitz and Boryta[45] assert that lithium will remain stable for days. Wayne Ronald Irvine[46] confirmed that the moisture pretreatment significantly enhances the reaction rate

While Reaction (1) describes the primary reaction that occurs when lithium is exposed to nitrogen, when thinking about NG, lithium can be helpful to imagine other relevant species besides nitrogen (i.e., impurities), such as H_2, CO_2, and O_2. For example, Gu et al.[14] summarized 21 reactions, including lithium, lithium hydride, and lithium hydroxide with the aforementioned gases and calculated the activation energy for each reaction. Some of these reactions are highlighted with their Gibbs-free activation energies, reactions (2–4). Notably, most of these reactions do not theoretically or experimentally occur due to the favorability of reactions with low activation energies. According to Reactions (2)–(4), the reaction of Li presents in the reaction system as LiH, and LiOH due to the moisture pretreatment. After the sufficient reaction time, complete conversion is nearly achieved and the metal nitride Li_3N is left.

TABLE 1 Thermochemistry data for relevant species.[43]

Species	S^0 (J/mol K)	ΔH_f^0 (kJ/mol)
Li (s)	29.09	0
N_2 (g)	191.61	0
Li_3N (s)	62.66	−164.56
H_2O (l)	69.95	−285.83
H_2O (g)	188.84	−241.83
LiOH (s)	42.81	−484.93
LiOH (l)	47.97	−474.42
NH_3 (g)	192.77	−45.94
O_2 (g)	205.15	0

TABLE 2 Summary of the most important and relevant reactions in the proposed Li-Cy.

Reaction	Type	Temperature cond.	Note
$6Li_{(s)} + N_{2(g)} \rightarrow 2Li_3N_{(s)}$	Spontaneous exothermic nitridation	25–100°C	Does not occur at such low temperatures without prior activation by moisture (vapor H_2O).
$Li_3N_{(s)} + 3H_2O_{(g)} \rightarrow 3LiOH_{(s)} + NH_{3(g)}$	Spontaneous exothermic hydrolysis	25–100°C	A highly exothermic reaction that requires cooling. Produces ammonia as a side product (side benefit).
$LiOH_{(l)} \rightarrow Li_{(s)} + 1/2H_2O_{(l)} + 1/4O_{2(g)}$	Nonspontaneous endothermic electrolysis	>325°C	Energy-intensive step, utilizing electric current at elevated temperatures to regenerate Li metal at the cathode.

$$6LiH + N_2 \rightarrow 2Li_3N + 3H_2 \quad \Delta G = 13.4 \, kJ/mol, \tag{2}$$

$$3LiH + N_2 \rightarrow Li_3N + NH_3 \quad \Delta G = 96.4 \, kJ/mol, \tag{3}$$

$$3LiOH + N_2 \rightarrow Li_3N + N(OH)_3 \quad \Delta G = 327.6 \, kJ/mol. \tag{4}$$

2.2 | Hydrolysis of lithium nitride

The "used adsorbent" can be regenerated in two different ways, the hydrolysis and hydrogenation methods. The hydrolysis method differs from the hydrogenation of Li_3N, which uses H_2 gas instead of water to produce ammonium.[21,24] While not the focus of this study, hydrogenation can be an alternative to hydrolysis, especially if H_2 gas is required. As demonstrated by Reaction (5), in the hydrolysis method the Li_3N reacts with water in a violent exothermic reaction to produce lithium hydroxide and ammonia as a side product.

$$Li_3N_{(s)} + 3H_2O_{(g)} \rightarrow 3LiOH_{(s)} + NH_{3(g)}. \tag{5}$$

The hydrolysis reaction can occur at room temperature with thermodynamic parameters ΔH, ΔS, and ΔG of $-610.6 \, kJ/mol$, $-307.9 \, J/mol \, K$, and $-518.8 \, kJ/mol$, respectively.[43] As concluded from the enthalpy of the reaction, this reaction is exothermic and spontaneous as confirmed by the research by Jain et al.[22] on ammonia production by lithium nitride hydrolysis. Following this reaction, it was noted that the reactor temperature and pressure increased from room temperature and 0.1 Pa to 80°C and 0.8 MPA, respectively. It was confirmed through the same study that that reaction can reach 100% conversion at room temperature and generate hydrogen gas. In Reaction (5), water must be in vapor phase form to avoid an excessive dissipation of energy that c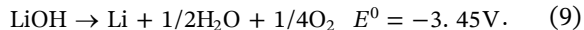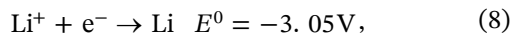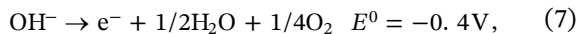ould dissociate the formed NH_3. Moreover, as ammonia is fairly soluble in water at the desired reaction conditions the reaction should be conducted using water vapor on solid surfaces away from water liquid to allow the ammonia gas to escape.[47] The hydrogenation of lithium nitride is also expected to happen simultaneously with the hydrolysis process. This is due to the presence of H_2 as an impurity in the NG stream or as a side product from the aforementioned reactions. As demonstrated in Reaction (6), the reaction will consume lithium nitride and hydrogen gas to produce lithium hydride and ammonia.

$$Li_3N_{(s)} + 3H_{2(g)} \rightarrow NH_{3(g)} + 3LiH_{(s)}. \tag{6}$$
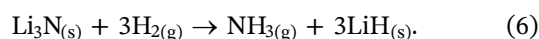
However, this reaction was reported to occur at relatively high temperatures up to 500°C.[21,23,24] If lithium hydride forms, it can always be turned into lithium nitride by reacting with nitrogen per Reactions (2) and (3). Though, this reaction is not expected to be significant due to the limited reaction conditions.

2.3 | Electrolysis of lithium hydroxide

The hydrolysis of lithium nitride primarily yields lithium hydroxide (LiOH), which must be processed to generate Li that can be used again for the chemisorption step. Most industrial generation of lithium by electrolysis is conducted with LiCl–KCl molten salt mixtures. In this step, a eutectic mixture of LiOH–LiCl is introduced as the analyte inside the electrochemical cell at elevated temperatures. The anode and cathode half-reactions occur according to Reactions (7) and (8), respectively. Then, Reaction (9) describes the overall reaction. This reaction is the most complex in the cycle in terms of reactor setup, conditions, and complexity. The heating and electricity flow requirements also make the maintenance process more complicated.

$$OH^- \rightarrow e^- + 1/2H_2O + 1/4O_2 \quad E^0 = -0.4V, \quad (7)$$

$$Li^+ + e^- \rightarrow Li \quad E^0 = -3.05V, \quad (8)$$

$$LiOH \rightarrow Li + 1/2H_2O + 1/4O_2 \quad E^0 = -3.45V. \quad (9)$$

The cell potential of the reaction indicates that it is not spontaneous and requires an electric current. The reported potentials for Reactions (7)–(9) are standard values at 25°C, which are not useful for this paper as the melting points for LiOH and LiCl are 462°C and 605°C, respectively. Levin and McMurdie[48] note that LiOH–LiCl has a eutectic melting point of 325°C with a molar concentration between 70% and 30%. The operating temperature inside the reactor for this step is expected to be quite high. This significant increase in temperature from standard conditions (300+°C) seems to only have a small impact on the dissociation potential, which was reported to be 3.05 V at 380°C as reported by Laude et al.[25] and 2.9 V at 350°C as reported Takeda et al.[26] Conversely, Tang and Guan[27] identified the potential to be 2 V at 400°C, which was explained by their use of liquid Sn as the cathode. This was a modification that seems to decrease the dissociation potential. The electrolysis efficacy of LiOH in the molten salt is measured by the Faraday efficiency of the cell. Within this context, it is defined as the ratio between the actual amounts of metal deposited at the cathode (Li) divided by the theoretical current required for the deposition of the same metal according to Faraday's law (Equation 1). Where n is the number of moles precipitated on the electrode, t is the total time the current was constantly applied, F is the Faraday constant, and v is the valency.

$$n = \frac{It}{Fv}. \quad (10)$$

One area of concern noted in the literature is the undesirable precipitation of Li_2O on the cathode. This hinders the regeneration of Li as it reacts with LiOH via the spontaneous reaction outlined in Reaction (11). This reaction harms Li recycling and reduces the yield. When the Li_2O precipitates on the cathode, less surface area is available for Li to form. This can be prevented by adding a porous membrane to block the LiOH from traveling to the cathode section[27]

$$Li + LiOH \rightarrow Li_2O + 1/2H_2 \quad \Delta G^0 = -96.9 \text{kJ/mol}. \quad (11)$$
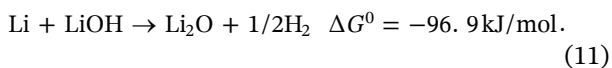
As water (H_2O) is a side product in Reaction (9) a possible interfering reactant present in the moisture with an electrolysis potential of 1.23 V (less than the main reaction), it is expected to have a negative effect on the reaction conditions. This uses up some of the electric currents, which leads to a decreased current efficiency as suggested by Laude et al.[25] The current efficiencies in the electrolysis of LiOH were reported to range from 38%[25] up to >80%.[26,27]

Given the nature of such reactions discussed in this section, it is concluded that such a pathway that starts with lithium metal and undergoes a regeneration cycle for continuous operation in an LNG plant is theoretically possible with attention to the highlighted details and the concerning reaction conditions. Some of these conditions include temperature, pressure, and energy requirements. It was observed that the required temperature and pressure are within operating conditions of the hot section in the LNG plant. That being said, integrating and operating such a cycle with an LNG plant will require better knowledge of the limitations and challenges that will be discussed in a later section. For example, hydrolysis of lithium nitride must be performed on a pure lithium nitride sample to avoid the evolution of hydrogen gas, but given that complete conversion in the nitridation step on a large-scale setup could be very difficult to achieve, it would be wise to account for the increase in reactor pressure that will inevitably build-up due to the "undesired" gas production. Regardless, most of these challenges can be easily remedied by simple solutions, such as modifications to the reactors and higher bed volume, with high surface area to compensate for "inactive" lithium that is not converted in the calculations to obtain the effluent methane purity.

3 | THE APPLICABILITY OF THE Li-Cy

This section focuses on analyzing techniques and technologies that use lithium metal (Li) to support the proposed lithium-based cycle. The majority of the research work that was examined whether experimental or theoretical widely differs from the perspective of this study. For example, the research typically focused on presenting the nitridation reaction between Li and nitrogen (N_2) or establishing an ammonia production process or cycle, rather than formulating a cycle for the UNR from the LNG plant. However, this study can be beneficial for this case as collecting the associated outcomes supports the visualization of the possible approach and performance of the cycle. Thus, this section aims to gather practical information, data, and results about one or more steps of the proposed lithium-based cycle. This helps to finalize the circumstances and conditions required for ensuring the practicability and

reliability of the lithium-based cycle. This section will serve as a summary of the work done that demonstrates the feasibility of the Li-Cy in each step, and a more critical discussion regarding the accuracy, reliability of reviewed literature, and the limitations and challenges of associated technology in the context of this paper's goal (LNG plants) will be further discussed in Section 5. Finally, much like the previous section, this section is divided into three parts, which encompass the three reactions of the lithium-based cycle.

Interestingly, there is research work in the literature that targets a similar desired goal for the upgrading of NG, though it primarily focuses on removing impurities instead of the possibility of a cycle. Gu et al.[14] presented an approach for NG purification by using pretreated lithium with moisture as a material for adsorbing the impurities from the NG stream. The performance of lithium as an adsorbent for selective separation when exposed to different gas mixtures was studied theoretically. The density functional theory (DFT) calculations were used for the reactivity analysis. In addition, the temperature-programmed kinetic Monte Carlo calculation (TP-KMC) method was used to analyze the effectiveness of the lithium to adsorb the impurities in the streams of the gas mixtures containing methane. The results highlighted thermodynamic favorability and confirmed the separation approach to occur spontaneously and provided outstanding conclusions that it may potentially achieve a high purity methane stream. The main problem with these results, however, was the reliance on the Arrhenius law for studying and predicting the reaction kinetics, which is problematic for several reasons, not the least of which is the assumption of temperature-independence of the reaction-free energy.[49] Nevertheless, the researchers found that the main mechanism influencing the process is the reaction between the captured gases and the components produced after the exposure of lithium to moisture. The TP-KMC calculations highlighted how the binary mixture of N_2 (10%) and methane at 35°C and 0.1 MPa can be effectively separated after operating the system for 70 min. This achieved a high purity of methane stream and collected N_2 as a solid (lithium nitride, Li_3N). The desired selectivity can still be achieved at higher temperatures due to the maintained differences in reaction kinetics. When the temperature is increased the reaction slightly increases and the separation time decreases.[14] It should be reminded that the pressure of the proceeding and succeeding units (dehydration, NGL recovery, liquefaction) operate at much higher pressures. The NG dehydration unit is commonly operated at 70 bar and can go up to 200 bar,[50] which would only make the nitridation process more attractive as the chemisorption would positively benefit from higher pressures.

3.1 | Nitridation of lithium

The nitridation of the Li reaction is considered to be the first reaction in the proposed cycle. This specific step was introduced as the first step in work that focused on the N_2 reduction reaction and the ammonia production process or cycle. For instance, Jain et al.[22] introduced Li metal as a test start material for the nitridation process at room temperature in a differential scanning calorimetry (DSC). The DSC profile of the nitridation reaction indicated how exposing fresh Li to N_2 with pressure no less than 0.8 MPa starts the reaction. After that, the reaction continuously occurred and an exothermic peak was identified at a temperature of approximately 50°C, which increased from room temperature. The DSC profile and the x-ray diffraction analysis (XRD) pattern in this study confirmed the complete transition of Li to Li_3N as no endothermic peak was observed at 180°C (the melting point for Li). In addition, the metal surface of the Li affects the characteristics of the nitridation, meaning that it has a clear influence on the temperature and pressure needed for the reaction to occur. When the Li is exposed to air for 6 h, the reaction could not be initiated at room temperature even when the pressure of N_2 increased to 1 MPa. The required temperature for a reaction increased when the Li sample was exposed to the air for 6 h. After the sample was exposed to the air for 24 h, the temperature reached values closer to the melting point of Li.

The relation between temperature and reactivity was also studied. It was found that the preheated Li (at 100°C) required less pressurized N_2 (0.5 MPa) than the non-preheated Li (0.8 MPa).[22] The required pressure can be less than 0.35 MPa when preheating the Li to higher temperatures such as 150°C. While thermodynamically the reaction can proceed at room temperature with a pressure of 0.1 MPa, it has activation energy to overcome. Given that, high pressure is essential for the initiation of the reaction. As a result, for the reaction to occur at lower pressure values, the Li needs to be heated to higher temperatures.

McEnaney et al.[42] presented the nitridation of Li reaction as part of a proposed ammonia production cycle. The cycle was principally designed based on the Li–N–O–H phase diagram, which is constructed with a reference pressure of 1 bar, a pH 1, a temperature of 300 K, and a Li^+ ion concentration of 10^{-6} M. Throughout the cycle steps, it is possible to adjust for optimized conditions because the diagram's energy differences are quite large. Consequently, the physical state of the cycle is not greatly affected by parameter changes. Importantly, before the nitridation reaction, voltage is applied to the Li sample to produce an electronically activated

surface. Then, it is exposed to N_2 gas in a tube furnace with a maintained temperature range between 22°C and 100°C. Next, the Li_3N product is created.

The outcome of the nitridation reaction was pronounced beginning at the ammonia production point, meaning that the conversions were based on the ammonia production from reacting the product of the nitridation reaction with water. The conversion was analyzed at three different temperatures of the nitridation reaction, including 22°C, 50°C, and 100°C, and in two different time frames of 30 min and 12 h.[42] Increasing the temperature of the nitridation reaction led to higher conversion values. In addition, exposing the N_2 flow to 100°C for 30 min produced conversion values higher than 80%. In contrast, exposing the N_2 flow for 12 h resulted in near-complete conversion values. Moreover, XRD analysis substantiated the presence of Li_3N and traces of LiOH and Li_2O, which resulted from transferring the Li sample from the electrochemical cell to the furnace tube of N_2. The exposure of O_2 and H_2O found in the atmospheric air seemed to increase the rate of the nitridation reaction.

3.2 | Hydrolysis of lithium nitride

This section focuses on the hydrolysis of Li_3N, which is the second reaction in the proposed cycle. In the research literature, the reaction was discussed within the context of ammonia production reactions or cycles. Jain et al.[22] presented a new experimental approach using nitride hydrolysis for the production of ammonia, a hydrogen storage material comprised of 17.8 wt% of hydrogen at temperatures lower than 100°C. Hydrolysis controls the atmosphere at a temperature of 80°C, and the Li_3N must react with the water vapor rather than the liquid water. This approach converts nitrides to receive ammonia through exhaust heat, solar heat, or thermal energy. The conversion was conducted in a simple reactor system that turns heated water into water vapor, which then passes through a metallic filtrate with a Li_3N sample. As an initial trial, the experiment was performed with a pressure of 0.1 Pa and at room temperature in the reactor system with a closed chamber. This was repeated multiple times to optimize the reaction conditions. The optimized temperature for the reaction to occur was 80°C, with a considerably high amount of Li_3N consumption and the lowest possible hydrogen generated value. Importantly, the XRD analysis substantiated the LiOH as a product of the hydrolysis reaction and the calculations confirmed a reaction fraction of 95% after 2 h of reaction at 80°C.

McEnaney et al.[42] examined an innovative production procedure for ammonia to find a substitute for the Haber–Bosch process, which is an energy-intensive and unsustainable approach for ammonia production. The hydrolysis reaction was conducted between Li_3N and deionized water (10 ml) in scintillation vials. The determination and quantifying of ammonia were accomplished using two approaches with high accuracy: the colorimetric test connected to the ultraviolet–visible light spectroscopy (UV-Vis) and Fourier transform infrared spectroscopy (FTIR). The results of this proposed cycle, depending on the individual step, exhibited an 88.5% current efficiency for ammonia yield. Moreover, the results of the ammonia conversion achieved high values of more than 80% when the temperature of the nitridation reaction was 100°C after 30 min of exposure to N_2. Higher values were obtained when the exposure to N_2 was for 12 h at different temperatures. The source of the N_2 in the cycle was also confirmed using FTIR, which came from the provided gaseous N_2 and not from an unexpected source

3.3 | Electrolysis of lithium hydroxide

This subsection focuses on the electrolysis of LiOH, which is the final step of the Li-Cy. In the research literature, this reaction was investigated within the context of the techniques used for hydrogen storage. Takeda et al.[26] explored the practicality of Li recovery from LiOH by electrolysis in molten chloride. This was aimed at forming a system for hydrogen storage and transportation. A potential diagram for the Li–H–O system formed, which was dependent on the thermodynamic data. The recovery of Li from LiOH cannot be accomplished if the molten salt from the electrolysis had LiOH as one of the components. This is because the recovered Li from the electrolysis will react with the LiOH available in the molten salt generating Li_2O. In this approach, it was preferable to assemble the components of the experimental setup in the Quartz tube to prevent the direct contact of freshly generated Li with LiOH. Instead, molten LiCl–42 mol% KCl or molten LiCl–17 mol% KCl–26 mol% CsCl was used as the molten salt. Then, the LiOH was inserted into the anode section away from the Li metal, which is deposited in the cathode section.

Following this approach, the Li metal was collected at the end of the electrolysis. The hydrogen generated from reacting Li with water also enabled the calculation of the lithium deposition current efficiency.[26] The two proposed molten salts, through different conditions, were used to analyze their impact on the cathode and anode reactions as well as the overall electrolysis. The temperature of the molten salt did not have a strong effect on the cathode

current efficiency. Using LiCl–KCl or LiCl–KCl–CsCl molten salts at lower temperatures also did not cause a major difference in the cathode current efficiency, which can reach a value up to 84%–86%.

Laude et al.[25] proposed a three-step cycle designed to ensure an efficient hydrogen supply from LiH. The cycle process is based on recycling the LiOH, which is the by-product of the LiH hydrolysis (i.e., first step). The electrolysis of LiOH (i.e., second step) is considered to be the recycling reaction, where Li metal is created through a hydrogeneration reaction (i.e., third step). The researchers also focused on the electrolysis of the LiOH, which was conducted in a quartz reactor at 380°C using a LiOH–LiCl mixture as the molten salt. This achieved a 37.9% current efficiency. During electrolysis, constant values of current electrolysis (1.5 A) and current density (1.5 A/cm^2) were used. The amount of hydrogen generated from dropping the collected Li metal from the electrolysis enabled the determination of the amount of metal generated. The first 30 min of the experiment exhibited a low current efficiency (12.5%) due to the moisture in the LiOH–LiCl mixture. Then, after 16 min the current efficiency increased to 37.9%, and the metal produced was established as Li by the DSC. Moreover, with the cyclic voltammetry measurement, the anode behavior exhibited no LiCl dissociation and no anode corrosion as there were no corresponding peaks and only one main reaction was identified ($LiOH \rightarrow Li^+ + e + \frac{1}{2}H_2O + \frac{1}{4}O_2$).[25] Conversely, for the cathode, only one reaction was determined ($LiOH + e \rightarrow OH^- + Li$), which confirmed the Li metal deposition. Although other peaks were found, it is likely only due to some water electrolysis and impurities. The nongeneration of Cl_2 was also confirmed with the KI solution test.

McEnaney et al.[42] demonstrated how the LiOH electrolysis in the LiCl–KCl/LiOH–LiCl molten salt mixture is a step in the cycle for ammonia production. The setup used for the electrolysis was designed to ensure that there was no direct contact between the produced Li with LiOH, H_2O, or O_2 to avoid any possible side reactions. Depending on the melting temperature of the molten salt mixture, the temperature of the electrolysis was maintained at 450°C to ensure the liquid phase of the molten salt. In addition, cyclic voltammetry was used to analyze the behavior of the electrolysis process. It was determined that the total cell potential for LiOH was approximately 3.0 V, which is consistent with the theoretical values of 2.8 V at 427°C. The current efficiency of the LiOH electrolysis associated with Li production was examined and the average yield reached 88.5%.

As highlighted, each article provided its perspective on one or more of the reactions of interest. Analyzing the research helps to understand the exact conditions and circumstances needed for the reactions as well as the outcomes. As such, the following Table 3 summarizes the relevant research conclusions that should be considered.

3.4 | The Li-Cy: Against the current and the alternatives

After discussing each step of the proposed Li-Cy, it is worth briefly discussing what it is supposed to replace/enhance and the other currently researched technologies in the separation of CH_4/N_2 gas mixture. After a literature review of the most recently published work in the last couple of years, the most prevalent technologies are summarized in Figure 4, which classifies such technologies into physical, chemical, and gas hydrate formation. Hybrid technology is possible and is discussed by the work of Almomani et al.[5] who present several designs that incorporate multiple technologies into one LNG plant. The technology in the figure can all be operated in the hot section of the LNG plant (ambient temperatures), hence they are the best candidates for UNR, and more research is still being conducted into their selectivity and performance, so while they may not all be competitive with current practice, they are the focus of the scientific community in this subject.

Physical separation processes rely on differences between N_2 and CH_4 in terms of physical properties, such as volatility, van der Waals forces, and molecular size among others. The most important and commonly used technology in nitrogen separation from NG is cryogenic distillation, and it essentially consists of a series of heat exchangers, compressors, a refrigerant, and a distillation column in which the CH_4–N_2 stream is cooled to extremely low temperatures such that methane liquefies due to its BP of −162°C while nitrogen remains mostly gaseous due to its lower BP of −196°C by a refrigeration cycle that utilizes mixed refrigerants and propane, before being directed to the distillation column where they are naturally separated the same way as a regular distillation column (volatility differences), though at low temperatures, hence the "cryogenic" term. Cryogenic distillation is currently the go-to option for most operating LNG plants due to its well-established nature and reliability in achieving high-quality LNG with satisfactory heating values and energy recovery ratios. The main "problem" with such technology is, unsurprisingly, the vast amount of monetary investment due to the high energy demands of the liquefaction, which is ultimately manifested in fuel requirements. This problem is usually moderated by the utilization of nitrogen-rich methane gas streams as fuel, which are

TABLE 3 Summary of research literature on the three steps of the proposed cycle.

| Step	Literature work	Advantages or beneficial conclusions	Drawbacks, concerns, or areas of improvement
Nitridation	Gu et al.[14]	1. Specific semi-related scope of work, utilizing Li as an adsorbent for NG upgrading. 2. In 70 min of operation at 35°C and 0.1 MPa, a high purity methane stream can be achieved.	1. No experimental work was provided.
	Jain et al.[22]	1. A confirmation of the complete transition from Li to Li_3N, by the DSC profile, and XRD analysis. 2. The reaction was performed at 55°C and 0.8 MPa and was completed in 15 min.	1. Preheating Li to reduce the required pressure for the nitridation reaction, when lithium is exposed to air for hours, needs further investigation.
	McEnaney et al.[42]	1. Conversion efficiency calculations and XRD analysis confirmed the transition from Li to Li_3N. 2. Conversion efficiency reached more than 80%, after 0.5 h of reaction at 100°C.	1. The results of the conversion of the reaction are related to the NH_3 production, meaning that there are no separate results represented for the reaction, which could have been helpful in comparison with other approaches. 2. The complete conversion was only achieved when the reaction between Li and N_2 was for 12 h.
Hydrolysis	Jain et al.[22]	1. Well-represented setup that provides an easy collecting of LiOH. 2. A high value of Li_3N consumption reached 95% after the reaction was performed at 80°C.	1. The experimental setup requires a vacuum pressure, which can be hard to achieve in some circumstances. 2. It is mandatory to control the atmosphere of the reaction properly and to work with water vapor. 3. The setup needs modifications for it to work in continuous production and be applicable in the industry.
	McEnaney et al.[42]	1. High-accuracy analysis methods were applied.	1. The setup needs extra investigation for it to work continuously. 2. As this step was mainly focused on ammonia production, the LiOH yield was not elaborately demonstrated.
Electrolysis	Takeda et al.[26]	1. Cathode's current efficiency reached 84%–86%. 2. Using molten salts that do not have LiOH and a setup that prevents the direct contact of LiOH with generated Li.	1. At the graphite anode used, there was CO_2 generation. 2. Possible Cl_2 generation.
	Laude et al.[25]	1. No CO_2 generation. 2. KI solution test was performed, and it was found that No Cl_2 production on the anode confirmed no LiCl decomposition.	1. Not very high current efficiency, 37.9%, that needs improvement. 2. Chemical crossing in the Castner cell causes current loss. 3. Using molten salt that has LiOH as one of its components could be a reason for the low current efficiency. 4. The remaining moisture in the LiOH–LiCl mixture wasted 30 min.
	McEnaney et al.[42]	1. An average current efficiency to Li of 88.5% 2. This study pointed out experimental details for collecting Li from the electrolysis reaction and properly preparing it for the nitridation reaction. 3. Comparable value of total cell potential for LiOH. 4. Cell stability was tested. 5. Negative results for the Cl_2 generation test.	1. The used graphite rods can cause CO_2 generation.
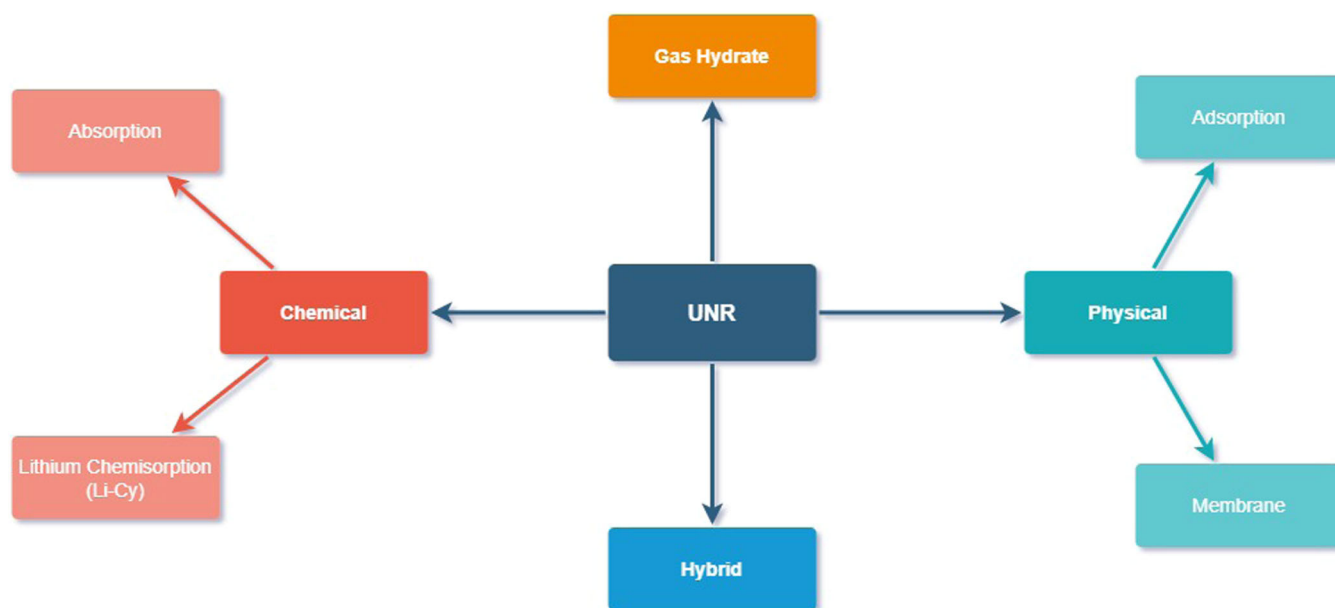
FIGURE 4 Different alternatives for upfront nitrogen removal (UNR) according to recent research.

produced at the LNG plant, due to having low qualities are not feasible to sell, but these can only do so much. Even when utilizing such gas streams for fuel demands, it is reported that most of the LNG plant costs are attributed to the cold section of the plant, which includes the liquefaction and distillation units. This technology's intense energy demands are the driving force behind the authors' proposal of the Li-Cy in which the nitridation of lithium is documented to occur at ambient temperatures, that is, in the hot section of the LNG plant. The Li-Cy would be able to remove nitrogen without the need for cooling, and if such technology manages to remove N_2 even partially, serious economic savings could be made, which will be further discussed in Section 4.

Once the appeal of removing nitrogen upfront before the cold section is understood, the remaining question to be laid is what the candidates for such a goal are. Most literature investigated focuses on two processes, namely adsorption and membrane technology, and a summary of the different options along with some of their reviewed performances is found in Tables 4 and 5. It should be noted that the numbers of the process performances are extracted from preferred papers, that is, work based on: (a) experimental results: as they are more representative of real scenarios and no assumptions or simplifications are made regarding the removal process and (b) N_2-containing mixture gas' separation process since research exists that investigates the removal of acidic gases among others, but for the sake of comparison with the proposed Li-Cy, our interest only lies in the separation between N_2 and CH_4.

Adsorption is driven by the van der Waals attraction forces between one of the NG components and the surface of the adsorbent, either natural or synthetic. Existing literature contains the usage of many types of materials for CH_4–N_2 separation, such as activated carbon,[56] zeolites,[54,55] metal–organic frameworks (MOFs),[51–53] and carbon molecular sieves (CMS),[57] and reviewed work published in the recent few years is summarized in Table 4. However, the selection process must be conducted carefully since they may (and do) differ in selectivity of which component. For example, Tu et al.[64] propose and test out a nickel-based MOF called Ni-BPZ for the separation of a binary mixture of CH_4/N_2, and the authors reported a methane selectivity and uptake rate of 6.6 and 1.56 mmol/g, respectively, at ambient temperature and pressure, and while this may initially seem competitive with other options, this study's adsorbate is methane and not nitrogen, which might make sense in the context of retrieving methane from coal mine gas (hence the binary mixture), but to enhance NG streams which are ~90% in methane content by the time they arrive in the adsorption unit, CH_4-selective adsorbents are highly uneconomical as large amounts of adsorbents would be required which would lead to high costs of both initial one-off purchase of adsorbent and the regeneration step. Unfortunately, much of the existing literature regarding adsorbents for the separation of N_2/CH_4 mixtures for the purpose of fuel enhancement prioritizes methane selectivity over nitrogen. Ghazi-MirSaeed and Matavos-Aramyan[57] target the rejection of N_2 utilizing silica-modified CMS derived from pistachio and walnut and achieve a relatively low

TABLE 4 Summary of results using adsorbents for N_2/CH_4 mixtures separation.

Adsorbent	Feed conditions	Favored component	Separation	Reference
MOF: Ni(4-DPDS)$_2$CrO$_4$	T: 25°C P: 1 bar CH$_4$:N$_2$: 50:50	CH$_4$	Selectivity: 7.3 Uptake: 0.95 mmol/g	Zheng et al.[51]
MOF: Co(AIP)(BPY)$_{0.5}$	T: 25°C P: 5 bar CH$_4$:N$_2$: 50:50	CH$_4$	Selectivity: 7.3 Uptake: 1.03 mmol/g	Zhang et al.[52]
MOF: SBMOF-1	T: 25°C P: 1 bar CH$_4$:N$_2$: 50:50	CH$_4$	Selectivity: 11.5	Chang et al.[53]
Zeolite: Ag-ZK-5(n)	T: 25°C P: 1 bar CH$_4$:N$_2$: 50:50	CH$_4$	Selectivity: 11.8 Uptake: 1.6 mmol/g	Kencana et al.[54]
Zeolite: NaY (Amine-modified)	T: 25°C P: 1 bar CH$_4$:N$_2$: 50:50	CH$_4$	Selectivity: 6.5	Wu et al.[55]
AC	T: 25°C P: 1 bar CH$_4$:N$_2$: 50:50	CH$_4$	Selectivity: 7.62 Uptake: 1.01 mmol/g	Li et al.[56]
CMS: Silica-modified and pistachio/walnut-derived	T: 25°C P: 40 bar	N$_2$	Selectivity: 2.1 Uptake: 8.8 mmol/g	Ghazi-MirSaeed and Matavos-Aramyan[57]

TABLE 5 Summary of results using membranes for N_2/CH_4 mixtures separation.

Membrane	Feed conditions	Favored component	Separation	Reference
CMS: PI-LPSQ	T: 35°C P: 1 bar CH$_4$:N$_2$: 80:20	N$_2$	Selectivity: 28	Yu et al.[58]
MMM: PBI-CLINOm	T: 35°C P: 3.4 bar CH$_4$:N$_2$: 90:10	N$_2$	Selectivity: 22.4	Montes Luna et al.[59]
MMM: ZIF-8@VR	–	CH$_4$	Selectivity: 3.1	Gu et al.[60]
MMM: CNTs/PES	P: 4 bar	CH$_4$	Selectivity: 1.62	Yousef et al.[61]
Zeolite: SAPO-34	T: 25°C P: 3 bar	N$_2$	Selectivity: 4.4	Alam et al.[62]
Zeolite: SSZ-13	T: 25°C P: 3 bar CH$_4$:N$_2$: 50:50	N$_2$	Selectivity: 13.5	Yanmei et al.[63]

selectivity of 2.1 though it is one of the highest regarding N_2 adsorption. This may also imply the superiority of CMS over other adsorbent materials when the to-be-rejected component is required to be nitrogen. The existing literature on using adsorption for N_2/CH_4 separation is also compromised by two additional crucial pieces of information: first, most of such research if not all conducts experiments on equimolar feeds, which is unrepresentative of NG in LNG before the cold section,

and second, many rely on numerical and theoretical calculations to determine mixture selectivities instead of experimental results. For example, the ideal adsorbed solution theory is often used,[53–56] which is a theoretical method commonly used to calculate said selectivities using only adsorption results for individual pure components, but such a method assumes homogenous gas molecules distribution on the adsorbent surface and similarity in surface area occupation for that of the

mixture molecule and the pure gas molecule, which was proven not to be necessarily the case in many systems.[65]

Membranes have also been investigated in the separation of NG components as summarized in Table 5 of the last two years in literature. Membrane technology is based on the rejection of certain components and permeation of others by semi-permeable "barriers" due to differences in molecular sizes of approaching gas components. While membranes are often traditionally made from polymers,[66] other options in recent literature look into other materials such as zeolites,[62,63] and increasingly, mixed matrix membranes,[59–61] which are synthetic membranes made from the combination of organic polymers with inorganic materials to enhance its performance and selectivity. Unlike adsorption, membrane technology does not require a regeneration step, making it more attractive economically, and more importantly, summarized reviewed research in Table 5 shows the membrane research to be more oriented toward the removal of nitrogen than adsorption literature. This is a positive aspect because the pressure drop across membranes is often significant, and it is preferred to preserve the methane pressure as high as possible to minimize required energy demands for compression in later stages, and for this reason, N_2 permeable membranes are more appropriate. Otherwise, when the membrane is CH_4-selective, it is essential to recompress the gaseous product afterward.[66] One criticism that could be levied against much of the currently existing research regarding membrane usage for nitrogen–methane separation is the method of determining the selectivity. Ideally, to get reliable results that could be made to argue in their favor, membranes would have to be experimentally tested with gaseous mixtures replicating compositions similar to those of the NG and then measuring the effluent concentration/composition to calculate the selectivity by the mol fractions method. Instead, it was more common to simply measure individual gas permeability through the membrane and use theoretically derived equations to calculate a hypothetical mixture.[60,61] The accuracy of these results is shaken by the deviancy of the experiments from realistic gas influents expected to be encountered in an LNG plant, and as previously stated, it is difficult to safely assume that individual gas molecules interact with solid phases the same way they would as a part of a mixture. This is proven by the work of Yanmei et al.,[63] who compare such "ideal" calculated selectivities with experimental results from mixture feeds and notice the ideal ones to be noticeably larger. The authors report an N_2/CH_4 selectivity of 13.5 for an equimolar gas mixture at room temperature and 3 bar. Furthermore, reviewed literature on membrane technology repeats

some of the flaws witnessed in adsorption, which are low-pressure values of the feed gas not representative of the NG stream in LNG plants and equimolar compositions in the rare cases where mixtures are tested instead of predicted by theoretical equations from individual gases permeation tests. According to Baker and Lokhandwala,[67] a selectivity of at least 17 toward N_2 must be achieved to reduce an NG stream from 10% to 4% N_2, and as of currently, this selectivity is rarely achieved by membrane technology despite its seemingly obvious superiority to adsorption. A selectivity of 28 was reported by Yu et al.,[58] but their mixture contained 20% N_2, making the selectivity calculated overestimated if compared to 10% N_2 NG. Montes Luna et al.[59] report a selectivity of 22.4 toward N_2, which does pass the threshold, which may suggest that innovations in preparing MMMs are the most productive pathway for this technology, but it is hard to say due to the insufficient amount of work investigating such issue as the material type with similar adsorption conditions. Membranes are reported to be most effective when multiple units in series are installed,[5] which will increase the cost of installation, operation, and maintenance of the technology while also increasing the recompression demands.

Though these are the most relevant in research, other technologies have been reported for the separation of N_2/CH_4 mixtures. One of the newer technologies in this application is the formation of gas-hydrates, which are in essence mostly water that is turned to ice by changing pressure and temperature while exposed to the target gases. Some of the gaseous components (methane) are trapped in the "cage-like" structure in the process, while other components are allowed to flow outside the hydrate container, therefore recovering the methane. Extracting the entrapped gaseous molecules is done by reversing the process, liquefying the hydrate, and releasing the gas. The most important and determining parameter in this process is the hydrate formation pressure, which is different for both nitrogen and methane. Though relatively new, gas-hydrate technology has been investigated in the enhancement of coal-mine gas containing low amounts of methane, increasing the methane molar fraction from 0.5 to 0.7 at 2°C and 10–14 bar,[19] The same quality improvement was also achieved at 4°C and 15–45 bar when using promoters (SDS and THF).[68] Sun et al.[69] utilized natural polyphenols as promoters and reported an almost doubled methane composition (34%–61%) and a methane separation factor of 5.31 at 1°C and 55–90 bar. The use of promoters is common in this technology to encourage hydrate formation and reviewed literature includes some examples of chemicals reported to enhance CH_4

recoveries, such as amino acids[70] and alkyl polyglucosides.[71] Although intriguing, gas-hydrate technology has not been proven from literature to process NG with relatively low nitrogen content (<10%) and most of the reported results deal with low-quality NG. More research is required in this area to study the technology's performance on UNR in the hot section of an LNG plant containing mostly methane and lower hydrocarbons with low amounts of nitrogen before making any confident state in the feasibility of the process. That being said, gas-hydrates were investigated for another purpose, though relevant to the subject of LNG, and that is the storage and transport of NG by using gas-hydrates as mediums, which are reported to increase the economic efficiency when compared to liquid phase storage and transport.[72,73]

Besides the physical processes discussed so far, nitrogen could also be removed chemically, and this always entails a chemical interaction occurring between some component of the NG with material brought in contact with it, either solid or liquid (solvent) phase. The most obvious and relevant example of this is the nitridation reaction, which is the first step of the Li-Cy proposed in this study. This process is advantageous over physical adsorption due to its highly selective nature of it. When exposed to both major gaseous components of NG ($CH_4 + N_2$), experimental results revealed that no methane sorption was detected while the nitrogen uptake rate calculated was 22–24 mmol/g,[16] which is magnitudes higher than most of those recorded in literature. This extremely high selectivity toward nitrogen is demonstrated by the energy of activation values for the reactions of lithium with nitrogen compared with methane, with the former having a lower value of 87 kJ/mol (compared to 106 kJ/mol).[14] In addition, the proposed regeneration of Li involves the hydrolysis of Li_3N, which produces ammonia (and possibly H_2).[22,42] The revenue generated from the sale of ammonia and/or H_2 has a significant economic benefit that can offset the cost of the electrolysis step and sometimes generate profit. Lithium nitridation does not require multistage operation as membranes do; however, it must undergo sorbent regeneration like adsorption, with the latter having no positive aspect/economic side products. With research regarding adsorption centered around methane separation, and membrane technology showing decreased separation performance at higher pressures,[5] causing the need for costly pressure reduction and copression, the Li-Cy is an option worth investigating for NG streams with low N_2 content in the hot section of the LNG plant, and Table 6 summarizes the comparison between the different separation technologies discussed in this subsection.

Another chemical option is N_2 absorption by transition metal complexes/chelating agents, which shows a promising future, although much like gas-hydrate technology, very little research is done in this area. Much like other previously mentioned processes, it is preferred for the nitrogen component to be absorbed due to the high volume of methane gas in NG. This method was investigated by Gilbertson et al.[78] more than a decade ago, and while the authors report the technical feasibility of using $trans$-$Fe(DMeOPrPE)_2Cl_2$ complex for the absorption of N_2 from N_2/CH_4 mixtures, they do not elaborate on performance parameters and no selectivities/separation efficiencies were provided. On the other hand, Li et al.[15] report an N_2/CH_4 selectivity in the range of 1.7–2.4 by K-$[Ru^{II}(EDTA)]$ depending on feed temperture and pressure at 30°C and 3–30 bar, respectively. The use of this technology's for nitrogen removal is severely hindered due to lack of interest in this kind of research. However, chelating agents were commonly used for wastewater treatment purposes[79-81] and medical applications.[82,83] Regardless, the absorption of N_2 by chelating agents under ambient conditions has a promising potential over the cold section nitrogen removal. As a result, more research is required to drwa firm conclusions about this process.

4 | ECONOMIC CONSIDERATIONS

The primary appeal of the proposed Li-Cy is the UNR in the LNG production line. Liquefaction occurs in the cold section of conventional LNG plants. In this section, the gas stream is mostly composed of nitrogen and methane. The gas stream is cooled by a complex web of heat exchangers, pumps and compressors, fractionation units, and phase separation units, which use the propane and refrigerant cycles. According to Pal et al.,[84] the energy cost of the cold section is reported to be approximately 60%. However, the cost can be optimized with improved resource management, structural design changes, and mathematical optimization techniques.

After designing a basic conventional cold section of an LNG plant, the researchers attempted to optimize the specific power consumption (SPC) of the section, which was a variable defined as the total amount of power (MW) needed for LNG production (MTPA). The researchers used the commercial simulation software Aspen HYSYS for the process design and the programming language MATLAB in which a particle swarm optimization (PSO) code was developed to maximize the SPC value of the plant. This program considered 27 parameters, including flow rate, temperature, pressure,

TABLE 6 Summary of the different technologies and candidates for UNR along with cryogenic distillation.

Technology	Description	TRL	Pros	Cons	Reported performance	References
Cryogenic distillation	1. Extreme cooling of N_2/CH_4 mixture gas utilizing propane and mixed refrigerants to liquefy methane while keeping nitrogen gaseous.	9[a]	1. Efficient and reliable. 2. Well-established.	1. Energy-intensive. 2. Investment demands are relatively higher. 3. Process design is more complex—must be given continuous care.	—	—
Adsorption	1. Selective attachment of a gaseous mixture component to the surface of an adsorbent due to weak van der Waals forces.	5–9[a]	1. Simpler regeneration of physical adsorption than that of chemical. 2. Can utilize cheap and/or natural adsorbents.	1. Most research done on CH_4. 2. Requires regeneration (no economic benefit). 3. Research favors its usage in coal mine gas treatment (low CH_4 content).	1. CH_4/N_2 Selectivity: 1.2–28. 2. N_2/CH_4 Selectivity: 1.32–2.1.	Chang and colleagues[53,57,74–76]
Membrane	1. Selective rejection of a gaseous mixture component by a semipermeable barrier due to differences in molecular sizes.	5–9[a]	1. Increasingly gaining traction. 2. Existing literature is oriented toward N_2 rejection. 3. CO_2 gas removal capability—can be used upstream to remove acid gas.	1. High N_2 selectivity is required to achieve a satisfactory product. 2. Multistage units may be required—higher installation costs. 3. Gas recompression may be required proceeding with treatment to maintain high pressure.	1. CH_4/N_2 Selectivity: 1.62–3.1. 2. N_2/CH_4 Selectivity: 4.4–28.	Yu and colleagues[58,60–62]
Gas hydrate	1. Primarily ice structures with gaseous molecules trapped in them upon formation by decreased temperature and/or increased pressure.	4[a]	1. Pressure requirements can be satisfied by high feed pressure. 2. Regeneration is easy—no need for a separate regeneration tank.	1. Relative Lack of research (novel subject for LNG plants). 2. Not enough promising results relevant to encountered NG. 3. Too high a pressure could cause hydrate formation containing nitrogen impurities.	1. CH_4 molar fraction increased by 40%–79%.	Dong and colleagues[19,68,69]

TABLE 6 (Continued)

Technology	Description	TRL	Pros	Cons	Reported performance	References
Absorption	1. Selective absorption of nitrogen component by chelating agents containing ligands and a transition metal molecule(s).	1–3	1. High N_2 selectivity due to chemical interactions. 2. Current literature regarding CO_2 absorption was shown to have similar nature.	1. Requires regeneration. 2. Severe lack of research on the subject. 3. The solvent may experience losses, which will increase costs.	1. N_2 selectivity: 1.7–5.8.	Li and colleagues[15,77]
Lithium chemisorption	1. Chemical nitridation of Li metal to form Li_3N upon contact with nitrogen under sufficiently moist conditions.	1–3	1. Highly selective toward N_2. 2. Significantly higher theoretical uptake rate (24 mmol/g). 3. The regeneration process produces ammonia.	1. Relatively novel for application of NG separation. 2. Requires regeneration. 3. The reckless operation could lead to a hazardous reaction (violent exothermic reaction with H_2O).	1. Uptake: 22–24 mmol/g.	Li[16]

Abbreviation: UNR, upfront nitrogen removal.

aExtracted from Almomani et al.[5]

and split fractions inside the section. The optimal model improved the LNG production capacity by 16 KTA and decreased the total power consumption and SPC by 4.83% and 5.52%, respectively. In addition, the optimized model reduced the compression power requirements for fuel gas and mixed refrigerants by 56.1% and 2.1%, respectively.

While these results are promising for the cryogenic distillation process, the potential energy savings are limited. In contrast, employing an NRU to remove nitrogen from the hot section could reduce the load needed for the expensive refrigerant and propane cycles, which are the main sources of the high energy requirements. As nitrogen is present throughout the entire cold section in high quantities, it significantly adds to the load in the cold section. Removing the nitrogen almost entirely or partially before entering the cold section removes the dead volume that it occupies and increases the LNG capacity of the plant. For example Almomani et al.,[5] reported preliminary engineering calculations that exemplified a removal of 70% of N_2 upfront at the hot section decreases the energy required for the propane/refrigerant cycle by 6.1%. According to the thermodynamic calculations, the required compression work (30% efficiency) for the upfront removal of nitrogen (70%) would require 55% of the energy. The researchers also highlighted how the modification to the process would lower the boil-off gas in the storage and shipping stages without impairing the fuel requirements in the plant.

Mkacher et al.[85] conducted a thorough experiment in which LNG optimization for cost PSO was performed. In the seven experimental scenarios there was a corresponding UNR of 12.5%, 25%, 37.5%, 50%, 62.5%, 75%, and 87.5%. In each of these scenarios, 11 variables including flow rate, temperature, pressure, and split fraction, were isolated to reduce the SPC and maintain the LNG production rate and high heating value (HHV) to satisfactory industrial specifications. The optimization technique indicated that removing 87.5% of the nitrogen in the NG stream upfront would lower the total power requirement and exergy losses by 0.24% and 0.23%, respectively. In addition, at optimal conditions, the plant can produce a 4.4% more LNG flow rate with an HHV of 1105 Btu/Scf.

Rather than replacing the conventional cryogenic distillation with a new method, using upfront removal before the cold section decreases the energy load. Ohs et al.[86] provide an example of an upfront NRU using selective membranes. The researchers conducted an economic analysis based on the mathematical optimization (integer programming) of methane selective and nitrogen selective membranes. The reported cost savings

were 40% under optimal conditions in comparison to conventional plants. However, membrane technology has a few disadvantages, such as fouling, low selectivity, and inverse selectivity. Adsorption is also an option, although it has similar problems with selectivity. In particular, most adsorbents are methane-selective, which would require large quantities of adsorbent for the NG stream and drastically increase costs. Lithium chemisorption has also been proposed and experimentally shown to achieve maximum nitrogen uptake rates[16] according to the reaction's stoichiometry at significantly lower costs because the reaction can be initiated at or below 100°C (hot section) following the moisture pretreatment. Currently, there is minimal research on the economic feasibility and challenges associated with operating a lithium-based NRU on a large scale as well as incorporating the process into an overall cycle that includes metal regeneration. However, this paper aims to address these issues.

Figure 5 illustrates the appeal of the upfront removal of nitrogen. The savings obtained in the cold section are more than enough to accommodate the UNR with a net profit. For the Li-Cy, the UNR unit also produces ammonia, which increases the economic value of the process but is not exhibited in the diagram.

Reaction conditions for the nitridation and hydrolysis steps in the proposed Li-Cy are not extreme. Neither step exerts pressure on the energy load. However, the opposite is true for electrolysis as costs are expected to increase for three main reasons. First, the feed flow to the electrolytic cell must be at a high temperature of up to 400°C, which requires heating energy. Second, the electrodes must either be replaced as the anode experiences corrosion or extracted as the cathode must have the solid deposits (i.e., layer) scraped off. Both of these procedures add to the maintenance cost and suggest that there is a need for more than one electrolytic cell to ensure continuous operation. Third, electrolysis requires a continuous supply of energy in the form of electricity to initiate the RedOx reactions, which produce lithium metal. As such, energy losses generated by Faraday/current efficiencies must be considered.

One common way to quantify the economic impact of the electrolytic cell is by determining the process energy demand, which is defined as the amount of energy (kWh) required to produce the lithium metal (kg). For example, Takeda et al.[26] performed LiOH electrolysis in their cycle of hydrogen storage, which included hydrogenation of lithium to produce LiH, and hydrolysis of lithium hydride to produce hydrogen and LiOH, and electrolysis of LiOH. The researchers conducted four experiments with different temperatures, initial LiOH added (mols), and electrolytic baths used (LiCl–KCl vs. LiCl–KCl–CsCl). The temperature, amount of LiOH, electricity passed, and current efficiency (η_c) of the cathode for the four experiments were 673°K, 673°K, 573°K, 573°K, 0.0194, 0.0297, 0.0196, 0.0301 mol, 1871°C, 2866°C, 1893°C, 2904°C, and 84.5%, 84.2%, 83.8%, 85.5%, respectively. The voltage for the two temperature points was 2.8 V for 673°K and approximately 2.9 V for 573°K. In addition, it is important to note that the reaction stoichiometry states that for each mol of LiOH used,
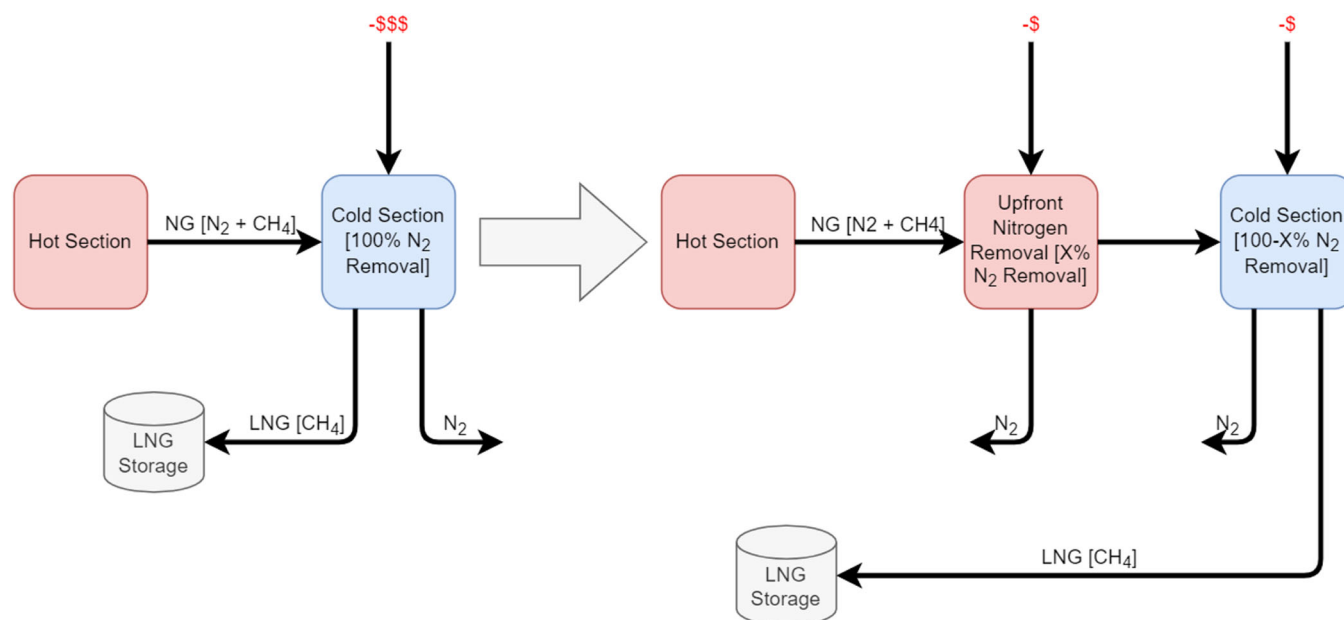

FIGURE 5 Block diagram visualizing the economic benefit of upfront nitrogen removal.

1 mol of Li is deposited. The energy demand for the electrolytic cell can be calculated using the equation provided by Takeda et al.[26]

$$\text{Energy demand} = \frac{\text{Energy used}}{\text{Lithium deposited}}$$

$$= \frac{V \times Q \times \frac{1\,\text{kWh}}{3.6 \times 10^6\,\text{J}}}{\eta_c \times n_{Li} \times M_{Li} \times \frac{1\,\text{kg}}{1000\,\text{g}}}.$$

After conducting these four experiments, the energy demand values were 12.79, 12.84, 13.38, and 13.10 kWh/kg Li, respectively. As expected, the energy demand is less at higher temperatures because higher temperatures have been reported to decrease the reaction potential required.[26]

Beyond exhibiting high theoretical nitrogen uptake rates, the proposed Li-Cy outperforms the competition by producing ammonia as a side product through the reaction of Li_3N hydrolysis. The produced ammonia could be directed toward another process to convert it into useful products that can be sold. However, this is a low priority for the LNG plant. Instead, produced ammonia can be directly sold to other manufacturers. Though, it is challenging to predict the revenue from ammonia and ammonia-based fertilizer as the market prices of these products have exhibited significant fluctuations over the years. At the time of writing data on ammonia for Qatar was not available, though Jiang[87] reports that the FOB price (Jebel Ali) in Saudi Arabia spiked to 870 USD/T as of December 17, 2021. This price is significantly higher than the average from the past two decades. The sudden rise in ammonia prices has been attributed to the arrival of the winter season and the decline in NG storage. Moreover, as of December 16, 2020, the ammonia prices from the US Gulf Coast, Middle East, and the Far East had estimated values of 1090, 1000, and 1020 USD/T, respectively.[88] According to Schnitkey et al.,[89] the price of ammonia (anhydrous) has increased by 278 USD/T as of July 2021. Identical patterns were observed for ammonia-based products, such as fertilizers and urea. The cost for all UNR technologies can be offset by a portion of the energy savings in the propane/refrigerant cycle and the Li-Cy. Furthermore, the production of ammonia can compensate for the cost of the electrolysis without the need to redirect the cold section costs.

A quick preliminary calculation can exemplify this point. In this scenario, we will assume the electrolysis energy demand is 13 kWh/kg Li[26] and the electricity price is 0.036 USD/kWh according to Qatar's standards for businesses, which yields an electrolysis cost of 0.468 USD/kg Li deposited in the cathode. To calculate the economic benefit of ammonia, the price is assumed to be approximately 800 USD/T. For the stoichiometric values, Equations (1) and (5) will be used.

Ammonia return (USD/kg Li)

$$= 800\frac{\text{USD}}{\text{T NH}_3} \times \frac{1\,\text{T NH}_3}{10^6\,\text{g NH}_3} \times \frac{17.031\,\text{g NH}_3}{10^6\,\text{mol NH}_3}$$

$$\times \frac{1\,\text{mol NH}_3}{1\,\text{mol Li}_3\text{N}} \times \frac{2\,\text{mol Li}_3\text{N}}{1\,\text{mol Li}} \times \frac{1\,\text{mol Li}}{6.941\,\text{g Li}}$$

$$\times \frac{1000\,\text{g Li}}{1\,\text{kg Li}} = 0.654.$$

As the calculations exemplify, the economic value of the produced ammonia (0.654 USD/kg Li) exceeds the cost of the electricity supply for the electrolysis process (0.468 USD/kg Li). These calculations are made with the assumption of complete conversion for nitridation and hydrolysis reactions, though they are not necessarily accurate for realistic applications. The price of ammonia can also fluctuate over weeks, months, or years. Thus, the exact value for the net profit is difficult to pinpoint.

Figure 6 highlights a cycle with an additional step that is similar to the one proposed in this paper. Li[16] provided a summarized economic analysis of the proposed regeneration loop. It consisted of the nitridation of lithium to lithium nitride, followed by the hydrolysis of lithium nitride to lithium hydroxide. Thereafter, lithium hydroxide is reacted with hydrochloric acid to produce lithium chloride. Then, it is electrolyzed to obtain lithium metal for reuse to close the loop. Li[16] made a few assumptions to make the calculation possible, including NRU feed specifications of $10N_2/90CH_4$ mol%, outlet gas specifications of $1N_2/99CH_4$ mol%, and an LNG production capacity of 5 MTPA. The nitrogen removal rate and the corresponding lithium requirement (from stoichiometry) were 99 and 149 tonne/h, which required three separate adsorption columns each containing 447 tonnes of lithium. The
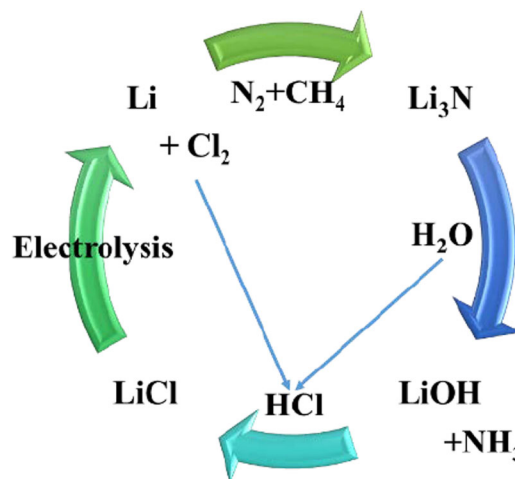

FIGURE 6 Lithium regeneration Loop as proposed by Li.[16]

TABLE 7 Summary of the main economic benefits and costs to be considered for Li-Cy.

LNG capacity (MTPA)	Ammonia production (TPA)	Ammonia revenue (USD)	Lithium consumption (TPA)	Electrolysis cost (USD)	Net profit (USD)
1	9.0E04	$72MM	1.1E05	$51MM	$21MM
2	1.8E05	$144MM	2.2E05	$103MM	$41MM
3	2.7E05	$216MM	3.3E05	$154MM	$62MM
4	3.5E05	$280MM	4.3E05	$201MM	$79MM
5	4.5E05	$360MM	5.5E05	$257MM	$103MM

Abbreviation: Li-Cy, lithium cycle.

cycle operated for 3 h and regenerated for 6 h. In addition, a one-time purchase of industrial-grade lithium metal for all the towers would cost USD 147 million assuming the price of the pure material is USD 110,000 per tonne. Moreover, the hydrolysis of Li_3N requires water, but this cost is negligible because water can be supplied internally from produced water in the LNG plant (e.g., dehydration). Ammonia is expected to be produced at a quantity of 1.05 MTPA, which would generate annual revenue of USD 421 million. In such process, HCl can also react with LiOH to form LiCl. The cost of this step is negligible because chloride is generated within the cycle in the electrolytic cell.

More important to this process is the cost of the electrolysis cell, which is manifested in the electricity demand. With a process energy demand of 8 kWh/kg for the electrolysis of LiCl and an electricity unit price of 0.033 USD/kWh with a methane gas turbine, the annual cost of the electrolysis is estimated to be USD 344 million for approximately 1.3 MT of lithium metal produced. The net annual profit using this Li-Cy is estimated to be around USD 77 million with the profit made from ammonia production and the cost associated with electrolysis considered. However, it should be stressed that these are preliminary calculations, and a more comprehensive economic assessment is expected to differ in many ways. For example, Li[16] assumes conversion in all reaction steps to be 100% as the values are extracted from stoichiometric relations. While this assumption can be somewhat validated by laboratory experiments, large-scale application of this technology would likely show that such high values are difficult to achieve. In addition, the price values can differ by location (i.e., a country's economy) and time (i.e., inflation). As of June 2021, the electricity price for businesses in Qatar was 0.036 USD/kWh and the average world electricity price was reported to be 0.124 USD/kWh. Considering Qatari prices is of greater relevance to this paper. As such, the electrolysis of LiCl would cost approximately USD 375 million, which would lower the annual net profit to USD 46 million. The ammonia market

price has also increased in value, which correspondingly increases the appeal of this process. The process is especially appealing if the market price continues to trend upwards or stabilize above 400 USD/T. Finally, the regeneration cycle proposed by Li[16] differs from the one proposed in this paper. It includes the reaction of LiOH with HCl to produce LiCl to be electrolyzed. In comparison, the proposed cycle electrolyzes LiOH directly, which is more economical. This difference also leads to different process energy demands, which as previously noted would be 13 kWh/kg Li as reported by Takeda et al.[26]

According to the rough calculations by Li,[16] there is an expected yearly ammonia production rate of 1.05 MT and a yearly lithium electrolysis demand of 1.3 MT. However, with more realistic numbers related to the type of electrolysis (13 kWh/kg Li), Qatar's electricity price (0.036 USD/kWh), and the current ammonia market price (800 USD/T), the annual electricity cost is expected to be USD 609 million with ammonia revenue of USD 840 million. This equals a net profit of USD 231 million.

Table 7 summarizes the main economic costs and benefits that have been calculated from preliminary calculations of the annual revenue and costs of ammonia production and lithium hydroxide electrolysis, respectively. These results are obtained from the hypothetical scenarios corresponding to LNG plant capacities of 1–5 MTPA. The conversions for all three reactions are assumed to be complete and the influent to the Li-Cy contains 5 mol% N_2 and 95 mol% CH_4, while the effluent specification is 99 mol% CH_4. Other than the complete conversion assumption, it should be noted that these numbers do not represent the ultimate profit value for the entire plant as doing so would require a more in-depth technoeconomic analysis of equipment capital cost, operation, and maintenance requirements, and adjusting to inflation for both basic scenarios (traditional liquefaction) and UNR, while also calculating the energy savings made in the liquefaction section, which was done recently by Pal et al.[90] These results merely represent the attractiveness of ammonia production as a side product when compared to electrolysis economic losses. Even if one

were to assume other costs associated with equipment installation and maintenance of Li-Cy would offset revenue made by selling ammonia, the main benefit of this proposed cycle remains to be the profits made in the liquefaction section in which high volumes of nitrogen no longer exists, which leads to lower costs of mechanical energy requirements in the refrigerant/propane cycle due to the decrease of the volume nitrogen previously occupied.

A more detailed technoeconomic analysis of using the Li-Cy was recently conducted by Pal et al.[90] and their findings are summarized in Table 8, which includes the profits calculated for the UNR in the range 12.5%–87.5% compared to the basic scenario where the stream is directly fed to the liquefaction cycle. The authors developed and the detailed cost analysis of the Li-Cy based on the process parameters extracted from Li and colleagues.[16,26,42,44,91-93] Although Pal et al.[90] resultsdo show that employing the Li-Cy on the LNG plant is feasible, several comments can be observed. First, some of the process parameters, such as the lithium bed L/D ratio and porosity, were assumed to be equal to beds from other studies that do not involve lithium. This goes against the fundamental idea behind how nitrogen from NG reacts with lithium to generate lithium nitride . Kherdekar et al.[92] determined the optimum L/D ratio for a catalytic water gas shift reaction bed, while Afzal and Sharma[91] assume the bed porosity to be 0.5 for a Ti bed for hydrogen storage, which is more forgivable for the lithium nitridation reactor due both being metals despite the differences in properties. In addition, the process parameters obtained from Li[16] such as ammonia prices and electricity costs are not based on the value reflected in Qatar, which would require modifications as previously stated. in addition, in the work of Li[16] three fixed bed reactors were proposed to be used; each has 3-h of operation and 6-h for regeneration, but they never explain the reason for such selection. Moreover. it was not justified whether or not the three beds are necessary. Finally, the results in Table 8 are based on the

complete conversion of lithium to lithium nitride. If the complete conversion is deemed impractical in large-scale applications of this technology, then additional lithium must be supplied to maintain the same nitrogen removal rates, and lower quantities of ammonia are expected to produce, which would lead to lower revenue from their sale.

To fully understand the economic benefits of the Li-Cy and how it compares with other UNR technologies, more research is needed, but this section highlights that from previous experimentation and analysis made for this process, along with some preliminary calculations made in this section, the novel Li-Cy process is shown to be a promising alternative/addition for the selective removal of nitrogen from NG streams in LNG plants.

5 | PROSPECTS, LIMITATIONS, AND FUTURE CHALLENGES

The performance of the proposed lithium-based cycle must be tested to ensure its reliability. This is accomplished by analyzing potential approaches and examining the strengths, limitations, and challenges. As such, this section summarizes the relevant research outlined in Table 3, including setup designs, outcomes based on the reaction conditions, useful analysis, calculation approaches, issues that should be avoided, and challenges to overcome. For the nitridation of lithium reaction, the theoretical work exhibited a binary mixture stream containing 10% nitrogen and methane, which can be effectively separated within 70 min at 35°C and 0.1 MPa by lithium (moisture-pretreated) with Li_3N received as a solid.[14] According to Jain et al.[22] the reaction can also be conducted at 55°C and 0.8 MPa and completed within 15 min. Another experimental work conducted at atmospheric pressure indicated more than 80% conversion from lithium to ammonia, which can be achieved after 30 min at 100°C.[42] Moreover, 100% conversion can be achieved after 12 h at 22°C.[42]

The reaction can thermodynamically proceed with 0.1 MPa; however, it needs to be initiated by a high pressure because it has an activation barrier.[22] Conversely, the lithium can be heated to a higher temperature, which reduces the needed pressure.[22] The temperature and pressure play a significant role in the reaction and the time it takes to complete. Thus, a decision must be made regarding the pressure and temperature range that should be experimentally tested. Though it is preferable for the reaction to occur at a moderate temperature and pressure as this requires less time and exhibits high values of conversion. A set of experimental trails can be started from an experiment conducted at atmospheric pressure and room temperature. Then, the conditions of the next experiment should have one parameter (e.g., pressure) that is constantly maintained and

TABLE 8 Percentage increase in annual profits based on the results from conducted by Pal et al.[90].

UNR	LNG price ($/MBTU)				
	7	9	11	13	15
12.5%	0.10%	0.16%	0.20%	0.23%	0.25%
25%	0.94%	1.00%	1.04%	1.07%	1.09%
37.5%	0.87%	1.02%	1.11%	1.18%	1.22%
50%	1.89%	2.09%	2.21%	2.29%	2.35%
62.5%	1.87%	2.15%	2.32%	2.44%	2.53%
75%	3.51%	3.62%	3.68%	3.73%	3.76%
87.5%	3.92%	4.07%	4.16%	4.22%	4.27%

Abbreviations: LNG, liquefied natural gas; UNR, upfront nitrogen removal.

the other (e.g., temperature) increased by small intervals while observing the conversion values and the time required for complete conversion. Thereafter, the effect of the previously constant parameter (e.g., pressure) should be studied by varying it and keeping the other parameter (e.g., temperature) constant. Again, the conversion time and values should be recorded.

The theoretical calculations and models can be conducted in parallel with the performed experiments to gain reliable insights into the accuracy of the experiments. The DFT is an example of theoretical work that can be conducted and used for reactivity analysis. The TP-KMC method can also be used for analyzing lithium separation from nitrogen in the NG stream.[14] Beyond theoretical methods, experimental analysis techniques are equally beneficial and essential for the confirmation of the lithium transition to lithium nitride. The effect of different reaction conditions on the nitridation reaction can be obtained using DSC and the product of the reaction can be identified using XRD.

The moisture pretreatment of lithium can support the nitridation step for the needed activation energy. The pretreatment step avoids the requirement for a high temperature and pressure by releasing the required energy to overcome the activation barrier.[14] The moisture pretreatment also creates active sites for the reaction to occur.[16] For the experimental setup, the nitridation of lithium reaction can be conducted in a DSC[22] or a purged tube furnace under the atmosphere of nitrogen.[42]

For the hydrolysis of the lithium nitride reaction, Jain et al.[22] showed that the most optimized conditions were 80°C and 0.1 Pa with a 95% consumption of lithium nitride after 2 h. More than 80% of the conversion from the lithium sample to ammonia can be achieved after 30 min when the nitridation reaction is conducted at a temperature of 100°C under an atmospheric pressure nitrogen stream.[42] In addition, an experimental setup can act as a reactor system with a closed chamber and vacuum pressure of 0.1 Pa, which produces water vapor to react with the lithium nitride placed above it.[22] A scintillation vial that contains 10 ml of deionized water can also be used.[42]

However, both setup configurations need further modification because they seem to be impractical. For instance, vacuum pressure is energy-demanding and the reaction of lithium nitride with water is not advisable. Using liquid water in the hydrolysis reaction causes an immediate dissociation of the ammonia formed in situ and the remaining ammonia is dissolved in water because the reaction is highly exothermic.[22] As such, the hydrolysis reaction requires more work as the setup and conditions cannot be confirmed. Additionally, the authors mention the pressure inside the reactor increased significantly from 0.1 Pa to 0.8 MPa, which when considering the application

in an LNG plant where the dehydration unit before the Li-Cy can vary between 70 and 200 bar[50] is very worrying. This increase in pressure is explained by the evolution of large amounts of hydrogen gas besides ammonia in the product inside the closed reactor chamber, which the authors suggest is the result of water reacting with pure lithium, but given the sample, they performed the reaction on is almost pure lithium nitride (≥99.5%), it is still odd and yet unexplained how such quantities of hydrogen gas were detected by gas chromatography. Nevertheless, because the pressure increase is caused by the production of gaseous products, such pressure changes inside the reactor in the proposed cycle could easily be controlled by continuous extraction of the evolved gases to maintain operating pressure at acceptable levels, and in the rare case of an emergency (pressure build-up) by pressure relief valves. While not the goal of the proposed cycle, if the production of hydrogen is confirmed to be inevitable under this pressure, it could serve as an additional economic benefit, seeing how hydrogen as a source of alternative fuel is picking up speed.[94,95] Although in this study the hydrolysis of lithium nitride reaction is proposed by reacting lithium nitride with water, other research has highlighted the reaction between lithium nitride and other sources of protons, such as sulfuric acid[96] and ethanol.[97] Furthermore, H_2 was used to react with lithium nitride to produce ammonia.[21,24] However, the other product from the reaction was not lithium hydroxide; consequently, the third step in the cycle was quite different from the electrolysis of lithium hydroxide. For future research, the hydrolysis reaction requires greater analysis as well as the examination of possible alternatives to water as the source of protons for the hydrolysis reaction.

Two analysis approaches can be used for this reaction including a gas chromatography system connected to the experimental setup to analyze the reaction products, and XRD analysis to identify the products after the reaction.[22] Two analysis techniques can be conducted at this stage. First, UV-Vis spectroscopy is used to detect and verify the presence of ammonia. Second, FTIR spectroscopy helps to confirm that the generated ammonia comes from the nitrogen provided in the experiment and not from other sources.[42] Further research should be carried out to understand the possibility of applying these techniques to identify the presence of ammonia and lithium as well as to confirm the source of nitrogen is the one supplied for the experiment. In addition, as a safety precaution, reaming lithium in the lithium nitride sample used for hydrolysis can cause a violent reaction.[42] Before the hydrolysis reaction, ensuring the full conversion of lithium to lithium nitride is essential.

For the electrolysis of the lithium hydroxide reaction, the potential diagram was constructed for a Li–O–H

system depending on the thermodynamic data, as shown in Figure 7. It showed that obtaining lithium from lithium hydroxide requires no direct contact between them because the deposited lithium reacts with the lithium hydroxide to generate lithium oxide and hydrogen.[98] As described by Equation (11), the lithium oxide precipitates on the cathode, which affects the normal accumulations of produced lithium on the cathode.[27] To explain, for the experimental setup, the lithium hydroxide must only be placed on the anode to ensure there is no interference with the lithium deposition on the cathode. In addition, there is concern regarding the handling of lithium hydroxide as it can easily absorb carbon dioxide from the atmosphere.[98]

For the obtained outcomes, a current efficiency of 37.9% was achieved by the lithium hydroxide electrolysis at 380°C using the molten salt LiOH–LiCl (70%–30% mol $\pm$ 1%) mixture.[25] In comparison, a cathode current efficiency of 84%–86% was obtained using LiCl–41 mol% KCl or LiCl–17 mol% KCl–26 mol% CsCl as the molten salt, which has a high decomposition potential for the electrolysis of lithium hydroxide at 548–673 K (274.85–399.85°C).[26] Although the molten salt mixture of LiCl–KCl/LiOH–LiCl has lithium hydroxide as a component, an 88.5% current efficiency was achieved for the lithium yield, while the lithium hydroxide electrolysis was held between 400°C and 450°C.[92] This o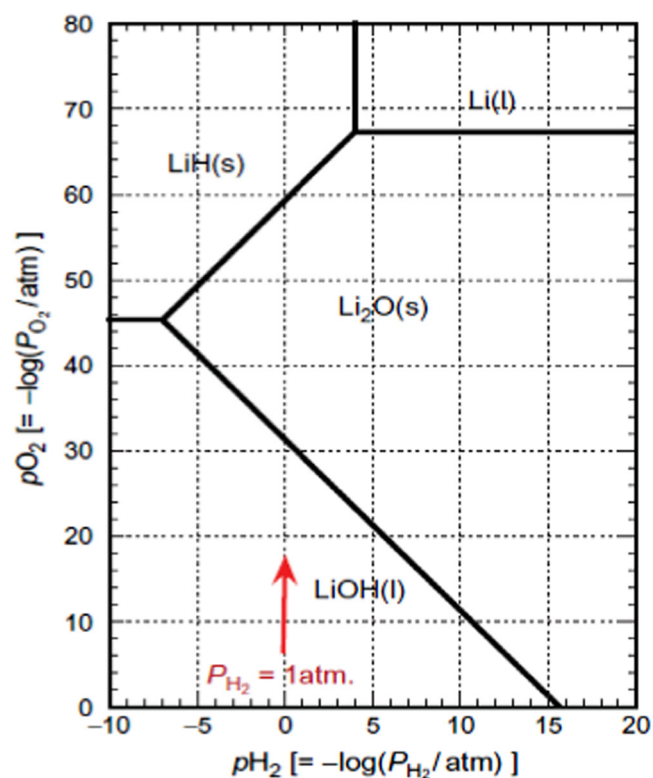ccurred because the experimental setup was designed to effectively separate the lithium product from other components in the electrolysis cell to avoid potential side reactions. The molten salt mixture used for electrolysis that does not contain lithium hydroxide can mitigate undesirable side reactions and produce a relatively high current efficiency. However, the current efficiency may be higher if there is the addition of lithium hydroxide in the molten salt mixture. This would ensure there is no direct contact between the produced lithium and lithium hydroxide.

For the experimental preparation, the molten salt preparation is highly dependent on the molten salt mixture, which each has a unique melting point. The melting points for LiOH–LiCl (70%–30% mol $\pm$ 1%), LiCl–41 mol% KCl, and LiCl–17 mol% KCl–26 mol% CsCl are 325°C,[48] 355°C, and 260°C,[11] respectively. The molar ratio for the molten salt LiOH–LiCl (63%–37% mol) has a melting point of 275°C.[100] The complete dehydration of lithium hydroxide must also be ensured,[25] as it may negatively affect the electrolysis, which can be verified by XRD analysis.[26] In addition, the experimental setup plays a vital role in the electrolysis reaction. It can be a quartz reactor surrounded by an electric furnace with an alumina crucible inside it to contain the molten salt.[25,26] It can also be an alumina crucible inserted into a heating tape or mantle in a cylindrical shape containing all the parts.[42]

Moreover, an essential part of the electrolysis cell is the electrode, which is primarily comprised of three electrodes, including the cathode, the anode, and the reference electrode. Some electrode materials may be cause for concern such as nickel and graphite anode electrodes, which may cause corrosion when working with molten hydroxide.[42] A graphite anode can also produce carbon dioxide emissions.[26] There are multiple analysis and measurement techniques that can be used, including cyclic voltammetry measurement to measure the potential between the electrodes, reacting lithium with water to determine the amount of lithium produced from the hydrogen generated, $Ba(OH)_2$ solution test, and/or gas chromatography to assess the generation of CO_2 (if needed), XRD analysis to measure the product phase, KI solution test to ensure there is no decomposition of the LiCl, and DSC to observe the formation of lithium around the cathode.[25,26]

Several strategies, conditions, and analysis techniques have been identified for future research, though further investigation is required to determine whether they are appropriate for implementation, and what, if any, substitutions or modifications are required. Challenges and limitations within the three steps have also been clarified. A summary of these important points is provided in Table 9. Moreover, future research should

FIGURE 7 Li–O–H system's potential diagram.[99]

TABLE 9 Summarized points for future work.

	Reaction conditions	Setup	Possible analysis methods or calculations	Challenges	Limitations
Nitridation	1. Start with moderate values, and increase by small intervals, while observing the time and the conversion values. 2. Experimental setup for moisture pretreatment.	1. Differential scanning calorimetry or N_2 purged tube furnace.	1. Theoretical: DFT and TP-KMC 2. Experimental: DSC and XRD	1. Lithium surface activation. 2. Preheating lithium if it was exposed to air for a long time and no moisture pretreatment applied.	1. The activation energy of the reaction if no moisture pretreatment for lithium. 2. Handling moisture-pretreated lithium.
Hydrolysis	1. Reaction with water vapor instead of water under a controlled atmosphere or using another source of protons (not confirmed).	1. Reactor system with closed chamber or Scintillation vials (not suitable setups and need modifications).	1. Gas chromatography system analysis. 2. XRD analysis. 3. UV-Vis and FTIR (not confirmed if suitable and needed or not).	1. Suitable experimental setup. 2. Give attention to lithium hydroxide rather than ammonia. 3. Confirm the usage of water vapor if water is the source of protons.	1. If the only way suitable found for hydrolysis is to apply vacuum pressure. 2. No lithium can remain in the lithium nitride sample.
Electrolysis	1. LiCl–KCl or LiCl–KCl–CsCl (at lower temperatures) molten salt mixtures. 2. Investigate if the molten salt mixture of LiCl–KCl/LiOH–LiCl would produce higher current efficiency or not. 3. The temperature held through the electrolysis depends on the molten salt mixture used.	1. Quartz reactor surrounded by an electric furnace or alumina crucible inserted in heating tape or mantle. 2. Electrodes choice that does not cause any or have very minimal corrosion or carbon dioxide emissions. 3. Molten salt preparation according to the melting temperature of the molten salt mixture.	1. XRD analysis to confirm no moisture available in the preparation steps. 2. XRD analysis for the phases of the product. 3. Reacting lithium with water to know the amount of lithium produced from the water generated. 4. $Ba(OH)_2$ solution test evaluation CO_2 emissions. 5. Gas chromatography to check for CO_2 emissions. 6. KI solution test to check the decomposition for LiCl. 7. Differential scanning calorimetry (DSC) for observing the lithium disposition.	1. Ensuring no direct contact between produced lithium and lithium hydroxide. 2. Preparing mixtures with no remaining moisture 3. Possible Cl_2 evolution. 4. Possible CO_2 emissions. 5. Li_2O precipitate on the cathode.	1. High-temperature demand for the reaction and the molten salt preparation. 2. Corrosion by nickel and graphite concern. 3. Handling of LiOH.

Abbreviations: DFT, density functional theory; DSC, differential scanning calorimetry; FTIR, Fourier transform infrared; TP-KMC, temperature-programmed kinetic Monte Carlo; UV-Vis, ultraviolet–visible; XRD, x-ray diffraction.

FIGURE 8 A potential setup of the three-steps Li-Cy for continuous operation.[42]
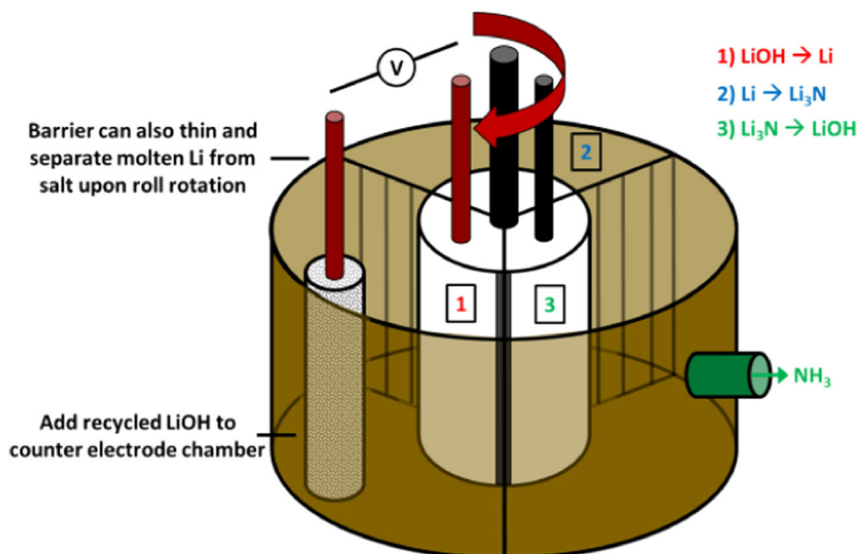
focus on approaches and techniques that can be applied to achieve continuous operating cycles. Primarily, attention should be given to the transportation and preparation of the product from one step to the next. For example, experimental work by McEnaney et al.[42] detailed the preparation required for lithium produced from the electrolysis step to be suitable for the nitridation step. Then, designing an experimental setup that connects the three steps and collects the side products for continuous operation should be considered. McEnaney et al.[42] also created an experimental setup for the three steps, as shown in Figure 8, but it needs some modification as it currently supports the reaction of lithium with water, which can cause violent reactions. Finally, achieving a setup for the three steps would help to determine how it could be transferred to a large-scale operation.

6 | CONCLUSION

To conclude, a lithium-based cycle was proposed for UNR from the NG stream as a substitution for the NRU. Typically, the NRU has a high cost of operation and complex maintenance. After providing a brief representation of the cycle and its steps, it was essential to review the chemistry of each reaction to provide the necessary background on the reaction types and conditions. Theoretical knowledge of the chemistry of nitridation, hydrolysis, and electrolysis affirms that such a cycle is possible, although attention to process design must be paid to account for heat generation and energy demands. Then, the applicability of the cycle was investigated by analyzing the relevant research literature and identifying the experimental and theoretical outcomes. Despite the

fact that there is little research has been conducted into the proposed cycle. However, some exist that discuss the three different steps either separately or together in the context of overall processes with different aims. It is concluded that each step, which was discussed in the chemistry section has been experimentally verified to occur, with some deviations regarding expected products, conversions, and efficiencies. Next, the economic feasibility of the cycle was examined, which indicated that the Li-Cy has some advantages. For example, ammonia produced in the hydrolysis reaction as a side product would provide a valuable economic benefit. The produced ammonia could cover the cost of electricity required for the electrolysis reaction plus a profit. In addition, the annual net profit for a plant incorporating the Li-Cy confirmed that the process benefits the overall economic aspect of LNG processing due to energy savings made in the liquefaction cycles. Finally, the outcomes highlighted in the research literature were combined to formulate guidelines that targeted areas of importance, such as reaction conditions, experimental setup, analysis approaches, challenges, and limitations to form a base for future studies.

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