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(REVIEW ARTICLE)

Blue ammonia an attractive pathway to decarbonize conventional ammonia plants

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Abstract

Ammonia is one of the basic ingredients for the fertilizer and mining explosive industries. Conventional ammonia production technologies have a high environmental impact owing to its high carbon dioxide (CO_2) emissions. This study evaluates the prospects of blue ammonia through integration of different available technologies within conventional ammonia plants: the Kellogg Braun & Root (KBR) Purifier process, Topsoe and the Linde Ammonia process. Carbon Capture and Sequestration (CCS) and Gas Switching Reforming (GSR) technology are attractive pathways toward blue ammonia due to cost effectiveness and ease of implementation. Blue ammonia technology development has its own challenges to overcome while it has massive advantages and opportunities like blue ammonia utilization as an alternative fuel, availability of pre-existing infrastructure available for storage, enhanced oil production through CO_2 pressurization. Given the increasing demand and international ammonia trade, advanced blue ammonia production from different available technologies like CCS & GSR offers an alluring way for natural gas exporting regions to contribute to global decarbonization.

Keywords: Blue Ammonia; Gray Ammonia; Decarbonization; Technologies; Carbon Capture and Sequestration; Gas Switch Reforming**.**

1. Introduction

Recent commitment by major oil producing countries toward decarbonization of the world economy (IEA. [1]) has increased the focus toward the development of low carbon energy vectors. Green and blue ammonia (NH3) production has received notable interest especially in the U.S., Europe and the Middle East as it constitutes a major component for production of nitrogen-based fertilizer (Lim et al. [2]) to feed the world. It has very good potential to be used as fuel in thermal power generation plants (Ezzat et al. [3]) and transport sectors (Hansson et al. [4]), especially ships/cargos considering its convenience for handling and storage (Bartels et al. [5]). It can be also used to produce H2 through thermolysis at the point of consumption (Cechetto et al. [6]). Existing ammonia production through conventional KBR, HT and LAP technologies are negatively contributing toward world CO_2 emissions. Thus, alternatives such as blue ammonia have been identified to overcome (Pereira et al. [7]) the inherent difficulties of handling CO_2 emissions of conventional ammonia plants. Carbon Capture and Sequestration (CCS) for decarbonization of conventional ammonia plants (Kolster et al. [8]) is suitable technology as CO_2 produced from this has a purity of 99%. Highly pure CO_2 can be liquified at high pressure and disposed of at suitable underground locations, such as empty reservoirs with a well-developed pre-existing infrastructure for transportation (Elishav et al. [9]). Additionally, highly pure CO_2 can be utilized in the beverage industry and, to a lesser extent, in the chemicals industry. An alternative option of installation of urea fertilizer complex is also considered to convert gray ammonia to blue. This endeavor requires energy inputs and large equipment thus making it challenging to implement and execute.

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Gas switching reforming (GSR) can be an alternative option, which also has the potential to reduce the CO_2 emissions from future ammonia plants. It has some inherent challenges like the operation of pressurized interconnected fluidized beds (Mattisson et al. [10]) and the undesired mixing of the outlet streams from each reactor (Wassie et al. [11]), which could negatively contribute toward emission reduction.

Considering blue ammonia as a pathway to global transition and decarbonization, interest is rising in conversion of the existing conventional ammonia plant to blue ammonia complex with CO_2 capture. Regarding blue NH3 production, CCS technology and urea fertilizer complex are the best available options to minimize CO_2 emissions. The primary strategy for reducing the carbon footprint of gray NH3 plants is enhancing effective CO_2 capture and its underground storage (Kolster et al. [8]) and utilization in the oil, beverage and urea fertilizer industries. One of the promising routes to accomplish this goal is the utilization of mostly pre-existing infrastructure available at underground reservoirs (Elishav et al. [9]) and well-established urea technology. Construction of complex plants to achieve the required purity and dew point is challenging. Recent studies evaluated various technologies and are well-suited to achieve the required purity for CCS and the beverage industry. These technologies have power and cooling requirements that can be achieved through integration with existing ammonia plant utilities. Alternatively, a dedicated wind/solar/fossil fuel power (IRENA [12], IRENA [13]) and water supply unit can be one of the substitutes. Similarly, the prospects of blue NH3 production depend primarily on the cost at which a sufficiently steady stream of liquid CO_2 with required purity is available, since it would reduce the overall profit margin of ammonia production. Given the rapidly falling costs of wind and solar power, this pathway is also attracting increasing research and demonstration interest.

Installation of urea fertilizer complex is also an attractive option as it's a value-added product that can meet world food requirements. Recently, a decline in the use of urea as fertilizer due to its detrimental impact on soil fertility and greater interest in the utilization of phosphate fertilizers by agriculture dependent economies left a question mark on the urea plant.

In this paper, the suitability of different technologies for blue ammonia production is assessed along with associated challenges and opportunities.

1.1. Conventional Ammonia Plants Technologies Overview

The first reference plant is the KBR (Kellogg, Braun & Root) purifier process (Pattabathula et al [14], (Gosnell [15]), schematically represented in Fig. 1. It consists of fired tubular Primary Reformer (PR) for Steam Reforming and Autothermal Secondary Reformer (SR) where N2 required for ammonia synthesis reaction is supplied through combustion of process gas with air in SR. A two-shift reactor train maximizes H2 production and CO_2 by Water Gas Shift Conversion (WGSC), followed by a CO_2 removal step, which produces a CO_2 stream with 99.5% purity for utilization in urea plant or storage. The subsequent methanation and cryogenic purification unit adjusts the make-up syngas composition suitable for ammonia production and removes inert like methane that would otherwise build up in the synthesis loop.

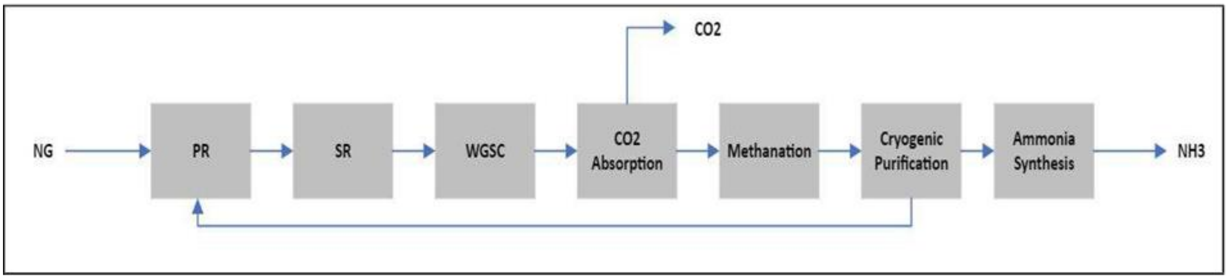

Figure 1 Block flow diagrams of KBR ammonia production technology

Topsoe ammonia process (Pattabathula et al [15]) is illustrated in Fig. 1. In comparison to the KBR process, it has no cryogenic purification step. Because of the high inert level in make-up syngas, there are significant synthesis loop purging requirements. To make system cost competitive, a hydrogen recovery unit downstream of synthesis loop is required to recover valuable hydrogen from the purge system and recycle back to the synthesis loop.

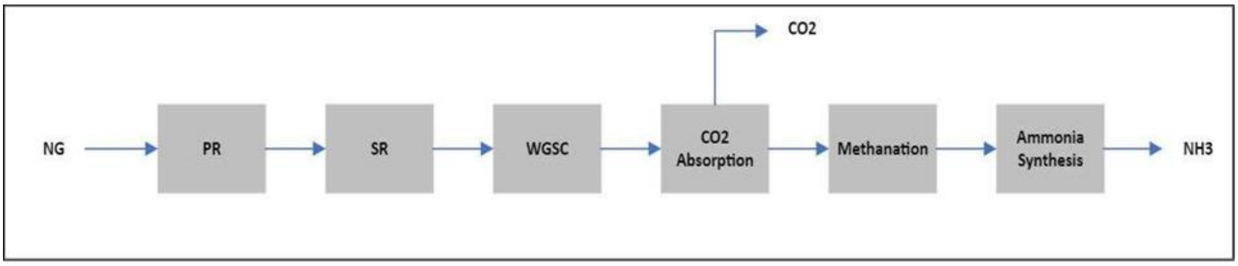

Figure 2 Block flow diagrams of Topsoe ammonia production technology

Linde Ammonia Process (LAP) is briefly illustrated (Pattabathula et al. [15], Linde-engineering [16]), in Fig. 3. In comparison to the KBR process, it only employs a primary reformer (PR), while the N2 for the ammonia synthesis reaction is generated in dedicated cryogenic inert generation unit (IGG). The process gas undergoes Shift Conversion (SC), which is an isothermal process followed by CO_2 removal through absorption. Syngas is further purified in a Pressure Swing Adsorption (PSA) unit to remove an inert and get a purified hydrogen and nitrogen gas mixture favorable for ammonia synthesis reaction. Thus, in comparison to the KBR process, there is no methanation step and the fresh make-up syngas quality is better in LAP and the synthesis loop purging requirements are reduced. All of the above three processes have an almost identical synthesis loop, with only Topsoe having an additional hydrogen recovery unit in the loop.

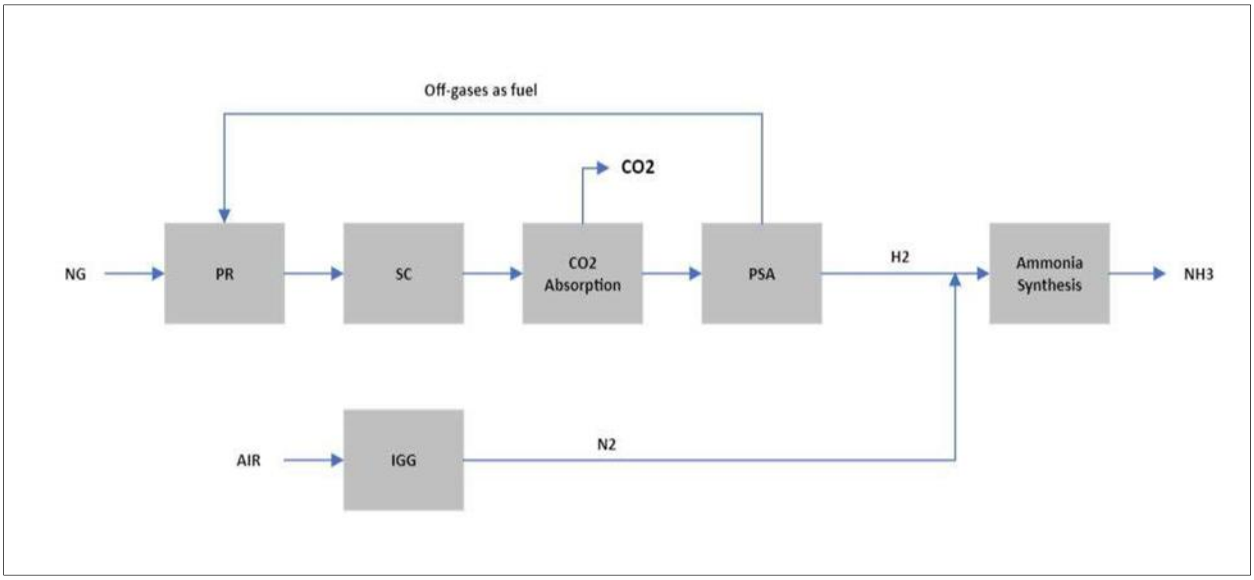

Figure 3 Block flow diagrams of LAP ammonia production technology

In terms of CO_2 emissions, it is evident that the LAP concept can only capture 76.3% of the CO_2 produced (Carlos et al. [17]) in the absorption section as PSA off gases have higher concentrations of methane recovered from syngas that is burned as secondary fuel. Higher carbon emissions arise from unconverted methane in the primary reformer with no secondary reforming ending up in PSA off gases, CO slip from the isothermal shift conversion and imperfect CO_2 capture in the absorption unit. The KBR and Topsoe concept accomplish a higher degree of capture by 6.5%-points in comparison to LAP (Carlos et al. [17]), in virtue of the higher conversion of CH4 and CO taking place in the Primary Reformer (PR) and Secondary Reformer (SR), and the conventional WGSC train respectively. Higher CO conversion results in higher CO_2 absorption and capture. Secondary reformer also reduces methane content in off gases generated from cryogenic purification.

2. Blue Ammonia Technologies

This section includes a more detailed description of the technologies that can be employed to reduce the carbon footprint of the conventional ammonia plants with emphasis on their characteristic features and suitability with respect to gray ammonia.

2.1. Carbon Capture and Sequestration

The Carbon Capture & Sequestration (CCS) process is investigated as a quick blue NH3 pathway for existing conventional gray ammonia producers (Kolster et al. [8]). In this scheme, as illustrated in Fig. 4, CO_2 – typically available at ambient temperature and pressure – is flashed off to remove water and other liquid droplets. Dry CO_2 gas stream is compressed to the desirable required pressure (30 Bar) and is cooled down in a cooler. Power, chilling ammonia and other utilities can be imported from ammonia plant utilities supply section, while recovered condensate can be recycled to the ammonia plant. Moisture contents of CO_2 needs further adjustment to avoid corrosion unless the system can be demonstrated to be non-corrosive (AS/NZS-2885 [18]). Two technologies for dehydration are the molecular sieve dryers that can achieve a dew point of 1ppmV (-72°C) and the glycol dehydration (Advanced) that can bring the dew point to 30ppmV (-52°C). As per European standards, a typical gas pipeline's acceptable dew point is 0.05ppmV (3 lb/MMSCF). The most suitable technology for dehydration of CO_2 is glycol with greater capacity for future enhancement flexibility. Conversely, molecular sieve dehydration has a fixed capacity with ease of operation as an advantage. The critical pressure of the CO_2 gas mixture is 73.47 bar, and the critical temperature is 29.47°C with a density of 285.37 kg/m3. Preferred operating conditions are supercritical/dense phase gas properties, which necessitate transportation pipelines must be operated at a much higher pressure and temperature. To attain dry gas with a squeezed dew point, CO_2 is compressed up to 150 bar in a multistage compressor and cooled in inter stage coolers and chillers up to 38°C.

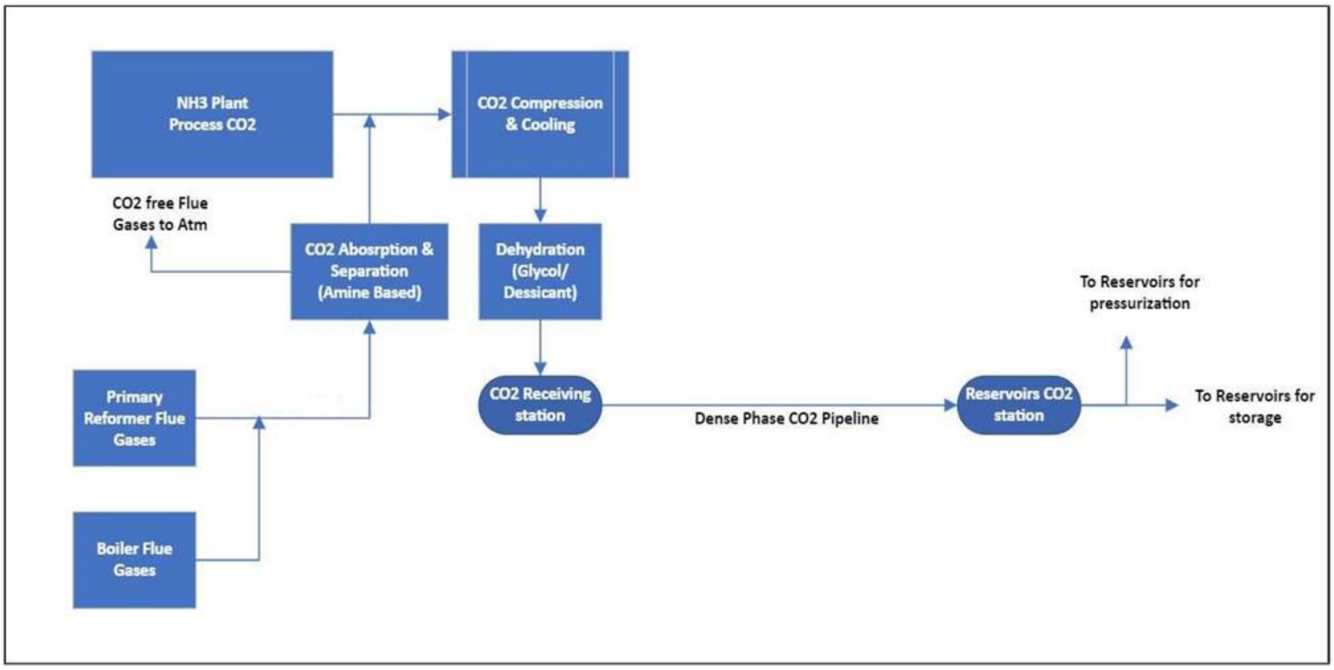

Figure 4 Block flow diagrams of CCS blue ammonia production technology

Flue gas streams available from gray ammonia plant's furnaces and boilers usually has a low CO_2 concentration, a low partial pressure, and a high temperature. In a specialized wash-water system, gas is pre-treated to cool down and remove NOx. Direct contact cooler lowers gas temperature through countercurrent water circulation and the product gas stream is made NOx free in a high-pressure amine-based absorption system. A CO_2 rich solution is regenerated in both the stripping section and absorption section where CO_2 lean flue gas leaves the absorber column at the top and is sent to the atmosphere as treated Flue Gas. Pure CO_2 with water contents are cooled down and flashed off in the flashing column to make it liquid free before its injection to the sequestration section at high pressure.

2.2. Gas Switching Reforming Ammonia Technology

The Gas Switching Reforming (GSR) NH3 process depicted in Fig. 5 is considered a long-term blue NH3 for future ammonia plants (Carlos et al. [17]). A cluster of dynamically operated fluidized beds produce syngas from the reforming, which undergoes a shift conversion to increase H2 yield and further purified in a Pressure Swing Adsorption (PSA) section. The flue gas stream from PSA is pressurized and injected back to the GSR as fuel, providing the heat for the endothermic reforming reaction. The compressed N2 stream resulting from the oxidation stage outlet is further cleansed and mixed with PSA step outlet H2 (Carlos et al. [17]). The resulting gas mixture is injected into the synthesis loop for ammonia production.

The GSR design also has a two-phase exchanger to maximize heat recovery from the reduction step outlet stream (Nazir et al. [19]). The S/C is controlled in GSR reactor to achieve required reforming reaction at 1000 °C. The GSR technology requires sophisticated heat management in its GSR reformer: owing to the high-pressure interaction between multiple inlet and outlet streams of the reformer. Hence, closer temperature approaches between streams is achieved due to higher heat exchange rates in GSR when compared to heat recovery from atmospheric pressure flue gases in a conventional reformer (Carlos et al. [17]). Additionally, the heat of N2 product from the GSR oxidation step can be utilized to preheat the inlet air and also produce superheated steam generated from synthesis loop of plant. The pressurized N2 stream is purified to remove moisture and CO_2 to ppm levels (Rege et al. [20]) and injected to synthesis loop at suitable temperature and pressure. The reformed gas from the GSR reforming step undergoes shift conversion to enhance hydrogen production and directed to the PSA unit for H2 recovery at high pressure (68bar) with further improve H2 recovery. GSR design has flexibility to include the methanation step before PSA but at the cost of overall low ammonia generation owing to hydrogen consumption in methanation (Pereira et al. [7]). The N2 stream is compressed in a compressor up to required synthesis loop inlet pressure and then mixed with the PSA H2 stream. This stream undergoes further compression (up to 150 bar) before conversion in the ammonia convertor in the synthesis loop. Heat generated in the shift reaction, GSR oxidation outlet and NH3 convertor synthesis reaction is used to generate high pressure (HP) steam required for power generation. High consumption of the air and PSA- off gas recycle compression demands a high-power input. Hence, the GSR-NH3 technology's overall electricity demand is the highest of the blue ammonia plants, against a much higher H2 production efficiency.

The GSR technology has efficiency of CO_2 capture of 94.4%, with main emissions originating from undesired mixing in the cluster outlet stream. This CO_2 is captured and vented during the purification of the main N2 stream, and through outlet stream of the Cryogenic Purification Unit (CPU). In terms of specific emissions (CO_2 per ton of ammonia), the GSR based concepts clearly outperform the reference benchmarks due to a higher degree of capture and lower natural gas feed requirements for the nominal production.

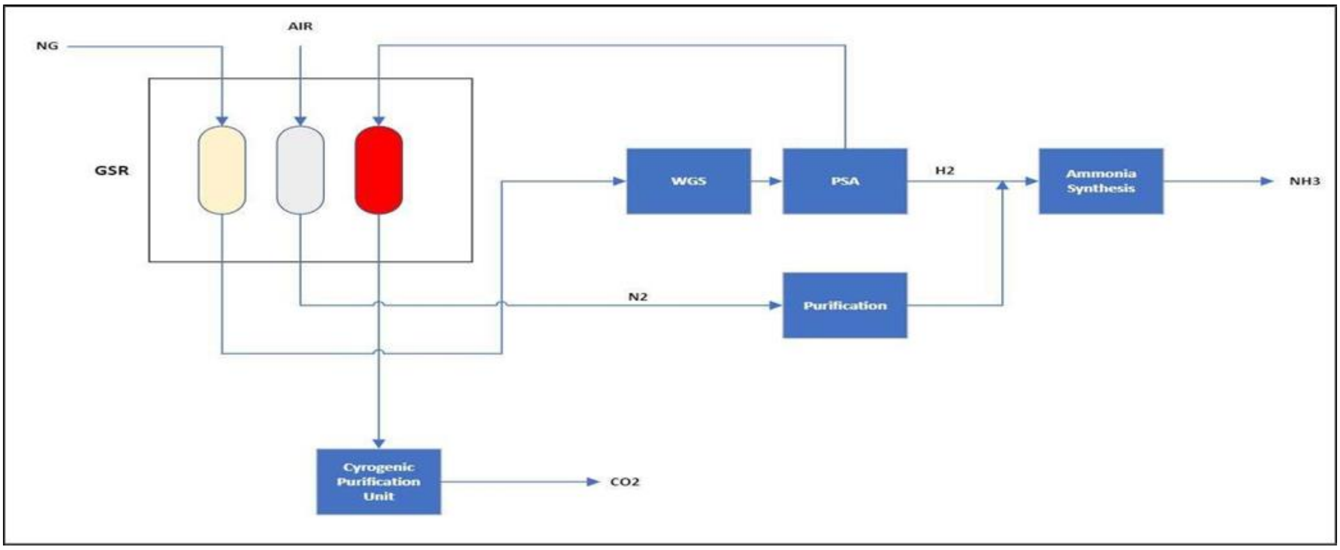

Figure 5 Block flow diagram of GSR ammonia production technology

3. Blue Ammonia Challenges

Most nations are constantly looking into creating new blue ammonia processes and converting existing gray ammonia plants to blue ammonia due to their strong commitment to decarbonization. Around the world, there are numerous initiatives and study projects underway to discover reliable and affordable blue ammonia technology. Although CCS and GSR technologies have promising futures, there is still much work to be done. Capturing all CO_2 emissions requires purity of CO_2 to avoid reliability and corrosion related issues in existing pipeline networks for reservoirs and demands further technological development. A lot of questions are still to be answered concerning CCS & GSR technology, especially sequestration with the required purity, operation of fluidized beds and heat recovery, respectively. Another crucial factor that should be considered and integrated into the new developing processes for blue ammonia is technology's impact on company business sustainability. Before being implemented on a large industrial scale, pilot technology houses are needed to demonstrate these technologies. Large piping networks for transportation of CO_2 at high pressure and low temperature emphasis on evaluation of carbon steel or stainless-steel or other materials suitability for required service. Major upfront and ongoing costs are involved for these technologies implementation to make them cost attractive.

CO_2 is difficult to capture and store, particularly from boiler and furnace flue gases. Flue gases are unsuitable to carbon capture processes because they have a low concentration and partial pressure of CO_2 and a high temperature. Carbon capture is heavily reliant on the partial pressure of CO_2 in the gas mixture; low partial pressure calls for significant effort and expensive infrastructure that is not cost-effective to make the investors appealing. A lot of research work is happening to find the right and economical solution for complete carbon capture from gray ammonia producers. Some available technologies from various renowned licensers are still in the design phase and its large-scale implementation is still to be validated. To transport the captured CO_2 under supercritical conditions, a sizable piping network is required. CO_2 moisture content, and other inert severely impair the stability and dependability of pipelines. Currently, worldwide operational CO_2 transportation networks are experiencing serious corrosion problems as a result of varying CO_2 supply quality from various CO_2 processes. More work needs to be done on standardizing the piping specifications to guarantee that they are appropriate for receiving CO_2 of varying qualities from various sources.

The task of effectively storing the captured CO_2 is difficult and necessitates more study and technological advancement. When CO_2 is stored under pressure in reservoirs, leaks from various places may cause CO_2 to escape into the atmosphere. Effective storage pathways require more research, especially in remote reservoir locations where there is little oversight and monitoring controls. The pre-selection of locations with lower susceptibility to leaks and damages could be one step in the right direction. This presents a significant obstacle for blue ammonia technology because efficient storing could fundamentally alter how the technology is applied.

High financial risks and expenses are involved on the road to blue ammonia. The reliable and economical technology must be developed, which will require significant financial flows. It may also be difficult to maintain the competitiveness of the ammonia industry given the significant capital and operational costs associated with the adoption of blue ammonia technologies. Although the cash flow from carbon credits may encourage efforts to adopt these technologies, the business owner still has to endure some costs that may have an effect on the balance sheets and revenues of the entire business. To meet the decarbonization goal for the year 2050, serious efforts must be made without regard to the financial effect. To save the world, major developed nations must take the initiative and make contributions to blue and green technologies.

4. Blue Ammonia Opportunities

Exploring a dependable and cost-effective technology for producing blue ammonia from gray ammonia is one of the key opportunity available in hand. Numerous technological advancements are anticipated to convert existing gray ammonia to blue ammonia on a big industrial scale, considering the potential it possesses and the quantity of work currently being done around the globe. It could also provide a breakthrough for blue ammonia technology that can be used for the future ammonia plants design. Since technological development is in initial stage, this could be great opportunity for fertilizers, O&G producers to investment more in this sector and become a leader in achieving a patent technology that could lead world to decarbonization. Collaboration between top businesses might be a means to advance blue ammonia technology.

The interest of developed countries in decarbonization may lead to the development of a sizable market for blue and green ammonia. It could also show a path to developing and under developed countries to decarbonization. In hindsight, this could be a big opportunity in the form of business diversification for leading fertilizers and O&G producers. Additionally, it also provides a pathway to shift world economy to renewable energy sources.

The possibility of using blue ammonia as propellant is another promising development. This could prove to be a fast track toward decarbonization, as proven technologies are available with respect to ammonia transfer, handling and storage. To decrease carbon emissions, a lot of technical work is currently being done to convert cargo powered by diesel to ammonia. The power sector in Europe, Japan, and Australia is actively working to replace fuel with ammonia. For gray ammonia plants, the capture of CO_2 generated from a fossil fuel burned in boilers and furnaces is difficult to attain, hence utilization of ammonia as fuel could solve this problem and reduce carbon emission from gray ammonia plants. Despite having lower energy content than carbon-based fuel, ammonia is still a desirable route with enormous potential.

Carbon captured from a blue ammonia facility can be used as an advantage in the form of increasing flow from reservoirs reaching to end of run (EOR). To get the greatest output, high pressure CO_2 provides sufficient power to push out from reservoir bottoms. Upstream oil exploration locations can bring about additional financial gains. Additionally, a fully depleted exploration site could be used as a CO_2 storage site for a blue ammonia facility, resulting in high carbon credits that would add value to the company's balance sheet and avoid the carbon tax.

5. Conclusion

This paper evaluates different technologies available to produce blue ammonia from several ammonia production plants using natural gas and/ or other carbon-based components as feedstock. Three reference plants using existing technologies were assessed as benchmarks: the Kellogg- Braun and Root (KBR) Purifier process, Topsoe and the Linde Ammonia Process (LAP). These reference plants create a basis of comparison of: Carbon Capture and Sequestration plant design and a gas switching reforming (GSR) plant design producing blue NH3 (natural gas fuel with CO_2 capture). The main conclusions drawn from the study are summarized as follows:

- The KBR and Topsoe plant have higher potential for carbon capturing compared to LAP plant. CCS technology looks attractive with 80% of CO_2 emission reduction from conventional ammonia plant. This option with ammonia as fuel could result carbon capture comparable to GSR technology.
- The GSR technology also looks very promising and need further research work to achieve maximum carbon capture for blue ammonia. The CO_2 capture attained by GSR makes it attractive as a low-carbon hydrogen production technology, while additional benefits are derived for NH3 synthesis from the co-production of a high-purity N2 stream. It has potential to achieve considerable cost reductions relative to conventional process routes and that these plants will remain more cost competitive.
- There are few challenges to overcome for attaining blue ammonia from gray ammonia, especially finding right technology that is most suited for gray ammonia plant with respect reliability and cost-effectiveness. Other challenges like capturing CO_2 from flue gas and storage in empty reservoirs are major barriers to be crossed to attain reliable and cost-effective blue ammonia solution.
- Blue ammonia itself present many opportunities for investment in form of its massive potential for further research work to obtain optimum solution for future global blue and green ammonia market.

Ammonia has a lot of potential to evolve into a carbon-free fuel in the future because its industrial synthesis is well-known, it is simple and inexpensive to transport and store, and it already has a sophisticated pre-existing infrastructure. In areas like Saudi Arabia with the least expensive energy input, blue ammonia will be a more appealing choice. Blue NH3 may present a cost competitive export energy vector alternative to LNG, even at mild CO_2 carbon credit pricing. Additionally, with increased regulations on carbon-based fuels and the implementation of carbon taxes, commitment to decarbonization can only be accomplished through blue ammonia produced by conventional gray ammonia plants while keeping sustainability of businesses in mind.

Compliance with ethical standards

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Disclosure of conflict of interest

The authors have no conflicts of interest to declare. All co-authors have seen and agree with the contents of the manuscript and there is no financial interest to report. We certify that the submission is original work and is not under review at any other publication.

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