



Review article

Decarbonization in ammonia production, new technological methods in industrial scale ammonia production and critical evaluations

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ABSTRACT

With the synthesis of ammonia with chemical methods, global carbon emission is the biggest threat to global warming. However, the dependence of the agricultural industry on ammonia production brings with it various research studies in order to minimize the carbon emission that occurs with the ammonia synthesis process. In order to completely eliminate the carbon emissions from ammonia production, both the hydrogen and the energy needed for the operation of the process must be obtained from renewable sources. Thus, hydrogen can be produced commercially in a variety of ways. Many processes are discussed to accompany the Haber Bosch process in ammonia production as potential competitors. In addition to parameters such as temperature and pressure, various plasma catalysts are being studied to accelerate the ammonia production reaction. In this study, various alternative processes for the capture, storage and complete removal of carbon gas released during the current ammonia production are evaluated and the current conditions related to the applicability of these processes are discussed.

In addition, it has been discussed under which conditions it is possible to produce larger capacities as needed in the processes studied in order to reduce carbon gas emissions during ammonia production in order to provide raw material source for fertilizer production and energy sector. However, if the hydrogen gas required for ammonia production is produced using a solid oxide electrolysis cell, the reduction in the energy requirement of the process and in this case the reduction of energy costs shows that it will play an important role in determining the method to be used for ammonia production. In addition, it is predicted that working at lower temperature (<400 °C) and pressure (<10 bar) values in existing ammonia production technologies, despite increasing possible energy costs, will significantly reduce process operating costs.

1. Introduction

Ammonia production began in the 1910s when scientist Fritz Haber and engineer Carl Bosch developed methods as shown in Reaction 1 and later called the Haber-Bosch Process [1]. However, the related process remains the main industrial process for producing ammonia all over the world.



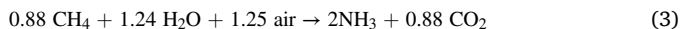
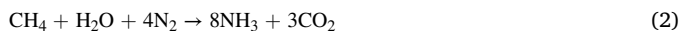
There are 2 main raw materials in the production of ammonia: Since nitrogen is used as a raw material in ammonia production, the nitrogen in the air is separated from the air by means of an air separation unit. As such, nitrogen and thus air can be considered as one of the raw

materials used in ammonia production. Nitrogen (N₂) in the air and Hydrogen (H₂) which can be produced from various sources [2]. In the early days of ammonia production hydrogen production by both water electrolysis powered by hydroelectric power plants and hydrocarbons are used [3]. Later, hydrocarbons became the preferred choice in industrial applications as technological developments and availability/continuity in supply favored hydrocarbons [4]. First plant that uses Haber-Bosch process had 20 tons/day ammonia production capacity but today, ammonia is produced around 170 million tons per year worldwide [5]. Production costs and energy consumption have been reduced from 110 kWh/kg to 7.7–10.1 kWh/kg [6], with the improvements in engineering and the increases in production scale over the course of 100 years.

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Natural gas and coal are the two main hydrocarbon sources used today to produce hydrogen and ammonia by the equations shown in 2 and 4.



However, hydrocarbon use in the process resulted a by-product, CO_2 as ammonia is a carbon-free molecule [7]. In the most efficient ammonia production factory, 1.6 tons of CO_2 is produced per ton of ammonia production, and the global CO_2 production average is 2.86 tons of CO_2 for each ton of NH_3 production [8]. Even though the operational efficiency improved significantly in the process since the early days, today ammonia causes 1.4% of total GHG emissions in the world [9]. Therefore, alternative ways to make ammonia production carbon-free by carbon capture and storage technologies or renewable energy powered water electrolysis are being developed and considered for future applications.

Ammonia is divided into 3 general categories according to its CO_2 emissions in the production without any specific limitations on the CO_2 amount released in the process [10]: Grey ammonia (traditional method, Haber-Bosch process) is produced via hydrocarbons as it is the mainstream application today, Blue ammonia follows the same route as grey ammonia in the ammonia production but uses carbon capture and storage (CCS) technologies to reduce CO_2 emissions, and Green ammonia uses renewable energy sources to generate hydrogen via water electrolysis (Figure 1).

Industrial hydrogen production can be carried out in several different ways, mainly depending on the availability of raw materials and the raw material chosen for the process [11]. The most used methods in hydrogen production can be listed as "Fossil Fuel Methods", "Electrolysis method", and "Thermal Chemical Method" [12]. Hydrogen production with Fossil Fuel Methods is mostly obtained from fossil fuels such as natural gas, petroleum products or coal, and the most used methods are catalytic steam reclamation of natural gas, partial oxidation of oil, steam iron treatment, and coal gasification [13]. On the other hand, electrolysis method, which is another hydrogen production method, is known as the simplest method for hydrogen production [14]. Ideally 1.23 V are sufficient for the electrolysis of water at normal pressure and temperature [15]. Theoretically, 2.8 kWh of electrical energy is sufficient for every cubic meter of oxygen, but in practice the amount of electrical energy used varies between 3.9-4.6 kWh per cubic meter of hydrogen production [16]. In the method of hydrogen production by Thermal Chemical Method, it is based on the separation of hydrogen in the water by using heat energy [17]. In this method, a temperature of at least 2,500 °C is required to decompose water with heat energy [18]. Here, instead of a one-step thermochemical treatment, several-step processes are envisaged [19]. As a result of the studies in this field, the required temperature in

multi-step thermal chemical processes was reduced to 950 °C, and the total efficiency was found to be 50% [20]. Studies on the thermo-chemical method are continuing intensively.

In the process of reforming methane with steam, the reaction between water and methane is an exothermic reaction and takes place in the presence of a heterogeneous catalyst [21]. This exothermic catalytic reaction between water and methane is the most important stage in hydrogen and ammonia production and can occur at high temperatures (320–450 °C) and low temperatures (200–250 °C) [22]. While iron-based catalysts are used in ammonia production processes at high temperatures, copper-based catalysts are used in low temperature applications [23]. Hydrogen and carbon dioxide released as a result of the reaction of water vapor and methane are formed [24].

Hydrogen gas formation as a result of reaction of water vapor and methane consists of three interrelated processes [25]; decomposition of methane, reaction of products resulting from the decomposition of methane with water, purification of the gases formed as a result of this reaction. Before all this reaction, desulfurization process is applied to prevent the possible interaction of sulfur in methane with the catalyst in the reaction medium. Hydrogen gas is used for desulfurization [26].

The hydrogen sulfide (H_2S) compound is then removed from the zinc oxide (ZnO) deposits, and after the preliminary treatment, the natural gas is sent to the natural gas vapor regulator at a pressure of 2.6 MPa [27]. This mixing gas is then transferred to high temperature conversion and low temperature conversion reactors. In these reactors, the water-gas conversion reaction converts 92% of carbon dioxide (CO_2) to hydrogen and is purified using a pressure swing adsorption (PSA) unit [28]. The regulator is primarily filled with PSA gases, but some natural gas is used to provide the fuel demand of the total regulator. PSA gases consist of CO_2 (55 mol%), H_2 (27 mol%), CH_4 (14 mol%), CO (3 mol%), N_2 (0.4 mol%) and some water vapor. Generally, the efficiency of the steam methane reforming system varies between 65-75% [29].

Carbon dioxide gas can be purged from hydrogen using various methods [30]. Separation and recovery of carbon dioxide by solvent absorption and stripping or adsorption and stripping on solid adsorbents are some of these methods [31]. Consisting of two reactors used consecutively, the PSA method stands out as the most advanced and economical carbon dioxide separation process used, today [32]. Pressure swing adsorption (PSA) method, which consists of two reactors used consecutively, stands out as the most advanced and economical carbon dioxide separation process used in hydrogen production process as a result of steam treatment of methane [33]. High pressure is applied to one of the reactors to keep carbon dioxide on the surface of a solid adsorbent such as activated carbon [34]. As a result of this process, pure hydrogen is released. Carbon dioxide is also released under low pressure in the second reactor. Then the flow in these two tandem beds is reversed and the cycle is started again [35].

If fossil fuels (coal, oil, and natural gas) are used to produce hydrogen, carbon dioxide is inevitable to be released into the environment [36]. However, carbon separation technology can be used to overcome this

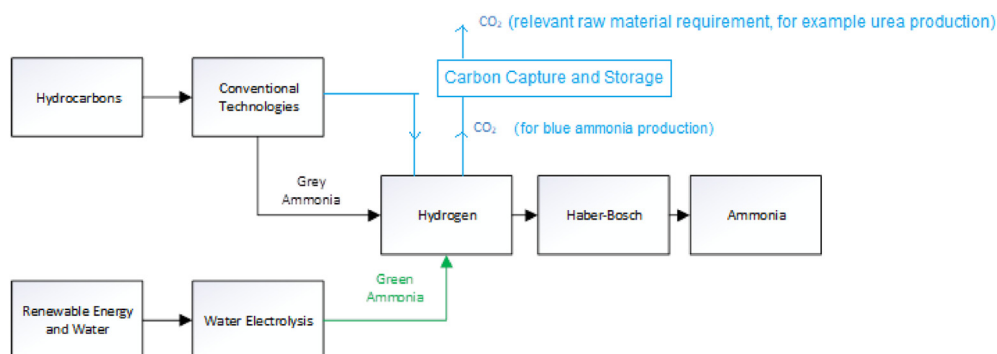


Figure 1. Technical classification and process technology according to carbon emission in ammonia production.

problem. Separating carbon consists of two main steps: capturing carbon dioxide emissions from a process and storing it safely underground or in the ocean (briefly capture and storage) [37]. In the production of hydrogen from natural gas with the steam-methane reformation process, 80–85% of the carbon dioxide captured adds an additional burden of approximately 25–30% to the cost of the hydrogen produced [38]. The energy use of the main steps in the carbon dioxide separation process is 3000 kJ, 281 kJ and 2000 kJ for capture, pressurization (80 bar) and transport (100–500 km pipeline), respectively [39].

2. Carbon dioxide capture technologies

Various methods have been developed to minimize carbon dioxide emissions while producing ammonia with the Haber-Bosch process, known as the traditional ammonia production method. These technologies are commonly known as "carbon dioxide capture systems". The realization of ammonia production by reducing carbon dioxide emissions with this method is known as the "Blue ammonia production process". The process differs from the Haber - Bosch process only in terms of the carbon dioxide reduction step. However, in processes such as the blue ammonia production process, it may be possible to use the carbon dioxide obtained by storing or keeping the carbon dioxide emission in different sectors such as "urea production" [40]. Among the technologies that can be used for carbon dioxide capture, amine absorption technology is the most common commercially available [41]. Amines are organic compounds and functional groups and contain only one pair and a basic nitrogen atom [42]. Alkanolamines separate carbon dioxide from the gas stream through the exothermic reaction of carbon dioxide with the amine functionality of alkanolamine [43]. Alkanolamines are divided into three groups as shown below [44]:

Primary amines → RNH_2 - MonoEhanolAmine (MEA)

Secondary Amines → R_2NH - DiEhanolAmine (DEA)

Tertiary amines → R_3N - MethylDiEhanolAmine (MDEA)

Another technique in carbon dioxide capture is that carbon dioxide from any gas mixture can be separated by cooling and condensation [45]. Cryogenic separation allows direct production of liquid carbon dioxide and is also suitable for long distance transport [46]. The disadvantages are that the amount of energy required to provide cooling is high for this proposed process, and some components such as water must be taken during the process to prevent the gas flow from cooling the blocks. However, the use of membranes for gas separation in carbon dioxide capture processes is an emerging process and has good potential for both purification and cleaning purposes [47]. Membranes are a wall that allows certain substances to pass, and they are specially prepared for any substance. Membranes used to decompose carbon dioxide are polymeric membranes, palladium membranes and zeolites [48].

Another technique uses an adsorption device rotary concentrator on solid. Some of the solid materials used in adsorption are as follows:

Activated carbons

Inorganic substances - activated aluminum oxide (Al_2O_3), silicon dioxide (SiO_2) gel, clays, zeolites.

Synthetic polymers, negative ion exchange polymers (styrene), positive ion exchange polymers (acylamine groups), acrylic ester polymers.

In pressurized swing adsorption (PSA), the gas mixture flows towards the packed bed of the adsorbent at increased pressure until the desired gas concentration reaches equilibrium. The bed is rearranged by lowering the pressure [49].

3. CO₂ storage methods

Another method developed to reduce carbon dioxide emissions during the production of ammonia with the Haber-Bosch process is known as

the CO₂ storage method. It has been technically developed as a system integrated into the carbon dioxide capture method and is designed for the natural use of stored carbon dioxide.

There are several alternative methods for carbon dioxide capture. These are to provide agricultural lands or forests capable of using carbon dioxide for their own nutritional needs during underground storage in geological formations, storage in oceans, solid mineralization or during photosynthesis [50]. Geological formations, oceans and forests are thought to have storage capacity of 300–3200, 1400–20 million and 100 gigatons, respectively. New sectors are needed to transport, collect and send carbon dioxide to the warehouse environment in the processes of capturing and holding carbon dioxide [51]. In addition to leaching, the carbon dioxide captured can be used in the development of oil remediation, the production of methane in coal deposits and to maintain pressure in depleted gas reservoirs [52].

Deep salt reservoirs are saline underground water basins that reach a depth of 800 m and allow carbon dioxide to be stored in dense supercritical form [53]. These watersheds are widely spread and often have gaps that can accept a limited amount of carbon dioxide. However, some of these basins have separate structures and allow for more storage as carbon dioxide dissolves slowly in water.

In "Increased Oil Recovery" as a CO₂ storage method, as a conventional improvement, even if there are more reserves, the pressure in the oil field pushes it to the surface and this pressure slowly decreases until it is over [54]. Carbon dioxide separated from the hydrogen production process can be injected to maintain water or gas pressure and increase oil extraction [55].

In the Coal Bed Methane Extraction method, Coal reserves generally have a high content of methane [56]. If the captured carbon dioxide is pumped into the coal mine, methane will be released because the chemical bonding affinity of the coal with carbon dioxide is better than methane [57]. This methane can then be used to generate electricity.

In Deep Ocean Injection as a carbon storage technique, the ocean is considered to be the unique stop of carbon dioxide in the atmosphere, but the system takes a long time to set up [58]. Therefore, the ocean injection method is seen as the accelerator of the natural process. Although the oceans have high potential for carbon dioxide storage, obstacles to this process include issues such as environmental, legal and public acceptance [37].

The carbon dioxide generated from the hydrogen production process can be transferred to targets to be thrown in compressed gas, liquid, solid or supercritical form at high pressure [59]. If the pipeline can be provided, it is generally more convenient to transfer carbon dioxide in supercritical form [60]. Although this method is shown as a new technology, it is predicted that the future amount of carbon dioxide that needs to be transported is higher due to concerns about climate change [61]. The pipeline can be difficult to set up and security problems can arise, especially in populated areas. In addition, the danger of pipeline damage from uninformed excavations can lead to inconveniences, insurance-related complexities, and reliability issues. Another issue is the problem of finding a suitable place for the disposal of carbon dioxide [62]. In cases where high volumes of carbon dioxide need to be disposed cannot be met by storage areas, international transport of carbon dioxide by ships may be economically and safely necessary [63]. This method also requires broader and more complex laws.

Oceans are areas that will store 85% of anthropogenic carbon dioxide emissions [64]. But this process happens very slowly. When carbon dioxide is injected into the near-surface levels of the ocean, the gas must be injected into deeper layers as it can escape back into the atmosphere [65]. This increases the cost. Another problem is that the pH balance changes when large amounts of injections occur. Injecting small amounts into different areas can overcome this problem. But again, it will increase the cost. What kind of changes the storage of carbon dioxide will cause in geological formations raises questions such as whether the technique has an adverse effect on the integration of the formation, or the storage is safe and environmentally acceptable [66].

The main problem with the geological decomposition of carbon dioxide found in oil and gas reservoirs is the potential for leakage due to both natural deterioration and damage to unused wells [67]. To overcome this problem, carbon dioxide can be transferred in solid form by forming a carbonate stone [68]. However, this process has financial difficulties. If existing technology is used, the carbon separation cost of unwanted carbon emissions ranges from \$100/tons to \$300/tons [69].

4. Electrochemical ammonia synthesis

One of the steps to reduce or completely remove the carbon dioxide released in the Haber-Bosch process, which is traditionally used for the production of anhydrous ammonia on an industrial scale, is to minimize the system pressure and thus reduce the carbon dioxide concentration. However, such a study would also serve to reduce the energy requirement of the ammonia production process. However, the latest effort to lower the pressure and temperature during ammonia synthesis has not yet solved the biggest problem of the Haber-Bosch ammonia production process [70]. Efficient use of energy is an important problem for all ammonia production processes, and research continues to solve the energy problem in processes such as electrochemical ammonia synthesis. This type of ammonia synthesis requires low pressure and low temperature compared to the Haber-Bosch process [71].

It has been determined that the energy efficiency of the electrolysis process applied during the electrochemical synthesis of ammonia is the same as the energy efficiency applied during the electrolysis of water. Efficiency defined here; It is directly related to pressure, temperature, circulation rate and insulation of the produced ammonia. The electrochemical synthesis of said ammonia is three steps; The electrolysis of water is the pressurization of hydrogen obtained as a result of electrolysis and the final ammonia synthesis [72].

Many different electrolytes can be used for ammonia synthesis by electrochemical methods. Liquid electrolyte group includes solid electrolytes that requires high temperatures such as polymer electrolyte membrane (PEM) and anion exchange membrane, and acidic electrolytes in liquid form, melt hydroxides and chlorine salts [73]. Electrolysis in acidic electrolytes can occur by the deposition of ammonium salts in solution, causing sudden changes in the pH of the solution. In addition, electrolysis in their solutions is hampered by the low solubility of nitrogen. Therefore, gas diffusion in electrodes is an important criterion for high production rates.

In the electrochemical synthesis of ammonia, precious metals, metal oxides, metal nitrides can be used for electrocatalyst purposes, depending on the physical state and pH of the electrolyte [74]. It has been reported that transition metal-free catalysts such as nitrogen-doped carbons and black phosphorus can also be used as electrolysis in such ammonia synthesis.

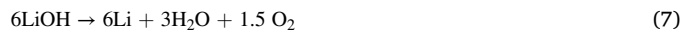
The use of ammonia selective catalysts to minimize nitrogen losses during ammonia synthesis by electrochemical method is important in terms of process efficiency and high ammonia synthesis [75].

Standard electrochemical potentials for reactions 1 and 2 are -0.057 V and 1.172 V. These potentials depend on the physical conditions and pH of the catalyst used. Nitrogen reduction reactors are more preferred for low temperature applications because hydrogen generation reactors are reactors that can be used instead of nitrogen reduction reactors [76]. However, the difference between the electrochemical potentials of reactions 5 and 6 decreases with temperature, and hydrogen generation reactors above 390 °C provide better thermodynamically efficiency.

Hydrogen generation reactors and nitrogen reduction reactors produce similar results in the electrochemical synthesis of ammonia [76]. However, the yield of reactions 1 and 6 results in a low conversion rate. This low efficiency is achieved with high energy consumption.

There are two approaches to reduce the underproduction problem in the hydrogen generation reactor [77]. The first is the choice of catalyst for these reactions in the presence of catalysts. For example, adding ZrO₂ to Ruthenium catalyst provides higher ammonia production efficiency. A

second approach is to reduce the amount of protons on the catalyst surface. This may be possible by using high pH electrolytes. Thus, the use of AEM catalyst results in higher yields than the use of PEM catalysts. In liquid electrolytes, it is possible to decrease the proton activity by increasing the salt concentration that forms the electrolyte solution.



Li salts at the anode and propylene carbonate at the cathode can be separated in various ways. Li accumulated at the cathode can react with nitrogen, reducing the nitrogen concentration [78]. The production efficiency in ammonia synthesis using Li ion is $1.88 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$, and the reaction efficiency can be expressed as 50%. The amount of energy needed by reactions such as 7, 8, 9 is more than the amount of energy required by the electrolysis of water for ammonia synthesis, and it is known that this energy consumption is more than the energy required in the Haber-Bosch process. The advantage of this process over a typical Haber-Bosch process can be expressed as investment cost and cheap energy generation.

In the production of electrochemical ammonia, there are many parameters that affect the reaction efficiency [79]. For example, the use of air as the nitrogen source and the moisture content of the air in a typical Haber Bosch process is an important parameter affecting the ammonia conversion rate. Using high purity nitrogen during the process will significantly increase ammonia production efficiency. Successful results were obtained at 180–260 °C with the use of nickel electrodes containing Fe₃O₄ and NaOH/KOH as another catalyst in the synthesis of ammonia by electrochemical method.

If the hydrogen produced by reaction 4 can be fed back to the cathode where it reacts with nitrogen through conventional reaction, it is possible to increase the yield of ammonia. However, combining plasma nitrogen activation and electrochemical ammonia synthesis can increase ammonia production efficiency by up to 100% [80]. Although there is no need to use any catalysts for such a reaction, the electrochemical current density is reported as 200 mAcm² and the energy consumed during the process as 2270 kWh. Such an electrochemical ammonia synthesis can be considered as an important alternative to the Haber-Bosch process, where chemical ammonia synthesis is primarily carried out, considering the amount of energy consumed and ammonia production capacity.

Today, although the production of electrochemical ammonia by alternative methods to the Haber-Bosch process takes place at very low capacity (10^{-9} to $10^{-11} \text{ mol cm}^{-2} \text{ s}^{-1}$), energy consumption is unacceptably high [81]. This is due to the high current density applied for hydrogen production during the electrolysis process. Until now, the highest efficiency in electrochemical ammonia synthesis has been achieved with reaction number 5. This reaction efficiency was achieved by adding Li₃N and alkali metal chlorides into the electrolyte.

5. Water electrolysis technologies with renewable energy sources

It is obvious that the carbon dioxide capture or carbon dioxide storage methods developed to minimize the carbon dioxide emissions that occur during the production of anhydrous ammonia produced on an industrial scale with the Haber-Bosch process will not provide beneficial results in the long run. In order to completely eliminate the carbon emissions from ammonia production, both the hydrogen and the energy needed for the operation of the process must be obtained from renewable sources [82]. Thus, hydrogen can be produced commercially in a variety of ways. These can be classified as proton exchange membranes, anion exchange membranes, or electrolysis of water. Many processes are discussed as potential competitors to the Haber-Bosch process. Besides parameters such as temperature and pressure, various plasma catalysts can be used to

accelerate the ammonia production reaction [83]. However, the rate of plasma catalyzed ammonia production is very low. It is uncertain how much energy will be unnecessarily used in an inefficient plasma catalyst and its cost. This entails three logical scenarios for a potential renewable ammonia production. As shown in reaction 5, hydrogen production can take place by electrolysis of water. In this form, it can be fed to the Haber-Bosch process after being oxidized to the required temperature and pressure value. Here, the electrochemical reduction of diazole in the presence of water is a system that does not require high pressure. Another hydrogen production scenario is the electrochemical synthesis of ammonia from reaction # 1 with renewable hydrogen production [84]. However, the usefulness of this system has not been proven yet.



Current research on ammonia production assumes that ammonia production is carried out with renewable energy sources. The pressure and temperature values at which the ammonia production reaction takes place requires an energy consumption of 100–200 MW. Today, the energy production capacity needed for ammonia production can be considered as 200 MWh for an average of 20 tons of ammonia per hour [85]. A typical Haber-Bosch process investment has a significant cost advantage over an ammonia plant operating with a renewable energy source, but it does not appear to be profitable for many producers. Energy production from renewable energy sources is limited in terms of resources and this can be seen as a disadvantage since it does not have the advantage of continuous operation such an ammonia production facility is associated with the power generation facility [86]. Unless a storage system is set up to compensate for the disruption caused by the lack of sun or wind, ammonia production from renewable sources will be considered as the disadvantage of this system.

In addition to all these, various techniques such as solid oxide electrolysis, Proton exchange membrane (PEM) fuel cells have been developed as hydrogen generation technology and the same technologies allow ammonia to be used as a clean energy source [87]. Production of hydrogen is accomplished using membranes such as proton exchange membrane (PEM) fuel cells, Deployable Membranes [88], and absorption-based systems [89]. Although these membrane technologies have different uses such as energy production, their use for hydrogen production is one of the most important processes studied for development. In hydrogen production technology in which the solid oxide electrolysis cell is integrated, hydrogen production takes place at high temperatures without using an air separation unit. The energy consumption of such a process is less than conventional ammonia production methods. Other technologies developed like these systems where hydrogen and therefore ammonia are used as clean energy sources at the same time, Proton exchange membrane (PEM) fuel cell, Alkali fuel cell (AFC), Solid oxide fuel cell (SOFC), Internal combustion engine (ICE), Boilers and Furnaces, and Combined cycle gas turbine (CCGT) are the most used efficient fuel technologies [6].

6. Haber-Bosch process improvement

Many research studies have focused on new methods to increase production efficiency by separating active catalysts and ammonia, thereby reducing pressure and temperature, thus reducing operating costs [90].

Commercial Haber-Bosch catalysts consist mostly of low ionization energy potassium activated iron [70]. Kellogg's advanced ammonia production process, an expensive ruthenium catalyst, is used as another ammonia production process [91]. However, in terms of efficiency, it did not find a wide enough scope of application to evaluate catalyst cost. In recent years, two new types of catalysts have been developed. It was concluded that the catalysts formed by the coating of calcium oxide and aluminum oxide on ruthenium and the triple bonds formed by N_2 with hydrogen could not be controlled in the synthesis reaction. The same result is valid for the ruthenium catalyst with iron content as with the ruthenium catalyst. It has also been reported that such a catalytic

reaction provides the highest efficiency at 200–350 °C under 1–10 bar pressure. The best catalyst recommended to be used for ammonia synthesis is Co-CNT-3Ba (NH_2)₂, and ammonia could be synthesized over 10 mmol $\text{g}^{-1} \text{h}^{-1}$ at 350 °C and 10 bar pressure. However, as an alternative production process, Kellogg's advanced ammonia production process, an expensive ruthenium catalyst, is used as another ammonia production process. However, in terms of efficiency, it has not found a wide enough scope of application to evaluate catalyst cost. Catalyst activity occurs between nitrogen, hydrogen and ammonia surfaces, and this activity is defined as the "Mars–van Krevelen Mechanism" [92]. Two new types of catalysts have been developed in recent years. It was concluded that the catalysts formed by coating calcium oxide and aluminum oxide on ruthenium and the triple bonds formed by nitrogen with hydrogen could not be controlled in the synthesis reaction. The same result applies to the ruthenium catalyst with iron content as well as to the ruthenium catalyst.

7. Conclusion

A Haber-Bosch ammonia production plant, designed and optimized with traditional features, consumes approximately 7.9 kWh.kg⁻¹ from fossil fuels. However, as the ammonia production capacity decreases, this production value does not decrease linearly, and energy consumption is expected to be higher due to increased heat losses. In ammonia synthesis by the electrochemical method, the amount of energy required for the electrolysis of water varies between 54 kWh and 44.7 kWh per kg H_2 , and its value corresponding to 1 kg ammonia production varies between 9.9 kWh and 11.5 kWh. If the Hydrogen produced in the process is produced through a solid oxide electrolysis cell that uses the heat of the process, the amount of energy needed will likely be even less.

In ammonia production technologies, the lowest amount of energy used is expected to be realized by electrochemical methods. Currently, the biggest cost share in ammonia production with the Haber-Bosch process is the amount of raw materials and energy used. While energy production costs are constantly changing in today's conditions, the approximate cost of Haber-Bosch production process for hydrogen production from fossil fuels is \$ 90 per 1 ton of ammonia, while the cost of hydrogen production by electrochemical method is \$ 232 for 1 ton of ammonia. However, with the rapid decline in renewable energy prices, the difference between renewable energy sources and energy production from fossil fuels will decrease and the importance of capital costs will increase. However, it is difficult to estimate the capital costs of new technologies. Nevertheless, it is clear that lowering the working pressure and temperature will reduce operating costs.

In conclusion, blue ammonia route will be the preferred choice in decarbonizing ammonia production in the short term where technological developments and process improvement will favor green ammonia production where all carbon emissions are evaded. During ammonia synthesis, the most important research focuses on lowering the pressure and temperature of the synthesis while maintaining the catalyst cost. These technologies are expected to be developed in the next few years. Although the production of ammonia by electrochemical methods is far from commercialization for now, the potential benefits of ammonia production by electrochemical methods are the reduction of energy consumption during production, lower process pressure and temperature, and lower purity requirement of the nitrogen needed. This suggests that more research needs to be done for electrochemical ammonia production in ammonia production. Future research aims to optimize and improve ammonia production capacity and cost, especially in ammonia production facilities where carbon emissions do not occur.

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