

## Ammonia, 4. Green Ammonia Production

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### 1. Introduction

About 50% of fixed nitrogen is nowadays produced by the fossil-based Haber–Bosch process [1, 2]. The Haber–Bosch process accounts for about 1–2% of energy and 5% of natural gas consumption worldwide, at the cost of 1.6% of CO<sub>2</sub> emissions worldwide [2]. In this article, ammonia production based on green feedstocks is discussed.

A classification is required to distinguish between fossil-based and renewable ammonia. Synthetic ammonia can be classified as *brown* ammonia, *blue* ammonia, and *green* ammonia. Brown ammonia is classified as ammonia synthesized with hydrogen production based on carbon sources such as methane, naphtha, heavy fuel oil, and coal. Hydrogen produced from coal, natural gas, and lignite is

referred to as *black*, *gray*, and *brown* hydrogen, respectively [3]. Currently, ammonia synthesis technologies emit about 2.0 t<sub>CO<sub>2</sub></sub>/t<sub>NH<sub>3</sub></sub> on average (see Table 1). In the European Union, the total CO<sub>2</sub> equivalent emissions have decreased from about 33.4 × 10<sup>6</sup> t<sub>CO<sub>2</sub></sub> in 1990 to 23.9 × 10<sup>6</sup> t<sub>CO<sub>2</sub></sub> in 2016 [17]. Brown ammonia synthesis technologies are discussed extensively in → Ammonia, 2. Production Processes and → Ammonia, 3. Production Plants. A comparison of various technologies for brown ammonia, blue ammonia, and green ammonia in terms of energy requirement, CO<sub>2</sub> footprint, and relative investment is listed in Table 1.

Blue ammonia is classified as ammonia synthesized in a similar manner to brown ammonia, with reduced carbon footprint. Firstly, this reduced carbon footprint can be

**Table 1.** Energy requirement and CO<sub>2</sub> footprint of brown ammonia, blue ammonia, and green ammonia based on the conventional high-pressure ammonia synthesis loop

Technology	Energy requirement, GJ/t <sub>NH<sub>3</sub></sub>		CO <sub>2</sub> footprint, t <sub>CO<sub>2</sub></sub> /t <sub>NH<sub>3</sub></sub>		Relative investment
	BAT	Potential	BAT	Potential	
<b>Brown ammonia</b>	<b>26</b>	<b>26</b>	<b>1.6</b>	<b>1.6</b>	<b>1.0</b>
SMR	26	26	1.6	1.6	1.0
Naphtha	35	–	2.5	–	1.1–1.2
Heavy fuel oil	38	–	3.0	–	1.5
Coal	42	–	3.6	–	1.8–2.1
<b>Blue ammonia</b>	<b>33</b>	<b>26</b>	<b>0.4</b>	<b>0.2</b>	<b>1.5</b>
By-product hydrogen	–	–	1.5–1.6	0.6	–
SMR with CCS	33	27	0.4	0.2	1.5
Coal with CCS	57	–	1.0–2.0	0.5	2.5–3.0
eSMR	–	26	–	1.1	1.0
<b>Green ammonia</b>	<b>33</b>	<b>26</b>	<b>0.1</b>	<b>0.0</b>	<b>1.2–1.5</b>
Low-temperature electrolysis	33	31	0.1	0.0	1.2–1.5
High-temperature electrolysis	–	26	–	0.0	1.5–2.0
Biomass (with CCS)	–	33	1.1–1.2*	0.5*	1.2–3.0
<b>Global average</b>	<b>35</b>	<b>27</b>	<b>2.0</b>	<b>1.4</b>	

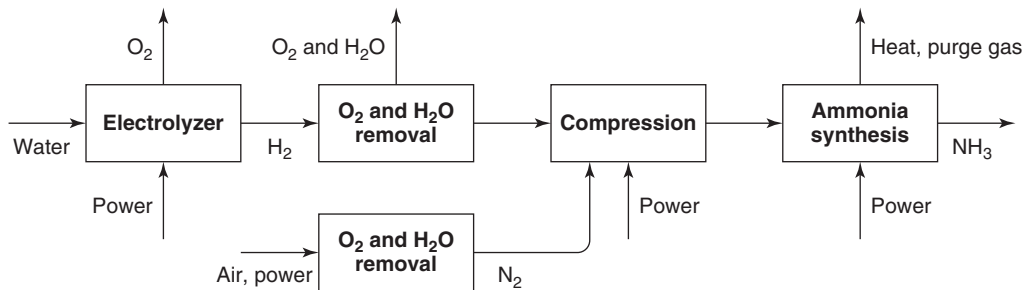
The best available technology (BAT) represents the BAT in the year 2020, while the potential represents the year 2050. Estimates based on [4–16].

\*The CO<sub>2</sub> emitted is part of a short carbon cycle, as opposed to the CO<sub>2</sub> emitted for natural gas, naphtha, heavy fuel oil, and coal feedstocks.

obtained by combining hydrogen production processes with carbon capture and storage (CCS). Electrification of heating processes in steam methane reforming (SMR) can reduce the carbon footprint as well [18]. The footprint of electrified steam methane reforming (eSMR) is two orders of magnitude smaller than that of gas-fired SMR [18]. Electrification of ammonia synthesis plants is primarily attractive in areas with low-cost renewable electricity, as was already pointed out by ERNST in the 1920s [19]. Hydrogen can also be obtained as a by-product in other processes, resulting in a reduced carbon footprint for ammonia synthesis. Examples of sources for by-product

hydrogen with reduced carbon footprint are ethylene crackers, chlorine plants, carbon black plants, and plastics gasification [14, 20].

Green ammonia is classified as ammonia synthesized with essentially zero carbon footprint. Green ammonia can be produced using conventional technology for the ammonia synthesis loop in combination with electrolysis-based hydrogen (see Fig. 1) or using nonconventional technologies for ammonia synthesis. Before the availability of cheap natural gas in the 1950s and onward, electrolysis-based ammonia synthesis was one of the most widely used technologies, second only to coal gasification. Lastly, biomass-based

**Figure 1.** Schematic of green ammonia synthesis process with electrolysis-based hydrogen production

hydrogen production with CCS can be considered as an alternative for decentralized green ammonia synthesis [12, 15, 21, 22].

The first electrolysis-based Haber–Bosch process started up in the 1920s, with an energy consumption of about 46–48 GJ/t<sub>NH<sub>3</sub></sub> [19, 23]. Four drivers can be identified for the production of green ammonia, namely sustainability of the reactants, low energy consumption, modular scalability, and economic viability [6, 19, 24]. Green ammonia technologies based on the conventional high-pressure ammonia synthesis loop with electrolysis-based hydrogen are discussed in Chapters 2 and 7. The theoretical minimum energy required for ammonia synthesis from air and water is 22.5 GJ/t<sub>NH<sub>3</sub></sub> [7]. Nonconventional technologies are discussed in Chapter 8. An overview of the ammonia economy is given in Chapters 9 and 10.

## 2. Electrolysis-Based Hydrogen Production

Green hydrogen is synthesized by electrolysis, as discussed in → Hydrogen, 2. Production. Various technologies for electrolysis are commercially available for coupling with ammonia synthesis, such as alkaline electrolysis and proton-exchange membrane (PEM) electrolysis

(see Table 2). Other technologies are in the demonstration stage, such as solid oxide electrolysis (SOE). Other technologies are currently researched in academia, such as anion-exchange membrane (AEM) electrolysis [25]. The efficiency and capital cost depend on the scale of application. All commercial systems have load responses in the seconds range in hot standby [26], which is required for adequate coupling with intermittent renewable electricity. However, in cold standby, PEM electrolysis is the only technology capable of ramping times in the range of seconds. A comparison of electrolysis technologies is listed in Table 2.

Combinations of electrolysis-based hydrogen and hydrogen derived from methane are also possible. For instance, a hybrid plant with a solid oxide electrolyzer and an autothermal reformer (ATR) can be beneficial, as purified oxygen is required for the ATR. An ATR operates by partial combustion of methane with purified oxygen, and is especially attractive for large-scale ammonia synthesis owing to the expensive oxygen purification plant, which is only economic at large scales. In a solid oxide electrolyzer, purified oxygen is produced in any case, making autothermal reforming feasible at smaller scales. It is estimated that such a configuration can save up to 22% in terms of natural gas consumption [30].

**Table 2.** Electrolysis technologies

		Alkaline	PEM	Solid oxide
Temperature, °C		60–90	50–80	600–1000
Pressure, bar		1–30	10–200	1–25
System energy consumption	kWh/m <sub>H<sub>2</sub></sub> <sup>3</sup>	4.2–6.6	4.4–6.6	3.4–3.9
	GJ/t <sub>NH<sub>3</sub></sub>	29–46	31–46	24–27
Current density, A/cm <sup>2</sup>		0.2–0.45	0.6–2.0	0.3–2.0
Hydrogen purity, vol%		>99.5	99.99	99.9
Maximum installed capacity, MW		165	20	0.2
Load range, %		10–110	0–160	20–100
Installed capital cost*, k€/tpd <sub>NH<sub>3</sub></sub>	2020	165–465	365–600	935–1865
	2030	135–285	215–500	265–935
	long term	65–235	65–300	165–335
Electrolyte		20–40 wt% KOH	Nafion	YSZ/SSZ
System size		large	compact	compact
Stack lifetime, 1000 h	2020	60–90	30–90	10–30
	2030	90–100	60–90	40–60
	long term	100–150	100–150	75–100
TRL**		9	8–9	5–6

Estimates based on [3, 5, 25–29].

\*tpd, tonnes per day.

\*\*TRL, technology readiness level.

### 3. Biomass-Based Hydrogen Production

Biomass-based hydrogen production is an alternative to electrolysis-based hydrogen production for ammonia synthesis [12, 15, 21, 22]. Biomass-based hydrogen production is discussed in → Hydrogen, 2. Production. Typical biomass-based facilities are limited by the logistics (i.e., the supply of biomass), so that plant capacities are generally below 50 MW [31]. The key metric for the cost of hydrogen is the cost of biomass, which varies strongly with the type of biomass and the location.

Biomass-based hydrogen can be produced by thermochemical or biochemical processes [32, 33]. Various biomass-based hydrogen production technologies are listed in Table 3. A benefit of biomass-based hydrogen production is the compatibility with the conventional brown hydrogen production process. The products of thermochemical or biochemical processing of the biomass are the feedstock of the SMR reactor used in brown ammonia synthesis. A drawback of biomass-based hydrogen is the complex processing of the biomass [3]. Furthermore, the technical potential of biomass to satisfy the demand for hydrogen is orders of magnitude smaller than that of renewable electricity resources such as solar, tidal, and wind, owing to the limited availability of biomass [3]. Typical sources of biomass are bagasse, crops, straw, switchgrass, wood, and wood chips [32, 34, 40, 41]. The typical products are biogas, bio-oil, and biochar [33].

An alternative for natural biomass feedstocks is the use of municipal waste [42]. An example of a waste-to-ammonia process is the use of recycled plastic, as is operated in Japan for selective catalytic reduction purposes [43].

Biogas from biomass can be combined with renewable electricity. An example of such a system is anaerobic digestion for biogas production coupled with electrified tubular steam reforming reactors. Another alternative is the combination of a biogas reactor with a solid oxide electrolyzer and an ATR.

### 4. Nitrogen Production

Purified nitrogen gas is produced from air by various technologies, namely an air-separation unit (ASU, cryogenic distillation), pressure-swing adsorption (PSA), membrane permeation, and hydrogen combustion (→ Nitrogen). In SMR, air separation is usually integrated with hydrogen production, and the oxygen is combusted with part of the hydrogen. Similarly, hydrogen combustion can be employed in a solid oxide electrolyzer to generate the heat for hydrogen production from water [5, 44]. The three other technologies can be employed in combination with alkaline or PEM electrolyzers, wherein nitrogen and hydrogen are produced in separate units (see Table 4).

The preferred alternative depends on the nitrogen purity and the scale of application [45]. For both PSA and membrane permeation, a deoxo system is required to remove residual

**Table 3.** Technologies for biomass-based hydrogen production

	Thermochemical		Biochemical	
	Pyrolysis	Gasification	Anaerobic	Fermentation
Temperature, °C	350–750	500–1150	20–80	30–70
Pressure, bar	1–5	225–350	1	1
Energy consumption	kWh/m <sub>H<sub>2</sub></sub> <sup>3</sup>	–	7.1–10.1	–
		GJ/t <sub>NH<sub>3</sub></sub>	–	50–72
Hydrogen yield, vol%	–	20–65	–	–
Biomass conversion products	bio-oil, gas, char	H <sub>2</sub> , CO, CO <sub>2</sub> , CH <sub>4</sub>	biogas	acids, alcohols, gases
Capacity range, MW	0.1	0.1–100	<10	<2
Load range, %	–	–	–	–
Cost of hydrogen, €/kg	2020	–	>1.3	–
	potential	–	0.6–1.1	–
TRL	3–5	5–7	6–9	9

For reference, the best steam methane reformers operate at 26 GJ/t<sub>NH<sub>3</sub></sub>. Estimates based on [3, 33–39].

**Table 4.** Nitrogen purification technologies

		ASU (cryogenic)	PSA	Membrane
Temperature, °C		−195 to −170	20–35	40–60
Pressure, bar		1–10	6–10	6–25
Purity, wt%		99.999	99.8	99.5*
Energy consumption	kWh/kg <sub>N<sub>2</sub></sub>	0.1	0.2–0.3	0.2–0.6
	GJ/t <sub>NH<sub>3</sub></sub>	0.3	0.7–1.0	0.7–2.0
Capacity range, m <sup>3</sup> /h		250–50 000	25–3000	3–3000
Load range, %		60–100	30–100	–
Investment cost, k€/tpd <sub>NH<sub>3</sub></sub>		<8	4–25	25–45
TRL		9	9	8–9

Estimates based on [45–49].

\*In most cases membranes are used for nitrogen enrichment of air, rather than the production of highly purified nitrogen.

oxygen [46]. Oxygen is removed by catalytic combustion with hydrogen, after which water is removed in a regenerative dryer [46]. Oxygen must be removed before the synthesis loop, as oxygen compounds are detrimental for the ammonia synthesis catalyst.

## 5. Ammonia Synthesis Loop

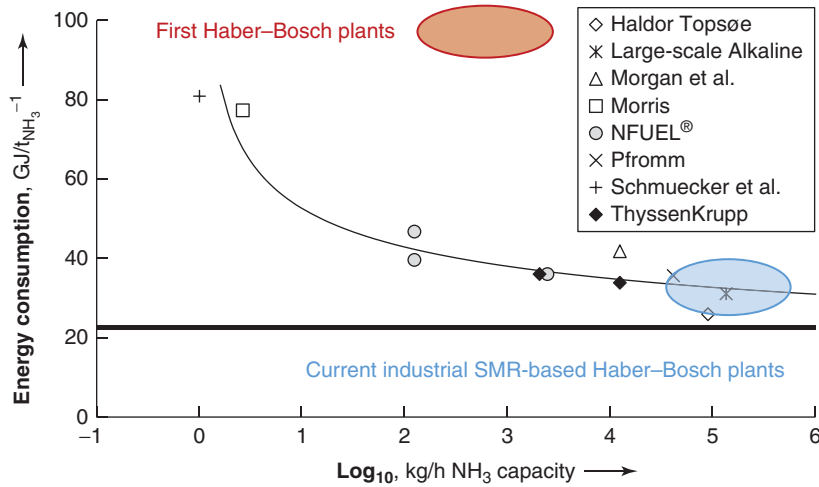
Ammonia synthesis loops and the associated equipment and catalysts are extensively discussed in → Ammonia, 2. Production Processes and → Ammonia, 3. Production Plants. In principle, the ammonia synthesis loop is not changed by the source of the hydrogen and nitrogen, although impurity levels may change. In principle, the choice of catalyst has little influence on the operating efficiency of the synthesis loop [50, 51]. However, the operating temperatures and pressures vary, depending on the choice of catalyst. This is especially relevant on scale-down and intermittent operation with renewables, as milder operating conditions lead to less heat losses with decreasing degree of heat integration. Furthermore, green hydrogen production implies different heat and mass flows in the process, which require different heat integration schemes [52]. Various catalysts are often combined in a single reactor with different beds [53, 54].

## 6. Scale-Down and Intermittency

Recent trends in ammonia synthesis technologies are scale-up, for minor improvements

in energy consumption (mega conventional, mostly for *brown* and *blue* ammonia production), and scale-down, for coupling with intermittent, renewable energy sources (small decentralized, for *green* ammonia) [30]. Decentralization of ammonia synthesis processes is mainly conducted along two pathways, namely using the conventional electrolysis-based Haber–Bosch technology, and using nonconventional technology with milder reaction and separation conditions [55]. The nonconventional technologies are discussed in Chapter 8.

Up to the 1990s, the electrolysis-based Haber–Bosch process was operated in various places with hydropower [56]. Thus, electrolysis-based Haber–Bosch processes are proven technology at large scale (300 t<sub>NH<sub>3</sub></sub>/d with alkaline electrolyzers of 135 MW capacity). Currently, only one large-scale, alkaline electrolysis-based Haber–Bosch plant with hydropower resources remains in Cusco, Peru (built in 1962). The current aim is to operate these electrolysis-based Haber–Bosch processes as energy efficiently as possible and at the scale of single wind turbines or on the scale of wind or solar farms. Demonstration plants were recently opened in Japan and the United Kingdom. Demonstration plants in the USA include solar- and wind-powered systems located in areas with large farmlands [57–61]. Commercial PEM electrolysis-based Haber–Bosch plants operating with a PSA unit and a high-pressure synthesis loop are in operation in various countries including Argentina, China, and Switzerland [62, 63]. A benefit of small-scale plants (≤50 t<sub>NH<sub>3</sub></sub>/d) is that these are not considered to be industrial sites, and hence regulatory obstacles are smaller [64].



**Figure 2.** Energy consumption of various electrolysis-based Haber–Bosch processes (academic and industrial estimates). The bold line represents the thermodynamic minimum energy consumption ( $22.5 \text{ GJ/t}_{\text{NH}_3}$ ). Adapted from [55] with permission of Elsevier

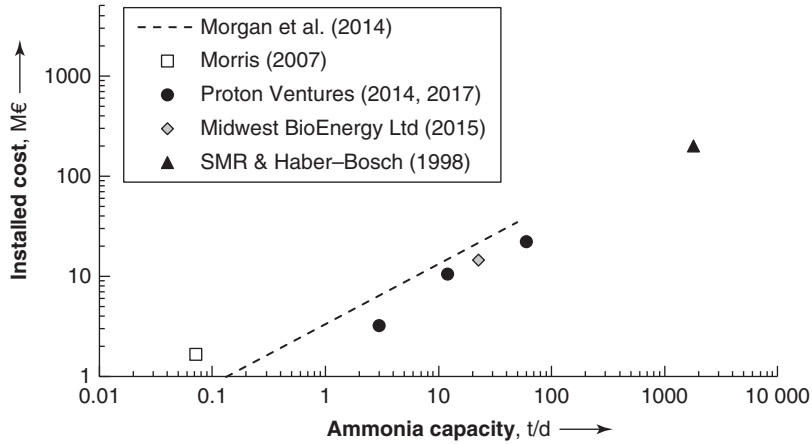
On scale-down, heat losses increase and the energy consumption goes up (see Fig. 2). A large-scale plant ( $\geq 1000 \text{ t}_{\text{NH}_3}/\text{d}$ ) consumes about  $2\text{--}7 \text{ GJ/t}_{\text{NH}_3}$  for pressurizing, heating, pumping, and utilities. At intermediate scales ( $3\text{--}20 \text{ t}_{\text{NH}_3}/\text{d}$ ), this energy consumption increases to about  $13\text{--}14 \text{ GJ/t}_{\text{NH}_3}$  [65, 66]. As ammonia synthesis scales down to  $5 \text{ t}_{\text{NH}_3}/\text{d}$ , losses in high-pressure synthesis processes are mainly due to scale effects. At very small scales ( $< 0.1 \text{ t}_{\text{NH}_3}/\text{d}$ ), heat is even required to keep the ammonia synthesis reactor at the synthesis temperature due to radial heat losses, and hydrogen and nitrogen production becomes less efficient as well [60, 67, 68]. Thus, milder conditions in the synthesis loop are required for effective scale-down.

Intermittent wind power and solar power cause variations in electricity supply. Therefore, the synthesis loop should either be able to ramp up and down, or batteries should be installed to operate the synthesis loop at constant load. The latter option is technically feasible, but cost intensive [6]. Ramp up and down can be achieved to some extent by varying the  $\text{H}_2:\text{N}_2$  ratio in the synthesis loop [55]. Nitrogen can act as an inert gas in the synthesis loop when small amounts of hydrogen are present. However, at all times some ammonia must be present in the synthesis loop to enable condensation. The

energy consumption per amount of ammonia produced can drastically increase on ramping down [47], although control strategies have been proposed with minimum increase in energy consumption [69]. To put ramping up and down in perspective: the cold start-up time of large-scale plant is  $1\text{--}2 \text{ d}$  [9]. Thus, shutdown can be considered when electricity supply is absent for a few weeks (i.e., beyond the storage time of a battery). Again, milder conditions in the synthesis loop are expected to make intermittent operation less energy intensive. Furthermore, separation of ammonia in the gas phase rather than by condensation can be beneficial [55].

## 7. Economic Aspects of Green Ammonia Production

The installed investment cost of an electrolysis-based Haber–Bosch plant consists of equipment for hydrogen production, nitrogen production, ammonia synthesis, and ammonia storage. Various cost-scaling relations were proposed for alkaline electrolysis-based and PEM electrolysis-based Haber–Bosch processes with PSA for nitrogen purification [45, 70, 71]. The installed costs of various electrolysis-based Haber–Bosch processes and proposed scaling relations are shown in Figure 3.



**Figure 3.** Estimated and realized installed costs of electrolysis-based Haber–Bosch processes with PSA for nitrogen production. The estimated installed costs of Morgan et al., Sánchez et al., and Morris plants include equipment for H<sub>2</sub> production, N<sub>2</sub> production, NH<sub>3</sub> synthesis, and storage. The data from Proton Ventures only includes the NH<sub>3</sub> synthesis loop. The Midwest BioEnergy Ltd. plant is based on biogas rather than electrolysis. As a point of reference, a 1800 t<sub>NH<sub>3</sub></sub>/d SMR-based ammonia plant is included as well (lumped turnkey cost of plant). Based on [45, 47, 70, 72–74]

The installed costs of electrolyzers and nitrogen purification units are listed in Tables 2 and 4. About half to two-thirds of the investment is required for the electrolyzer [47, 75]. As listed in Table 2, the cost of electrolyzers is expected to decrease in the next decade. The most accurate cost-scaling relation including hydrogen production, nitrogen production, ammonia synthesis, and storage was proposed by MORGAN et al. [70]. The cost-scaling relation is given by Equation (1), where  $C_{\text{I tot}}$  is the installed cost in € and  $X$  the ammonia capacity in t<sub>NH<sub>3</sub></sub>/d (1 MW  $\approx$  3 t<sub>NH<sub>3</sub></sub>/d). The cost-scaling relation is valid in the range 0.1–50 MW. For comparison, a biogas-based plant with a capacity of 22.5 t<sub>NH<sub>3</sub></sub>/d has an investment cost of about 14.4 M€ [76]. An SMR-based plant with a capacity of 1800 t<sub>NH<sub>3</sub></sub>/d has an investment cost of about 199 M€ [72].

$$C_{\text{I tot}} = 3.3 \times 10^6 \times X^{0.6} \quad (1)$$

The operating costs of an electrolysis-based Haber–Bosch process can be divided into the electricity costs and the owner’s costs. About 75–95% of the electricity is required for the electrolyzer in a large-scale electrolysis-based Haber–Bosch process [5, 51, 63, 77]. The electricity consumption and cost depend on the scale and location of the plant, as shown

in Figure 2. The owner’s costs are about 120 k€ a<sup>-1</sup> tpd<sup>-1</sup> for a 3 t<sub>NH<sub>3</sub></sub>/d plant [47].

Hydrogen production is the main cost contributor for ammonia synthesis. Depending on the location, various alternatives can be considered. Brown hydrogen produced by SMR costs 845–1585 €/t (excluding CCS, costs increase to 1305–2145 €/t with CCS) [3]. On the other hand, the cost of electrolysis-based, renewable hydrogen ranges from less than 1440 €/t to more than 3605 €/t, depending on the cumulative solar and wind load hours at a given location [3]. Electrified SMR may be of interest when the electricity cost is below 15–25 €/MWh, depending on the cost of natural gas at a given location. Compared with electrolysis, a benefit of eSMR is the compatibility with existing SMR plants for hydrogen production and the lower capital investment.

Biomass-based ammonia with thermochemical processing costs 380–1875 €/t, depending on the scale of application, the source of the biomass, and the location [21, 32, 40, 41]. The cost of ammonia produced from municipal waste is as high as 2135 €/t [42].

## 8. Nonconventional Technologies

Even though green ammonia synthesis is feasible with technology existing for about

a century, nonconventional technologies are widely researched to allow for scale-down, intermittent operation, and potentially higher energy efficiency. Various alternatives to the Haber–Bosch process for nitrogen fixation are discussed in → Nitrogen Fixation. The focus here is on ammonia synthesis, rather than nitrogen fixation in general.

Nonconventional technologies focus on enhancing the catalytic ammonia synthesis reaction under milder conditions and on enhancing ammonia separation using sorbents. Research varies from fundamental concepts to the use of commercial materials in pilot plants. Examples of research areas include nonconventional heterogeneous catalysis, adsorbents, absorbents, nonthermal plasma technology, electrochemical synthesis, photochemical synthesis, homogeneous catalysis, and chemical looping approaches [6, 78–82]. Typically, the nonconventional technologies allow for scale-down and operation in remote areas. Thus, the economic risks of the innovations are smaller compared to large-scale conventional plants, and a faster pace of innovation may occur.

Discoveries of new catalyst systems nowadays involve a combination of laboratory and computer-aided experiments [78, 83, 84]. Comparative assessment with calculated ammonia synthesis for heterogeneous catalysts has

become reliable [85]. Cross-cutting approaches among enzyme catalysis, homogeneous catalysis, and heterogeneous catalysis also allow for new insights and potential pathways toward ammonia synthesis under mild conditions and at high rates [78, 86]. An example of this is the similarity between heterogeneous catalysis over a ruthenium catalyst and enzyme catalysis in an  $\text{MoFe}_6\text{S}_9$  complex [86]. Furthermore, progress in in situ and operando spectroscopy enhances the understanding of the ammonia synthesis reaction under relevant conditions [78].

Various researched nonconventional technologies are listed in Table 5. Some technologies were investigated even before the Haber–Bosch process, such as plasma technology and thermochemical looping, commercialized as the Birkeland–Eyde process and the Frank–Caro process (→ Nitrogen Fixation). On the other hand, novel approaches such as single-atom catalysis have also been proposed for various categories of catalytic ammonia synthesis [92, 93]. Electrochemical ammonia synthesis, photochemical ammonia synthesis, homogeneous ammonia synthesis, nonthermal plasma technology, and chemical looping approaches are discussed in → Nitrogen Fixation. Herein, catalysts and sorbents that allow for operation of ammonia synthesis under milder conditions are discussed.

**Table 5.** Best reported and potential energy requirement of various nonconventional technologies

	Energy requirement, $\text{GJ}/t_{\text{NH}_3}$		Relative cost of ammonia
	Reported	Potential	
<b>Benchmark electrolysis-based Haber–Bosch process</b>	<b>33</b>	<b>26</b>	<b>1.0</b>
<b>Electrolysis-based Haber–Bosch processes with</b>	<b>46–50</b>	<b>30–35</b>	<b>1.0–1.5</b>
Absorbent-enhanced synthesis loop	47–50	30–35	1.0–1.5
Adsorbent-enhanced synthesis loop	46–50	30–35	1.0–1.5
Nonthermal plasma technology	155	60–70	2.0–4.5
<b>Electrochemical and photochemical synthesis</b>	<b>135</b>	<b>27–29</b>	–
Electrochemical synthesis	135	27–29	–
Photochemical synthesis	–	200*	–
<b>Other technologies</b>	<b>64</b>	<b>55</b>	–
Electrothermochemical looping	64	55	–
Redox cycles	–	79**	–
Homogeneous catalysis	900	159	–

Estimates based on [4, 5, 63, 81, 87–91].

\* About  $199 \text{ GJ}/t_{\text{NH}_3}$  is required as direct solar energy.

\*\* About  $35 \text{ GJ}/t_{\text{NH}_3}$  is required as direct solar energy.



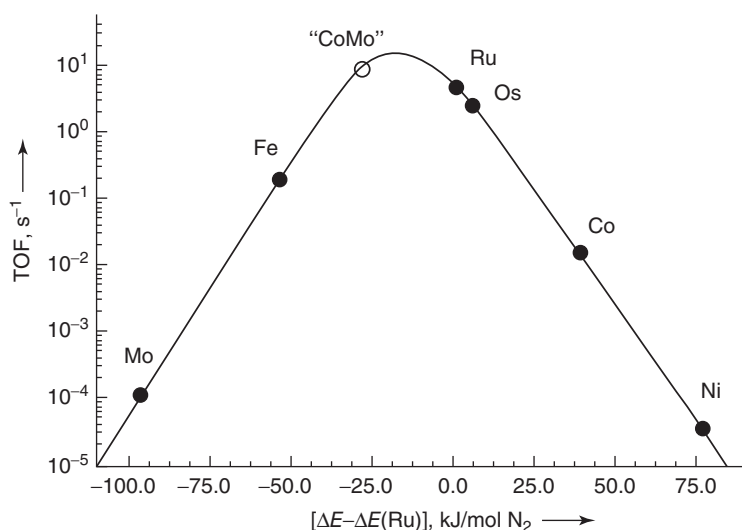
### 8.1. Nonconventional Heterogeneous Catalysis

Even though heterogeneously catalyzed ammonia synthesis has been studied for over a century, new discoveries are still common for the bellwether reaction in heterogeneous catalysis [94, 95]. The search for new efficient heterogeneous catalysts for ammonia synthesis in the 21st century is fundamentally different from that in the 20th century. While thousands of catalysts were experimentally tested in laboratory reactors in the facilities of MITTASCH and FRANKENBURG [96], nowadays predictive computer-aided experiments are performed, based on scaling relations among transition metals and first-principles calculation [83, 84, 97–101]. Even though early attempts for the volcano curve in ammonia synthesis date from the 1970s [102], predictive theory provided additional evidence on the most active transition metals for ammonia synthesis in the early 2000s. As follows from the volcano curve in Figure 4, the binding strength of nitrogen is a descriptor for the rate of ammonia synthesis, and Fe, Ru, and Os are the best transition metals for ammonia synthesis [103–105]. Metals binding nitrogen very strongly have low barriers for  $N_2$  activation, but the activity is low due to the desorption limitations of ammonia from

the surface. On the other hand, metals binding nitrogen weakly have too high an activation barrier for  $N_2$  dissociation. The optimum activity is found in between these extremes. While the choice of the transition metal is of fundamental importance, the electronic factor influenced by the support and promoters can alter activity by orders of magnitude [106, 107]. Industrially used Fe and Ru catalysts are discussed in → Ammonia, 2. Production Processes.

Bimetallic catalysts represent the first generation of discoveries coinciding with computational activity trends. By combining two transition metals, the resulting binding energy for nitrogen is of intermediate strength (see Fig. 4), giving rise to interpolation in the periodic table [103]. Examples of bimetallic catalysts with activities on par with or better than those of industrial Fe and Ru catalysts are Co–Mo catalysts [103, 108, 109], Co–Re catalysts [110, 111], and Fe–Co catalysts [112, 113].

The Co–Mo catalysts are the most active of a series of nitride structures ( $Co_3Mo_3N$ ,  $Fe_3Mo_3N$ , and  $Ni_3Mo_3N$ ) that show higher activity than industrial iron-based catalysts, especially in the low-temperature regime (325–400°C) [114]. This activity enhancement in the low-temperature regime can be understood from nitrogen adsorption by



**Figure 4.** Calculated turnover frequencies for ammonia synthesis as a function of the adsorption energy of nitrogen (at 400°C, 50 bar,  $H_2:N_2 = 3:1$ , and 5%  $NH_3$ ). Reproduced from [103] with permission of American Chemical Society

a Mars–van Krevelen mechanism rather than a Langmuir–Hinshelwood mechanism [115–117]. A drawback of  $\text{Co}_3\text{Mo}_3\text{N}$  is the high-temperature nitrification process for catalyst synthesis, which makes the production of catalysts with high surface areas difficult [118]. Similar to Fe- and Ru-based catalysts, the activity of bimetallic nitride catalysts is enhanced by the addition of alkali metal promoters [114]. Bimetallic rhenium-containing catalysts such as Co–Re are of scientific interest. However, Re is far too expensive (even more expensive than Ru), and activities are not higher than for Fe or Ru catalysts. Similarly, studies on barium-promoted Fe–Co alloys supported on carbon offer scientific insights into the reduced ammonia inhibition due to the presence of Co, while the observed activity is not higher than for industrial Fe catalysts [112].

The majority of recent research has focused on improving ruthenium-based catalysts [119]. While mechanistic understanding has substantially increased over the past decades regarding the effect of nanoparticle sizes and the distribution of sizes (i.e., the structural factor) [97, 120–124], most research focuses on the electronic factor by altering the support and promoter formulation [125]. The first focus area is the development of oxide-supported ruthenium-based catalysts to replace activated carbon as a support [7]. Activated carbon is known to be prone to methanation [7, 126]. A wide range of oxides (and nitrides) has been tested [127–129]. A general observed trend is an increased activity for ammonia synthesis with decreasing electronegativity of the oxide support [130]. The catalyst activity can be enhanced further by the addition of alkali (Cs, K) and alkaline earth metals (Ba), which enhance the nitrogen dissociation rate and lower the surface coverage of  $\text{NH}_x$  species on the catalyst [131, 132].

The development of Co and Ru catalysts with substantially enhanced electronic properties has led to catalysts with hydrogenation as the rate-limiting step rather than  $\text{N}_2$  dissociation [133]. Examples of these catalysts are Co and Ru on  $12 \text{ CaO} \cdot 7 \text{ Al}_2\text{O}_3$  electride [133–137], metallic electrides [138, 139], and Ba– $\text{Ca}(\text{NH}_2)_2$  [140–142]. The electride acts as an electron-donating support for ruthenium-based catalysts with rates an order

of magnitude higher than those of conventional oxide-supported catalysts [134]. Furthermore, hydrogen can be stored in the electride cages, and thereby the hydrogen poisoning effect generally observed for ruthenium-based catalysts is minimized [136]. The  $\text{NH}_2$  groups in the support and the Ba layer on the Ru particles enhance the ammonia synthesis rate, such that hydrogenation is the rate-limiting step [140]. The aim is to commercialize the Ru/Ba– $\text{Ca}(\text{NH}_2)_2$  catalyst for low-pressure (10 bar) ammonia synthesis [143]. Furthermore, transition metals combined with metal hydrides have been developed, which separate the  $\text{N}_2$  dissociation and hydrogenation steps, resulting in high catalytic activity at low temperatures (200–350°C) and pressures (1–10 bar) [6, 144].

Nowadays, science-based approaches are used to predict possible catalysts [83, 97–100]. Computational methods can be used to search for nonconventional catalysts not on the scaling line of transition metals [84, 100]. This allows for the identification of ammonia synthesis catalysts based on three-dimensional structures rather than two-dimensional transition metal planes. Inspiration can be obtained from nitrogenase structures for the development of single-metal-atom catalysts. Such catalysts operate with an associative mechanism instead of a dissociative mechanism [145], which may eventually allow for ammonia synthesis under ambient conditions. A few practical issues associated with such catalysts are transport limitations to such sites and the lack of high active-site densities.

## 8.2. Absorbent- and Adsorbent-Enhanced Haber–Bosch Processes

Academic research has focused on enhancing the activity of ammonia synthesis catalysts to lower the ammonia synthesis temperature and pressure [146]. More active catalysts allow for a lower operating temperature and consequently a lower operating pressure matching  $\text{H}_2$  and  $\text{N}_2$  production pressures [55]. This can save about  $1 \text{ GJ/t}_{\text{NH}_3}$  for syngas compression [147]. However, even when substantially more active catalysts are developed, the separation efficiency by condensation is limited by the ammonia vapor pressure. Other

ammonia-separation technologies are required to lower the pressure to 10–30 bar.

A proposed solution is a low-pressure absorbent- or adsorbent-enhanced ammonia synthesis loop (at 10–30 bar) [55, 148, 149]. This technology utilizes an absorbent or adsorbent to remove ammonia more sharply than by condensation (see Table 6). This allows for operation of the synthesis loop at lower pressures, less temperature swing in the synthesis loop, and less feed compression [55, 65, 67, 68, 154]. Combining nonconventional heterogeneous catalysts with an absorbent or adsorbent for separation allows the temperature swing in the process to be further reduced [55]. Separation of ammonia with membranes was also proposed [155–157]. However, due to low selectivities at low partial pressures of ammonia and poor thermal stability, membranes have not been researched widely [158].

The absorbent- or adsorbent-enhanced Haber–Bosch process is considered to be a low-hanging fruit for the upcoming decade, as a major decrease in pressure can be achieved with little technological innovation [6, 55]. In principle, the synthesis loop can operate at the same pressure as the hydrogen and nitrogen production units [55]. At the low ammonia concentrations in the absorbent- or adsorbent-enhanced ammonia synthesis loop, the catalysts are generally more active than at the high ammonia concentrations in the conventional ammonia synthesis loop [104, 159]. The resulting energy consumption of a small-scale absorbent- or adsorbent-enhanced Haber–Bosch process is lower than that of a small-scale conventional Haber–Bosch process [55, 65, 67, 150, 160].

Interactions of absorbents and adsorbents with ammonia can be classified as electrostatic interactions, metal ammine formation, and ammonium ion formation [161]. Wide ranges of solid and liquid materials have been proposed for ammonia separation, such as activated carbon, covalent organic frameworks, deep eutectic solvents, ionic liquids, metal–organic frameworks, metal halides, oxides, porous organic polymers, and zeolites [150, 151, 162–167]. Ammonia capacities of up to 55 wt% have been reported for metal halides [152]. The wide range of materials researched shows the academic interest to improve the ammonia-separation and storage method. Hereafter, activated carbon, metal halides, and zeolites are discussed, as these materials are applied in industry for various processes and the material cost is low [151]. Furthermore, the mechanisms for ammonia separation on these sorbents are well understood, and reasonable ammonia capacities are achieved. The ammonia-separation characteristics of condensation, activated carbon, metal halides, and zeolites under practical conditions are listed in Table 6.

Activated carbon is widely used for catalyst supports and separations. Various types of activated carbon have been investigated [151, 161]. Surface-modified activated carbon can reversibly store up to 5 wt% ammonia [151, 161]. The introduction of metal oxides on the surface increases the ammonia capacity due to electrostatic attractions [151]. On the other hand, hydrogen present in the loop removes functional groups at elevated temperatures, thereby lowering the ammonia capacity [151]. Both the reversible and irreversible ammonia adsorption increases on treating the activated

**Table 6.** Comparison of ammonia-separation technologies

	Condensation	Activated carbon	Metal halides	Zeolites
Separation temperature, °C	–20 to 30	20–50	150–250	20–100
Desorption temperature, °C	–	200	350–400	200–250
Pressure, bar	100–450	20–50	10–30	10–30
Energy consumption, GJ/t <sub>NH<sub>3</sub></sub>	3–5	15–35	6–11	8
Ammonia at outlet, mol%	2–5	0.5–2.0	0.1–0.3	0.1–0.3
Ammonia capacity, wt%	100	2–5	5–30	5–15
Ammonia density, kg/m <sup>3</sup>	680	10–25	100–600	30–90
Chemical stability	–	high	low/medium	high
TRL	9	3	4–5	4–5

Based on [55, 150–153].

carbon with acid or metal oxides [151]. Due to the low reversible ammonia-storage capacity, activated carbons are not the preferred ammonia adsorbents.

Metal halides are proposed for ammonia absorption and storage due to their high ammonia-storage capacity of up to 6–8 moles of ammonia per mole of metal halide with formation of metal ammine complexes [148, 149, 152, 154, 159, 168–177]. For example, the incorporation of ammonia into calcium chloride proceeds according to  $\text{CaCl}_2 + 6\text{NH}_3 \rightarrow [\text{Ca}(\text{NH}_3)_6]\text{Cl}_2$ . The cation affinity to ammonia determines the minimum partial pressure of ammonia for absorption [170]. Inert supports are used to stabilize the nanoporous metal halide structures and to prevent agglomeration of particles [149, 152, 169, 175, 178, 179]. Nanoporosity is introduced during the desorption of ammonia [175, 177, 180]. Due to the high volumetric density of ammonia (see Table 6), metal halides can also be used to store ammonia after separation from the gas stream [55]. The absorption is kinetically limited, while the desorption is diffusion limited [154, 176]. Metal halides have low ammonia vapor pressures under ambient conditions, making these sorbents safer alternatives for ammonia storage compared with liquefied ammonia [181]. The absorption and desorption cycles can be operated in both pressure- and temperature-swing approaches [154, 170, 182]. Economically, pressure-swing absorption may be more feasible than temperature-swing absorption [153], but so far temperature-swing absorption has been most successfully applied [149, 152]. The investment in an absorbent- or adsorbent-enhanced ammonia synthesis loop is similar to that of a conventional ammonia synthesis loop [71]. If a solid oxide fuel cell is used for electricity generation from ammonia in an islanded system, the heat of the solid oxide fuel cell can be used for the desorption of ammonia, and thereby the round-trip efficiency is increased [55]. The current challenge is the stabilization of metal halides on inert supports to give a high reversible ammonia absorption rate over multiple cycles, while maintaining a high surface area and nanoporosity [152].

Zeolites have also been proposed for ammonia adsorption. Typically, 5–15 wt% ammonia can be adsorbed on zeolites, depending

on the zeolite structure and ion exchange used [151, 163, 183]. Ammonia can be adsorbed effectively at low temperatures, while the decreasing adsorption capacity with increasing temperature facilitates desorption [163]. Ammonia adsorption and desorption from zeolites can be described by the Langmuir–Freundlich isotherm [163, 184]. Technology with commercially available molecular sieves has also been developed and patented [160, 185]. Both chemisorption and physisorption phenomena occur during ammonia separation from nitrogen and hydrogen using zeolites [186], even in the presence of water impurities in the stream [187]. Ammonia adsorption can be due to ammine complex formation with an alkali metal ion, ammonium ion formation with a proton, and electrostatic attraction with ions on the zeolite [188]. Various ion-exchange faujasites have been investigated [188]. The current challenge is to develop zeolite materials with a higher reversible ammonia adsorption capacity, which may be achieved by investigating various zeolite families.

## 9. Role of Ammonia in the Hydrogen Economy

A circular economy without fossil carbon is required to decrease greenhouse gas emissions [189]. Renewable energy sources such as wind, solar, and tidal power can be used for this. Such renewable technologies are becoming increasingly cost competitive with fossil-based technologies [31]. Over the past 40 years, the cost of solar power has halved for every order of magnitude capacity increase, which has been coined Swanson's law [190]. However, a drawback of renewable energy sources such as solar and wind is their intermittency, which implies that energy storage is required. Even though batteries can be used for energy storage of up to a few weeks, seasonal energy storage can only be accommodated by chemical energy storage.

The conversion of surplus renewable electricity to hydrogen is often proposed. In such a *hydrogen economy*, the hydrogen is stored and combusted for electricity (and heat) generation when the demand for electricity is higher than the renewables can accommodate at that

specific moment [191, 192]. However, the storage and transport of hydrogen is difficult. Therefore, hydrogen carriers are required [193]. Proposed hydrogen carriers include organic hydrides, methane, methanol, and ammonia [194–196]. An example of organic hydrides is the hydrogenation of toluene to cyclohexane for hydrogen transportation. About 6 wt% hydrogen can be stored in organic hydrides. Methane and methanol can be produced from electrolysis-based hydrogen and CO<sub>2</sub> captured from point sources or from the air. Ammonia can be produced from electrolysis-based hydrogen and nitrogen from air. A major difference between the conversion to methane and methanol as compared to the conversion to ammonia is the high cost of carbon capture as compared to nitrogen purification [197]. Furthermore, the power-to-fuel-to-power roundtrip efficiency for ammonia synthesis is higher than that of carbon-based hydrogen carriers (see Table 7), which may be attributed to high degree of exothermicity and water formation in the conversion of CO<sub>2</sub> to carbon-based hydrogen carriers.

If ammonia is used as a hydrogen carrier, it can be used for both fertilizer and power applications. In such an *ammonia economy*, energy can be stored in time (i.e., for islanded power systems) and in space (i.e., for transportation from places with abundant, low-cost renewable ammonia production to other places) [55, 181, 198–202]. There is significant infrastructure for transportation of ammonia over sea, and ammonia can be used as a marine fuel [203]. In Japan, an infrastructure is currently set up for the use of imported blue and green ammonia as a fuel in gas turbines and fuel cells [204]. Furthermore, islanded ammonia power systems may be installed in areas with limited electricity infrastructure and limited fertilizer input, and thereby facilitate the organic growth of these

economies [47, 55]. For example, the average fertilizer input in Africa is significantly lower than on other continents. On industrialization and urbanization, fertilizer is required in any case, and local, green production is desirable.

## 10. Outlook

The Haber–Bosch process is one of the most impactful inventions in human history by making *bread from air*, thereby facilitating a dramatic increase in the world population [205]. The Haber–Bosch process has been optimized from an energy consumption of about 100 GJ/t<sub>NH<sub>3</sub></sub> in the 1930s down to about 26 GJ/t<sub>NH<sub>3</sub></sub> today. A century later, the challenge is no longer to make bread from air, but rather to store *energy from sun and air* in a potential *hydrogen economy*, in which green ammonia synthesis can play a crucial role [58, 82, 201, 206]. When ammonia is used as a hydrogen carrier, it is converted to electricity in a gas turbine, engine, or fuel cell. Typical roundtrip efficiencies reported for power-to-ammonia-to-power are 33–43% [5, 55, 194, 207].

Current trends in ammonia synthesis technologies are electrification and decarbonization. Technologically, green ammonia synthesis has been feasible at scale for almost a century. The transition to green ammonia is a matter of economics and electrolyzer production capacity [19]. The main driver for green ammonia synthesis is low-cost electricity from renewables. Furthermore, electrolyzers with high electrical efficiency and low investment cost enable the transition to green ammonia synthesis [3]. Little academic attention has been given to improving the industrial iron-based catalysts in recent years [208, 209]. However, minor improvements in the commercial catalyst can decrease

**Table 7.** Power-to-fuel-to-power (P2F2P) roundtrip efficiencies and gravimetric hydrogen fraction for various carbon- and nitrogen-based hydrogen carriers

Hydrogen carrier	P2F2P roundtrip efficiency, %	Hydrogen fraction, wt%
Methane (CH <sub>4</sub> )	27–31	25.0
Methanol (CH <sub>3</sub> OH)	27–32	12.5
Dimethyl ether (CH <sub>3</sub> OCH <sub>3</sub> )	28	13.1
Ammonia (NH <sub>3</sub> )	35	17.8

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the operating temperature and pressure and enable scale-down.

The second transition is concerned with ammonia synthesis under mild conditions, which remains a topic of active research [78]. Lowering the operating pressure from 100–300 bar to 10–30 bar in an absorbent- or adsorbent-enhanced Haber–Bosch process is already technologically possible, albeit at a higher energy cost (see Table 5). Furthermore, nonconventional heterogeneous catalysis and plasma catalysis may lower the operating temperature to 250–350°C and thereby allow higher equilibrium conversions. The direct synthetic production of ammonia from air and water via electrochemical or photochemical synthesis routes remains an unsolved challenge. Ammonia synthesized directly from air and water may find applications in small-scale, remote fertilizer production.

All in all, it can be concluded that there has been an extensive research effort on ammonia synthesis using nonconventional technologies [95]. Potentially, some of these technologies may find widespread application in the long term, or niche applications in the short term. However, the electrolysis-based Haber–Bosch process will remain the preferred alternative on a large scale for the upcoming decade(s). In areas with insufficient solar, tidal, and wind power, biomass-based ammonia synthesis can be considered.

Strategies for the next five years include the transition from brown ammonia to blue ammonia using less carbon-intensive hydrogen sources, as well as carbon capture technologies. Furthermore, existing plants based on SMR technology can be revamped to provide a hybrid solution with both electrolysis-based hydrogen production and SMR-based hydrogen production [5, 30, 210, 211]. After 2025–2030, fully electrolysis-based technology is expected to be commercially viable on an industrial scale in some locations [5, 30, 211]. Electrolysis-based green ammonia is already becoming cost competitive with imported brown ammonia in some regions in Argentina, Chile, and China [212, 213]. The choice among the electrolysis technologies depends on the scale of application. At a scale of 3–150 t<sub>NH<sub>3</sub></sub>/d, alkaline electrolysis or PEM electrolysis coupled with PSA for N<sub>2</sub> generation

combined with a conventional Haber–Bosch process or absorbent- or adsorbent-enhanced Haber–Bosch process appears to be most feasible, at an energy consumption of about 30–35 GJ/t<sub>NH<sub>3</sub></sub>. At larger scales (300–15 000 t<sub>NH<sub>3</sub></sub>/d), SOE technology combined with a conventional Haber–Bosch process is expected to be most feasible, at an energy consumption of about 26 GJ/t<sub>NH<sub>3</sub></sub>.

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