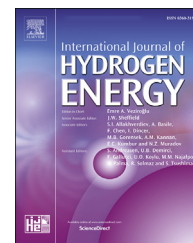


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Steady state process simulations of a novel containerized power to ammonia concept

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HIGHLIGHTS

- A novel small-scale power to ammonia cycle is proposed.
- The cycle focusses on low investment cost and operating flexibility.
- A comprehensive design study of the reactor as the key component has been conducted.
- The cycle has been optimized with regards to maximum ammonia production.

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ABSTRACT

A simple novel small-scale time flexible containerized power to ammonia concept, employing conventional technology only, which is going to be realized in 2023 in Italy, is being investigated.

The design focuses on investment cost minimization and time-flexibility, presenting a middle way between large-scale conventional ammonia plants and more sophisticated small-scale power to ammonia designs.

Reducing the investment cost of the cycle components shall be achieved by a simple cycle design and by operating at lower pressures and temperatures.

Time-flexibility, desired for the concept to act as chemical energy storage for the fluctuating renewables, is achieved by the novel cycle design, mainly by electrical start-up heaters.

Process simulation results regarding the optimum sizing of the reactor, reactor temperature profile, and inlet ratio for hydrogen to nitrogen are presented.

Due to the simple design, the resulting energetic degree of efficiency is, as expected, lower than the values in the literature.

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Introduction

Carbon neutrality requires either a carbon-free energy vector such as hydrogen or fuel that closes the carbon cycle, e.g. methane produced from biomass.

One of the challenges of hydrogen is its rather low energy density and thus its unsuitability to act as a long-term storage medium. To liquefy hydrogen at ambient pressure, a temperature of $-252,76\text{ }^{\circ}\text{C}$ is required. In contrast, for the hydrogen carrier ammonia, a temperature of only $-33,41\text{ }^{\circ}\text{C}$ is required. At $25\text{ }^{\circ}\text{C}$ ambient temperature, 11 bar are required to liquefy ammonia, whereas at that temperature hydrogen cannot be liquefied by increasing the pressure [1].

Thus, ammonia seems to be a suitable long-term medium to fix and store hydrogen.

As such an energy vector, ammonia is being researched more and more often in academia [2–6], research initiatives [7–9], and industry projects [10–13].

Ammonia is the main feedstock for fertilizers. Traditionally, the ammonia in the fertilizer industry is being produced from fossil fuels such as natural gas or coal. However, the fertilizer industry is starting to shift away from fossil fuels and turning to a green production of ammonia via water electrolysis [14–16].

As an early adapter of ammonia as a fuel, the maritime industry is a potent candidate. Ammonia is a commodity that is shipped worldwide in large quantities with an existing port infrastructure for storing, loading, and unloading vessels. Replacing the marine diesel with ammonia seems to be very sensible for ammonia vessels and efforts are being undertaken to retrofit the ship engines to be able to run on ammonia [17–20].

Big ammonia plants largely use the Haber-Bosch process. Hydrogen and nitrogen are generated from natural gas and air, respectively. The former via methane steam reforming and the latter via cryogenic air separation. The reagents are then combined to produce ammonia in a heterogeneous catalytic reaction. The operating conditions lie at 100–350 bar and 400–550 $^{\circ}\text{C}$. To increase efficiency, extensive heat integration efforts are being undertaken in the plants. Iron-based or more recently ruthenium-based catalysts are employed. Daily capacities reach up to 3300 tonnes of ammonia. On average 1,33 tonnes of carbon dioxide per tonne of ammonia are produced. In this context, green ammonia generated from renewable sources of energy becomes more and more crucial [21,22].

In this paper, a small-scale containerized power to ammonia (P2A) system, e.g. for remote areas, is being presented. The concept is being planned and built in the European Union's (EU) Flexibilize combined cycle power plant through power-to-X solutions using non-conventional fuels (FLEXnCONFU) project and will be installed at the Savona Campus of the University of Genova, Italy. There it will be incorporated into a small smart heat, cooling, and electricity grid. The test campaign will start in 2023.

The P2A design focuses on both the investment cost minimization and the high process flexibility. Moreover, the modular “plug-and-play” containerized solution allows for an easy and lower cost installation suitable also for remote areas, acting as a cheap and fast-reacting chemical energy storage for the fluctuating renewable sources of energy.

Process simulations are carried out, both to size the reactor as the key component and to optimize the operation of the design. It is the aim to produce fast a maximum amount of ammonia at a reasonable power to fuel to power (P2F2P) efficiency with proven components at low investment costs.

Today's large-scale stationary ammonia plants have both high investment costs and high efficiencies. They are geared towards a maximum and constant ammonia production, employing standard and long-proven technologies such as cryogenic air separation, iron-based catalysts in the reactor and condensation to remove the ammonia produced. As a feedstock for hydrogen, fossil fuels are used.

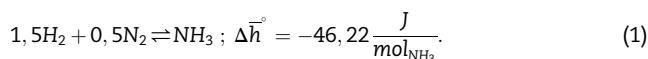
In contrast, recently suggested sophisticated small-scale systems use water electrolysis to derive hydrogen. In addition, more modern unit operations are proposed, such as pressure swing adsorption to derive nitrogen from the air and to separate the ammonia produced. The use of novel catalysts is also suggested. These systems have lower production capacities but are more time-flexible. They also display high P2F2P efficiencies, employing fuel cells [23] rather than gas turbines or internal combustion engines for power generation, but likely at both higher investment costs and a higher likelihood of process failure due to the suggested use of not yet fully long-term-proven technologies [6,24].

The FLEXnCONFU P2A concept presented in this paper can be regarded as an in-between solution. It aims at a low cost of investment with a rather small production capacity, at time-flexibility with proven technology, and a moderate cycle efficiency.

Process description

In Fig. 1 the process diagram of the proposed P2A cycle is depicted. The inlet hydrogen is generated by an electrolyzer with a maximum capacity of 15 kW_{el} to produce 3 Nm³/h of hydrogen at 8 barg from the feedstock water [25]. The 8 barg are also taken as the recycle pressure of the P2A cycle. As a start to prove feasibility, the inlet nitrogen is provided from research-grade 99,998 vol% nitrogen bottles [26]. The high-pressure nitrogen from the bottles is reduced also to 8 barg. Once feasibility is shown, a pressure swing adsorption (PSA) unit working close to 8 barg can replace the nitrogen bottles.

The recycle stream with the gaseous components of unreacted hydrogen, nitrogen, and not removed ammonia is mixed with the two inlet streams. The mixture enters a compressor with an outlet pressure of 80 barg. During the compression, the mixture heats up. An electrical heater raises the temperature further to the temperature required by the catalyst in the reactor. The electrical heater thus enables a fast start-up of the reaction by providing the necessary activation energy. The exothermic gaseous ammonia equilibrium reaction is given in Eq. (1) [22]:



Once the reaction is started, the heat of the reaction should supply the required activation energy. If this is the case, the electrical heater can be switched off. This means that the electrical heaters are only required for start-up or quick

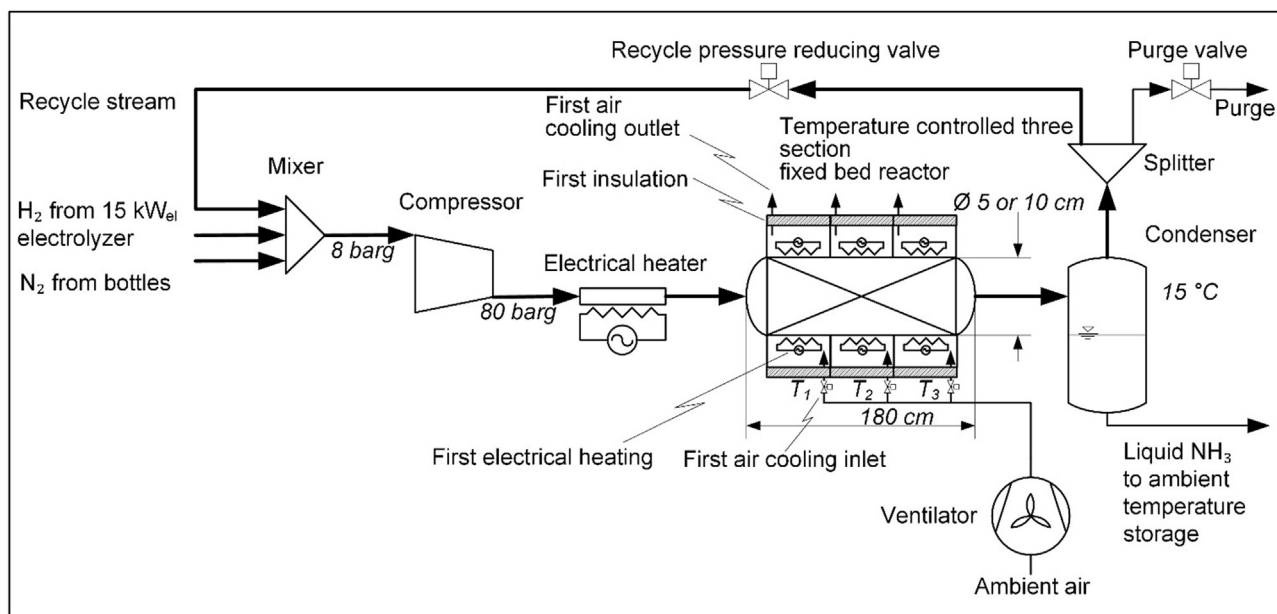


Fig. 1 – Power to ammonia cycle process diagram.

changes to higher reaction temperatures but not for steady-state.

The reactor is a fixed bed tube in tube design. The inner high-pressure tube contains the iron catalyst. The outer tube is subdivided into three sections. Each section consists of an electrical heating coil wrapped around the outside of the inner tube and the possibility of an air stream flowing through the space between the inner and outer tube.

Around the outer tube, a layer of easily removable insulation is installed. The purpose of the reactor heating coils is the same as the electrical preheater before the reactor, i.e. to bring the catalyst bed to the required start-up temperature. These coils are required during the start-up and for a quick reactor temperature increase. Then, they are deactivated in steady-state operation, when instead the heat of the reaction has to be removed. For this purpose, the cooling air will flow through the sections and, if necessary, the insulation can also be taken off.

With these means of heating and cooling, any combination of idealized temperatures T_1 , T_2 , and T_3 in the three sections (see Fig. 1) should be achievable. Thus, the full range of temperature profiles between a fully adiabatic reactor and an isothermal reactor can be specified.

The reaction products leaving the reactor are cooled down to 15 °C in a condenser. At this temperature, only a part of the ammonia produced is being condensed. The liquid ammonia leaves the cycle and is stored in a pressure vessel but at ambient temperature. The moderate 15 °C are chosen, to be able to cool either with ambient air or with a simple vapour compression refrigeration (VCR) cycle. Should ambient air temperatures allow for cooling all year, this would pose the cheapest option investment cost-wise, as the VCR could be left out in the design and be replaced by a fan to ensure the flow of ambient cooling air. To decrease investment costs further, it may also be possible, to use the same ventilator that provides the cooling air for the reactor (see Fig. 1). But even if ambient

air temperatures should be too high, a VCR cycle working at 15 °C and down to –10 °C should come at a low investment cost, since this is in the normal temperature range of household appliances.

A fraction of the gaseous phase leaving the condenser may be removed from the system by a purge valve. First, the purge valve controls the pressure in the high-pressure section of the cycle. Second, the purge can remove unwanted accumulating components in the cycle, e.g. argon, which is present in the nitrogen bottles. At a later stage with PSA supplying the nitrogen, such impurities will increase, as the PSA process produces less pure nitrogen than nitrogen from bottles, thus increasing the necessity to purge the cycle from time to time.

The by far larger part of the gaseous phase from the condenser is being recycled. The pressure of this stream is reduced to 8 barg by a recycle valve to match the pressure of the hydrogen and nitrogen entering the cycle. If driven solely by electricity from renewable sources of energy, the operation of the P2A concept described has a zero carbon footprint and a maximum daily ammonia production capacity of 35 kg.

In comparison with conventional ammonia production cycles [21,24,27,28], the suggested concept differs in the following aspects:

1. No heat integration is made use of. Electrical heaters are employed instead.
2. No second compressor, i.e. a recycle compressor is made use of. A pressure reducing valve is employed instead.
3. No radial flow, counter-current flow, quenching, intermediate cooling, or similar concepts, which lead to a complex design of the reactor, are used. A conventional fixed bed tube reactor is employed instead. The three-section heating and cooling concept described is rather straightforward as well, whilst still ensuring a full temperature control of the reactor.

4. The reaction conditions in the reactor are below 80 barg and below 420 °C and thus far below the conditions of 100–350 barg and 400–550 °C, which are common for large ammonia plants.

Regarding aspect 1, in most layouts, a gas-gas-heat exchanger is installed before the reactor as a means of an internal heat exchanger. Sometimes, an additional external heater is placed after the internal heater, to increase the temperature further [28]. The reactor educts are warmed up by the reactor products. Gas-gas heat exchange is rather inefficient and requires a large surface area, resulting in high investment costs for the heat exchanger. In addition, the space taken up by such a heat exchanger is rather inconvenient for the proposed containerized solution. On top of that, such an internal heat exchanger makes a fast start-up rather difficult. An internal heat exchanger causes feedbacks and thus may cause problems of stability in the reactor, i.e. temperature fluctuations and thus composition fluctuations, in the worst case resulting in a blowout of the reactor [29]. In contrast, the suggested electrical start-up heating system causes no feedbacks and instabilities, and also displays a very fast start-up behaviour. In this way, the proposed P2A concept can almost instantaneously make use of renewable excess electricity and store it chemically in the form of ammonia. Every power to fuel (P2F) concept is based on the availability of cheap excess electricity. An internal heat exchanger would increase the efficiency of the cycle, decreasing the energy input for the cycle. This however is rather unnecessary in the case of excess electricity. The general economic trade-off between investment and operating costs comes into effect. In this case, cheap excess electricity means low operating costs thus making a high investment into a cycle with a high efficiency unnecessary.

Regarding aspect 2, and using the same argument as in the paragraph above, the commonly found recycle compressor is unnecessary as well and can be replaced by a pressure-reduction valve. This means, that the required power input for the one remaining compressor is increased drastically. But, since the operating cost is assumed to be low, the cost impact of the increase in power input is negligible. Furthermore, the replacement of the recycle compressor with a pressure reduction valve results in a significant investment cost reduction, as the investment costs of both compressors, no matter the actual pressure difference that is achieved by the compressors, are comparable [30]. Another option for requiring just one compressor in the P2A cycle would be if hydrogen and nitrogen were stored above the reaction pressure [28]. This however just shifts the compression to the production and storage of hydrogen and nitrogen.

Regarding aspect 3, the reactor diameter is rather small. Thus, radial heat transfer limits should be kept to a minimum, with rather smooth radial temperature profiles and no extreme hot spots expected in the middle of the reactor bed. In addition, the reactor length is rather big. This should allow for an adequate temperature profile control along the reactor length. Via the three electrical heating coils, the three reactor insulations, and the three motionless layers of air in the outer tube, if the air-cooling is not active, acting as additional insulation, the temperatures of the three reactor sections can

be increased fast and independently from one another. Similarly, via the air-cooling and the removal of insulation, the reactor can be cooled down and again separate for each section. The combination of these simple heating and cooling mechanisms allows for a good temperature control along the length of the reactor, being able to establish any profile between an isothermal and an adiabatic profile. More sophisticated temperature control mechanisms commonly found in large plants, for example, quenching, intermediate cooling, and changing the direction of flow in the bed from horizontal to radial or vice versa are not considered. Such more sophisticated temperature control mechanisms would entail a more complex reactor design as well, leading away from the proposed simple fixed bed tube. Since in industry ammonia production is much bigger, leading to much bigger reactors with much bigger catalyst beds, the risk of temperature hot spots resulting in catalyst sintering or simply in ammonia being cracked is great. This explains the need for more complex cooling methods. The production capacity of the suggested cycle is far less than what is found in industry, making the use of a simple tube reactor possible. On top of that, such a standard type of reactor can be simulated in common process simulation software, thus enabling the simulation of the whole P2A cycle. Even such a small modification as from a tubular to a radial flow reactor, as is realized in a comparable small-scale P2A system [28], would prove difficult to simulate. For such a more complex reactor design, computational fluid dynamics (CFD) simulations for the reactor would need to be carried out to establish the efficiency of the reactor. Lastly, the inner tube of the reactor is designed in such a way, that it can be removed easily, making the renewal of the catalyst bed easy as well and thus reducing the downtime of the system. A catalyst replacement is necessary for the event of catalyst poisoning, degeneration, or if a better catalyst should be available, or if the guard bed before the catalyst bed needs to be renewed.

Regarding aspect 4, the desired low pressure of 80 barg in the cycle is aimed at reducing the investment costs of the cycle components. Pressure correlates positively with e.g. the compressor power input and pipe thickness and both, in turn, correlate positively with investment cost [31–34]. However, as Eq. (1) shows, regarding ammonia conversion, low pressure is not favorable. To counter the negative impact of a pressure reduction, as the equilibrium reaction is exothermic, the reaction temperature has to be decreased, in order to have the same equilibrium as in a high-pressure, high-temperature scenario. The problem with low temperatures is, that catalysts require a high enough temperature, first, so that the activation energy is provided for the catalyst to function, and second, the rate of ammonia production, the kinetics of the reaction, is favoured by high temperatures. In commercial plants with high investment costs, both a high-pressure and high-temperature regime is chosen. Concerning the equilibrium and ammonia production, the high pressure counteracts the high temperatures. In FLEXnCONFU, to keep down investment costs, pressure is kept low. However, in order to still have a favorable equilibrium, the temperature is kept low as well. As a consequence, catalyst activity should decrease. The aim of FLEXnCONFU is to show that a modern generation iron-based catalyst can be employed at moderate pressures and

temperatures, whilst still ensuring a satisfying ammonia production rate. In this regard, Reese et al. have taken the first step, also having employed an iron-based catalyst at reaction conditions of about 115 bar and 290 °C [28].

On the other hand, compared to more sophisticated small-scale systems [6,24], the main differences in the FLEXnCONFU layout are:

1. No advanced catalysts are made use of. A conventional iron-based catalyst of the newest generation is used instead.
2. No adsorption concept is made use of for ammonia removal. Conventional condensation at moderate temperatures is used instead.

Regarding difference 1, conventional iron-based catalysts are commercially available, cheap, and reliable, i.e. their lifetime and catalyst poisons, are known. All these characteristics are not yet fully known or industrially proven by ruthenium-based or more advanced catalysts, such as ruthenium or barium supported on calcium amide [24,36–38]. Price quotations from two suppliers of ruthenium catalysts were in the range of 5000 €/kg [39,40] while the iron catalyst is far below this figure [35]. Aspen Plus® simulations using the kinetics given in Table 1 below led to required masses of 5 and 40 kg for the ruthenium and iron catalyst respectively for the same production of ammonia and keeping all other design specifications the same. Thus, to save 25 000 € in investment cost for the catalyst, the iron catalyst was chosen.

Regarding difference 2, the efficiency of the removal of ammonia via condensation is dependent on the pressure, i.e. the higher the pressure the higher the partial pressure of the ammonia and the more ammonia condenses. For a very low-pressure regime, i.e. below 30 barg, condensation is less efficient than adsorption onto adsorbents, e.g. active carbon and zeolites [41] and metal halides [42,43], such as magnesium chloride. However, adsorption and the mentioned adsorbents are still being researched [7,24]. Furthermore, the 80 barg in the cycle are high enough for condensation to take place at the aimed 15 °C, which is why condensation is chosen in FLEXnCONFU.

Process simulation aims and set-up

The aims of the process simulations employing the software Aspen Plus® are to determine:

1. A suitable kinetics reaction model by testing and fitting various kinetics models from literature to data provided by the catalyst supplier.
2. The optimum diameter of the fixed bed tube reactor assumed to be an ideal plug flow reactor, with regards to conditions found in ammonia production plants and other phenomena e.g. mass transport and flow regime.
3. The optimum temperature profile for the reactor with regards to the maximum hydrogen production capacity of the electrolyzer.
4. The optimum cycle inlet hydrogen to nitrogen ratio for the optimum reactor temperature profile.
5. The P2F2P efficiency of the concept and how this efficiency value compares to other values of alternative synthetic fuels given in the literature.
6. The influence of the cycle variables pressure and condensation temperature and by how far the condensation temperature has to be decreased if the cycle pressure is decreased further, again with the aim to reduce investment cost further, when at the same time the amount of liquid ammonia produced is being kept constant.

For the set-up of the simulations, the property method Aspen HYSYS® Peng Robinson (HYSPR) is employed. The components present are hydrogen, nitrogen, and ammonia. Trace amounts of argon etc. are neglected. For ammonia synthesis simulations, other methods are mentioned in the literature as well, such as Peng Robinson (PR) [29,44] and Redlich Kwong Soave (RKS) [6,44]. Simulation comparisons with these models yielded similar results. HYSPR was chosen in the end, because for this model adapted and tested interaction parameters from the project partner Proton Ventures B.V. were available.

Adapting the manufacturer data [25], the electrolyzer is being modeled as a simplified black box having a linear correlation between electrical power input and hydrogen production from zero to the maximum of 15 kW_{el} and 3 Nm³/h. The hydrogen leaves the electrolyzer at 8 barg. For the compressor, an isentropic degree of efficiency of 80% is assumed. Condensation takes place at 15 °C. In the test plant, the purge will be automated and only activated if required, based on gas analysis results from the reactor outlet. Thus, in absence of test data, the purge is assumed to be continuous 0,5 mol% of the gas stream from the condenser.

The reactor is assumed to be an ideal plug flow reactor. The build-in Aspen Plus® LLHW kinetic model is implemented, as suggested by Tripodi et al. [44], and given in Eq. (2):

Table 1 – Overview of literature reaction kinetics used for ammonia synthesis.

Name of kinetics	Abbreviation	Formula	Source
Temkin-Puzhev	TEMPUZ	$r = c_1 \exp\left(-\frac{c_2}{RT}\right) \left(c_3(T) p_{H_2}^{2,25} p_{N_2}^{1,5} p_{NH_3}^{-1,5} - c_4(T) p_{H_2}^{-1,5} p_{NH_3}^{1,5} \right)$	[21,44]
Iron oxide wustite	WUSTITE	$r = c_1 \exp\left(-\frac{c_2}{RT}\right) \left(c_3(T) f_{H_2}^{2,25} f_{N_2}^{1,5} f_{NH_3}^{-1,5} - c_4(T) f_{H_2}^{-0,75} f_{NH_3}^{0,5} \right)$	[44]
Ruthenium supported on carbon	RUC	$r = \frac{c_1 \exp\left(-\frac{c_2}{RT}\right) \left(c_3(T) f_{H_2}^{0,375} f_{N_2}^{0,5} f_{NH_3}^{-0,25} - c_4(T) f_{H_2}^{-1,125} f_{NH_3}^{0,75} \right)}{c_5(T) + c_6(T) f_{H_2}^{0,3} + c_7(T) f_{NH_3}^{0,2}}$	[44]
Langmuir Hinshelwood modified	LHMOD	$r = \frac{c_1 \exp\left(-\frac{c_2}{RT}\right) \left(c_3(T) p_{H_2}^{1,5} p_{N_2} - c_4(T) p_{H_2}^{-1,5} p_{NH_3}^2 \right)}{c_5(T) + c_6(T) p_{NH_3}}$	[49]

$$r = \frac{c_1 \exp\left(-\frac{c_2}{RT}\right) \left(c_3(T) \int_{H_2}^{c_4} \int_{N_2}^{c_5} \int_{NH_3}^{c_6} - c_7(T) \int_{H_2}^{c_8} \int_{N_2}^{c_9} \int_{NH_3}^{c_{10}} \right)}{\left(\sum_{i=11}^m c_i(T) \int_{H_2}^{c_{H_2,i}} \int_{N_2}^{c_{N_2,i}} \int_{NH_3}^{c_{NH_3,i}} \right)^{c_n}} \quad (2)$$

In Eq. (2), the parameters c_1 , c_2 , ..., c_m and c_n are partly dependent on temperature in degrees Kelvin. Eq. (2) is the general kinetics formulation of the most common equations suggested in the literature for ammonia synthesis, which are listed in Table 1.

The length of 1,8 m of the reactor is chosen as long as possible, restricted both by the height of and the space available in the P2A container. A horizontal installation of the reactor would allow for an even greater reactor length. However, the vertical installation chosen makes use of the full height of the container and does not interfere with the space needed for the other cycle components. It holds, that the longer the reactor the more precise a desired temperature profile can be ensured.

The cooling of the reactor is achieved first by free convection of air in and around the outer tube, second by the ventilation of air between the inner and outer tube, and third by adjusting the insulation. Assuming the electric power input for the ventilator to be negligible, the energetic degree of efficiency of the P2A process depicted in Fig. 1 is given in Eq. (3):

$$\eta_{P2A} = \frac{LHV_{NH_3} \cdot \dot{M}_{NH_3(l) \text{ to storage}}}{P_{el, Electrolyzer} + P_{el, Comp} + P_{el, Heaters} + \dot{P}_{el, VCR}} \quad (3)$$

In Eq. (3), the energetic output is given by the lower heating value multiplied by the mass stream of liquid ammonia leaving the condenser. The energetic input in the denominator is given by the sum of the electrical powers of the electrolyzer for the hydrogen production, the compressor, the electrical heaters, and the vapour compression refrigeration, which is assumed to provide the cooling for the condenser. For a more realistic energetic degree of efficiency of the P2A process, the production of nitrogen needs to be considered as well. Thus, instead of the nitrogen bottles in Fig. 1, a pressure swing adsorption unit with the conservative value of 0,36 kWh_{el}/Nm³_{N₂} from Ref. [45] is considered. Further, a conservative coefficient of performance of one [46,47] is assumed for the vapour compression refrigeration, which means, that the required cooling energy is equal to the required electric power input of the vapour compression cycle. With these two alterations, Eq. (3) becomes Eq. (4) for the P2A energetic degree of efficiency:

$$\eta_{P2A} = \frac{LHV_{NH_3} \cdot \dot{M}_{NH_3(l) \text{ to storage}}}{P_{el, Electrolyzer} + 0,36 \cdot \dot{V}_{N_2} + P_{el, Comp} + P_{el, Heaters} + \dot{Q}_{Condenser}} \quad (4)$$

Finally, for the complete P2A2P energetic degree of efficiency, the power consumptions for the ammonia storage and the degree of efficiency for power generation from the stored ammonia need to be considered. In FLEXnCONFU, the ammonia is stored pressurized at ambient temperature. Thus, ammonia storage requires no energy. Assuming further an ammonia-fired micro gas turbine with 20% thermal efficiency [48], Eq. (4) becomes Eq. (5) for the P2A2P energetic degree of efficiency:

$$\eta_{P2A2P} = \frac{LHV_{NH_3} \cdot \dot{M}_{NH_3(l) \text{ to storage}} \cdot 0,2}{P_{el, Electrolyzer} + 0,36 \cdot \dot{V}_{N_2} + P_{el, Comp} + P_{el, Heaters} + \dot{Q}_{Condenser}} \quad (5)$$

Results and discussion

Regarding aim 1 defined in the previous section, the four kinetic equations in Table 1 were tested and compared to measurement data in the range of 75–125 barg and 350–450 °C provided by the catalyst supplier [35]. Using the Aspen Plus® data fit tool, the parameters of the equations were fitted to the provided data. The best fit was reached with a modification of the Langmuir Hinshelwood kinetics, named LHMOD, as can be seen in Fig. 2.

In Fig. 2, the weight time yield (WTY) of selected data is normalized to the value of one (black horizontal line). The corresponding fitted and also normalized WTY results of the four kinetics are plotted as bars. For example, the value of 1,2 of the first data point of the ruthenium supported on carbon kinetics (RUC) means, that the WTY is 20% higher than the test data value. The variance between the fitted WTY values of a kinetic model and the test values is taken to determine which kinetic model fits the test data best, i.e. the lowest variance is the best fit. The variance values are given in Fig. 2 on the bottom right, LHMOD displaying the lowest value of 0,00554. Thus, LHMOD is chosen as the kinetic model for all following calculations. The values of the LHMOD parameters from Table 1 are given in Table 2.

Regarding aim 2 defined in the previous section, given the fixed reactor length, the remaining free variable, the reactor diameter, determines e.g. the total mass of the catalyst and the flow regime and thus the capacity of the ammonia production and the mass transfer to and from the active sites of the catalyst. Keeping the reactor at 380 °C, the electrolyzer capacity at a maximum of 15 kW, and the hydrogen to nitrogen input ratio at the stoichiometric value of three, and conducting a variation analysis in Aspen Plus® by changing the reactor diameter from 4 to 12 cm, a number of flow regime and mass transfer variables can be calculated. The most relevant variables for selected diameters are listed in Table 3.

From Table 3 it can be seen, that a greater diameter correlates positively with the mass of the catalyst, the amount of liquid ammonia produced, the ratio of reactor diameter to particle diameter, and correlates negatively with the power input of the compressor, the Reynolds number, the mass transfer coefficient, and the gas hour space velocity (GHSV), being defined as the norm volume gas flow entering the reactor divided by the reactor volume. More catalyst leads to a higher capacity to produce ammonia and thus a higher amount of ammonia is being produced.

From Table 3 it can further be seen, that while the differences between 8 and 10 cm are small, the differences between 10 and 12 cm are very small and rather negligible. A high diameter ratio is desired to minimize wall effects. All ratios are above the recommended minimum ratio of eight [50] or ten [51].

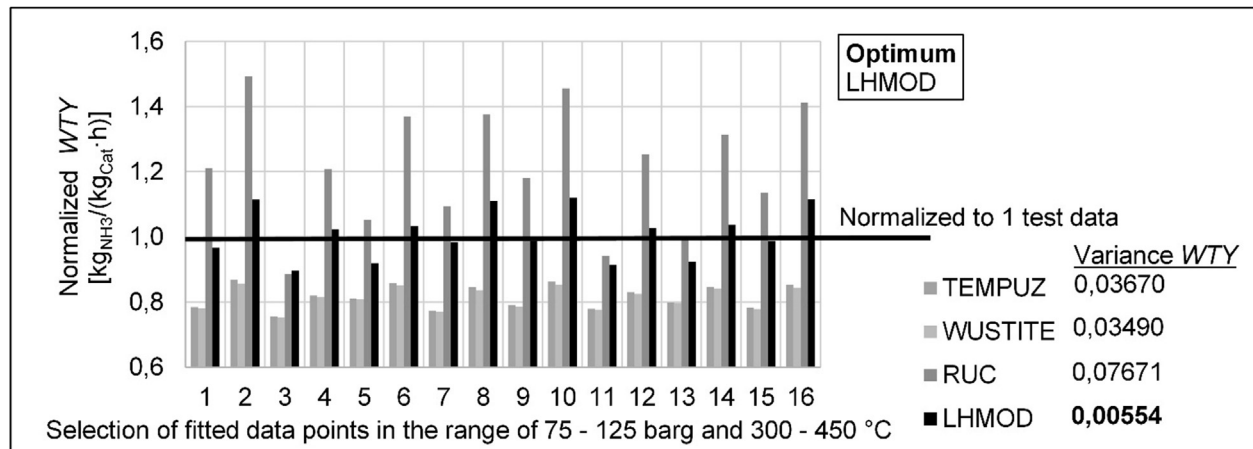


Fig. 2 – Results of the kinetic model fit.

Table 2 – Parameters of the LHMOD kinetics.

Parameter	Value	Unit
c_1	0,016	$\text{kmol}/(\text{kg} \cdot \text{s})$
c_2	0	J/mol
$c_3(T[\text{K}])$	$\exp\left(1,604 - \frac{10488\text{K}}{T[\text{K}]}\right)$	$\frac{5}{\text{bar}^2}$
$c_4(T[\text{K}])$	$\exp\left(29,194 - \frac{23235\text{K}}{T[\text{K}]}\right)$	$\frac{1}{\text{bar}^2}$
$c_5(T[\text{K}])$	1	–
$c_6(T[\text{K}])$	2	bar^{-1}

Another important ratio is the ratio of the reactor length to the particle diameter. If it is above the value of 100, a plug flow profile can be assumed [51], which is the case in the reactor setup. Thus, the assumed plug flow reactor model in Aspen Plus® is likely to be justified. A plug flow profile should also reduce the risk of a radial temperature profile with temperature hotspots in the middle of the bed.

A decrease in the diameter of the reactor leads to a lower catalyst mass. Less ammonia is being produced in one pass of the reactor. This means, that the amount of gas that is being recycled increases, increasing the required power input of the compressor and leading to a higher superficial gas velocity in the reactor. This increases the Reynolds number. The higher the Reynolds number, the more the flow regime changes from laminar to turbulent. A value below two indicates a laminar regime, and a value above 10 000 indicates a turbulent flow regime [51]. As can be seen from Table 3, all regimes are in

between laminar and turbulent, with a multiplying factor of 100 between the 12 cm and the 4,5 cm diameter. A turbulent regime ensures a good mixing in the bulk gas phase, thus leading to a higher mass transfer coefficient. A turbulent regime also makes a plug flow profile more likely, thus again decreasing the risk of a radial temperature profile and hotspots in the middle of the bed. Lastly, a higher recycle stream also increases the GHSV. In literature, values between 7800 and 400 000 are given [44,49,50]. Only the 4,5 cm and 5 cm diameters lie in that range. However, the diameter of 4,5 cm presents a lower limit, as can be seen in Table 3, that for a diameter of 4 cm, the Aspen Plus® simulation did not yield any liquid ammonia. At 4 cm the recycle stream becomes so great, that the partial pressure of the ammonia is not high enough for condensation to take place at 15 °C.

However, the information in Table 3 does not include some critical aspects, which cannot be determined by Aspen Plus® simulations, such as if pore diffusion is a limiting factor. In addition, the true radial temperature profile can only be determined by CFD simulations. Further, the assumptions of an isothermal reactor and a stoichiometric inlet ratio affect the values in Table 3.

Considering these unknowns and acknowledging, that Table 3 delivers both arguments for a smaller and a larger reactor diameter, the two diameters, 5 and 10 cm, which are close to the extremes in Table 3, shall be tested in FLEXnCONFU.

Regarding aim 3 defined in the previous section, for each of the two reactor diameters, a variation analysis, varying the

Table 3 – Selected variable results of the reactor diameter variation analysis.

	Unit	Source	Reactor diameter [cm]					
			4	4,5	5	8	10	12
Catalyst mass	kg	–	7	9	11	27	42	61
Mass flow liquid ammonia	kg/h	–	0	1,06	1,37	1,48	1,49	1,49
Ratio reactor diameter to particle diameter	–	–	19	20	22	36	44	53
Power input of compressor	MJ/h	–	–	84	27	7	6	6
Reynolds number	–	[51]	–	3500	890	80	50	33
Mass transfer coefficient	m/s	[51]	–	0,048	0026	0,011	0010	0,009
Gas hour space velocity GHSV	1/h	–	–	74 600	19 200	1800	1000	700

three temperatures T_1 , T_2 , and T_3 in the three sections (see Fig. 1) between 300 and 450 °C, was carried out. The electrolyzer capacity was kept at maximum 15 kW, and the hydrogen to nitrogen input ratio was kept at the stoichiometric value of three. The results are depicted in Fig. 3 and Fig. 4. In these figures, the amount of liquid ammonia leaving the condenser is depicted over the temperatures in the second and third compartments. The temperature profile optima with regards to liquid ammonia production are depicted as black columns and are summarized in Table 4.

According to Table 4, for both diameters, the optimum profile is a decreasing profile. The results seem to be in accordance with reactor profiles in literature [21] and make sense thermodynamically, since the reaction requires a higher temperature at the inlet, for the catalyst to reach its working temperature, but once ammonia is produced, the heat of the reaction has to be removed and the temperature has to be lowered for a more favorable equilibrium. The fact, that the smaller reactor diameter requires a higher temperature profile, can be explained by the larger recycle stream and the smaller amount of catalyst present. For a smaller amount of catalyst to produce the same amount of ammonia, the temperature must be increased to increase the activity of the catalyst. However, high temperatures are counterproductive to the equilibrium. This is compensated by a higher recycle flow, i.e. throughput to the reactor. For a fast start-up of the P2A system, lower temperatures are favorable, but since more catalyst needs to be heated up, it is unclear if the smaller or bigger reactor will display a faster start-up time.

Regarding aim 4 defined in the previous section, taking the optimum temperature profiles from Table 4, again for each reactor diameter, another variation analysis, varying both the inlet hydrogen to nitrogen ratio entering the P2A cycle and the electrolyzer power input, was conducted. The results are depicted in Fig. 5 and Fig. 6, in which the amount of liquid ammonia leaving the condenser is depicted over the varied electrolyzer power and inlet ratio.

In both figures, the optimum inlet ratio with regards to liquid ammonia leaving the system, indicated by the black columns, is not the stoichiometric value of three, but 2,96, for

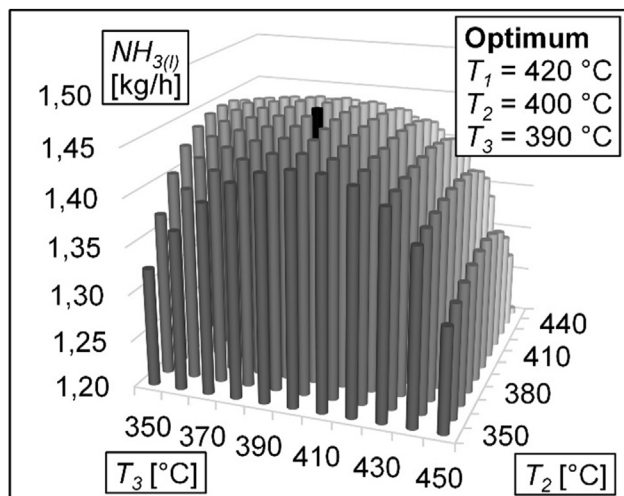


Fig. 3 – Results for the 5 cm reactor temperature variation.

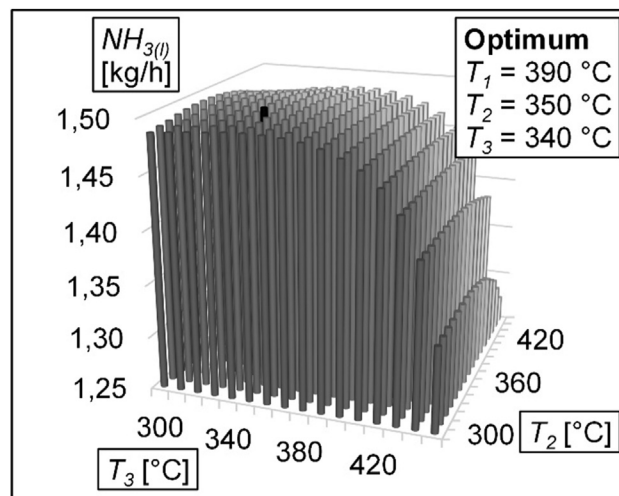


Fig. 4 – Results for the 10 cm reactor temperature variation.

Table 4 – Optimum reactor temperature profiles.

Reactor diameter [cm]	T_1 [°C]	T_2 [°C]	T_3 [°C]
5	420	400	390
10	390	350	340

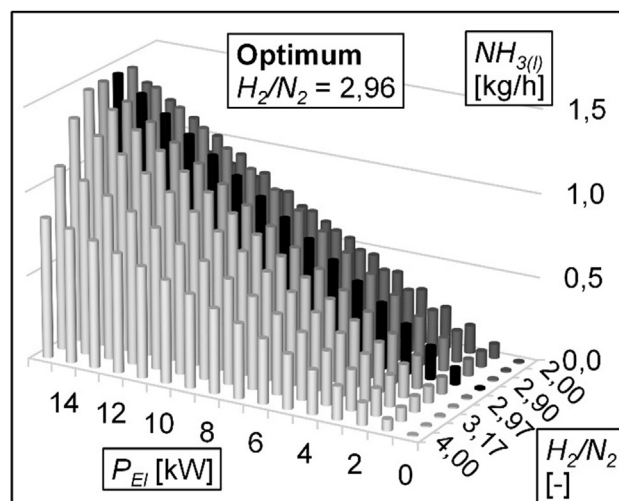


Fig. 5 – Molar inlet hydrogen to nitrogen variation results for the 5 cm reactor.

every electrolyzer power input. Both lower and higher ratios lead to a lower output of liquid ammonia. The fact, that the optimum ratio is not stoichiometric, can be explained by the condenser. Some of the nitrogen is being condensed in the condenser, changing the input ratio of hydrogen to nitrogen to higher values. This change is increased by the recycling stream. Thus, a less than stoichiometric input ratio is required. Nevertheless, the optimum inlet ratio is still close to three, which is dictated by the overall mass balance of the P2A system, which is determined by the stoichiometry of the reaction given in Eq. (1), because for every ammonia particle leaving the cycle, three particles of hydrogen and one particle

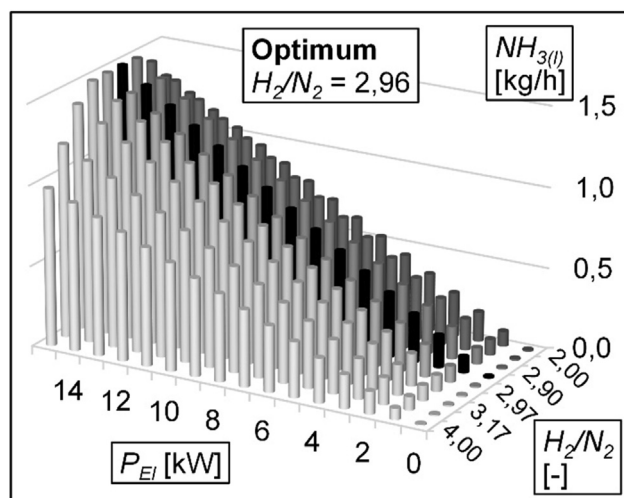


Fig. 6 – Molar inlet hydrogen to nitrogen variation results for the 10 cm reactor.

of nitrogen need to enter the cycle to balance the mass balance.

However, the optimum inlet ratio does not give the inlet ratio in the reactor. In systems without recycling, the optimum reactor inlet ratio with regard to maximum ammonia production depends on the catalyst and may not be the stoichiometric value [21]. Not only the inlet ratio in the P2A system but also the reactor inlet ratio needs to be considered. These ratios are given in Table 5.

Table 5 shows, that for both reactor diameters, the reactor inlet ratio is smaller than the stoichiometric value of three, i.e. for the 5 cm reactor the value is ca. 1.9 and for the 10 cm reactor the value is even lower at ca. 1.5, i.e. half the stoichiometric value. The differences between the two diameters and between the almost stoichiometric system inlet ratio may be explained by both the different temperature profiles in the reactors and by the different ammonia concentrations entering the reactors, as not all ammonia is being condensed in the condenser, but accumulates in the system because of the recycle. Both the temperature and the composition affect the chosen LHMOK kinetics in Table 1. The kinetics influences the amount of gas being recycled. This, together with the fact that the overall mass balance for the P2A system still has to hold true, leads to lower than stoichiometric inlet ratios into the reactors in both setups.

Lastly, it should be critically remarked, that the described procedure of first determining the optimum reactor diameter, then the optimum temperature profile, and last the optimum inlet ratio, is a practical way, but may not lead to the optimum solution. Instead, a variation analysis varying all three variables together would lead to a solution close to the real

optimum. Similarly, an optimization calculation with the three variables would lead to the exact optimum. However, both methods are restricted practically by the Aspen Plus® software, as it is not designed for large variation analyses let alone optimization calculations.

On top of that, the above-mentioned uncertainties regarding the diameter would remain. For this reason, the chosen two diameters are kept. For each of the two diameters, another variation analysis, this time of the inlet ratio and the reactor temperatures together, is carried out. For sake of practicability in Aspen Plus®, the variables are varied just in small intervals around the optimum values stated above, i.e. between 2.94 and 2.98 for the inlet ratio and plus-minus 20 °C for each reactor temperature. The results are listed in Table 6.

The optimum values in Table 6 are identical to the values of Tables 4 and 5, apart from the first temperature for the 10 cm diameter, which is 10 °C lower, i.e. 380 instead of formerly 390 °C. Since the combined variation analysis leads to similar results as the consecutive variation analyses and most importantly does not contradict them, it can be assumed and is assumed here, that the values in Table 6 are close to the optimum values. However, it needs to be stressed, that only an optimization calculation could verify this.

Regarding aim 5 defined in the previous section, taking the optima from Table 6, the P2A and P2A2P efficiencies of Eq. (4) and Eq. (5) for the two reactors' diameters are calculated and given in Table 7.

The P2F2P efficiencies of 7 and 8% in Table 7 are rather small, compared to values for other fuels such as methane (27%), methanol (27%), dimethyl ether (23%), and ammonia (35%) [52] and for ammonia even up to 53 [53] and 61% [6] from literature. However, both [6,53] suggest using very advanced technology, such as not yet commercially available catalysts and fuel cells instead of a gas turbine. Furthermore, it should be emphasized again, that the suggested P2A system is designed for low investment cost and a fast start-up behaviour and not for maximum efficiency. Systems with low investment costs usually display low degrees of efficiency, as there is a trade-off between investment cost and efficiency. Internal heat integration and other efficiency raising means are left out in the design as well, as they are a hindrance to a fast start-up.

Regarding aim 6 defined in the previous section, without changing the design of the cycle, two free variables remain, i.e. the compressor outlet pressure and the condenser temperature. Higher pressure and lower condensation temperature both lead to a higher liquid ammonia production, as a high pressure favours the formation of ammonia in the reactor (see Eq. (1)) and a lower condensation temperature leads to more condensation of ammonia. Fig. 7 and Fig. 8 confirm this.

Table 5 – Optimum hydrogen to nitrogen ratios.

Reactor diameter [cm]	P2A inlet H_2/N_2 ratio [–]	Reactor inlet H_2/N_2 ratio [–]
5	2,96	1,9
10	2,96	1,5

Table 6 – Optima of inlet ratio and reactor temperature variation analysis.

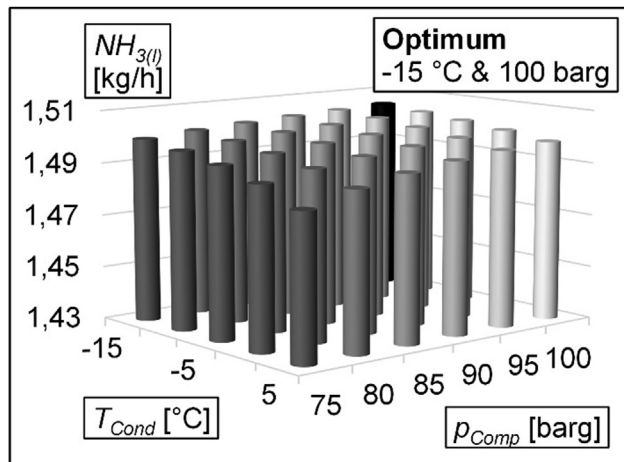
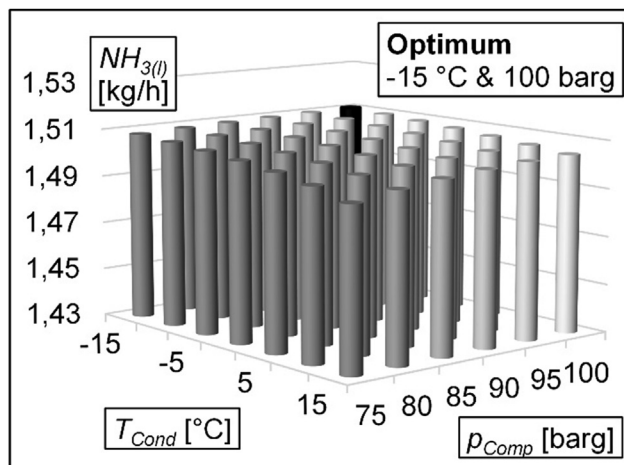
Reactor diameter [cm]	P2A inlet H_2/N_2 ratio [–]	T_1 [°C]	T_2 [°C]	T_3 [°C]
5	2,96	420	400	390
10	2,96	380	350	340

Table 7 – Energetic degrees of efficiency.

Reactor diameter [cm]	η_{P2A} [–]	η_{P2A2P} [–]
5	0,33	0,07
10	0,39	0,08

Table 8 – Design specification results.

Reactor diameter [cm]	$NH_{3(l)}$ [kg/h]	p_{Comp} [barg]	T_{Cond} [°C]
5	1466	75	11,36
10	1499	75	11,42

**Fig. 7 – Compressor outlet pressure and condensation temperature variation results for the 5 cm reactor.****Fig. 8 – Compressor outlet pressure and condensation temperature variation results for the 10 cm reactor.**

In Figs. 7 and 8 the pressure is varied between 75 and 100 barg, to be in accordance with the kinetics fit pressure range (see Fig. 2), and the temperature is varied between -15 and 15 °C, to be able to employ a conventional VCR cycle. The opposing effects of pressure and temperature on the amount of liquid ammonia produced, shown in Figs. 7 and 8, can be used, to further reduce the investment costs. Assuming, that the investment cost reduction of all cycle components of lower pressure is greater than the increase in investment cost for a more efficient VCR cycle, a design specification calculation is conducted in Aspen Plus®. This means, that with the optimum values from Table 6, the condenser temperature is calculated, which keeps the liquid ammonia output constant,

whilst reducing the compressor output pressure to 75 barg. The results of the design specification calculation are given in Table 8.

Table 8 shows, that a reduction in pressure of 5 barg can be compensated by a similar reduction in condenser temperature of ca. 4 °C for both reactor diameters.

Conclusions

A novel small-scale containerized P2A concept, aiming at low investment costs and time-flexibility, has been presented and verbally compared to competing large and small-scale designs found in practice and literature.

To size the reactor, being the vital component for the desired time-flexibility and mild operating conditions below 420 °C and 80 barg, Aspen Plus® simulations were conducted. First, a kinetics fit to determine a suitable reaction kinetics for the iron-based catalyst, which will be employed, was carried out, leading to the best fitting model LHM0D (see Tables 1 and 2).

With this model, three consecutive variation analyses were carried out to determine the optimum reactor diameter, reactor temperature profile and cycle inlet molar ratio of hydrogen to nitrogen, all three with the objective to maximize the amount of liquid ammonia being produced. The analysis of key variables, e.g. the Reynolds number, and a comparison with data from the literature, provides arguments for both a larger and smaller reactor diameter. As a consequence, two diameters, 5 and 10 cm, will be tested in the pilot plant container. For these diameters, the optimum temperatures T_1 , T_2 , and T_3 (see Fig. 1) for the three sections were calculated to be decreasing profiles of 420, 400, and 390 °C and 380, 350, and 340 °C (see Table 6). The optimum molar cycle inlet ratio of hydrogen to nitrogen was calculated to be 2,96 for both diameters (also see Table 6).

Comparing the calculated P2F2P efficiencies of both scenarios to data of other renewable fuels in the literature, the new cycle is rather close to 10% than close to 30% of the other fuels. However, all data has not been tested in practice. Additionally, the new simple cycle employing conventional technology has been designed for low investment cost and not a high cycle efficiency. Thus, a poorer cycle efficiency compared to data found in literature was to be expected.

Lastly, it was found, that decreasing the cycle pressure further to 75 barg, and with it likely decreasing the investment cost further as well, can be compensated by a relatively small reduction in the condensation temperature from 15 to 11 °C, all the while keeping constant the amount of the produced liquid ammonia.

The proposed containerized concept will be ready to be tested starting in early 2023. The optimum start-up and

steady-state reactor temperatures will be determined. For this, the presented simulation results will be used as starting points. Then, the true P2F2P efficiency will be known and a fair comparison with other cycles and fuels will be possible.

Furthermore, both investment and operation costs will be known by then, which will allow for a thorough cost analysis, including a thermo-economic analysis, i.e. exergy costing [31,54] or exergo-environmental costing [55], again, with the aim of a fair comparison with other cycles and fuels.

The data from the tests will also be used to verify the Aspen Plus® model as well as to optimize it. Building on this, a dynamic model of the process shall also be developed using the software Aspen Plus Dynamics®. Dynamic models are crucial to analyze the compatibility of P2A systems with the fluctuating renewable sources of energy [56,57].

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Nomenclature

$\Delta \bar{h}^\circ$	Molar standard reaction enthalpy (1 bar, 298 K) (J/mol)
c_i	Parameter ($i = 1, \dots, m$ and n)
f	Fugacity (bar)
GHSV	Gas hour space velocity (Nm ³ /h _{Gas inlet} /m ³ _{Reactor volume})
LHV	Mass specific lower heating value (J/g)
\dot{M}	Mass stream (g/s)
p	Partial pressure (bar)
p_{Comp}	Compressor outlet pressure (barg)
P_{el}	Electrical power (W)
\dot{Q}	Heat flow (W)
r	Rate of reaction (mol/g _{Catalyst} · s)
\bar{R}	Ideal gas constant (J/mol · K)
T	Temperature (K)
T_{Cond}	Condenser temperature (°C)
\dot{V}_N	Norm volume flow (Nm ³ /h)
WTY	Weight time yield (g _{NH₃} /g _{Catalyst} · h)

Greek letters

η_{P2A}	Energetic degree of efficiency P2A
η_{P2A2P}	Energetic degree of efficiency P2A2P

Acronyms

CFD	Computational fluid dynamics
FLEXnCONFU	Flexibilize combined cycle power plant through power-to-X solutions using non-conventional fuels
EU	European Union
H ₂	Hydrogen
HYSR	Aspen HYSYS® Peng Robinson
LHMOD	Langmuir Hinshelwood modified
LLHW	Langmuir Hinshelwood Hougen Watson
N ₂	Nitrogen
NH _{3(l)}	Liquid ammonia
P2A	Power to ammonia
P2A2P	Power to ammonia to power
P2F	Power to fuel
P2F2P	Power to fuel to power
PSA	Pressure swing adsorption
PR	Peng Robinson
RKS	Redlich Kwong Soave
RUC	Ruthenium supported on carbon
TEMPUZ	Temkin-Puzhev
VCR	Vapour compression refrigeration
WUSTITE	Iron oxide wustite

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