SolarPACES 2023, 29th International Conference on Concentrating Solar Power, Thermal, and Chemical Energy Systems

Solar Fuels and Chemical Commodities

https://doi.org/10.52825/solarpaces.v2i.744

Integrated Solar Production of Fertilisers and Fuels

Martin Roeb[1,*], Pablo Lopez Martinez[1], Nicole Neumann[1], David Baumstark[1], Lena Klaas[1,2], Dorottya Kriechbaumer[1], Nathalie Monnerie[1], Christos Agrafiotis[1], and Christian Sattler[1,2]

[1] German Aerospace Center (DLR), Institute of Future Fuels, Germany

[2] Faculty of Mechanical Engineering, RWTH Aachen University, Germany

*Correspondence: Martin Roeb, martin.roeb@dlr.de

Abstract. Solar fertiliser production including the internal utilisation of the side-product oxygen is analysed as one promising example of an innovative process utilising renewables energy resources and addressing the aspect of integrated production – here in the case of nitrogen containing fertilisers. Alternative methods to supply solar energy into the energy intensive generation of precursors needed for nitrate-based fertiliser via the Haber Bosch and Ostwald process are introduced. Those methods are assessed in a comparative way through process design and simulation with a focus on oxygen injection inside the NO_x combustion of the Ostwald process and through calculation of its economic impacts.

Keywords: Ammonia, Hydrogen, Solar Chemistry, Solar Fertiliser

1. Introduction

A characteristic for production plants, and especially for chemical production plants, is that the production plants for the individual processes consist of many individual unit operations and have a correspondingly complex structure. This applies in particular to plants with continuous process operation, as there must be an especially suitable arrangement for each interface between the individual process units. Thus, chemical processes and plants are characterized by a high degree of complexity.

Another special feature of such processes is that not only the desired product is obtained, but also co-products and by-products, depending on the reaction system. Co-products are inevitably formed due to the stoichiometry of the main reaction. By-products can be formed by parallel and subsequent reactions. Their formation can be controlled within certain limits by adjusting the reaction conditions - e.g. pressure, temperature, choice of catalyst. With suitable reaction control, it is possible to minimize such by-products, but their formation cannot usually be completely suppressed. Recently, environmental protection, resource conservation and sustainability have also become increasingly important. It is therefore necessary to try to recycle the co-products and by-products generated either internally or externally to the process. This is more likely to be possible in a larger plant complex with many product strands than in smaller plants.

In the near future not only the raw material base for such processes will shift toward substances that enable closed material cycles, but also the energy sources. These will be based less and less on the partial combustion of fossil raw materials and more and more on renewable energy sources. This requires a drastic restructuring of the established processes and their coupling to power and heat sources [1]. The present study analyzes scenarios, processes and key components necessary for this, production networks or integrated production of chemical products, fuels and basic materials produced using renewable energy. The central focus of the study is on the use of solar energy in production networks of common production of fuels and fertilisers.

2. Fertilisers and Fuels

One important aspect are synergies which can be raised through the co-production of fuels and fertilizers. Different routes to solar fertilizer production are being investigated, not only for the "Big 3" (nitrogen, potassium and phosphorus), but also for other important additives such as lime (regulates pH, helps release the other components) and sulfur. Different scenarios can be developed by combining innovative and state-of-the-art solutions to optimize the entire process chain in terms of energy efficiency and by-product management. Special attention is currently be paid to the production of ammonia, as it is the most produced fertilizer component and the chemical feedstock with the highest global demand. In addition, ammonia is also gaining importance as an environmentally friendly fuel and energy storage, which creates a direct link between the agricultural and energy sectors [2]. In this context, the main aspects to be investigated are the production of the raw materials (hydrogen and nitrogen), the energy integration of the process steps, the selection and scaling of the green ammonia production step, and the production of nitric acid from ammonia as the main precursor for nitrate fertilisers.

Solar production of feedstocks, as well as ammonia synthesis, was investigated. Solar production would enable on-site and on-demand production of fertilizer mixtures tailored to specific soil and crop needs, while providing a solution for fuel and energy storage for agricultural machinery. To ensure a circular approach, solutions for fertilizer recovery, waste management and smart fertilizer distribution are also to be considered.

The investigations in this contribution exemplarily focus on the search of synergies between solar-powered nitrogen and hydrogen production technologies to provide green ammonia, and the subsequent nitric acid process. Specific attention is put on the effect of utilizing the oxygen by-product from solar-powered thermochemical air separation to produce nitrogen, and from water splitting to provide green hydrogen. The main objectives are to study the technical and economic feasibility of producing nitric acid using green ammonia powered by solar energy and how oxygen injection might influence the nitric acid plant design and economics.

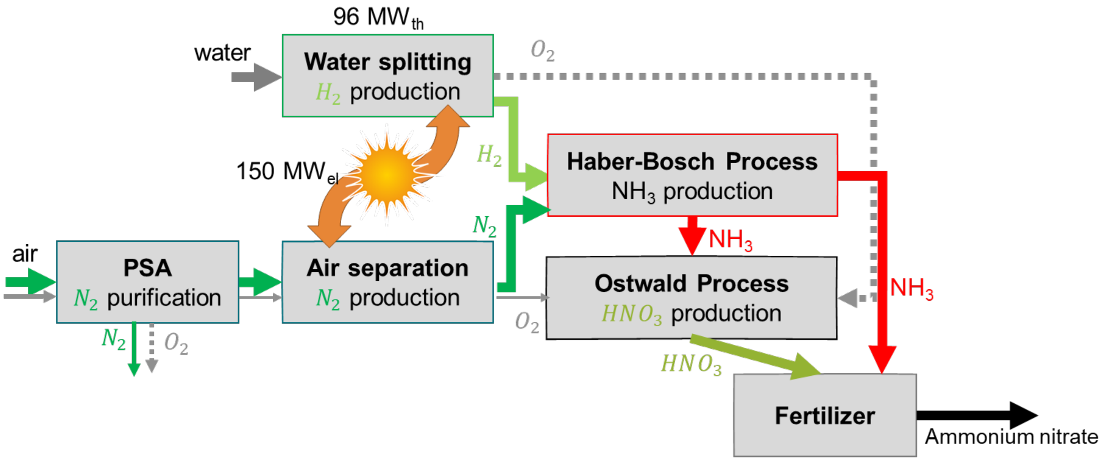

***Figure 1**. Scheme of solar-assisted nitric acid and fertilizer production.*

Figure 1 illustrates the concept of a nitrogen fertilizer plant based on concentrated solar energy as the resource and of thermochemical air separation of the nitrogen production and purification route. Nitrogen and hydrogen, also produced by a thermochemical cycle, are sent to a Haber-Bosch Process. The resulting ammonia is further processes in an Ostwald plant utilizing the oxygen side-stream from the air separation and water splitting to generate Ammonium Nitrate.

3. Haber-Bosch and Ostwald Process

3.1. Haber-Bosch Process

Ammonia is the main precursor of nitrate fertilisers and is mainly produced from natural gas and water and air. In this case, the fuel source that provides the hydrogen is a hydrocarbon commercially called natural gas. The conventional ammonia synthesis process consists of 8 stages as can be seen in Figure 2. The first process is the desulphurisation of natural gas. The natural gas is a dry gas containing up to 40 ppm by weight of sulphur. This sulphur must be removed as it acts as a poison for the reforming catalyst. This sulphur is removed by treating natural gas with zinc oxide. It absorbs the hydrogen sulphide and reduces the sulphur content to less than 5 ppm. Once the sulphur is removed, the natural gas is ready to enter the two reforming sections.

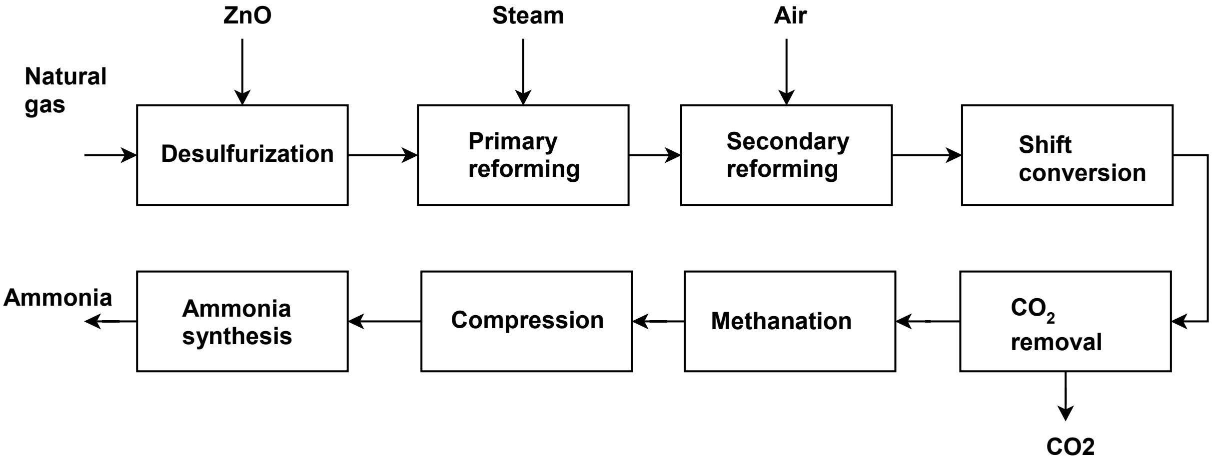

***Figure 2**. 8-step ammonia synthesis from natural gas.*

The primary reformer converts natural gas in the presence of steam into hydrogen and carbon monoxide. The reformed gas leaving the primary reforming unit enters the secondary reforming section to be treated with hot air to ensure that the methane content is reduced to less than 0.3 % by volume. The next step is the conversion of carbon monoxide into carbon dioxide. This process consists of two catalytic stages: the first at high temperature with Fe_3O_4 or CrO as catalysts and the second at low temperature with CuO, ZnO, or Al_2O_3 as catalysts.

The carbon dioxide is then removed and captured with ammonia, producing ammonium hydrogen carbonate as by-product. The purified gas with a CO_2 content of 0.1 % by volume is called synthesis gas. As it is mentioned above with the presence of sulphur, small amounts of CO and CO_2 also lead to catalyst poisoning in the ammonia synthesis. For this reason, the CO and CO_2 content is reduced by reacting the synthesis gas in the presence of a nickel-based catalyst.

In this way, the carbon oxides composition is reduced to less than 10 ppm. Once the synthesis gas (typically 74 vol% H_2, 24 vol% N_2, 0.8 vol% CH_4 and 0.3 vol% Ar) is free of impurities, it is compressed to the design pressure and fed into the converter to proceed with the substantially exothermic ammonia synthesis. According to the stoichiometry, the desired H_2/ N_2 molar ratio downstream the methanation process should be 3. The reaction is energetically demanding and kinetically complex as it requires high temperatures (400 - 500 °C) and pressures (100-200 atm).

3.2. Ostwald Process

The production of nitric acid from ammonia as the main precursor of nitrate-based fertilisers is one of the oldest and most important chemical processes. It was developed by the German chemist Wilhelm Ostwald at the beginning of the 20th century. This process consists mainly of three steps.

First, the catalytic oxidation of ammonia forms the basis of the nitric acid process (see Figure 3). The oxidation occurs when anhydrous ammonia in contact with air is led over a platinium-rhodium gauze catalyst made of 90% platinum and 10% rhodium. Under optimal temperature conditions and in the presence of such catalyst, the catalytic combustion efficiency of ammonia is quite high, around 93-98%. Ammonia penetrates through the gaseous film to the catalyst surface, where it is oxidized to form nitric oxide [3]. At the end of the combustion chamber, the gaseous mixture is promptly quenched with the aim of preventing the NO decomposition. This step is an extremely fast heterogeneous reaction, with a reaction time in the range of 0.1 milliseconds [4].

All reactions are sufficiently exothermic to be self-sustaining and are practically irreversible. In fact, in the absence of a catalyst, only nitrogen would be formed. For that reason, the presence of a suitable catalyst (e.g. Pt-Rh) is essential to produce nitric oxide. An important side reaction, the comproportionation of NO with NH_3 to form nitrogen, only takes place if the gas velocity is low enough for the already formed nitric oxide to diffuse towards the catalyst. Such side reaction can easily be avoided by decreasing the contact time between the reactants and the catalytic wire gauze [5].

The second step is the oxidation of nitric oxide into nitrogen dioxide and dinitrogen trioxide. Non-reacted oxygen remaining from ammonia combustion undergoes a reaction with the nitric oxide to generate nitrogen dioxide. This reaction occurs while the exit gas is cooled to recover the heat released by the strongly exothermic reaction. At the same time, nitrogen dioxide can dimerise to form dinitrogen tetraoxide. And as an undesirable side reaction, nitric oxide and nitrogen dioxide can react to form dinitrogen trioxide.

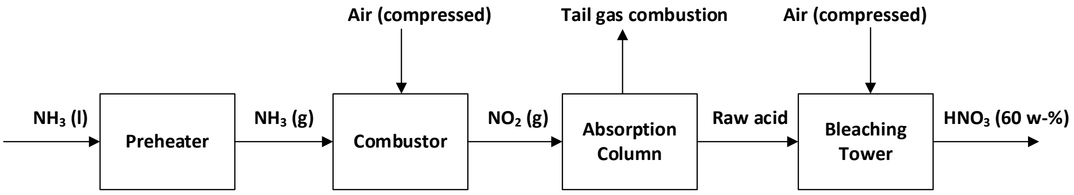

***Figure 3**. Scheme of main steps of Ostwald process for nitric acid production.*

Finally, the third and last step is the reactive absorption of nitrogen dioxide and dinitrogen tetraoxide in water. NO_x absorption has been defined by many researchers as one of the most
complex absorption mechanisms due to several reasons:

- NOx gas is a mixture of several nitrogen oxides (NO, NO_2, N_2O_3 and N_2O_4). The absorption of these nitrogen oxides in water results in two oxyacids, nitric acid and nitrous acid.

- More than forty equilibrium reactions occur in both gas and liquid phases.

- The absorption of NO, NO_2, N_2O_3, and N_2O_4 is accompanied by chemical reaction whereas the desorption of NO, NO_2 and HNO_2 is preceded by chemical reaction.

- Heterogeneous equilibrium prevails between gas-phase and liquid-phase components

For the production of fertilisers, such as ammonium nitrate, a nitric acid concentration of
50-70% by weight is required.

4. Solar production of the fertiliser's precursors

While the main reactions of the Ostwald process are highly exothermal and thus self-sustaining the reactions constituting the Haber-Bosch process are only slightly exothermal. Since there is a need to pre-heat reactants and to work under high pressures there is a net demand for external heat and electricity supply which can be covered from renewable and in particular solar energy sources to render the overall process carbon-lean or even carbon neutral.

Beyond that, since the highest share of energy demand comes along with it, is the provision of the required precursors hydrogen, nitrogen and oxygen. Since those species are not present in nature, energy needs to be introduced to gain pure hydrogen, nitrogen and oxygen from suitable feedstocks, which are ideally water and air, and which can be carried out by using solar energy and in particular by applying solar thermochemical methods.

4.1 Hydrogen

The environmental impact of the conventional hydrogen production, which is still the predominant method to produce the by far biggest share of hydrogen today, is huge. Steam methane reforming releases 9.26 kg CO2/ kg H_2 [6]. Over 79 % percent of global hydrogen production comes from fossil fuels. Accounting fossil-based hydrogen responsible of the 2 % of global CO_2 emissions in energy and industry in 2020 [7].

But there are already technologies that are in progressing towards scaling up and ramping up for a future mass production of green hydrogen. It is the case of water electrolysis, which is expected to be the main source of hydrogen production in the future, considerably reducing the use of natural gas as feedstock and the use of the steam methane reforming process.

Water electrolysis is an electrochemical process that by using electricity is able to split water molecules into hydrogen and oxygen. This process can be a much more environmentally friendly option, if the source of the electricity is a renewable energy source. Therefore, solar energy can be implemented into the process of producing hydrogen from water electrolysis.

There are mainly 4 electrolyser technologies: alkaline, proton exchange membrane (PEM), solid oxide electrolysis cells (SOECs), and anion exchange membranes technologies. Alkaline electrolysers dominate with 61% of installed capacity in 2020, while PEMs have a 31% share. The remaining capacity is of unspecified electrolyser technology and SOECs [7].

The cost per kg of hydrogen produced by means of electrolysis is still significantly higher than the cost by means of SMR. Still there is a perspective that a market penetration with a competitive price can be obtained by a ramp up of green hydrogen demand, by further improving this technology and by penalising the use of fossil fuels by 2030.

As an alternative to the electrochemical paths, also thermochemical paths can be applied for hydrogen production that use high-temperature heat from concentrating solar thermal technologies. The use of high-temperature thermal heat for water splitting potentially enables high efficiencies and thus competitive hydrogen production costs. Two paths of thermochemical hydrogen generation have emerged in research that are especially promising in terms of their efficiency: One family of processes are metal oxide redox processes and the other is the family of sulfur cycles [8, 9]. In the following only redox cycles are considered further because they can be combined with thermochemical nitrogen production in a synergetic and highly integrated way.

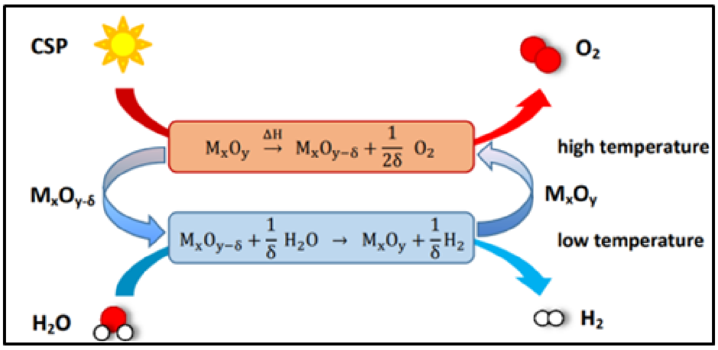

***Figure 4**. Redox cycle for solar thermochemical water splitting.*

In the cyclic process depicted in Figure 4, a redox material is typically first reduced in an endothermal process step and then oxidized in a second exothermal process step. In this process, the redox material is in contact with water vapor and captures the oxygen from it. These cyclic processes are called cycles because the redox material assumes different states but is not consumed itself. The reduction step usually takes place at temperatures above 1000 °C. There are a number of other thermochemical water splitting processes that consist of a higher number of process steps, which allows the required maximum temperatures to be lowered but exhibiting other process challenges.

4.2 Nitrogen

Nitrogen constitutes besides hydrogen constitute the second main feedstock for ammonia synthesis and its purity play a crucial role in the Haber-Bosch process. The presence of oxygen and water leads to the main deactivation of the catalyst, resulting in a considerable increase in the operating costs of the reactor [10]. The process most commonly used in industry for the separation of nitrogen from air is known as the Hampson-Linde process [11]. This process is very energy intensive (12 kJ/mol N_2) as cryogenic temperatures are needed to obtain oxygen and nitrogen in a liquid state [12]. There are other techniques based on adsorption at high pressures that also requires a high energy consumption such as pressure swing adsorption (PSA) or at low temperatures such as temperature swing adsorption (TSA) [13].

Apart from these physical separation methods, there are innovative thermochemical loops under investigation and development that can directly harness the solar heat from CSP plants to separate nitrogen and oxygen from air. Solar thermochemical air separation cycle uses a similar approach to the thermal water splitting process described before. The main difference is that air is used as oxidant instead of using water [13, 14]. Alternative approaches address the solar production of ammonia through the intermediate formation of metal nitrides like e.g. strontium nitride investigated at ETHZ [15] or iron-group-metal and molybdenum based ternary nitrides investigated at Arizona state university and Sandia NL [16].

4.3 Oxygen

The Ostwald process uses air and the oxygen contained therein to oxidize ammonia. Considering this it needs to be stated that in both air separation and hydrogen production, pure oxygen is obtained as a by-product. This gave rise to the idea of studying the feasibility and integration of this pure oxygen into the conventional Ostwald process. This research is doubly valuable in the quest to decarbonise chemical processes by 2050. It is a study aiming to optimise a nitric acid plant by integrating renewable technologies and making fertiliser production more sustainable. The implementation of oxygen-enriched air into the conventional nitric acid process is discussed in various patents [17, 18, 19]. This technique aims at optimising the nitric acid production process in several ways:

1. Maximising the catalytic combustion of ammonia conversion to generate an increase in nitric acid production

2. Increasing gaseous nitrous oxides conversion to reduce the final concentration of NO_x gases in the tail-gas

3. Boosting the bleaching process to increase the nitric acid strength and to improve the quality of the final product

5. Process Design and Simulation

One central aspect of the process design and evaluation was the integration of the by-product oxygen, stemming from water splitting and air separation, into the conversion process of ammonia to provide nitric acid as part of the Ostwald process. Therefore, the latter was modelled with AspenPlus and analysed under different boundary conditions with respect to the use of oxygen enriched air as oxidant.

The Aspen process flowsheet with the operating conditions (temperature and pressure) during the whole plant is shown in Figure 5. Liquid ammonia is first vaporized in and overheated at 150 ◦C before being mixed with the air stream. Filtered atmospheric air passes through a three-stages compressor train to remove air moisture and achieve the design pressure of 5.8 bar. This air-stream is split into two streams: a primary stream goes to the ammonia-air mixer and a secondary stream goes to the bleaching column (bleacher). The ammonia-air mixture is preheated at 200 ◦C before the catalytic combustion chamber. Ammonia is combusted in air while passing through a Pt-Rh catalytic gauze generating a gaseous stream containing nitrogen oxides, nitrogen and oxygen.

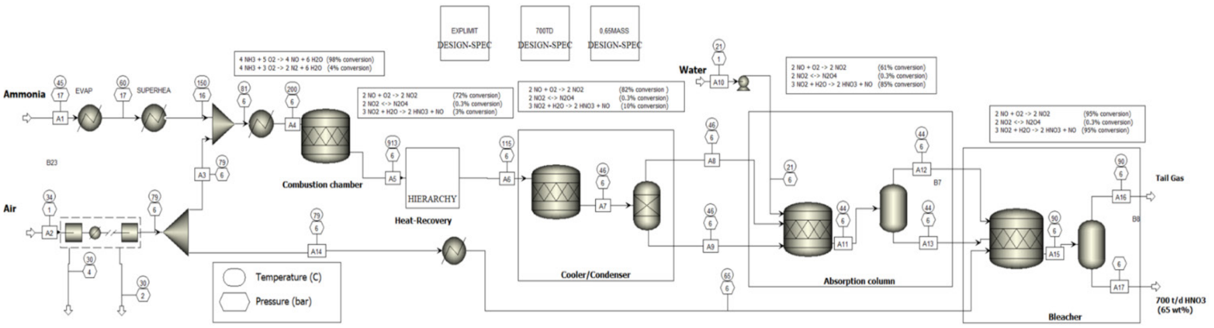

***Figure 5**. Flowsheet of Ostwald process for nitric acid production.*

In a heat recovery unit containing several heat exchangers is used to recover as much as possible of the heat released by the series of exothermic reactions of converting NH_3 to NO_x. Along with the heat recovery nitric oxide is oxidized to nitric dioxide in a first step and thereafter dimerised to form dinitrogen tetroxide. Then, this gas stream is partially condensed in a cooler-condenser by cooling water. Weak nitric acid is formed at the bottom of the condenser and redirected to the lower middle part of the absorption column.

To the remaining gas stream air is added which is taken from the bleaching column and led to the bottom of the absorption column. Then, NO_x gas stream is exposed to process water that enters at top of the column in countercurrent contact. This absorption process leads to obtaining the required nitric acid concentration at the bottom. In a final step, the yellow acid liquid is sent to the bleaching column to be bleached with additional air.

The NO_x gases leaving at the top of the absorption column are sent to a series of gas-gas heat exchangers. After that, they are treated in a removal NO_x section before being vented at a concentration lower than 50 ppm_v. As a result, 199.5 tons per day of ammonia, 3915.5 tons per day of air and 243.6 tons per day of process water are needed to produce 700 tons of nitric acid per day.

6. Techno-economics of a (solar) nitric acid production plant

The economic analysis is carried out on three different types of nitric acid plants based on the results of a process simulation to compare the main limitations and disadvantages of producing nitric acid in a more sustainable way compared to the conventional process:

1. Conventional nitric acid plant: Considering ammonia and electricity prices of fossil-based production

2. Solar-based nitric acid plant: Considering ammonia and electricity prices of solar-based production

3. Optimised solar-based nitric acid plant: Integrating the surplus oxygen from water electrolysis in the solar nitric acid production plant.

Sensitivity analyses were performed on profitability metrics such as return of investment (ROI), minimum selling price (MSEP) and payback period (PBP) among others. The results of the techno-economic analysis give a clear picture of the challenges and considerations when simulating and evaluating different types of nitric acid plants from an economic point of view.

The first and most fundamental step was to model and simulate the nitric acid plant in a rigorous way. The complexity of the simulation of the Ostwald process in process simulation software lies in the implementation of the kinetic reactions during the heat exchangers and mainly in the absorption column. As a result of the simulation, it is obtained that 199 tons/day of ammonia, 3916 tons/day of air and 244 tons/day of process water are necessary to produce 700 tons/day of nitric acid at a concentration of 60 wt%.

The feasibility of optimising nitric acid production and reducing the final NO_x concentration of the absorption column by injecting pure oxygen at different points of the plant was studied. The aim of this research is to find synergies between the remaining oxygen from green ammonia production and nitric acid production. The results indicate that the greatest benefits are obtained for the case in which oxygen is injected into the main air line and increasing the oxygen content by 6.1 wt% (from 22.4 wt% to 28.5 wt%), the daily nitric acid production could be increased by 0.34 % and the nitrogen oxides content decreased by 43.6 % [20].

The sensitivity analysis to changes in cooling water cost, ammonia cost and catalyst cost are consistent provided that the MSEP of nitric acid could decrease by almost 42 % with an 80 % decrease in the cost of ammonia which in turn is crucially dependent on the hydrogen production costs. In sum, the economic assessment shows that the final product price of nitric acid strongly correlates with the purchased ammonia. Therefore, the conventional process has the lowest production cost of 220 $/t of nitric acid which is 22% lower than the solar produced nitric acid including oxygen injection of 267 $/t. Taking into account CO2-certificates, a break-even point of the solar production route could be reached for a certificate price of 233 $/tCO2.

7. Conclusions

Different routes to solar fertilizer production have been considered. Different plant and process scenarios have been analysed by combining innovative and state-of-the-art solutions to improve the entire process chain in terms of emissions, energy efficiency, and by-product management. Special attention was paid to the production of ammonia, since this is the most produced fertilizer component and the chemical feedstock with the highest global demand and since it is also gaining importance as a potential fuel and energy storage medium, which creates a direct link between the agricultural and energy sectors. One well established production route for nitrate fertilizer, the combination of the Haber-Bosch and Ostwald process, has been analysed with respect to solar energy integration and in particular the potential benefits of integrating side products like oxygen into the NO_x oxidation as part of the Ostwald process has been evaluated techno-economically.

The feasibility of improving nitric acid production and reducing the final NO_x concentration of the absorption column by injecting pure oxygen at different points of the plant was studied. The simulation results indicated certain synergies through using oxygen as the side-product from green ammonia production for nitric acid production. By injecting oxygen into the main air line and by increasing the oxygen content the daily nitric acid production could be increased and the nitrogen oxides content decreased. Though the oxygen injection and solar energy supply introduce several technical benefits the overall production cost are about 22 % higher than in a conventional process, in which the product cost are dominated by the ammonia and more specific by the hydrogen cost. An economic break-even point is forecasted for the solar production route if potential certificate prices of 233 $/tCO2 are assumed.

Author contributions

MR: Martin Roeb; **LK**: Lena Klaas; **DK**: Dorottya Kriechbaumer; **PLM**: Pablo Lopez Martinez; **DB**: David Baumstark; **NN**: Nicole Neumann; **NM**: Nathalie Monnerie; **CA**: Christos Agrafiotis; **CS**: Christian Sattler

Conceptualization **NN, DB, LK, CS**; Data curation **PLM, NN, DB**; Formal analysis **PLM, NN, DB, DK**; Funding acquisition **MR, NM**; Investigation **PLM, NN, DB, DK**; Methodology **PLM, NN, DB**; Project administration **NN**; Resources **MR, NM, CS**; Software **PLM, NN**; Supervision **NN, DB**; Validation **PLM, NN, DB, CA**; Visualization **PLM, NN, DB, MR**; Roles/Writing - original draft **MR, PLM, NN, DB**; Writing - review & editing **PLM, NN, DB, MR, NM, LK, CA**.

Data availability statement

Due to the conditions given by the related project and concerning the cooperation with external partners the authors cannot place the used data in an openly available space.

Competing interests

The authors declare that they have no competing interests.

Funding

This work has received funding from project SESAM (EFRE-0801808), which is co-funded by the federal state of North Rhine-Westphalia, Germany and from project Mesowas (03SF0648A), which is supported by the German Ministry for Education and Research (BMBF.722).

References

[1] J. J. Klemes, P. Sabev Varbanov, S. R. Wan Wan Alwi, Z. A. Manan, “Process integration and intensification, saving energy, water and resources”, De Gruyter 2014. https://doi.org/10.1515/9783110306859

[2] S. Budinis, A. Gouy, P. Levi, H. Mandová, T. Vass, International Energy Agency, Ammonia Technology Roadmap, “Towards more sustainable nitrogen fertiliser production”, 2021.

[3] N. I. Ilchenko, “Catalytic Oxidation of Ammonia”, Russian Chemical Reviews 45.12 (Dec. 1976), 1119–1134

[4] M. Koukolik, J. Marek, “Mathematical model of HNO3 Oxidation-Absorption equipment”, In: Proc. Fourth European Symp. on Chem. Reaction Eng. (1968).

[5] M. Thiemann, E. Scheibler, and K. Wiegand, “Nitric Acid, Nitrous Acid, and Nitrogen Oxides”, In: Ullmann’s Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA, June 2000.

[6] P. Sun and A. Elgowainy, “Updates of Hydrogen Production from SMR Process in GREET 2019”; Argonne National Laboratory: Lemont, IL, USA, 2019.

[7] “Global Hydrogen Review 2021”. In: IEA Publications (2021). URL: http://www.iea.org/about/contact.

[8] C. Sattler, M. Roeb, C. Agrafiotis, D. Thomey, “Solar hydrogen production via sulphur based thermochemical water-splitting”, Solar Energy 156, 30-47, 2017, DOI: 10.1016/j.solener.2017.05.060

[9] C. Agrafiotis, D. Thomey, L. de Oliveira, C. Happich, M. Roeb, C. Sattler, N. I. Tsongidis, K. G. Sakellariou, C. Pagkoura, G. Karagiannakis, A. G. Konstandopoulos, D. Pomykalska, M. Zagaja, D. Janus, “Oxide particles as combined heat storage medium and sulphur trioxide decomposition catalysts for solar hydrogen production through sulphur-based cycles”, International Journal of Hydrogen Energy, 44, 2019, 9830-9840, https://doi.org/10.1016/j.ijhydene.2018.11.056

[10] A. A. Moghaddam, U. Krewer, “Poisoning of Ammonia Synthesis Catalyst Considering Off-Design Feed Compositions”, Catalysts 10.1225 (2020), 1–16, https://doi.org/10.3390/catal10111225

[11] R. Stokes. “A History of the International Industrial Gases Industry from the 19th to the 21st Centuries”. In: Cambridge University Press (2015)

[12] S. Li, V. M. Wheeler, P. B. Kreider, W. Lipiński, “Thermodynamic Analyses of Fuel Production via Solar-Driven Metal Oxide Redox Cycling”, Energy & Fuels 32.10 (2018), 10848–10863, https://doi.org/10.1021/acs.energyfuels.8b02081

[13] J. Vieten, D. Guban, M. Roeb, B. Lachmann, S. Richter, C. Sattler, “Ammonia and Nitrogen-based Fertilizer Production by Solar thermochemical Processes”, AIP Conference Proceedings, 2303, 170016. American Institute of Physics (AIP). DOI: 10.1063/5.0030980.

[14] J. Vieten, B. Bulfin, P. Huck, M. Horton, D. Gubán, L. Zhu, Y. Lu, K. A. Persson, M. Roeb, C. Sattler, “Materials design of perovskite solid solutions for thermochemical applications”. Energy & Environmental Science, 2019. 12: p. 1369-1384, DOI: 10.1039/C9EE00085B.

[15] D. Notter, M.-E. Gálvez, B. Bulfin, A. Steinfeld, “Solar-driven thermochemical production of ammonia via a metal nitride cycle”, AIChE Annual Meeting 2022, Phoenix, AZ, USA, November 13-18, 2022, https://www.aiche.org/academy/conferences/aiche-annual-meeting/2022/proceeding/paper/532ac-computational-screening-and-experimental-validation-binary-and-ternary-metal-nitrides-solar.

[16] X. Gao, H. E. van Bush, J. E. Miller, A. Bayon, I. Ermanoski, A. Ambrosini, E. B. Stechel, “Synthesis and Structural Study of Substituted Ternary Nitrides for Ammonia Production”, Chem. Matter, online preprint July 21, 2023, https://doi.org/10.1021/acs.chemmater.3c00606

[17] M. L. Wagner and W. Plains. “Direct oxygen injection in nitric acid production”, European Patent EP0808797B1, 2003.

[18] S. Bhatia, F. J. Jackow, R. Vlaming, J. Koenig, “Oxygen injection in nitric acid production”. European Patent EP0799794A1, 1997.

[19] R. W. Watson and P. G. Blakley, “Oxygen-enrichment columnar absorption process for making nitric acid”, US Patent US4183906A ,1980.

[20] N. Neumann, D. Baumstark, P. López Martínez, N. Monnerie, M. Roeb, “Exploiting synergies between sustainable ammonia and nitric acid production: A techno-economic assessment”, Journal of Cleaner Production 438 (2024) 140740.