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# **Ammonia as a hydrogen carrier: Process synthesis using superstructure optimization for the storage of renewable energy sources in chemical compounds**

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Hydrogen will play a key role in industrial and daily consumption decarbonization for the next decades, and prices for its production using renewables energy are predicted to decrease 60% of actual cost for the end user by 2030. Last decade showed an important fall in production cost of hydrogen using electrolysis technology, going from around 10-15 USD/kg in 2010 to 4-6 USD/kg in 2020, which suggest a similar behaviour for the next decade [1]. Interests for hydrogen not only remain on the zero-carbon emissions produced when used, for instance as a fuel for transportation, but focus must be orientated to upstream processes, which have to be transformed in order to reduce carbon emissions and, therefore, modify the methods for its obtention.

Nowadays trend of using renewable sources to shift from fossil fuel sources must deal with energy availability, as sources such as wind and solar energy depend on climate factors and periodicity. Renewable energy production does not correspond to the same period of its consumption. Thus, intermittency creates a barrier for a reliable immediate production-consumption pathway.

Chemical storage of energy, such as liquid ammonia, can perform a reliable and immediate available solution when energy is required. Furthermore, NH<sub>3</sub> is a high-dense hydrogen carrier, able to store 17.8 wt% of hydrogen, the highest in comparison with other liquid organic hydrogen carriers, such as methanol, and also can be stored in liquid conditions at almost ambient temperature, under moderate pressure of 10 bars [2], meaning an easier handling and storage than hydrogen.

Industrial synthesis of NH<sub>3</sub> using Haber-Bosch process has been performed for more than a century. Nitrogen, obtained from air separation units, and hydrogen, from steam methane reforming, are compressed and react at about 400 °C and 200 atm. Being an exothermic and reversible reaction, the system requires a heat removal system and the recycle of non-reacted gases.

However, in order to use renewable sources of energy instead of fossil fuels for energy storage, hydrogen is produced by electrolysis. Furthermore, the yield and the energy efficiency of the ammonia production process are key parameters of energy storage efficiency. Therefore, process synthesis requires modifying the architecture and even the operating conditions and the sizing of the process steps (reactors, separators and heat exchangers for energy integration) to optimize the system. To do so, a methodology of process synthesis using superstructure optimization is used, searching the best suitable process architecture and conditions to achieve an optimal solution for NH<sub>3</sub> production.

A superstructure can be defined as the interconnection of different processes that have the same main objective. It becomes advantageous in comparison with a single-process evaluation, as the superstructure estimates the best pathway of the process while assessing the operational conditions that allow achieving the optimum of one or a set of objective functions.

As observed in Figure 1, the superstructure contains logical integer switches which deviate the material streams through different pathways, allowing an external optimization algorithm to evaluate that specific zone of the flowsheet without considering the rest.

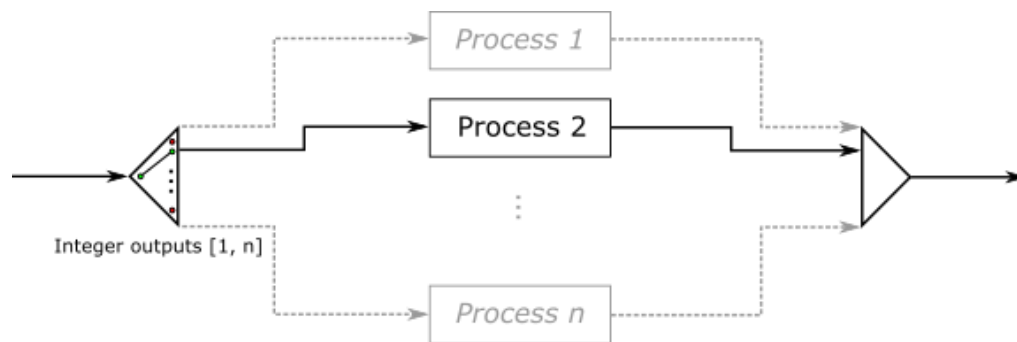


Figure 1. Superstructure logical switch for different pathways.

Treating superstructure problem means trying to solve complex optimization problems, containing continuous (temperature, pressure, etc.) and discontinuous (logical integers) variables, with or without equality or inequality constraints, while minimizing non-explicit objective functions, such as production cost or exergy destruction. In other words, the optimization algorithm used to solve these complex structures must be capable of treating MINLP (Multi-Integer Non-Linear Programming) problems [3].

For  $\text{NH}_3$  synthesis specifically, the optimal process structure is sought considering the production cost of  $\text{NH}_3$  and the ratio of the destroyed exergy over recovered exergy in form of  $\text{NH}_3$ , as the two objective functions to minimize. Compression, reaction and separation approaches are evaluated through this methodology, with multiple variables being considered, such as pressure and temperature of the reactors, stages of compression, the use of intercoolers, among other alternatives.

At this stage,  $\text{H}_2$  and  $\text{N}_2$  are considered to be obtained from renewable sources (wind turbines), and the focus is limited to the  $\text{NH}_3$  synthesis zone in a first step. Further studies will be devoted to upstream processes for gases obtention, to englobe from the wind turbines electricity production until the liquid ammonia storage.

## References

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