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Strategies for a More Resilient Green Haber-Bosch Process

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ABSTRACT

This work focuses on the dynamic analysis of a single-bed fixed-bed catalytic reactor (FBCR) used for ammonia synthesis. The single-bed model was configured in gPROMS® Process using Siemens' FBCR library, and subjected to a series of dynamic tests to gain insight into its operation under transient conditions. This study, still in its early stages, aims, in the long term, to explore flexibility strategies for the Haber-Bosch (HB) process, enabling it to accommodate variable hydrogen loads while maintaining safe operation. Taking a nominal operating point as a reference, a series of time ramps were enforced on the most relevant process variables, including the inlet reactor temperature, reactor operating pressure, feed composition and flow rate, and their effects on reactor performance have been observed. The results of this preliminary study will serve as the foundation for testing the flexibility measures currently proposed in the literature to ensure the safe operation of the green HB (gHB) process.

Keywords: gProms, Green Ammonia Production, Haber-Bosch Process, Flexibility

INTRODUCTION

With a global production of 183 million metric tons in 2020 **[1]**, ammonia (NH_3) stands out as one of the most important commodity chemicals on the global scene. The Haber-Bosch process has historically enabled large-scale NH_3 production, supporting agricultural practices in response to the unprecedented population growth over the past century, but it also accounts for *c.* 1% of global CO_2 emissions **[1]**. In the gHB process–a Power-to-Ammonia system–, hydrogen (H_2) produced through water electrolysis and nitrogen (N_2) from an air separation unit are compressed and fed into the NH_3 synthesis loop, which mirrors the general configuration of the conventional HB process. However, the fluctuating nature of renewable energy (RE) means that H_2 production is not constant over time. Therefore, the NH_3 synthesis loop is to be operated dynamically, as the H_2 content in the makeup gas to the synthesis loop varies with the RE availability. This presents a major operational challenge particularly at the reactor level.

Dynamic operation of NH_3 converters is typically associated with reaction extinction and sustained temperature oscillations, which can severely damage the catalyst and cause material fatigue. Morud and Skogestad (1998) **[2]** were among the first to study the dynamics of a FBCR coupled with a feed-effluent heat exchanger (FEHE) downstream of the catalytic beds. Their research, based on real plant data, explained the observed limit cycle behavior, which could be traced back to the positive feedback arising from the heat recycle, caused by the FEHE. Since then, other studies have built upon their work, including Rosbo *et al.* (2023) **[3]**, who developed a MATLAB model for the NH_3 synthesis loop and implemented a control structure capable of ensuring safe and flexible operation across 20% to 120% of the nominal capacity. Their study considered a three-bed FBCR with inter-bed quenching and a FEHE, as Morud and Skogestad had previously done **[2]**. In a similar line of work, Fahr *et al.* (2023) **[4]**, who developed a rigorous UniSim model of a Topsoe proprietary NH_3 converter, listed a series of potential flexibilization measures that could be applied industrially at the synthesis loop, based on information available in patents filed by technology licensors. A key aspect consistently addressed in patents is maintaining high loop pressure, which can be achieved by exploiting the NH_3 synthesis reaction equilibrium. As the NH_3 synthesis reaction proceeds, there is a decrease in the number of moles leaving the reactor. Therefore, any measures that shift the equilibrium towards the reactants' side are to be considered. This work is situated in this context, intending to explore flexibility strategies for the gHB process, including some already proposed in the literature, and, eventually, propose novel ones involving the implementation of control loops.

MATHEMATICAL MODEL DESCRIPTION

In this work, the authors have started by modeling an annular radial-flow FBCR filled with solid spherical pellets in gPROMS®

Process, based on an example provided by Siemens **[5]**. The FBCR features a single catalytic bed that is 2.5 m tall, with an outer radius of 0.25 m and an inner radius of 0.2 m. This first-principles model, formulated as a system of partial differential algebraic equations, is distributed in both the radial and axial directions within the tube and incorporates separate conservation laws for the fluid and solid phases. For the solid phase, the authors have opted to consider a lumped model to represent diffusion-reaction inside the pellet at the microscale. As a result, the model does not increase in dimensionality, and a simple effectiveness factor is used to account for internal mass transfer limitations. To the best of the authors' knowledge, no rigorous 2D models for this system have been reported in the literature. Temkin-Pyzhev reaction kinetics have been considered, as follows:

$$r = k\left[K_a^2\, a_{N_2}\left(\frac{a_{H_2}^3}{a_{NH_3}^2}\right)^{\alpha} - \left(\frac{a_{NH_3}^2}{a_{H_2}^3}\right)^{1-\alpha}\right] \qquad (1)$$

where r is the intrinsic reaction rate (mol kgcat^{-1}s^{-1}), k is the reverse reaction kinetic constant (mol kgcat^{-1}s^{-1}), K_a is the equilibrium constant, a_i the gas-phase activity of component *i*, and α an empirically determined parameter set to 0.5. k is calculated from an Arrhenius-type formula using the data shown in **Table 1**. The equilibrium constant is calculated using the Gillespie and Beattie equation, a description of which can be found elsewhere **[6]**.

Table 1. Kinetic model parameters applied to calculate k **[6]**.

Pre-exponential factor	4.4245×10^{11} kmol kgcat^{-1} h^{-1}
Activation energy	40765 cal/mol

METHODOLOGY/RESULTS/DISCUSSION

A single-bed FBCR has been considered. The objective was to examine the dynamic response of a single catalytic bed when subjected to changes in temperature, feed flow rate, pressure, and composition relative to the nominal conditions, and explore how these changes influence reactor performance. A base case scenario was simulated, considering the data provided in **Table 2**.

Considering ramp changes of -10% to 10% over one hour in the reactor inlet temperature, the reactor performance was analysed using the fractional conversion of H_2, as illustrated in **Figure 1**. A trade-off between reaction equilibrium and kinetics is evident. From a thermodynamic perspective, as the inlet temperature increases, the reverse (endothermic) reaction should be favored, thereby decreasing the conversion. However, the increased temperature also raises the reaction rate, which enables greater conversion, meaning the kinetic effect is the one that prevails.

Table 2. Base case (nominal) data inputted to the model.

Reactor feed flow rate	1 kg/s
Reactor inlet temperature	600 K
Inlet mass fractions	w(N_2) = 0.68; w(H_2) = 0.13; w(NH_3) = 0.07; w(Ar) = 0.12
Pressure	200 bar

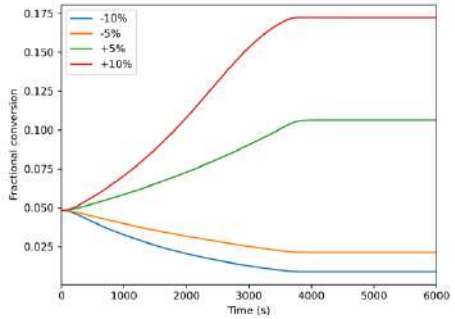

Figure 1. Fractional conversion profile at the reactor exit over time for ramp changes of -5%, -10%, +5%, and +10%, starting from nominal conditions.

This preliminary study investigates the dynamics of a single bed FBCR, acknowledging it does not fully reproduce actual process conditions. As such, future research will consider additional catalytic beds and analyse different reactor configurations.

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REFERENCES

1. Narciso, D. *et al*. (2025). Design and operation of Power-to-Ammonia systems: A review. *Ener Conv Manag*, 327, 119494
2. Morud, J. and Skogestad, S. (1998). Analysis of instability in an industrial ammonia reactor. *AIChE J.*, 44: 888-895.
3. Rosbo, J. *et al.* (2023). Flexible operation, optimisation and stabilising control of a quench cooled ammonia reactor for power-to-ammonia. *Comput. Chem. Eng.*, 176, 108316.
4. Fahr, S. *et al.* (2023). Design and thermodynamic analysis of a large-scale ammonia reactor for increased load flexibility. *Chem. Eng. J.*, *471*, 144612.
5. https://www.siemens.com [Retrieved Jan 28th, 2025]
6. Dyson, D. and Simon, J. (1968). A kinetic expression with diffusion correction for ammonia synthesis on industrial catalyst. *Ind. Eng. Chem. Fundamen.*, 7(4), 605-610.