

Dynamic Operation of a Haber-Bosch Loop with Quench-Cooled Converter for Power-to-Ammonia Systems

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ABSTRACT

This work presents a preliminary application of a developing methodology for assessing the operational flexibility of ammonia synthesis loops. Part of this methodology involves systematic dynamic testing in the synthesis loop. In the present case, a synthesis loop equipped with a two-bed, quench-cooled converter operating under variable feed conditions was considered. A high-fidelity model of the converter was developed in gPROMS Process using two-dimensional reactor models from its fixed-bed catalytic reactor library, and a synthesis loop configuration was modeled and designed in the same environment. A series of dynamic tests varied the make-up flow rate across four disturbance amplitudes ($\pm 25\%$ and $\pm 50\%$) and four disturbance durations (10 s, 600 s, 1800 s, 3600 s). The results showed that disturbances of $\pm 50\%$ magnitude led to the violation of one process operational constraint. These findings enable the construction of a preliminary operational map of this system, providing an initial determination of its process boundaries, and therefore its current degree of flexibility. Such knowledge is fundamental to understand how the synthesis loop can be made more flexible so that it suits Power-to-Ammonia applications. Overall, this study constitutes an initial step toward the development of a framework for enhancing the flexibility of ammonia synthesis loops.

Keywords: Dynamic Modelling, gProms, Process Design, Process Flexibility, Green Haber-Bosch Process

INTRODUCTION

In recent years, ammonia (NH_3) has attracted significant attention as a key piece on the strategic chessboard of energy transition, playing an important role in the value chain of green hydrogen. Ammonia possesses a higher volumetric energy density than hydrogen, making it easier to store. Furthermore, its handling and transport infrastructure is already well-established [1, 2]. Altogether, these features render ammonia an extraordinary carbon-free chemical energy carrier for hydrogen. Besides its potential novel role in the energy transition, ammonia is already one of the most important commodity chemicals worldwide. The expansion of its applications to include energy-related uses complements its traditional markets and is expected to further increase global demand. In 2021, the global ammonia market was valued at \$US 67 billion, representing about 5% of the total

chemical market value [3]. Looking ahead, ammonia demand is projected to increase to 223 million metric tons by 2030 [4, 5]. Despite these new applications, fertilizer production currently accounts for the majority of ammonia consumption, representing approximately 85% of the total demand, and remains its most significant use.

The Haber-Bosch (HB) process is the industrially relevant process when it comes to ammonia production, accounting for over 90% of global ammonia produced [1]. Conventional HB processes rely on an upstream operation to produce hydrogen (H_2) from fossil fuels, which is then mixed with dinitrogen to form the *synthesis gas* used for ammonia production. There are essentially two main process routes for producing hydrogen from fossil fuels, with the best available technology being steam methane reforming (SMR), which relies on a natural gas feedstock. The SMR section is responsible for much of the greenhouse gas (GHG) emissions associated with

ammonia production; in fact, for the SMR process route, it is estimated that 1.5 kilograms of CO₂-equivalent are emitted for every kilogram of ammonia produced [5]. As a result, about 1% of the global anthropogenic CO₂ emissions are attributed to the conventional HB process [5]. Shifting the hydrogen production route to electrolytically produced hydrogen greatly reduces the process dependence on fossil fuels, giving rise to the so-called green HB (gHB) process [1]. This shift entails a fundamental change in the nature of the HB process itself, which has traditionally been operated at a quasi-steady-state. The gHB process can therefore be viewed as a Power-to-Ammonia (P2A) process, which is a specific subclass of the broader Power-to-X (P2X) ones, wherein renewable energy is used to produce value-added commodity chemicals [1].

In a P2A process, green hydrogen is produced via a water electrolyser at a flow rate that is entirely dependent on the power supply to the electrolyser (*i.e.*, the availability of renewable energy). After being mixed with a nitrogen stream from an air separation unit (ASU), this stream is fed into the NH₃ synthesis loop [1]. The loop comprises an ammonia converter, a separator, and a recycle compressor, arranged as shown in **Figure 1**. Due to the low conversion-per-pass in the converter, unrecycled reactants must be recycled back to the converter, giving rise to the generic synthesis loop configuration. Different loop configurations exist depending on the quality of the make-up synthesis gas. For this reason, the gHB and the conventional HB process are expected to employ different loop configurations. In fact, even among commercial conventional HB process, several loop configurations are in use.

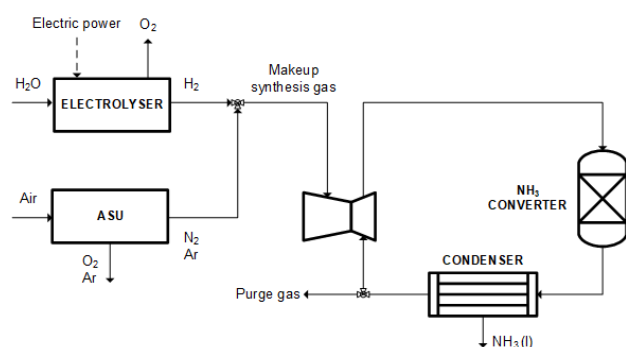


Figure 1. Generic Process Flow Diagram for the Green Haber-Bosch Process. Note that other loop configurations exist.

Under variable hydrogen supply (and hence variable make-up synthesis gas), the loop operates dynamically, requiring its unit operations to have a high degree of flexibility to accommodate different feed loads. This flexibility is currently missing in the conventional HB process.

In the context of Power-to-Ammonia systems,

quantifying process flexibility through dynamic testing is certainly a most relevant task, because it enables the identification of current process boundaries, thereby shedding light on existing operational limitations. In other words, dynamic analysis helps clarify the conditions under which the process can resume operation without issues following a disturbance and ultimately provides guidance for improving process flexibility.

Existing works on the flexibility of synthesis loops have restricted their analysis to the converter [2, 6] under steady-state conditions or considered the loop, but again at steady-state [7]. Cheema and Krewer [7] quantified the operational flexibility of a three-bed converter inserted into a given synthesis loop, finding that, among all process variables, the inert gas fraction and the molar H₂:N₂ ratio were those whose variation enabled greater operational flexibility (*i.e.*, yielded more flexible designs). In more recent years, Fahr *et al.* [2] modelled Topsoe's proprietary S-300 converter and performed a steady-state parametric analysis to understand how that converter concept could be made more flexible. Across these studies, the central idea is that, for a given steady-state, the operating window of the converter can be widened by appropriately selecting the values of the operating variables. In all these works, however, the methodology did not involve dynamic tests. Conversely, Burrows and Bollas [8] employed dynamic testing but did not quantify flexibility, focusing instead on identifying faulty operating conditions. They investigated a conventional synthesis loop under dynamic feed conditions and conducted several dynamic tests at three different productivity scales. These tests subjected the process to a range of operating conditions, allowing process faults under such conditions to be identified [8]. Furthermore, Gottheil and Bremer [9] briefly addressed a systematic methodology for quantifying the flexibility of ammonia converter concepts by categorizing a given disturbance. However, their analysis was essentially limited to ramp-type disturbances, which could be characterised by a "ramp height" and a "ramp length". Moreover, this methodology was only applied to the ammonia converter.

Increasing the flexibility of the ammonia loop is enabled by increasing the flexibility of the individual unit operations. Of all existing unit operations within the loop, the ammonia converter is the most critical. The converter roughly consists of multiple catalyst beds and an iFEHE, all enclosed within a single pressurized vessel, with the iFEHE positioned downstream of the catalyst beds. There are three well-established types of converters on the market, depending on the cooling principle used to control the heat liberated by the ammonia synthesis reaction: the *Adiabatic Quench Cooled Reactor* (AQCR), the *Adiabatic Indirectly Cooled Reactor* (AICR), and the *Internally Cooled Multi-Tubular Reactor* (ICMR). Current industrial trends favour the AICR type, as all feed passes through

the entire catalyst bed (*i.e.*, no fraction of feed bypasses a given bed), allowing higher reactant conversion than the AQCR, even though the latter has found widespread acceptance in the industry for its simple mechanical design [10, 11].

When operating it in steady-state, the converter exhibits multiplicity of steady-state behavior when proceeding towards a steady-state after startup, owing to external recycle of heat [10, 12]. This extreme sensitivity ultimately implies that it can easily extinguish when transitioning between operating points. Consequently, its autothermal behavior is lost and productivity decreases sharply. When operating it dynamically, *i.e.*, when subjected to disturbances over a given time horizon, the converter exhibits several characteristic behaviors that have been extensively investigated in earlier studies [10, 13]. The first is the inverse response dynamics due to the packed bed. Catalyst overheating may be observed in consequence, which may lead to its deactivation, which is highly unwanted. Additionally, this response, combined with the feedback that the iFEHE introduces in the system, may evolve into (self) sustained oscillatory behavior (*i.e.*, limit cycles) [10, 13]. Such oscillations are also undesirable, as they induce pressure and temperature cycles, leading to material fatigue [1]. All these characteristics make the converter extremely sensitive to changes in process variables, hence particularly vulnerable for continuous dynamic operation.

If the converter design is sufficiently flexible, these operational issues may be avoided because the operating windows are wide enough that such disturbances do not push the process beyond its boundaries, allowing operation to be safely resumed. Therefore, assessing how converter designs are developed, quantifying their actual flexibility, and understanding how they can be made more flexible are critical questions in this context.

This work focuses on the initial steps in the development of a comprehensive framework for designing flexible synthesis loops. The authors focus on one specific component of this framework: systematic dynamic testing for the determination of process boundaries. Through dynamic tests, operational issues are intentionally induced in the system to identify its operating limits. For the purpose of systematic dynamic testing, the methodology developed by Gottheil and Brewer [9] has been adopted in this work and applied to a synthesis loop equipped with a commercially available AQCR-type converter (Topsoe's proprietary S-100 converter). Applying this methodology to the synthesis loop has not been explored in the literature and is therefore the main contribution of this study. The objectives of this study are two-fold: (i) to assess the performance of this converter concept for Power-to-Ammonia applications, and (ii) to quantify the resulting flexibility of the synthesis loop when equipped with such a converter.

MODEL DEVELOPMENT

Reactor models belonging to the Advanced Model Library – Fixed Bed Catalytic Reactors (AML – FBCR) in gPROMS Process have been *composed* to assemble models of ammonia converters [14]. The model is a first-principles formulation, expressed as a system of differential-algebraic equations. In this model, variables are distributed over two spatial domains, namely the radial and axial directions, and separate conservation laws are written for the fluid and solid phases (heterogeneous model). The catalyst consists of Fe-based spherical pellets, which have been modelled as a lumped system, considering the selected particle granulometry (industrial-grade particles typically range between 1.5 - 3 mm for radial-flow converters). The particle sizes employed guarantee there are no appreciable intraparticle gradients, which is to say there are practically no internal mass and heat transfer limitations. This methodological option results in a model that does not increase in dimensionality. Modified Temkin-Pyzhev kinetics by Dyson and Simon [15] have been selected, as follows in eq. (1):

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

where r is the rate of formation of ammonia (mol kgcat⁻¹ s⁻¹), k is the kinetic constant (mol kgcat⁻¹ s⁻¹) calculated using an Arrhenius-type equation with data provided in **Table 1**, K_a is the equilibrium constant computed using Gillespie and Beattie's equation [16], a_i the gas-phase activity of component i and α an empirical parameter which was set to 0.5.

Table 1: Kinetic data employed in the developed model.

Pre-exponential factor [kmol/kgcat h]	4.42×10^{11}
Activation energy [kcal/kmol]	4.08×10^4

All heat exchangers were modeled as black box units that satisfied mass and energy balances and a given thermal specification (*e.g.*, temperature difference between outlet streams). As for the ammonia separator, a dynamic model for a flash separator has been used, using the gPROMS Separations Model Library. No compressors have been used to model this synthesis loop, since the pressure drop across the catalyst beds is negligible and the make-up stream is assumed to be available at the pressure of the synthesis loop. Simplifications in the compressors and heat exchangers design may influence the overall loop transient response. However, to keep the loop model simple yet functional and capture the physics of the system, these simplifying assumptions were adopted. Due to the packed-bed nature of the converter, the loop's response will be primarily determined by the converter's response, whose dynamics are much slower

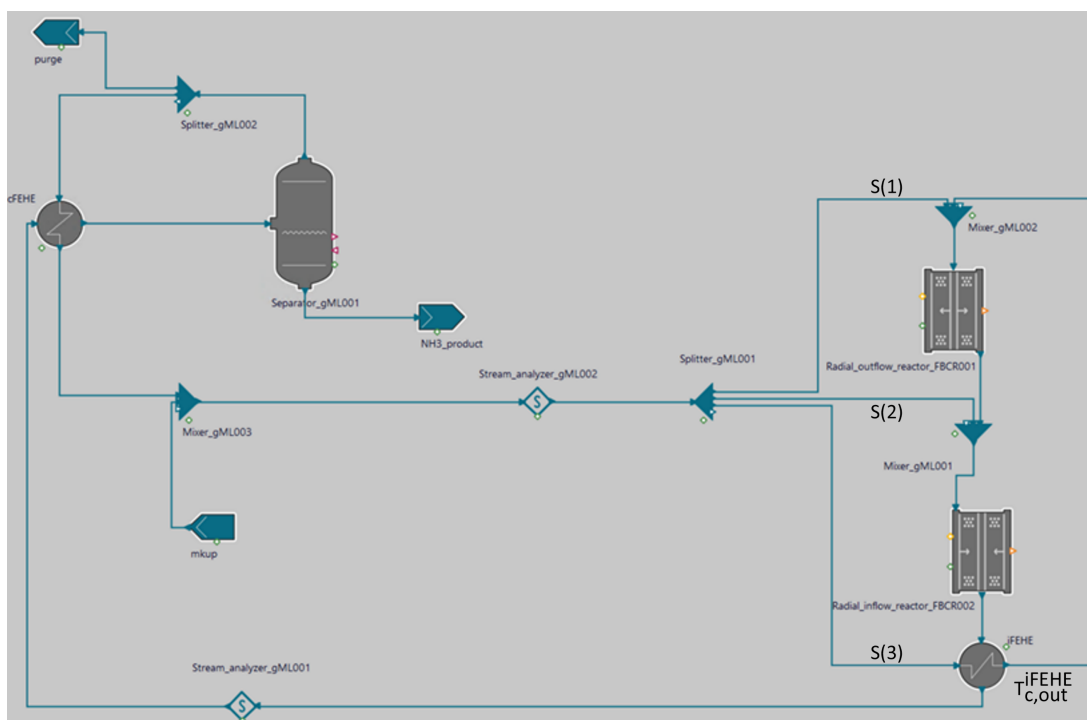


Figure 2. Flowsheet for the green ammonia loop modeled in gPROMS Process. In the loop, it is installed a 2-bed AQCR converter, reproducing Topsoe's S-100 proprietary converter. Selected key operating variables of the converter are shown in the figure.

than those of the compressors and heat exchangers.

These models were assembled to build a composite model of a synthesis loop, as illustrated in **Figure 2**. Overall, the mathematical model of the synthesis loop comprises approximately 14300 variables, and across all runs, simulation times reached a maximum of 7 seconds. Catalyst beds were discretized axially and radially, respectively, into 10 and 5 points.

METHODOLOGY

In this work, the authors detail a preliminary methodology for assessing the operational flexibility of the synthesis loop through systematic dynamic testing. Here, flexibility is evaluated by mapping the loop's operating window through a series of dynamic tests.

At this stage, the problem is formulated as a partial design problem, as it considers only performance. Economic considerations are not included in the present analysis.

Loop design and optimization

The loop was designed for a nominal ammonia production rate of 4 kt/year (approximating a small-scale ammonia production plant). In the selected loop configuration, the make-up synthesis gas is introduced downstream of the separator, since the existing trace amounts of water in the make-up gas do not pose a significant

threat to the catalyst to the point of deactivating it. Iron-based catalysts, such as those employed in ammonia synthesis, are extremely sensitive to any oxygen-containing compounds, which can result in catalyst poisoning. Heuristic criteria were used to specify the separator operating temperature ($-5\text{ }^{\circ}\text{C}$) and purge rate (6 %). As the pressure drop across the catalyst beds was found to be negligible, a constant 200 bar pressure was assumed for all process units, and no recycle compressor was considered at this stage.

Starting from the flowsheet presented in **Figure 2**, the loop design was then optimized to achieve maximum conversion per pass. The design problem is formulated as a non-linear optimization problem, solved using gPROMS Optimization Entity, which is written as follows:

$$\max_D X_{N_2} \quad (2)$$

$$D = [T_{c,out}^{iFEHE}, S(1), S(2)] \quad (3)$$

s.t.

$$f(D, Y) = 0 \quad (4)$$

$$T_{bed\ i} \leq T_{upper} \quad (5)$$

$$T_{lower} \leq T_{bed\ i} \quad (6)$$

where D is the set of decision variables (*i.e.*, degrees of freedom), which, for an AQCR-type converter, are the quench fractions, $S(1)$ and $S(2)$, and the outlet

temperature of the feed stream (*i.e.*, the cold stream) of the feed-effluent heat exchanger, $T_{c,out}^{FEHE}$.

$f(D, Y)$ represents the set of equations that define the model and must be satisfied at all times. Y denotes the remaining (dependent) model variables. Bed temperatures were constrained between 600 and 773 K, as literature reports 800 K to be the upper limit for catalyst operating temperature without risking deactivation [2, 17], while temperatures above 600 K are reported to yield appreciable reaction rates for the employed catalysts [18]. The results of this optimization study are presented in **Table 2** and reveal the optimal values for several key variables. Note that this represents an initial formulation, which at present considers only the reaction performance aspect of the problem. Process economic considerations and the extension of other loop variables to the design problem will be incorporated in future work.

Table 2: Results for the converter design before and after the optimization study.

Variable	Base design	Optimized design
Conversion [%]	22.52	23.61
$T_{c,out}^{FEHE}$ [K]	690	669
Split to cold shot to bed 1, $S(1)$ [-]	0.200	0.229
Split to quench in between bed 1 and bed 2, $S(2)$ [-]	0.350	0.422

Dynamic tests planning and quantification of operational flexibility

As noted in the **Introduction**, disturbances applied to the converter at a given operating point may trigger one of the following phenomena: catalyst overheating (with subsequent deactivation), reaction extinction, or oscillatory behavior. The occurrence of any of these phenomena indicates that a process boundary has been crossed, rendering normal operation of the Power-to-Ammonia process infeasible. These phenomena, therefore, define the criteria for feasible operation of the synthesis loop.

Any dynamic tests performed on the modeled synthesis loop can thus be used to deliberately induce these phenomena and, whenever any of them arises, a given range of operating conditions is deemed unfeasible. From this information, the process boundaries can then be determined, and an operational map can be constructed from which the current loop flexibility can be inferred.

For the modeled loop, all dynamic tests were performed on the make-up gas feed flow rate. According to the methodology proposed in this work, all dynamic tests are characterized by (i) the *type* of disturbance (ramp, step, pulse, or sinusoidal); (ii) the *magnitude* or *amplitude*

of disturbance, and (iii) the *duration* of disturbance. Specifically, the tests in this study consisted exclusively of linear ramps, applied with four different amplitudes (expressed as percentage deviations from the nominal value) and three disturbance durations. This resulted in a 4×3 test matrix, as summarized in **Table 3**.

Table 3: List of dynamic tests performed.

Type of disturbance	Linear ramp
Disturbed variable	Make-up gas flow rate
Magnitude of disturbances [%]	± 25 & ± 50
Duration of disturbances [s]	10, 600, 1800 & 3600

Therefore, the operational flexibility is defined by the maximum disturbance amplitude the system can withstand for a fixed disturbance time.

RESULTS AND DISCUSSION

In this section, the results for the dynamic tests conducted are presented, first focusing on the impact of these tests at the converter level and then expanding the study to the loop.

Table 4: Final steady-state values of relevant high-level converter variables for all dynamic tests considered.

	Disturbance	X [%]	θ_{conv} [s]	T_{out}^{conv} [K]
-50%	10 s	24.56	63.06	787.4
	600 s	24.56	63.09	787.5
	1800 s	24.59	63.19	787.3
	3600 s	24.61	63.22	787.2
-25%	10 s	24.54	42.52	787.0
	600 s	24.56	42.55	786.8
	1800 s	24.57	42.56	786.8
	3600 s	24.57	42.56	786.8
+25%	10 s	21.73	23.97	764.0
	600 s	21.71	23.96	763.8
	1800 s	21.70	23.95	763.6
	3600 s	21.69	23.94	763.5
+50%	10 s	4.580	8.33	624.2
	600 s	4.580	8.33	624.2
	1800 s	4.580	8.33	624.2
	3600 s	4.580	8.33	624.2

Converter performance

For all tests considered, the final steady-state values of the relevant high-level variables for the converter are summarized in **Table 4**. These include the conversion per pass, X , the overall average residence time, θ_{conv} , and the converter outlet temperature, T_{out}^{conv} .

From **Table 4**, it can be observed that decreasing

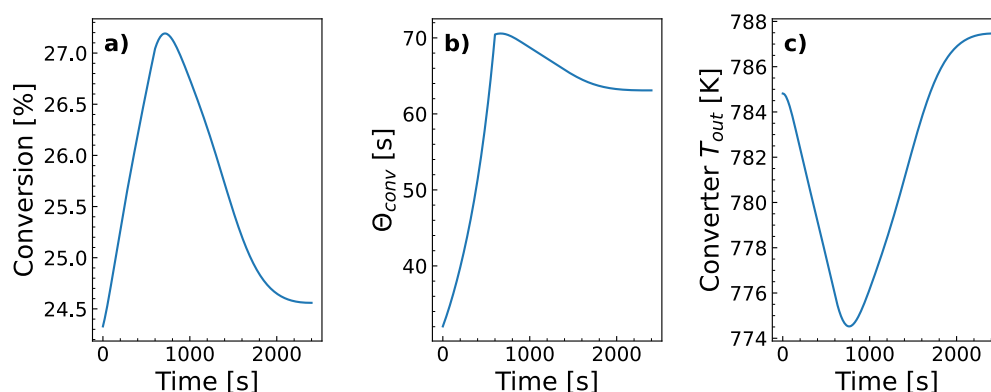


Figure 3: Profiles of percent conversion, overall average residence time, θ_{conv} , and outlet gas temperature, T_{out} , following a ramp disturbance of -50% on the make-up gas mass flow rate for 600 s.

feed flow rates lead to higher conversions (which are, in any case, limited by the equilibrium conversion). Conversely, admitting mass flow rates above the nominal to the converter reduces conversion and may even extinguish the converter if the superficial velocity becomes too high, substantially reducing the gas residence time. Furthermore, as expected, conversion and average residence time exhibit similar trends. That is, conversion is highest when the average residence time is greatest. Additionally, in cases where the conversion increased (*i.e.*, when the make-up flow rate decreased), the final converter outlet temperature (after the new steady-state was reached) was also higher, due to the enhanced occurrence of reaction. The opposite occurred when the conversion decreased. However, the transition between the two steady-state (initial and final) values of the converter outlet temperature is not as linear as it may seem. For that reason, the authors now restrict their analysis to the case in which the make-up gas flow was reduced by 50% over the course of 600 s. Along with the time variation of the make-up mass flow rate (and, by extension, the converter inlet mass flow rate), the profiles of the overall conversion, overall average residence time and converter outlet temperature are shown in **Figure 3**. The conversion profile exhibits a bell-shaped trend over time. As the inlet feed flow rate decreases, the gas superficial velocity reduces, and the gas spends more time in contact with the catalyst. Consequently, the increased residence time translates into higher conversion (see **Figure 3b**). Despite the increased conversion, which locally increases heat generation by the reaction, the solid bed temperature does not respond instantaneously due to its high thermal inertia, a consequence of the densely packed catalyst bed. Additionally, the reduced gas mass flow rate weakens radial convective heat transport. As a result, the gas cannot absorb as much heat from the bed as before, so less energy is transported to the converter outlet. Consequently, the gas

reaches the outlet at a lower temperature, explaining the decreasing trend observed in **Figure 3c**. Eventually, as the bed becomes progressively hotter by the enhanced occurrence of the reaction, part of this heat propagates by conduction, with the remainder carried by convection in the flowing gas. The gas temperature then rises, and when this temperature front reaches the converter outlet, the gas is seen as being hotter. This results in the outlet converter temperature profile shown in **Figure 3c**, where the outlet temperature initially decreases, goes through a minimum, and then increases again. Therefore, this sequence of a fast hydrodynamic effect followed by a slower thermal effect leads to the observed inverse dynamic response, characteristic of packed-bed reactors. However, as time goes by, the increase in the converter outlet temperature shifts the equilibrium conversion to lower values. Therefore, the maximum attainable conversion decreases, as does the actual conversion, giving rise to the decline observed in **Figure 3a**.

Loop performance

Table 5 presents the loop's key performance indicators. In this work, the following were considered: process yield and ammonia (loop) production rate.

When the make-up flow rate was increased, the loop production rate increased because more material circulated in the loop. Conversely, when the flow rate to the loop was decreased, the loop's productivity dropped. However, at the converter level, conversion per pass increased, which explains the rise in loop yield.

As more material circulated within the loop, the loop yield slightly increased reflecting the greater conversion per pass when the make-up flow rate is decreased. Moreover, for the disturbance with the largest absolute magnitude ($\pm 50\%$), two different operational problems were encountered: increasing the make-up flow rate led to virtually no conversion (reaction extinction), whereas decreasing it caused only slight bed overheating on the

order of 5 K while still allowing production to continue (albeit at lower rates). Thus, the sign of the disturbance magnitude (*i.e.*, the direction of change) explained why the process was affected so differently in these cases.

Table 5: Key performance indicators for assessing loop performance.

Disturbance	X [%]	Loop yield [%]	Loop production rate [kt/y]
-50%	10 s	24.56	98.16
	600 s	24.56	98.15
	1800 s	24.59	98.19
	3600 s	24.61	98.19
-25%	10 s	24.54	98.15
	600 s	24.56	98.16
	1800 s	24.57	98.17
	3600 s	24.57	98.17
+25%	10 s	21.73	95.80
	600 s	21.71	95.78
	1800 s	21.70	95.77
	3600 s	21.69	95.76
+50%	10 s	4.580	55.39
	600 s	4.580	55.39
	1800 s	4.580	55.39
	3600 s	4.580	55.39
Nominal	82.46	97.98	4.32

Loop operability

So far, the dynamic behavior of both the converter and the loop has been analyzed in terms of relevant process indicators. This analysis revealed how the system responded whenever subjected to ramp-type disturbances. In addition, it allowed the feasibility of the studied loop configuration to be assessed when operating within dynamic conditions. Recall that for each dynamic test performed, the following conditions were investigated: (i) reaction extinction, (ii) oscillatory behavior in any of the output variables, and (iii) catalyst bed overheating. The occurrence of any of the previous rendered the corresponding transition unfeasible, but also the operation at this range of conditions.

With the +50% disturbance, reaction extinction was observed, resulting in a converter *cold stop*. In contrast, for the -50% disturbance, a bed overheating of about 5 K was detected. In the long term, bed overheating leads to catalyst deactivation and entails additional operating expenditures to replace the catalyst bed that has experienced a reduced service lifetime. Therefore, these cases were classified as unfeasible operating ranges.

This information is summarized in **Table 6** and forms the basis for an operational map. From the results in Table 6, it can be concluded that the modeled loop configuration is $\pm 25\%$ flexible over the studied disturbance

duration.

Table 6: Operational map of the dynamic tests conducted by varying the make-up gas mass flow rate.

Amplitude Duration	-25%	-50%	+25%	+50%
10 s	OK ¹	CatH ²	OK ¹	RxnEx ³
600 s	OK ¹	CatH ²	OK ¹	RxnEx ³
1800 s	OK ¹	CatH ²	OK ¹	RxnEx ³
3600 s	OK ¹	CatH ²	OK ¹	RxnEx ³

¹ – denotes a final steady-state in which no process constraints are violated; ² – denotes a final steady-state in which catalyst overheating is observed; ³ – denotes a final steady-state in which reaction extinction is identified.

CONCLUSION AND FUTURE WORK

This work represents an initial application of a systematic methodology to assess the flexibility of an ammonia synthesis loop equipped with a quench-cooled converter (AQCR) for Power-to-Ammonia applications. The methodology builds upon that previously proposed by Gottheil and Bremer [9]. The presented methodology should be regarded as part of a higher-level framework for designing flexible synthesis loops.

Dynamic tests were conducted by varying the make-up flow rate across four disturbance amplitudes and four disturbance durations. The disturbance space in this study considered only ramp disturbances, which effectively become step disturbances for short or very short disturbance times. Future work will address multi-variable simultaneous disturbances and explicitly consider flow inputs from real renewable intermittency profiles, thus expanding the assessment beyond the present scope.

By compiling the results of the conducted transient simulations, it was possible to identify the effects of feed flow rate variations on overall loop performance (including converter performance) and, most importantly, to determine whether any operational limits were violated. If so, a process boundary is crossed, and the corresponding range of operating conditions must be considered infeasible. The present results therefore enable the construction of a preliminary operational map from which the current loop flexibility can be quantitatively inferred.

Advancing such methodological solutions is essential for overcoming the limited flexibility of conventional ammonia synthesis loops, which remain one of the main bottlenecks to the industrial deployment of Power-to-Ammonia systems, alongside plant economics.

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