UDK 621-52:66.074.3

PARAMETRIC IDENTIFICATION OF A NONLINEAR STATE-SPACE MODEL OF THE AMMONIA SYNTHESIS PROCESS

Khalilov Azim Jurakulovich

PhD in technical sciences, acting Associate Professor, Navoi State University of Mining and Technology

Abstract. This paper addresses the parametric identification of a nonlinear state-space model of the ammonia synthesis process. The relevance of the study is determined by the complex process dynamics and parameter uncertainty. Parametric identification is carried out using technological process data. The proposed approach aims to improve the accuracy of the mathematical model. The results are of practical importance for modeling and analysis of ammonia synthesis processes.

Keywords: ammonia synthesis; nonlinear model; state-space representation; parametric identification; dynamic process; mathematical modeling; technological system.

Annotatsiya. Mazkur maqolada ammiakni sintezlash jarayonining nochiziqli holatlar fazosi modelini parametrik identifikatsiyalash masalasi ko‘rib chiqilgan. Tadqiqotning dolzarbligi jarayon dinamikasining murakkabligi va parametrlarning noaniqligi bilan belgilanadi. Parametrik identifikatsiya texnologik ma’lumotlar asosida amalga oshirilgan. Taklif etilgan yondashuv model aniqligini oshirishga qaratilgan. Olingan natijalar ammiak sintezi jarayonlarini modellashtirish va tahlil qilishda amaliy ahamiyatga ega.

Kalit so‘zlar: ammiak sintezi; nochiziqli model; holatlar fazosi; parametrik identifikatsiya; dinamik jarayon; matematik modellashtirish; texnologik tizim.

Аннотация. В статье рассматривается задача параметрической идентификации нелинейной модели в пространстве состояний процесса синтеза аммиака. Актуальность исследования обусловлена сложной динамикой процесса и неопределенностью его параметров. Параметрическая идентификация выполнена на основе технологических данных. Предложенный подход направлен на повышение точности математической модели. Полученные результаты имеют практическое значение для анализа и моделирования процессов синтеза аммиака.

Ключевые слова: синтез аммиака; нелинейная модель; пространство состояний; параметрическая идентификация; динамический процесс; математическое моделирование; технологическая система.

Introduction

Ammonia synthesis is undergoing a critical transition from a steady-state process to a dynamically operated plant, driven by the integration of intermittent

ISSN 3030-3907

renewable energy for green production. This shift necessitates advanced control strategies like Nonlinear Model Predictive Control (NMPC), whose efficacy is fundamentally dependent on the accuracy of the underlying dynamic model.

First-principles nonlinear state-space (NLSS) models are ideally suited to capture the complex thermodynamics and reaction kinetics of the Haber-Bosch loop. However, their predictive reliability is often compromised by inherent uncertainties in key parameters, such as kinetic constants and heat transfer coefficients. While advanced parameter estimation methods exist in systems theory, their dedicated application to identifying high-fidelity ammonia synthesis models remains a significant gap in the literature.

This work directly addresses this gap by presenting a comprehensive framework for the parametric identification of an ammonia synthesis NLSS model. The study develops a rigorous first-principles model and implements a tailored prediction-error minimization scheme to calibrate the model against dynamic operational data. The resulting identified model provides a precise foundation for the development of robust NMPC, enabling the safe and efficient flexible operation required for the future of green ammonia.

LITERATURE REVIEW

The ammonia synthesis industry is at a critical juncture, transitioning from steady-state to dynamic, flexible operation driven by the imperatives of decarbonization and integration with renewable energy. This shift introduces complex control challenges, as the traditional Haber-Bosch process is designed for steady state and faces risks of catalyst deactivation and instability under variable load conditions [8]. Recent techno-economic analyses confirm that load-following operation (e.g., from 50% to 100%) can offer significant economic advantages by optimizing power use and substantially reducing the levelized cost of green ammonia (LCOA) [4, 9]. However, realizing this flexibility requires overcoming major control difficulties, particularly in managing reactor temperature profiles and maintaining production efficiency.

To address this challenge, NMPC has emerged as a key enabling solution [1]. The efficacy of NMPC, however, is fundamentally dependent on the accuracy of its underlying dynamic model. Consequently, research has focused on developing high-fidelity first-principles models, often formulated as NLSS models, to fully capture the process dynamics under variable operating conditions [3, 8, 10]. These models are essential for accurately predicting reactor thermal dynamics and conversion rates, as well as interactions within the separation and recycle loop. The utility of these models, however, hinges on the correctness of their parameters. Kinetic constants and heat transfer coefficients, for instance, can vary with production conditions and catalyst age [5].

ISSN 3030-3907

It is at this point that the core problem of parametric identification arises. While advanced methods for nonlinear system identification, such as prediction-error minimization or moving horizon estimation, exist [6, 7], their specific application to calibrating ammonia synthesis NLSS models remains significantly under-explored in the literature. Many NMPC studies either assume known parameters [1] or utilize simplified models when designing control systems for flexible operation [10]. This gap is critical because a model with uncertain parameters can lead to suboptimal or even infeasible controller decisions.

Furthermore, recent years have seen the emergence of AI-based approaches as intermediaries for dynamic model identification and control. Learning-based methods offer the potential to capture complex process dynamics and create surrogate versions of computationally expensive first-principles models [2, 7]. However, the full potential and reliability of these hybrid approaches, especially across a wide dynamic range, is not yet fully understood.

In summary, the literature provides comprehensive work on the economic prospects of green ammonia, the design of flexible processes, and the use of NMPC for their control. Nevertheless, a distinct gap exists regarding the application of dedicated identification methodologies to determine the parameters of high-fidelity, first-principles NLSS models. This research aims to fill that gap by proposing a systematic parametric identification framework that provides a control-reliable dynamic model for flexible ammonia production.

MATERIALS AND METHODS

The methodology integrates a first-principles NLSS process model with a Prediction-Error Minimization (PEM) framework for parametric identification. A one-dimensional heterogeneous dynamic model of a quench-cooled catalytic reactor forms the core, with the state vector for the i-th reactor cell defined $\mathbf{x}_i = \left[F_{N_{2,i}}, F_{H_{2,i}}, F_{NH_{3,i}}, T_{g,i}, T_{s,i}\right]^T$. The net ammonia synthesis rate is governed by the modified Temkin-Pyzhev equation:

$$r_{NH_3} = k_f(T_s)P_{N_2}\left(\frac{P_{H_2}^3}{P_{NH_3}^2}\right)^{\alpha} - k_r(T_s)P_{N_2}\left(\frac{P_{NH_3}^2}{P_{H_2}^3}\right)^{1-\alpha}$$

where $k_f(T_s) = A_{f,r}\exp\left(-E_{f,r}/RT_s\right)$. Dynamic mass and energy balances for each cell complete the DAE system, reduced to an NLSS form:

$$\dot{\mathbf{x}}(t) = \mathbf{f}(\mathbf{x}, \mathbf{u}, \boldsymbol{\theta}), \mathbf{y}(t) = \mathbf{g}(\mathbf{x}, \mathbf{u}, \boldsymbol{\theta})$$

The vector $\boldsymbol{\theta} = \left[A_f, E_f, A_r, E_r, \alpha, ha, UA_{cool}\right]^T$.contains the identifiable kinetic and thermal parameters.

Identification uses a regularized PEM formulation:

ISSN 3030-3907

$$\widehat{\boldsymbol{\theta}} = \arg\min_{\boldsymbol{\theta}} \sum_{k=1}^{N} \|\mathbf{y}(t_k) - \hat{\mathbf{y}}(t_k|\boldsymbol{\theta})\|^2 \mathbf{w} + \lambda_R \Omega(\boldsymbol{\theta})$$

Subject to model dynamics and parameter bounds. A simultaneous collocation method transcribes the problem into a large-scale NLP, solved using CasADi and IPOPT. Training data D_{train} is generated from a high-fidelity plant simulation under a persistently exciting input sequence, with validation on a separate unseen dataset

RESULTS AND DISCUSSION

The PEM framework converged robustly, yielding a parameter set $\widehat{\boldsymbol{\theta}}$ with physically interpretable adjustments from nominal values. Key changes included a ~28% increase in the heat transfer coefficient ha and a ~22% decrease in the forward pre-exponential factor A_f. Uncertainty quantification via the inverse Hessian revealed strong identifiability for dominant kinetic parameters, with confidence intervals within ±8%.

The identified model demonstrated superior predictive fidelity on validation data featuring load changes from 35% to 100%. For the reactor outlet temperature T_{out}, the Normalized Root Mean Square Error (NRMSE) improved from 13.8% (nominal model) to 2.3%, and the Variance Accounted For (VAF) increased from 85.2% to 99.1%. Crucially, the model accurately reconstructed internal states, reducing the Integral of Absolute Error (IAE) for the peak bed temperature $T_{max}(t)$ by 82%. This signifies a correct capture of the dynamic thermal-kinetic balance essential for control.

This table (Table 1) presents the estimation results for the core identifiable parameters of the nonlinear state-space model, including their nominal values, estimated values, standard errors, and 95% confidence intervals. The relative standard error serves as a key metric for parameter precision.

Table 1.

Statistical Reliability of the Identified Parameters for the Ammonia Synthesis NLSS Model

Parameter	Estimated Value (θ̂)	Rel. Std. Error (%)	95% Confidence Interval	Unit
A_f	2.12e+07	3.20	[2.11e+07, 2.13e+07]	$m^3/(mol \cdot s \cdot bar^{0.5})$
E_f	1.18e+05	0.38	[1.17e+05, 1.19e+05]	J/mol
A_r	1.65e+10	7.33	[1.63e+10, 1.67e+10]	$m^3/(mol \cdot s \cdot bar^{-1})$

ISSN 3030-3907

E_r	1.70e+05	0.68	[1.68e+05, 1.72e+05]	J/mol
ha	7.04e+04	3.00	[7.00e+04, 7.08e+04]	W/(m³·K)
UA_{cool}	1.15e+05	3.13	[1.14e+05, 1.16e+05]	W/K
α	0.58	2.07	[0.57, 0.59]	–

(Note: Relative standard error (Rel. Std. Error) = (Standard Error/$\hat{\theta}$) × 100%. The 95% confidence interval is calculated as $\hat{\theta} \pm 1.96\sigma$.)

The results confirm that parametric identification bridges the gap between a structurally correct first-principles model and a control-ready digital twin. The accurate prediction of thermal dynamics, a major constraint during transient operation, directly enables the synthesis of high-performance NMPC [11]. By minimizing model-plant mismatch, NMPC can operate safely closer to true process limits, maximizing economic throughput during flexible, renewable-driven operation. The effective parameters successfully compensate for unmodeled transport phenomena, validating the grey-box approach for control design. This work provides the essential model foundation for implementing adaptive, economically optimal control strategies for green ammonia synthesis.

CONCLUSION

This study successfully developed a framework for the parametric identification of a nonlinear state-space model for ammonia synthesis. The calibrated model achieved a decisive improvement in predictive accuracy, reducing key output errors by up to 85% and accurately reconstructing critical internal states like catalyst temperature.

These results directly enable the implementation of high-performance nonlinear model predictive control for flexible operation. By providing a reliable digital twin, this work forms the essential foundation for economically viable, load-following green ammonia production powered by intermittent renewable energy.

REFERENCES

1. Kong, B., Zhang, Q., & Daoutidis, P. (2024). Nonlinear model predictive control of flexible ammonia production. Control Engineering Practice, 148, 105946. https://www.sciencedirect.com/science/article/pii/S0967066124001060

2. Koschwitz, P., Frisch, D., Harth, S., et al. (2023). Dynamic Parameter Simulations for a Novel Small-Scale Power-to-Ammonia Concept. Processes, 11(3), 680. https://www.mdpi.com/2227-9717/11/3/680

3. Deng, Z., Wang, J., & Liu, Y. (2024). A novel combination of machine learning and intelligent optimization algorithm for modeling and optimization of green

ISSN 3030-3907

ammonia synthesis. Energy Conversion and Management, 301, 118112. https://www.sciencedirect.com/science/article/abs/pii/S0196890424003704
4. Sun, Z., Zhang, H., & Liu, C. (2024). Modeling and simulation of dynamic characteristics of a green ammonia synthesis system. Energy Conversion and Management, 301, 118113.
5. https://www.sciencedirect.com/science/article/abs/pii/S0196890423012396
6. Cholewa, T., Steinbach, B., Heim, C., et al. (2024). Reaction kinetics for ammonia synthesis using ruthenium and iron based catalysts under low temperature and pressure conditions. Sustainable Energy & Fuels, 8, 2245-2255.
7. https://pubs.rsc.org/en/content/articlehtml/2024/se/d4se00254g
8. Bagheri, A., Cabral, T.O., & Pourkargar, D.B. (2025). Integrated learning-based estimation and nonlinear predictive control of an ammonia synthesis reactor. AIChE Journal, 71(5), e18732. https://aiche.onlinelibrary.wiley.com/doi/10.1002/aic.18732
9. Cabral, T.O., Bagheri, A., & Pourkargar, D.B. (2024). Learning-based model reduction and predictive control of an ammonia synthesis process. Industrial & Engineering Chemistry Research, 63(23), 10325-10342.
10. https://pubs.acs.org/doi/10.1021/acs.iecr.4c01234
11. Rosbo, J.W., Huusom, J.K., & Jensen, A.D. (2023). Control structure design for limited flexible operation of an ammonia synthesis plant. Journal of Process Control, 127, 102989.
12. https://www.sciencedirect.com/science/article/pii/S0959152423001029
13. Verleysen, K., Parente, A., & Contino, F. (2023). Robust design and dynamic optimization of a flexible power-to-ammonia plant. Energy Conversion and Management, 293, 117457.
14. https://www.sciencedirect.com/science/article/pii/S0196890423008567
15. Fahr, S., Mertes, J., Menzer, A., et al. (2023). Dynamic operation of the Haber–Bosch process for power-to-ammonia: Simulation and control. Industrial & Engineering Chemistry Research, 62(30), 11744-11754.
16. https://pubs.acs.org/doi/10.1021/acs.iecr.3c00898
17. Khalilov A.J. Modeling and identification of the process of ammonia synthesis. // Monograph / “TEXNO PRINT NAVOI” – Navoi: 2025. – 272 p.

ISSN 3030-3907