

A multiscale modeling framework for complex chemical processes with
decision-making applications

by

Thiago Oliveira Cabral

M.S., Federal University of Rio de Janeiro, 2019

AN ABSTRACT OF A DISSERTATION

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DOCTOR OF PHILOSOPHY

Tim Taylor Department of Chemical Engineering
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KANSAS STATE UNIVERSITY
Manhattan, Kansas

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Abstract

Integrated process systems transform chemical manufacturing by enabling modular, decentralized, and multifunctional operations. The increasing integration of renewable energy technologies and sustainable practices reshapes industrial paradigms, introducing complex dynamics that demand advanced modeling and control strategies. This dissertation presents a robust computational framework grounded in fundamental chemical engineering principles—transport phenomena, reaction kinetics, and thermodynamics—to enable predictive modeling, process design, and decision support in chemical-energy systems, focusing on hydrogen and ammonia production and utilization. Mechanistic models were developed for various applications, including ammonia synthesis and separation, solar-thermal energy integration, carbon vapor deposition, and multiphase fluidization. These models provide a reliable basis for capturing system behavior and guiding operational strategies.

Where necessary and computationally tractable, multiscale representations were incorporated to reflect the hierarchical nature of physical phenomena across molecular, mesoscopic, and macroscopic domains. While multiscale effects are inherent in chemical processes, their use in modeling and optimization has historically been limited by measurement and computational challenges. At the smallest scales, atomic and molecular interactions determine surface kinetics and thermodynamic properties. At intermediate scales, transport mechanisms interact with reaction dynamics to shape local process behavior. At the plant level, interconnections among unit operations influence overall performance and economic outcomes. Capturing these interactions is essential for developing accurate and effective models that support informed decision-making.

Model predictive control (MPC) was integrated with the developed process models to enable optimal system-level operation. As an optimization-based control strategy, MPC offers a structured approach for handling nonlinear dynamics, constraints, and uncertainty.

This work conceptualizes MPC as a supervisory decision-making layer responsible for coordinating energy and material flows across integrated networks. Beyond regulation, MPC is utilized as a planning and scheduling tool for real-time operation under diverse scenarios. While the present framework demonstrates its effectiveness, future research opportunities remain in model reduction, data-driven modeling, and scalable distributed control.

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Muito obrigado a todos.

Chapter 1

Introductory Concepts

1.1 Process Integration, Intensification and Polygeneration Systems

The impact of human technology and industrial activities on the natural environment has been recognized since the mid-20th century. Although politically controversial, the issue has become a daily concern of the scientific community in the XXI century. The long-discussed solutions rely on developing and investing in renewable, environment-friendly, sustainable technologies^[1–4]. Given the context of sustainable technologies, the chemical industry is interested in implementing a wiser use of energy and material resources^[5–8]. Improving global efficiency and minimizing inherent losses can be realized through process intensification and integration. Due to the particularities of each process technology and system design, chemical-energy integration and intensification are relatively complex and case-specific. Still, some studies handle this topic with generality^[9–11]. In simpler terms, process integration implies the rational interconnection and recycling of material and energy streams between processing units, so that the manufacturing system still achieves specific techno-economic objectives. Process integration is therefore associated with economics, system design, and decision-making: what processing units must be used; how many are necessary, and how they should be connected.

On the other hand, process intensification has more subjective and diverse definitions. Keil et al.^[12] presents a few of them and explains that the premise of process intensification is understanding the intrinsic physics of a process (thermodynamics, kinetics, and transport phenomena) and their interactions. It requires strong interdisciplinary skills in chemistry, reaction engineering, applied physics, and materials science. Process intensification aims to take economic advantage of those physical-chemical interactions. It is also economically advantageous to achieve goals with reduced manufacturing costs and waste, as well as increased productivity and quality. Therefore, process integration and intensification are deeply linked to principles of lean/compact, smart, and efficient manufacturing. Concurrently, they are also related to automation, artificial intelligence, and process control applications. Stankiewicz and Mouljin^[13] and Moulijn et al.^[14] discuss that the components of integration in chemical engineering typically translates to creating multifunctional processes (reactive separation, reactive distillation, reactive absorption, membrane adsorption), innovative equipment (fuel cells, microreactors, monolithic reactors, bioreactors), unusual operation (periodic dynamics) and renewable energy incorporation.

Process integration and intensification concepts in chemical manufacturing are well embodied by the design of polygeneration (or polygenerative) systems (PGS). A polygeneration system comprises individual processes producing two or more utilities. Examples of utilities include electricity, heat (stored in a hot fluid), cooling potential (stored in conditioned air or chilled water), and chemicals (typically fuels or value-added substances)^[15]. According to Adams II and Ghouse^[16], a polygeneration system must involve an energy form and a chemical. They argue that polygeneration technologies in Chemical Engineering will center on the production of syngas/hydrogen and their subsequent utilization in turbines, fuel cells, or as a feedstock in other chemical manufacturing processes. That embraces the idea of manageable power-to-gas (P2G) systems. Newer works have also extended the concept of P2G to ammonia, which occupies a crucial position in industry, with versatile applications as a feedstock and energy carrier in several markets and supply chains^[17–19]. However, producing those gaseous chemicals through thermal reforming, biomass conversion (including fermentation and gasification), or even water electrolysis also requires a considerable amount

of energy, as these processes are typically high-temperature. So, incorporating energy inputs from renewable sources, such as solar, hydro, or wind power, is highly beneficial.

The renewabilization of chemical manufacturing (i.e., integrating renewable energy and chemical processes) is a promising yet challenging synergistic approach to maintaining or even increasing productivity and resiliency, while considering environmental concerns. This synergy leverages the flexibility of using chemicals as an energy storage medium, allowing for optimal chemical production and the subsequent, locally controllable, generation of chemicals or energy during periods of high and low demand. In general terms, controllability can be defined as the ability to lead a specific output to the desired state as quickly, stably, and smoothly as possible by manipulating the inputs reasonably. It becomes clear why polygeneration systems have been receiving attention: their implementation is aligned with the sustainability agenda, and they have high potential for integration and intensification.

PGS opportunely meets principles of predictability, renewability, sustainability, integrability, and controllability. Therefore, this review provides a concise state-of-the-art overview of the descriptive modeling and simulation of units integrated into a specific PGS. It is organized into primary, secondary, and tertiary technologies, as shown in Figure 1.1. It attempts to link processes through material pathways that resemble a transportation network with a lean specificity, conceived by the perception and incorporation of those principles into hydrogen and ammonia technology, as well as by methods of process intensification^[20], design and distributed control, which will be briefly touched on the following sections.

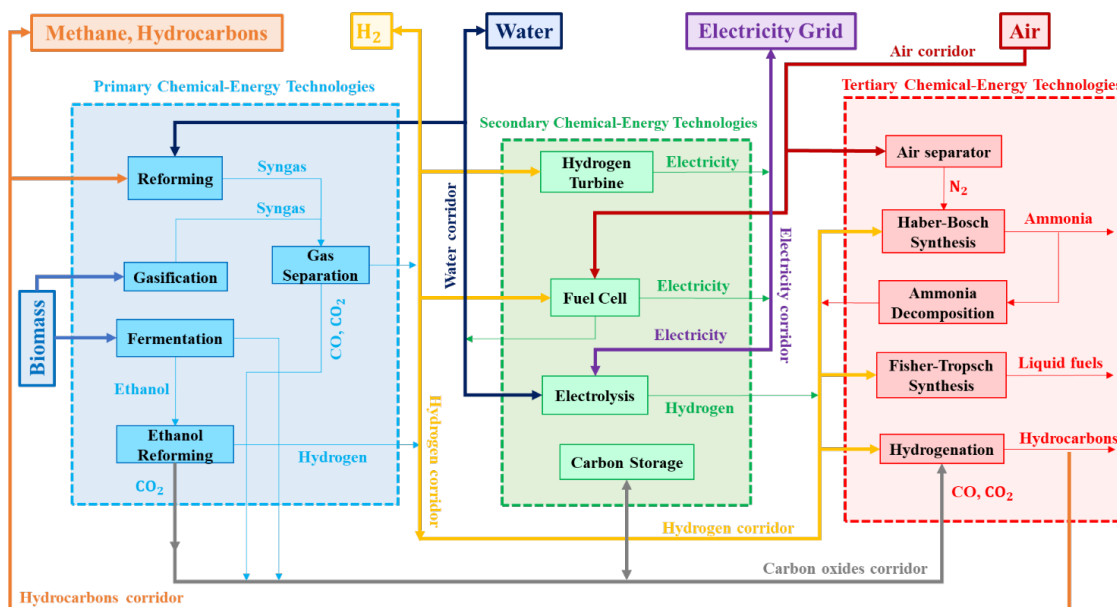


Figure 1.1: A polygeneration module conceived by the present author.

1.2 Chemical Process Engineering into Perspective: General Concepts for Multiscale High-Fidelity Modeling

Multiscale modeling is the mathematical consideration of interactions between physical-chemical phenomena at different spatial and time scales^[21]. The reader might notice similarities with the definition of process integration from section 2. The intensified process development promotes the investigation of technological challenges and gaps in multiscale and multiphysics modeling of chemical manufacturing processes. Figure 1.2 presents a comprehensive chart illustrating the multiscale modeling concept, spanning from quantum mechanics to process system dynamics. Although the chart is informative, it is also somewhat elusive: no single computational platform can currently encompass and describe those multiple levels of modeling. A hybrid and segregated approach is necessary for information flow between different scales.

At the macroscopic scale, a chemical plant network comprises several process units in-

terconnected through material, energy, and signal flows. At this scale, dynamic modeling, optimization, simulation, and control can be achieved within minutes or hours, as long as a predictive model is available for or a response is received from each processing unit. Ideally, a model should capture the spatial dependence of the process variables. Spatial homogenization is a significant source of uncertainty and discrepancy in lumped models (non-dimensional) because real processes are inherently non-homogeneous. For example, fluid properties in porous catalytic packed-bed reactors, bioreactors, and separation units can be highly space-dependent under certain conditions. This is due to interactions among reaction kinetics, thermodynamics, transport phenomena, and varying mixing degrees. Therefore, it is not an overstatement to say that spatial distribution profoundly affects the operation of a chemical unit and influences the operation of all subsequent connected units. Nevertheless, process units in which spatial variations are operationally determining (e.g., packed bed reactors, heat exchangers, and separators) are traditionally modeled at steady state. In other words, they do not contemplate time as a relevant variable due to complex mathematical formulations; therefore, they cannot be used for decision-making applications.

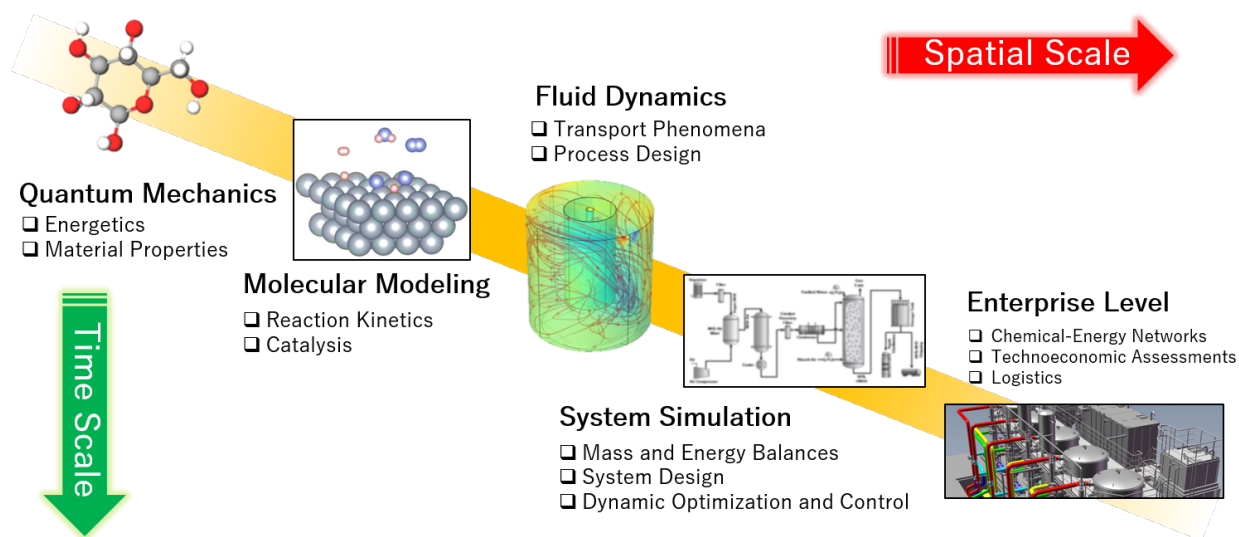


Figure 1.2: Modeling levels in packed-bed catalytic processes.

In the most general cases of laminar and turbulent fluid flow in chemical processing

units, such as porous catalytic reactors, it is observed that velocity, temperature, and concentration fields are formed, dictated by the multidimensional conservation of momentum, energy, and mass. They are generally described as intricately coupled partial differential equations (PDEs). The conservation field equations of fluid motion in porous media account for global mass conservation (Continuity Equation, 1.1), inertial forces (where the transient contribution lies), pressure forces, viscous forces, and external (gravitational) forces acting on the fluid. Those are usually expressed by the Navier-Stokes (Equation 1.2), which may be modified by a phase field parameter or function to addresses the presence of more than one fluid phase.

$$\frac{\partial(\varepsilon_b \rho)}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = S_{\text{mass}} \quad (1.1)$$

$$\begin{aligned} \frac{\rho}{\varepsilon_b} \left(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \right) \mathbf{v} \frac{1}{\varepsilon_b} = \nabla \cdot \left\{ -p \mathbf{I} + \left[\frac{\mu}{\varepsilon_b} (\nabla \mathbf{v} + (\nabla \mathbf{v})^T) - \frac{2}{3} \frac{\mu}{\varepsilon_b} (\nabla \cdot \mathbf{v}) \mathbf{I} \right] \right\} + \\ - \left(\mu \kappa^{-1} + \beta \rho |\mathbf{v}| + \frac{S_{\text{mass}}}{\varepsilon_b^2} \right) \mathbf{v} + \rho \mathbf{g} \end{aligned} \quad (1.2)$$

Brinkmann Equation (Equation 1.3) can be applied if the flow is not turbulent. Darcy's law (Equation 1.4) is a straightforward substitute if the assumption that the velocity field and the medium's permeability primarily govern the pressure gradients is valid. A common permeability correlation is given by the Kozeny-Carman (Equation 1.5). The combination of Darcy's Law and Kozeny-Carman correlation yields the famous Ergun equation, which describes the pressure drop caused by resisting frictional forces against fluid flow in a porous medium^[22–24].

$$\begin{aligned} \frac{\rho}{\varepsilon_b} \frac{\partial \mathbf{v}}{\partial t} = \nabla \cdot \left\{ -p \mathbf{I} + \left[\frac{\mu}{\varepsilon_b} (\nabla \mathbf{v} + (\nabla \mathbf{v})^T) - \frac{2}{3} \frac{\mu}{\varepsilon_b} (\nabla \cdot \mathbf{v}) \mathbf{I} \right] \right\} + \\ - \left(\mu \kappa^{-1} + \beta \rho |\mathbf{v}| + \frac{S_{\text{mass}}}{\varepsilon_b^2} \right) \mathbf{v} + \rho \mathbf{g} \end{aligned} \quad (1.3)$$

$$\nabla p = -\frac{\mu}{\kappa} \mathbf{v} - \frac{1.75 (1 - \varepsilon_b)}{d_p} \frac{\rho |\mathbf{v}| \mathbf{v}}{\varepsilon_b^3} \quad (1.4)$$

$$\kappa = \frac{\varepsilon_b^2}{150} \frac{\varepsilon_b^3}{(1 - \varepsilon_b)^2} \quad (1.5)$$

The heat transport equation, also referred to as the energy equation (Equation 1.6), describes Fourier's heat conduction and convection and includes heat sources/sinks caused by reactions. Because catalytic reactors are biphasic, volume-averaged heat capacities and conductivities (Equation 1.7) can be used to provide a more accurate description of the temperature field^[22–24].

$$\sum (c_{i,p,i}) \frac{\partial T}{\partial t} + \sum (c_{i,p,i}) \cdot \mathbf{v} \cdot \nabla T + \nabla(-k_{\text{eff}} \nabla T) = \sum Q \quad (1.6)$$

$$k_{\text{eff}} = (\theta \cdot k)_{\text{solid}} + (\varepsilon_b \cdot k)_{\text{fluid}} \quad (1.7)$$

The heat source terms on the right side of the equation include the heat released by the reaction inside catalyst pellets, for instance (Equation 1.8), which couples heat transport with species transport.

$$\sum Q = \frac{\int_V \Delta H_{\text{reaction}} \cdot R_{\text{reaction}} \cdot dV}{V_{\text{pellet}}} (1 - \varepsilon_b) \quad (1.8)$$

The species transport equation (Equation 1.9) contemplates Fickian diffusion and advection (dispersion, when both are combined) of individual species in a bulk fluid. Additional transport equations must be included in the model to describe the internal diffusion of species into small catalyst pellets^[22–24]. Equation 1.10 exemplifies a dimensionless transport equation for transient diffusion inside spherical porous pellets, whose surfaces are catalytically active. The reaction rates can be expressed in terms of volume or surface area, depending on the availability of kinetic data and catalyst properties.

$$\frac{\partial(\varepsilon_b c_i)}{\partial t} + (1 - \varepsilon_b) \rho_{\text{solid}} \frac{\partial c_{i,pe}}{\partial t} + \mathbf{v} \cdot \nabla c_i + \nabla(-D_{i,\text{eff}} \nabla c_i) = 0 \quad (1.9)$$

$$\frac{\partial(\varepsilon_{\text{pe}} c_{\text{i,pe}})}{\partial t} + \frac{1}{(r \cdot r_{\text{pe}})^2} \frac{\partial}{\partial r} \left(-r^2 D_{\text{i,eff,pe}} \frac{\partial c_{\text{i,pe}}}{\partial r} \right) = R_{\text{reaction}} \quad (1.10)$$

At the fluid-pellet interface, the mass transport resistance exerted by the fluid layer can be modeled with a Robin boundary condition (Equation 1.11). Frossling correlation can be used to estimate the Sherwood (Sh) number (Equation 1.12).

$$\frac{1}{r_{\text{pe}}} D_{\text{i,eff,pe}} \frac{\partial c_{\text{i,pe}}}{\partial r} \bigg|_{r=1} = \frac{\text{Sh} \cdot D_{\text{i,eff,pe}}}{r_{\text{pe}}} (c_{\text{i}} - c_{\text{i,pe}}) \quad (1.11)$$

$$\text{Sh} = 2 + 0.552 \cdot \text{Re}^{1/2} \cdot \text{Sc}^{1/3} \quad (1.12)$$

The effective species diffusivities are calculated employing Fuller correlation (Equation 1.13) and mixing rules for binary mixtures (Equations 1.14 -1.18)^[23]. Figure 1.3 exemplifies the main transport phenomena in a packed-bed catalytic process.

$$D_{\text{i,j}} = \frac{10^{-3} \cdot T^{1.75} \left(\frac{1}{M_{\text{i}}} + \frac{1}{M_{\text{j}}} \right)}{P \cdot \left(\nu_{\text{i}}^{1/3} + \nu_{\text{j}}^{1/3} \right)} \quad (1.13)$$

for T [K] and P [bar], $D_{\text{i,j}}$ is in $[\text{cm}^2/\text{s}]$.

$$D_{\text{i,mixture}} = \left[\sum_{j \neq i} \frac{\left(\frac{y_{\text{j}}}{1-y_{\text{i}}} \right)}{D_{\text{i,j}}} \right]^{-1} \quad (1.14)$$

$$D_{\text{i,eff}} = \frac{\varepsilon_{\text{b}}}{\tau} D_{\text{i,mixture}} \quad (1.15)$$

$$D_{\text{i,eff,pe}} = \frac{\varepsilon_{\text{pe}}}{\tau_{\text{pe}}} D_{\text{i,mixture}} \quad (1.16)$$

$$\tau = \varepsilon_{\text{b}}^{-1/3} \quad (1.17)$$

$$\tau_{pe} = \varepsilon_{pe}^{-1/3} \quad (1.18)$$

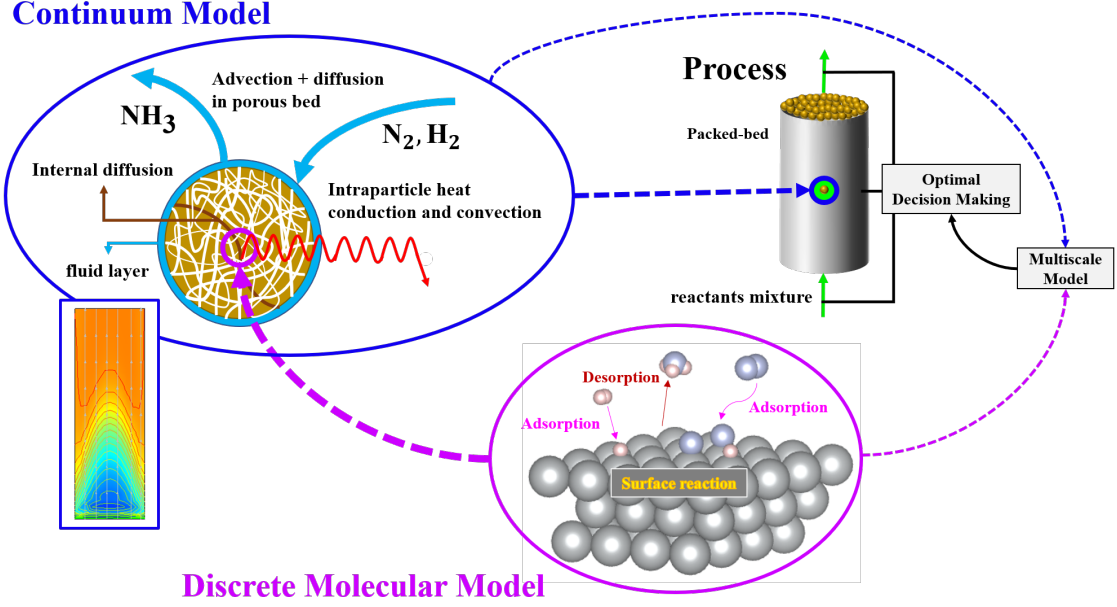


Figure 1.3: Modeling levels in packed-bed catalytic processes.

Even though we possess fundamental knowledge to describe dynamic/transient transport-reaction phenomena in a single process, its mathematical implementation and resolution are historically recognized as a complicated problem, as it not only substantially increases the process model complexity, but also makes the current computational solution arduous, hampering sophisticated real-time applications like MPC. Most renewable technologies are considered complex and advanced processes, inherently implying complex models. The tradeoff between model accuracy, complexity, and computational load remains in several engineering fields. However, some studies have noted that upgraded computational simulation tools have reached a maturity stage, allowing complex process models to be implemented with improved predictability and intensification [21,25,26].

Discussing integrability, Daoutidis et al. [27] state that, even with the assumption of spatial homogenization, non-linear system dynamics emerge from interactions between processes, causing time-scale multiplicity and the need for a hierarchical, supervisory system-level control architecture, either centralized or distributed. In centralized control, a single controller

makes decisions for the entire system, typically requiring significant computational power. Alternatively, distributed control is based on dividing the system into optimal subsystems with shared objectives, requirements, and outputs (referred to as communities) and assigning coordinated controllers to them, which communicate and lead to the best collective state for the system. The authors debate some open challenges involving distributed control with MPC: the detection and design of communities, the decomposition of the integrated system into an efficient distributed architecture, and the development of robust architectures promoting flexible system operation in response to dynamic market requirements. In recent studies, Daoutidis et al.^[28] and Allman et al.^[29,30] have discussed distributed control applied to sustainable chemical manufacturing systems, highlighting the production of biofuel and ammonia from solar and wind power.

A significant challenge arises when attempting to investigate the dynamic behavior of an entire chemical manufacturing system on a multiscale level. Solving the fluid dynamics for multiple processes together still seems too complicated with the current computational resources. Deeper-level modeling (molecular and quantum) is also too simplified and limited to be reliably extended to the system level. Our current interscale modeling capability is relatively narrow in the face of the spatial spectrum. Liu et al.^[31] believe that, in some decades, engineering and computational science will probably have evolved enough to conciliate a unified modeling framework that satisfactorily intertwines the fundamental physics and materials of processes in different scales and in real-time. They indicate a few critical gaps that must be surpassed: underdevelopment of physics-based models that link length and time, inability to conduct real-time characterization and measurements, lack of reliable optimization methods that bridge across scales, lack of appropriate code modernization in software employed in engineering applications, lack of community standards or schema for materials information storage, lack of multidisciplinary workforce.

Adjiman et al.^[32] also help elucidate pathways to broaden the capability of relating material-level physics and decisions to system-level dynamics with Computer-Aided Molecular Design (CAMD). CAMD is a series of methods that determine material structure and properties from high-fidelity models in computational quantum mechanics (QM) and molec-

ular dynamics (MD), which can be transposed to larger scales through surrogate machine learning (ML) or deep learning (DP) models. Statistics, data science, and artificial intelligence (AI) may indeed provide the tools to glue an approximately self-consistent multiscale framework. Regarding catalytic processes, the authors concluded that microkinetic or mechanistic modeling also represents a bridge for: (1) information traffic between micro and macroscale through the accountability of different elementary events and reactive sites, (2) controlling macroscopic outputs (productivity rates, for instance) through the manipulation of variables at the molecular level (particle size or shape, for instance), and (3) quantification of uncertainties and discrepancies at macroscale level for properties that we can and cannot measure accurately^[33]. Furthermore, the authors note that time-scale disparities pose significant computational difficulties; however, the numerical solution of microkinetic problems can be optimized to reduce these disparities. Rangarajan et al.^[34] give an exemplary framework for such optimized microkinetic modeling. Vlachos et al.^[35] also discuss a hierarchical multiscale model-based design to maximize the transmission of information from complex reaction mechanisms using microkinetic modeling and model reduction.

Table 1.1: Variables and their definitions.

Name	Definition
ε_b	Bed void fraction
ρ	Density of the material
t	Time
∇	Del operator, representing the gradient in space
$\mathbf{v}$	Velocity vector
S_{mass}	Mass source term for mass
p	Pressure
$\mathbf{I}$	Identity matrix
μ	Dynamic viscosity of the fluid
κ	Bed permeability
β	Drag coefficient
$\mathbf{g}$	Gravitational acceleration field
β	Drag coefficient
d_p	Particle diameter
T	Temperature
$c_{p,i}$	Specific heat of species i
k_{eff}	Effective thermal conductivity
$\sum Q$	Heat sources
θ	Solid phase proportion
k	Thermal conductivity
$\Delta H_{\text{reaction}}$	Heat released or absorbed in a chemical reaction
R_{reaction}	Rate of the chemical reaction
V	Volume
V_{pellet}	Volume of the pellet
c_i	Concentration of species i in the bulk
ρ_{solid}	Density of the solid phase
$c_{i,\text{pe}}$	Concentration of species i in the pellet
$D_{i,\text{eff}}$	Effective diffusion coefficient of species i in the bulk
ε_{pe}	Void fraction of the pellet
r	Radial distance in the sphere
r_{pe}	Radius of the particle
$D_{i,\text{eff,pe}}$	Effective diffusion coefficient of species i in the pellet
R_{reaction}	Rate of the chemical reaction
Sh	Sherwood number
Re	Reynolds number
Sc	Schmidt number
$D_{i,j}$	Diffusion coefficient between species i and j
M_i, M_j	Molecular weights of species i and j
ν_i, ν_j	Molecular volumes of species i and j
$D_{i,\text{mixture}}$	Diffusivity of species i in the mixture
y_i, y_j	Mole fractions of species i and j
τ, τ_{pe}	Bulk and pellet tortuosity

1.3 Integration of Fundamental Reaction Kinetics into Continuum Models

Traditional reaction engineering methods and CFD successfully communicate to size equipment and predict the operation of several processes. Nevertheless, properly incorporating fundamental reaction kinetics into the former is the most promising technological advancement in devising catalytic processes. To determine a fundamental reaction rate law, it is necessary to gain a deeper understanding of molecular interactions through the combination of quantum mechanics, surface chemistry, and molecular dynamics. The general approach of developing rate laws for heterogeneous reactions from power laws or even kinetic theories such as the Eley-Rideal or Langmuir-Hinshelwood-Hougen-Watson kinetics is often subject of criticism, due to invalid assumptions on equilibrium and rate-limiting steps, presence of unconsidered sites and species, occurrence of unpredicted elemental reactions, strict operational validity, regression overfitting and misinterpretations. However, a reasonable assumption about open atomic or molecular systems is that a steady-state configuration is attainable, even if equilibrium is not.

The integration of discrete molecular and surface dynamics with continuous fluid dynamics through a fundamental rate expression has been outlined in multiple articles and books on multiscale modeling^[21,36–44] and is given by the following sequence of steps:

1. Hypothesizing on the most important (rate-limiting or slowest) elementary reactions of a catalytic process and constructing its reaction mechanism. An example is provided in Table 1.2 for the NH_3 synthesis mechanism. Other elementary reactions may occur in this process and compete on the surface of a real catalyst.

Table 1.2: NH_3 synthesis mechanism.

Type	Elementary Reaction
Adsorption/Desorption	$\text{N}_2 + * \rightleftharpoons \text{N}_2^*$
Surface/Surface	$\text{N}_2^* + * \rightleftharpoons 2\text{N}^*$
Adsorption/Desorption	$\text{H}_2 + 2* \rightleftharpoons 2\text{H}^*$
Surface/Surface	$\text{N}^* + \text{H}^* \rightleftharpoons \text{NH}^* + *$
Surface/Surface	$\text{NH}^* + \text{H}^* \rightleftharpoons \text{NH}_2^* + *$
Surface/Surface	$\text{NH}_2^* + \text{H}^* \rightleftharpoons \text{NH}_3^* + *$
Desorption/Adsorption	$\text{NH}_3^* \rightleftharpoons \text{NH}_3 + *$

2. Determining the energy barriers of each elementary reaction with the aid of the Nudged Elastic Band (NEB) method. The NEB method is a quantum-mechanical approach, implementable with Density Functional Theory (DFT), consisting of estimating the ground-state energies associated with a series of static atomic configurations (or images/frames) that represent the evolution or transition of the spatial positions of the atoms along the reaction coordinate. This static frame approach is employed because time-dependent forms of the Schrodinger Equation are not easily tractable in commercial packages. The NEB calculations are centered on geometry optimizations of intermediate atomic configurations, interpolating between an initial and final configuration. The initial and final structures must be intuitively constructed by the user. Crystal structures and surfaces of metallic catalysts can be found on websites such as the Materials Project^[45] and Crystalium^[46]. A database of energy barriers of numerous elementary reactions can also be found at Catalysis Hub^[47].

3. Applying transition state theory (TST) to estimate theoretical values for the rate constants of elementary adsorption, desorption, and surface reactions (Equations 1.19, 1.20, and 1.21, respectively)^[44,48]. If an adsorption isotherm is available, k_{ads} and k_{des} are directly correlated through the equilibrium constant.

$$k_{\text{ads},i} = \frac{1}{N_{(\text{site/area})} \sqrt{2\pi m_i k_B T}} S_{\text{ref}} \exp \left[\frac{-\Delta E_{\text{act},i}}{k_B} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right] \quad (1.19)$$

$$k_{\text{des},i} = \frac{k_B T^3}{h^3} \frac{2\pi m_i k_B}{N_{(\text{site/area})} \sigma_i \theta_{i,\text{rot}}} \exp \left(\frac{-\Delta E_{\text{des},i}^\ddagger}{k_B T} \right) \quad (1.20)$$

$$k_{\text{surf},i} = \frac{k_B T}{h} \frac{q_{AB}^\ddagger}{q_A q_B} \exp \left(\frac{-\Delta E_{\text{surf},i}^\ddagger}{k_B T} \right) \quad (1.21)$$

4. Performing mean-field microkinetic modeling (MKM) by solving a set of transient ODEs that establish molecular balances of each adsorbed species and sites in terms of surface coverage fractions (Equations 1.22, 1.23, and 1.24). MKM targets the steady-state configuration of surface reactions at the molecular level. The “mean-field” expression implies spatial homogeneity of the surface domain or an “average” configuration of the reactive ensemble. The amalgamation between the NEB+MKM methods can be allegedly substituted by reactive Molecular Dynamics (MD), in which atomic interactions in an ensemble are approximated by Newton’s law of motion and parameterized with a reactive force field. The dynamic evolution of the atoms’ positions can be predicted for thousands of frames, reaching much longer time-scales than DFT^[49,50].

$$\frac{d\theta_i}{dt} = \sum \nu_{i,j} \cdot \text{TOF}_{i,j} \quad (1.22)$$

$$\sum \theta_i = 1; \quad (1.23)$$

$$\text{TOF}_{i,j} = k_j \prod a_i^{\nu_i} \prod \theta_i^{\nu_i} \quad (1.24)$$

5. Calculating the product’s turnover frequencies (TOF) for multiple temperatures and partial pressures at steady-state.

6. Performing numerical regression to coalesce and consolidate the TOF data generated by MKM into a rate model, most interestingly, deep-learning neural network models.

Although the algorithm has been known, very few studies have effectively implemented some form of molecular-fluid field integration in catalytic processes. Chen et al.^[51] combined a kinetic model for syngas dehydrogenation with CFD and validated the results with experimental data. Without experimental data, the validation could also be made against the traditional empirical rate laws employed in macroscopic modeling. Maestri et al.^[52]

conducted multiscale and multidimensional simulations with the complex kinetic mechanisms of H_2 combustion. Matera et al.^[53] applied the first-principles kinetic Monte Carlo (a discrete/probabilistic approach to microkinetic modeling) and addressed the disparate time scales between surface chemistry and gas-phase transport. Surface chemical interactions tend to be much faster than fluid dynamics. Therefore, they reasonably claimed that a steady-state approximation could be devised for the surface. Finally, Hus et al.^[54] studied ethylene epoxidation to show the feasibility and reliability of coupling deterministic mean-field microkinetics with CFD.

At this point, we should not expect an errorless description. The procedure introduces several levels of uncertainty, ranging from inaccuracies in energy estimates from DFT (which propagate exponentially according to TST) to the mean-field approximation (spatial uniformity of adsorbates and site distributions) in microkinetics, which impact the calculation of TOFs. Catalyst surfaces are not homogeneous and perfectly crystalline, as assumed in most first-principles calculations. Geometric and spatial defects, such as uneven atomic coordination, vacancies, asymmetric edges, ledges, interfaces, and other metastable structures, can all be catalytically active, frequently serving as the actual active sites in structure-sensitive reactions^[54]. Furthermore, structural surface changes driven by chemical interactions (fouling) or thermodynamics (sintering) also alter catalytic activity. Of course, modeling all those phenomena at the microscale is prohibitively complicated. Not surprisingly, mean-field MKM usually results in very stiff sets of ODEs, which most numerical implicit solvers hardly cope with or get reasonable steady-state solutions for, even for relatively simple mechanisms.

Maestri^[55] deliberates on how to escape the complexity traps in multiscale microkinetic modeling. He references pioneering contributions of Vlachos and collaborators in the concept of hierarchical multiscale modeling^[35,36,56]. According to them, an elegant resolution is the optimally refined identification and sensitivity analysis of the crucial mechanistic phenomena, which would rationally balance modeling accuracy and computation affordability. However, its generalization and systematization are complicated. The training of surrogate ML models that link molecular-fluid fields requires a large amount of kinetic data from MKM at various conditions, including those in which neglected phenomena may be relevant. So far, pondering

the model’s accuracy and complexity seems to be the most efficient way to create large datasets.

Multiscale integration will become more consistent as computational power in materials science improves. Ab initio methods, such as DFT, can optimize molecular geometry to reliably assess transition states, reaction pathways, and their associated energy barriers. Trends in consistency are already evident through screening optimized atomic configurations and identifying those with the lowest energies, which are likely to be closer to the actual configuration. Fortunately, fundamental data on material and physical chemistry are growing and becoming more organized. Regarding ammonia synthesis, for instance, we reference the works of Qian et al.^[57], Hellman et al.^[58,59], Honkala et al.^[60], McKay et al.^[61], Qiu et al.^[62], and Nakao et al.^[63]. They provide energies estimated with DFT for elementary reactions evaluated on different metals and conditions. DFT studies of methane reforming are also abundant: Zhu et al.^[64], Niu et al.^[65,66], Wang et al.^[67], and Chen et al.^[68] are examples. In the case of ethanol reforming and solid oxide cells, fewer efforts have been reported; noteworthy mentions include Wang et al.^[69], Li et al.^[70], Tao et al.^[71], and Yang et al.^[72]. More referential information on the material chemistry, electrochemical activity, and kinetics of hydrogen-based electrolyzers and fuel-cells can be found in Tucker^[73], Ahmad et al.^[74], Grondin et al.^[75], Pers et al.^[76], Wang et al.^[77], Lyagaeva et al.^[78], Zhu and Kee^[79,80], Zhu et al.^[81–83].

Table 1.3: Variables and their definitions.

Name	Definition
$k_{i,ads}$	Adsorption rate constant for species i
P_i	Pressure of species i
A_{ads}	Pre-exponential factor for adsorption
m_i	Molecular mass of species i
k_B	Boltzmann constant
T	Temperature
$k_{i,des}$	Desorption rate constant for species i
h	Planck constant
σ_i	Collision diameter of species i
$\theta_{i,rot}$	Rotational temperature of species i
$\Delta G_{i,des}^\ddagger$	Activation energy for desorption of species i
$k_{i,surf}$	Surface reaction rate constant for species i
$q_{i,0}^\ddagger$	Transition state partition function for species i
q_i	Partition function for species i
$\Delta G_{i,surf}^\ddagger$	Activation energy for surface reaction of species i
$\frac{d\theta_i}{dt}$	Rate of change of coverage of species i
$\nu_{i,j}$	Stoichiometric coefficient of species i in reaction j
$TOF_{i,j}$	Turnover frequency of reaction j for species i
θ_i	Surface coverage of species i
k_j	Rate constant of reaction j
a_i	Activity of species i

1.4 A Brief Overview on Model Predictive Control

Process control is a computer-based engineering method that connects real-time decisions to the operation of a process or system. The purpose is to make the system's outputs attain a desired quality after a finite, hopefully short, period. In the literature, it is common to find a hierarchy diagram (Figure 1.4), which identifies the levels of control applied to chemical manufacturing process systems. The highest level in the process control hierarchy is concerned with planning and scheduling operations for the entire processing plant. Techno-economic considerations and decisions are typically made based on profitability, productivity, costs, and safety. Real-time optimization (RTO) reconciles these high-level economic decisions with technical engineering restrictions by determining optimal steady state operating conditions, which are implemented as setpoints for controlled variables^[84].

In multivariable, constraint, and regulatory control, the set-points and information about specific process restrictions are transferred to controllers. They receive information from sensors and actuate directly on the process through control elements, like a valve or heating element. Multivariable and constraint control is an advanced feedback strategy with model predictive control (MPC). MPC utilizes process models to make predictions about the temporal dynamics of output variables. Online and systematically, traditional MPC determines values for process inputs that minimize an objective function involving the predicted output trajectories and their desired set-point trajectories within a prediction horizon^[84,85]. RTO and MPC share a numerical optimization component, which is not covered in this review. Apart from its capability to deal with multiple variables and constraints, MPC can be extended to variables that cannot be directly measured in real life. Formally, MPC represents an elegant decision-making method for input variables centered on the possession of dynamic, time-dependent models; without them, output predictions cannot be made, and the strategy cannot be implemented.

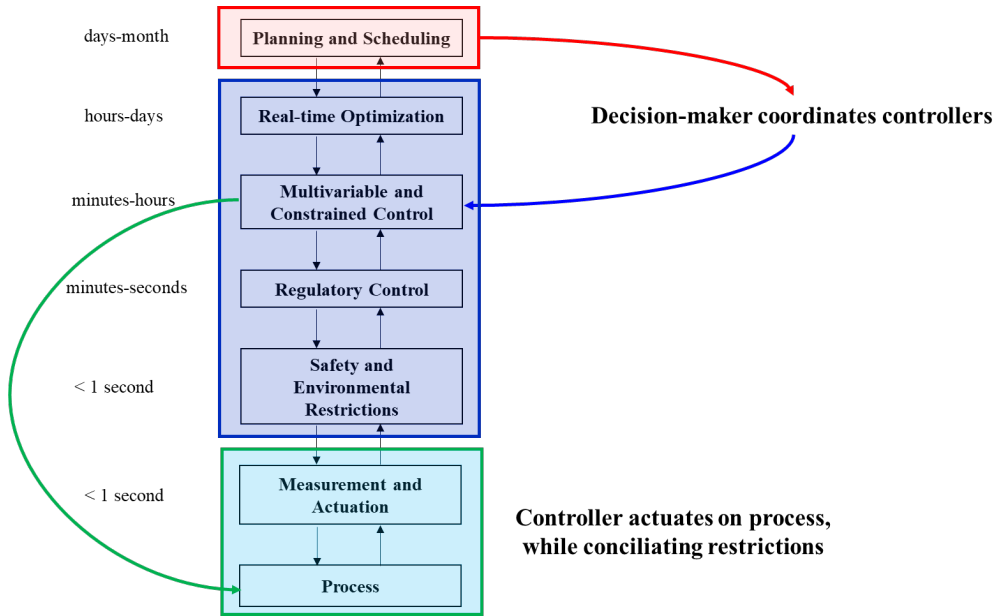


Figure 1.4: Process control hierarchy, adapted from Seborg et al.^[84]. Manipulating process dynamics as a strategy to achieve decided objectives.

In the multiple-input multiple-output (MIMO) MPC formulation for a regulation problem, the objective (or cost) function is most simply represented as a double summation of

quadratic residuals between the predicted and desired state values within a prediction horizon of length P , as shown in Equation 1.25: $y_{SP,j}$ is the set-point value for output j ; $y_{i,j}$ is the predicted value for output j at the i^{th} sampling time instant; $u_{\text{ref},j}$ is the reference or expected steady-state value for manipulated input j ; and $u_{i,j}$ is the optimal value determined for manipulated input j at the i th sampling time instant. They are vectors with lengths compatible with the time slots in the horizon. Weights can be assigned to reflect relative and normalized importances in the optimization. They are represented in matrices $\mathbf{P}$ (output weights) and $\mathbf{Q}$ (input weights), which multiply the residual matrices as shown in Equations 1.26 and 1.27.

$$\min \sum_{j=1}^{j=N_{\text{output}}} \sum_{i=k}^{i=k+P} ||x_{i,j} - x_{SP,j}||^2 + \sum_{j=1}^{j=N_{\text{input}}} \sum_{i=k}^{i=k+P} ||u_{i,j} - u_{\text{ref},j}||^2 \quad (1.25)$$

where

$$||x_{i,j} - x_{SP,j}||^2 = (x_{i,j} - x_{SP,j})^T \cdot \mathbf{P} \cdot (x_{i,j} - x_{SP,j}) \quad (1.26)$$

$$||u_{i,j} - u_{\text{ref},j}||^2 = (u_{i,j} - u_{\text{ref},j})^T \cdot \mathbf{Q} \cdot (u_{i,j} - u_{\text{ref},j}) \quad (1.27)$$

In deviational form, Equation 1.25 can be rewritten as shown in Equations 1.28. The advantage of choosing a deviational form for the cost function is that it can be more straightforwardly minimized by setting the deviational variables x' and u' to zero, thus avoiding a different steady state that would naturally be attained without control action from the initial state.

$$\min \sum_{j=1}^{j=N_{\text{output}}} \sum_{i=k}^{i=k+P} ||x'_{i,j}||^2 + \sum_{j=1}^{j=N_{\text{input}}} \sum_{i=k}^{i=k+P} ||u'_{i,j}||^2 \quad (1.28)$$

where

$$||x'_{i,j}||^2 = (x'_{i,j})^T \cdot \mathbf{P} \cdot (x'_{i,j}) \quad (1.29)$$

$$||u'_{i,j}||^2 = (u'_{i,j})^T \cdot \mathbf{Q} \cdot (u'_{i,j}) \quad (1.30)$$

A typical MPC code works as follows: (1) At time step k , the MPC controller evaluates the current states of a process and their desired set-points; (2) It performs the cost function minimization to determine the optimal control/input moves for time steps up to $k+P$ in the prediction horizon; the optimal evaluation of trajectories requires the dynamic model to make predictions within the horizon; (3) It applies the first move in the optimal sequence found in the optimization stage, proceeding to the next time step $k+1$ and setting it as the current state. In that sense, MPC recedes its operational loop to go further in time. (4) Finally, at the new time step k , it reassesses the states and their setpoints and repeats the procedures. Ideally, the higher the model fidelity and the faster the model predictions, the more reliable the optimized input decisions. An ODE or PDE mathematical formulation for chemical process models has been convenient for traditional, advanced, and adaptable feedback control methods. They are relatively efficient and have succeeded in the chemical industry and research.

Table 1.4: Variables and definitions.

Name	Definition
N_{output}	Number of outputs
N_{input}	Number of inputs
k	Current time index
P	Prediction horizon length
$x_{i,j}$	State variable at time i for variable j
$x_{\text{SP},j}$	Setpoint for state variable j
$u_{i,j}$	Input variable at time i for variable j
$u_{\text{ref},j}$	Reference input for variable j
$\mathbf{P}$	Weight matrix for state error
$\mathbf{Q}$	Weight matrix for input error
$x'_{i,j}$	Deviational state variable at time i for variable j
$u'_{i,j}$	Deviational input variable at time i for variable j

1.5 Dissertation Scope

The primary research subject detailed in this dissertation is the development and evaluation of a high-fidelity and dynamic multiscale modeling framework for advanced chemical systems, as well as an investigation into how they can be physically integrated within the scope of sustainable, renewable, and smart manufacturing, and real-time decision-making and optimization strategies. In that context, the research employed different computational platforms such as MATLAB and COMSOL to implement and combine methods and data from molecular modeling (microkinetic modeling, transition state theory and density functional theory), thermodynamics of fluids, reaction engineering and transport phenomena to study and propose innovative chemical systems, particularly technologies involving hydrogen, ammonia, air and other renewable resources. The models are typically constituted of complex partial differential equations, which are solved with finite element or finite difference methods. Machine learning has also been incorporated to allow faster communication and information flow through physics-informed data.

The process systems community has demonstrated interest in the projects and methods involved in this research, as integrated and dynamic multiscale models are rarely investigated in depth. This dissertation is structured into 7 main chapters. This chapter aimed to provide the foundational concepts of process integration and multiscale modeling. Chapter 2 presents the development of a feedback control loop for a 2-dimensional packed-bed ammonia synthesis reactor model, incorporating distinct dimensional considerations for the catalyst pellets and utilizing a machine-learning model reduction. Chapter 3 discusses a multiscale phenomenological model of a heterogeneous catalytic system for the growth of carbon nanotubes. Chapter 4 presents the modeling and regulation of an integrated hydrogen-ammonia production system sustained by solar and wind energy. Chapter 5 introduces concepts of integration at the largest scale, specifically a supply chain optimization problem within a chemical-energy community. Chapter 6 presents a collection of high-fidelity modeling methods for chemical engineering processes that are traditionally complex, including a biphasic fluidized bed reactor, a digital twin model for a bioreactor, additive manufacturing, elec-

trolisis/hydrogen fuel cells, intensified systems for ammonia synthesis and separation, and organ-on-chip technologies. Chapter 7 concludes the dissertation, summarizing relevant remarks from the previous chapter and highlighting new research directions. Hopefully, this dissertation elucidates the development of computational models that are more physically reliable, serving as a platform for informed decisions towards a more sustainable chemical industry.

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Chapter 2

Learning-Based Model Reduction and Predictive Control of an Ammonia Synthesis Process

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2.1 Introduction

Ammonia is the second most widely produced synthetic chemical and a key component in the production of fertilizers, plastics, refrigerants, explosives, pesticides, textiles, and dyes^[2]. Besides its critical role in establishing chemical and agricultural infrastructure, it has also been recognized as a versatile, carbon-free hydrogen carrier and a sustainable energy storage alternative^[3,4]. Ammonia synthesis has been industrially achieved for over a century through the Haber-Bosch process. This process involves a tubular reactor packed with iron-based catalyst pellets, onto which N_2 molecules, separated from air, adsorb and react with

activated H_2 at high pressure (50–200 bar) and moderately high temperature (500–1000 K). The ammonia synthesis reaction is exothermic, necessitating precise control of the reactor temperature, especially around hotspots, to achieve reasonable thermodynamic conversions, ensure process safety, and minimize catalyst degradation. The reaction mechanism is well understood and documented in the literature^[5–12]. It involves multiple intermediate reactions, including the breaking of the strong N_2 triple bond, the hydrogenation of NH_2^* species, and the desorption of NH_3^* as the kinetically dominant elementary steps. Experimental studies by Gillespie et al.^[13] and Temkin and Pyzhev^[14] provide thermodynamic and kinetic information on iron-based catalyzed ammonia synthesis.

The complex transport-reaction interactions at different scales need to be accurately described to capture the synthesis process. Transport mechanisms significantly impact reactor performance, as much as the catalyst activity. A high-fidelity model of ammonia synthesis relies on predicting the dynamic interplay between elementary surface reactions at the molecular scale and thermodynamics and transport phenomena at meso and macroscopic scales^[15–17]. Therefore, a multiscale model becomes indispensable to bridge microscopic features to macroscopic process variables that can be measured and manipulated. Although multiscale modeling approaches have been explored for various catalytic chemical processes^[18–26], there is an evident lack of studies on ammonia reactors^[27–30], with only a few directly analyzing process dynamics^[31–33].

Despite the accuracy of the multiscale modeling approach, the model solution is computationally demanding, rendering it impractical for real-time decision-making and control strategies, particularly when solving transient transport-reaction models using computational fluid dynamics (CFD) tools. Machine learning (ML)-based reduced-order surrogate models can be utilized to address the challenges of multiscale model-based control implementation by providing fast inference and information exchange^[34–36]. Recurrent neural networks (RNNs) have emerged as an efficient ML approach for model-based control because they can capture sequential dependencies in time-series data^[37,38]. Unlike feedforward neural networks (FNNs), RNNs possess distinctive recursive connections in each cell, enabling them to learn sequentially and leverage past data to make future predictions^[39–41]. However, conventional

RNN structures, such as Vanilla RNNs, encounter difficulties in learning long-term dependencies in sequential data. Long short-term memory networks (LSTMs) were developed to overcome this limitation by enhancing the ability to capture dynamics through advanced gating mechanisms that encompass input, output, and forget gates^[35,41–43]. These gates enable LSTMs to effectively manage long-term dependencies in time-series data, incorporating sigmoid and hyperbolic tangent functions. Recent works have demonstrated the promising application of LSTMs for various process systems. For instance, a model predictive control system was introduced to utilize LSTMs for optimizing the Kraft pulping process operation, catering to the increasing demand for various paper types^[44]. In another study, LSTMs were employed to model an electrochemical CO₂ reduction system^[45]. The limitations of LSTMs for surrogate modeling were also addressed, and an LSTM-based controller was proposed to extend the applicability of these types of networks in process control^[46].

Despite the promising applications of RNNs, their recursive architecture makes them computationally intensive for processing large-scale datasets. Moreover, proper handling of RNN hidden states could be elusive for some applications, potentially leading to less effective temporal learning^[47]. Transformers were introduced as a new sequential architecture that addresses the limitations of RNNs by incorporating the self-attention mechanism^[48]. This innovation eliminates the recursive architecture and is superior to RNNs, especially in time-series modeling. In this context, the application of time-series transformers (TSTs) was demonstrated for the data-driven modeling of batch crystallization of dextrose^[49,50]. In another study, transformers were employed for multi-step-ahead process modeling, highlighting their capability to learn from very long sequences effectively^[51].

This work advances a model predictive control (MPC) framework for ammonia synthesis by leveraging ML-based reduced-order surrogate models to address the computational challenges of real-time multiscale model solutions. A detailed multiscale predictive model is initially developed for catalytic ammonia synthesis by integrating microkinetics and continuum transport, comprising a set of nonlinear algebraic and differential equations. These equations are crucial for predicting the spatiotemporal dynamics of pressure, temperature, and species concentration. The feasibility of MPC hinges on the real-time solvability of a dynamic op-

timization problem, subject to the resulting multiscale model and constraints. To overcome the computational limitation of the model solution, an LSTM-based reduced-order model is trained on a large-scale dataset generated through offline high-fidelity simulations under various operational conditions. This dataset encompasses parallel, multivariate time-series data. The model solutions obtained using the finite element method yield heterogeneous time steps in the time-series data, resulting in a bimodal distribution that can potentially introduce bias in the training of surrogate models.

To address this issue, an FNN-based approach is employed to normalize the time series and regenerate the gappy data. Subsequently, a stacked LSTM network is trained on the regenerated dataset, providing a reduced-order representation of the reactor dynamics. Finally, the resulting LSTM-based reduced-order model is utilized for MPC design. Closed-loop simulation results demonstrate the effectiveness of the proposed approach in regulating the reactors' hotspot temperature and outlet concentration of ammonia. The rest of the chapter is structured as follows: Section "Multiscale-Multiphysics Ammonia Synthesis Reactor Model" introduces the proposed multiscale modeling framework for the ammonia synthesis reactor. The solution approach and open-loop simulation results are presented in the "Computational Details" section. This section also explains the LSTM approach for reduced-order modeling, large-scale dataset generation, and gappy data regeneration (GDR). The formulation of MPC for output regulation is presented in the "LSTM-based MPC Architecture" section. Finally, we summarize the results of our simulations and conclusions in the "Results and Discussion" section.

2.2 Multiscale-Multiphysics Ammonia Synthesis Reactor Model

Consider a cylindrical, homogeneous, packed bed reactor with uniform porosity. The reactor's symmetrical geometry allows for ignoring spatial variations in the azimuthal direction and describing the reactor through two-dimensional momentum, heat, and mass conservation

equations. Integrating these equations with catalytic reaction kinetics provides a multiscale-multiphysics modeling framework for quantifying the impact of feed properties and heat removal on the reactor's temperature and species concentrations. We are particularly interested in identifying the maximum temperature reached within the reactor and the ammonia concentration at the reactor outlet.

2.2.1 Momentum Transport

The momentum conservation in the homogeneously packed bed reactor is expressed by coupling the continuity equation,

$$\frac{\partial(\varepsilon_b \rho)}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \quad (2.1)$$

with Darcy's law,

$$\nabla p = -\frac{\mu}{\kappa} \mathbf{v} - \frac{1.75(1 - \varepsilon_b)}{d_p \varepsilon_b^3} \rho |\mathbf{v}| \mathbf{v} \quad (2.2)$$

where ε_b represents the bed porosity, ρ denotes the fluid density, $\mathbf{v}$ is the velocity field vector, p represents the gauge pressure ($p = P - P_{\text{ref}}$), μ is the fluid viscosity, κ is the bed permeability, d_p indicates the diameter of the catalyst pellet, and t denotes time. The density and viscosity of the fluid mixture are calculated using weight-average sums of the density and viscosity of each component, both of which vary with pressure and temperature. The fluid velocity field is determined by pressure gradients and the permeability of the packed bed, with the Ergun equation used to compute bed permeability,

$$\kappa = \frac{\varepsilon_b^2}{150} \frac{\varepsilon_b^3}{(1 - \varepsilon_b)^2} \quad (2.3)$$

2.2.2 Heat Transport

The heat transport within the reactor is predominantly governed by the convection and conduction mechanisms,

$$\sum_i (C_i c_{p,i}) \frac{\partial T}{\partial t} + \sum_i (C_i c_{p,i}) \mathbf{v} \cdot \nabla T + \nabla \cdot (-k_{\text{eff}} \nabla T) = \dot{Q} \quad (2.4)$$

where C_i represents the volumetric concentration of species i , c_p is the specific heat, k_{eff} indicates the effective thermal conductivity, $\dot{Q}$ is the volumetric heat source, T is the temperature, and the subscript 'eff' denotes an effective property obtained through averaging values across both fluid and solid volumes within the packed bed constituting the biphasic medium,

$$k_{\text{eff}} = \theta_{\text{solid}} k_{\text{solid}} + \varepsilon_b k_{\text{fluid}} \quad (2.5)$$

where θ_{solid} is the volume fraction of the solid pellets in the reactor. The heat source term on the right side of Equation 2.4 is exclusively equivalent to the heat released by the reaction inside the pellets, coupling heat transport with concentration field and species transport,

$$\dot{Q} = \frac{\int_V \Delta H_{\text{reaction}} r_{\text{NH}_3} dV}{V_{\text{pe}}} (1 - \varepsilon_b) \quad (2.6)$$

where V_{pe} is the the volume of the catalyst pellet and $\Delta H_{\text{reaction}}$ denotes the heat of the reaction obtained experimentally^[52],

$$\begin{aligned} \Delta H_{\text{reaction}} [\text{cal/mol}_{\text{NH}_3}] = & \left(0.54526 + 846.609 T^{-1} + 459.734 \times 10^6 T^{-3} \right) P + 5.34685 T \\ & + 0.2525 \times 10^{-3} T^2 - 1.69197 \times 10^{-6} T^3 + 9157.09, \end{aligned} \quad (2.7)$$

for T [K] and P [bar].

2.2.3 Mass Transport

The species transport more clearly reflects the multiscale nature of the model, as illustrated in Figure 2.1, where diffusion and advection emerge as the primary mechanisms governing mass transport within the porous space among the pellets, as described by Equation 2.8,

Continuum Model

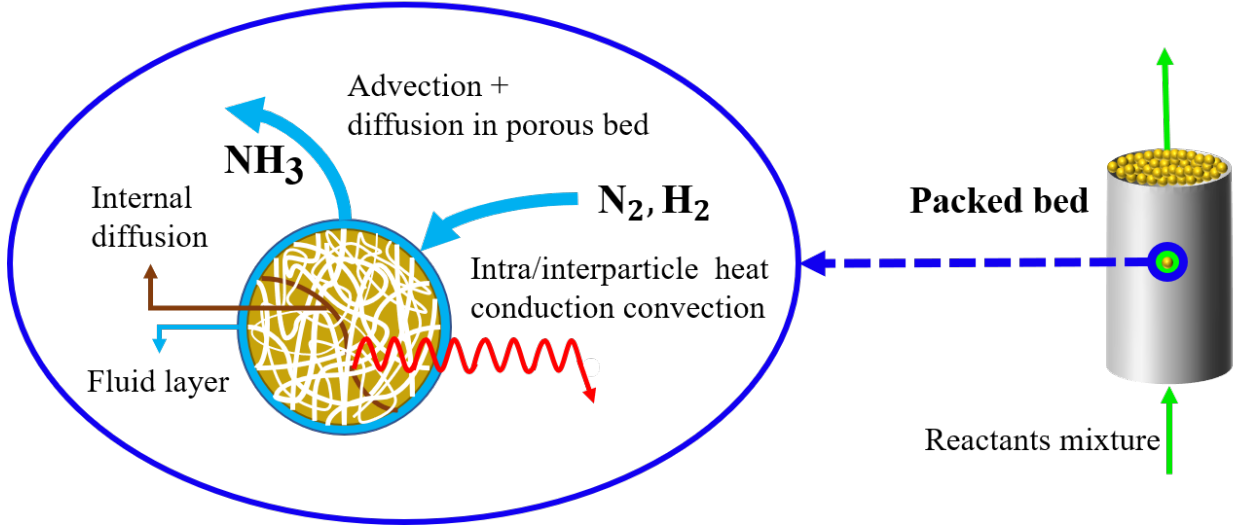


Figure 2.1: Transport phenomena in a packed bed ammonia reactor.

$$\frac{\partial(\varepsilon_b C_i)}{\partial t} + (1 - \varepsilon_b) \rho_{\text{solid}} \frac{\partial C_{i,\text{pe}}}{\partial t} + \mathbf{v} \cdot \nabla C_i + \nabla(-D_{i,\text{eff}} \nabla C_i) = 0 \quad (2.8)$$

where $C_{i,\text{pe}}$ represents the volumetric concentration of species i within the pellet, $D_{i,\text{eff}}$ denotes the effective diffusion coefficient of species i in the bulk fluid, and ρ_{solid} is the density of the solid pellet.

The narrower pores within the catalyst pellet hinder the internal diffusion of species, necessitating a more detailed description of diffusion coefficients for each species. An additional dimensionless transport equation is employed to describe internal diffusion within spherical pellets,

$$\frac{\partial(\varepsilon_{\text{pe}} C_{i,\text{pe}})}{\partial t} + \frac{1}{\tilde{r}^2 r_{\text{pe}}^2} \frac{\partial}{\partial \tilde{r}} \left(-\tilde{r}^2 D_{i,\text{eff,pe}} \frac{\partial C_{i,\text{pe}}}{\partial \tilde{r}} \right) = R_i \quad (2.9)$$

where ε_{pe} is the pellet porosity, $\tilde{r}$ denotes a dimensionless pellet radius coordinate, r_{pe} is the pellet radius, and R_i represents the volumetric reaction rate of species i . A fluid film is formed at the fluid-pellet interface, introducing transport resistance. To describe this, we

employ a combination of a Robin boundary condition,

$$\frac{1}{r_{\text{pe}}} D_{\text{i,eff,pe}} \frac{\partial C_{\text{i,pe}}}{\partial \tilde{r}} \bigg|_{\tilde{r}=1} = \frac{\text{Sh} \cdot D_{\text{i,eff,pe}}}{r_{\text{pe}}} (C_{\text{i}} - C_{\text{i,pe}}) \quad (2.10)$$

and the Frossing correlation^[15],

$$\text{Sh} = 2 + 0.552 \cdot \text{Re}^{1/2} \cdot \text{Sc}^{1/3} \quad (2.11)$$

to establish a relationship between bulk species concentrations and their concentrations on the pellet surface, where Sh, Re, and Sc denote the Sherwood, Reynolds, and Schmidt numbers, respectively.

The effective diffusivities of the species are determined using the Fuller correlation and mixing rules^[15],

$$D_{\text{i,eff}} = \frac{\varepsilon_{\text{b}}}{\tau} D_{\text{i,mixture}} \quad (2.12)$$

$$D_{\text{i,eff,pe}} = \frac{\varepsilon_{\text{pe}}}{\tau_{\text{pe}}} D_{\text{i,mixture}} \quad (2.13)$$

$$D_{\text{i,mixture}} = \left[\sum_{j \neq i} \frac{\left(\frac{y_j}{1-y_i} \right)}{D_{\text{i,j}}} \right]^{-1} \quad (2.14)$$

$$D_{\text{i,j}} [\text{cm}^2/\text{s}] = \frac{10^{-3} T^{1.75} \left(\frac{1}{M_i} + \frac{1}{M_j} \right)}{P \left(\nu_i^{1/3} + \nu_j^{1/3} \right)}, \quad (2.15)$$

for T [K] and P [bar], while the Millington and Quirk model is applied to determine pore tortuosity^[53,54],

$$\tau = \varepsilon_{\text{b}}^{-1/3}, \quad \tau_{\text{pe}} = \varepsilon_{\text{pe}}^{-1/3} \quad (2.16)$$

where $D_{\text{i,mixture}}$ represents the diffusivity of species i in the gaseous mixture, y_i is the molar fraction of species i in the gaseous mixture, $D_{\text{i,j}}$ denotes the binary diffusivity coefficient of species i in species j, M_i is the molecular mass of species i, P denotes the absolute pressure

in bars, ν_i is the molecular volume of species i , τ represents the tortuosity of the porous bed, and τ_{pe} is the tortuosity of the porous pellet.

2.2.4 Kinetics and Thermodynamics of Ammonia Synthesis

The reaction rates are calculated using the Temkin-Pyzhev equation (5.37), which postulates that the rate-limiting elementary reaction is the dissociation of N_2 ^[52],

$$R_{NH_3} = k_2 \left[K_{eq}^2 a_{N_2} \left(\frac{a_{H_2}^3}{a_{NH_3}^2} \right)^{1/2} \left(\frac{a_{NH_3}^2}{a_{H_2}^3} \right)^{1/2} \right], \quad a_i = y_i \phi_i P \quad (2.17)$$

where a_i denotes the activity coefficient of species i , ϕ_i is the fugacity coefficient of species i , and the kinetic constant k_2 and the equilibrium constant K_{eq} are determined by

$$k_2 = k_0 \exp \left(\frac{-E_a}{RT} \right), \quad k_0 = 8.8490 \times 10^{14} \left[\frac{\text{kmol}}{\text{m}^3 \cdot \text{h}} \right], \quad E_a = -1.7056 \times 10^5 \left[\frac{\text{J}}{\text{mol}} \right] \quad (2.18)$$

$$\log(K_{eq}) = -2.6911 \log(T) - 5.5193 \times 10^{-5} T + 1.8489 \times 10^{-7} T^2 + 2001.6 \cdot T^{-1} + 2.6899 \quad (2.19)$$

where T is the temperature in K, E_a is the activation energy, and R denotes the universal gas constant. The fugacity coefficients are also determined using the Peng-Robinson equation of state,

$$\ln(\phi_i) = \frac{1}{RT} \int_V^\infty \left(\frac{\partial P}{\partial n} \Big|_{T,V,n_j} - \frac{RT}{V} \right) dV - RT \ln \left(\frac{PV_m}{RT} \right) \quad (2.20)$$

$$P = \frac{RT}{(V_m - b)} - \frac{a \cdot \alpha}{V_m(V_m + b) + b(V_m - b)} \quad (2.21)$$

where V is the volume, n is the number of moles, V_m is the molar volume of the species and

$$\begin{aligned} a &= \frac{0.4572 R^2 T_c^2}{P_c}, \quad b = \frac{0.0778 R T_c}{P_c}, \\ \alpha &= \left(1 + (0.3746 + 1.5423 w - 0.2699 w^2)(1 - T_r^{0.5}) \right)^2, \quad T_r = \frac{T}{T_c} \end{aligned} \quad (2.22)$$

with T_c [K], P_c [bar], and w denoting the critical temperature, critical pressure, and the acentric factor for the species, respectively.

2.3 Computational Details

2.3.1 Finite Element Method, Boundary Conditions, and Solution Approach

The previously presented set of partial differential equations is solved simultaneously using the finite element method (FEM) in COMSOL 5.6. The system is discretized into non-curved triangular elements. A fine mesh is formed across the reactor domain, as shown in Figure 2.2. Additional studies have shown that square-shaped elements yield the same results. Table 2.1 provides an overview of the physical properties of the reactor, feed, and catalyst particles. The catalyst pellets are discretized separately, employing a cubic root sequence with ten elements. Initial and boundary conditions are explicitly detailed in Tables 3.2 and 3.3, respectively. These conditions are tailored to each transport phenomenon, with the vector $\mathbf{n}$ denoting the normal direction to the boundary. The heat flux removed from the walls is treated as a Neumann boundary condition.

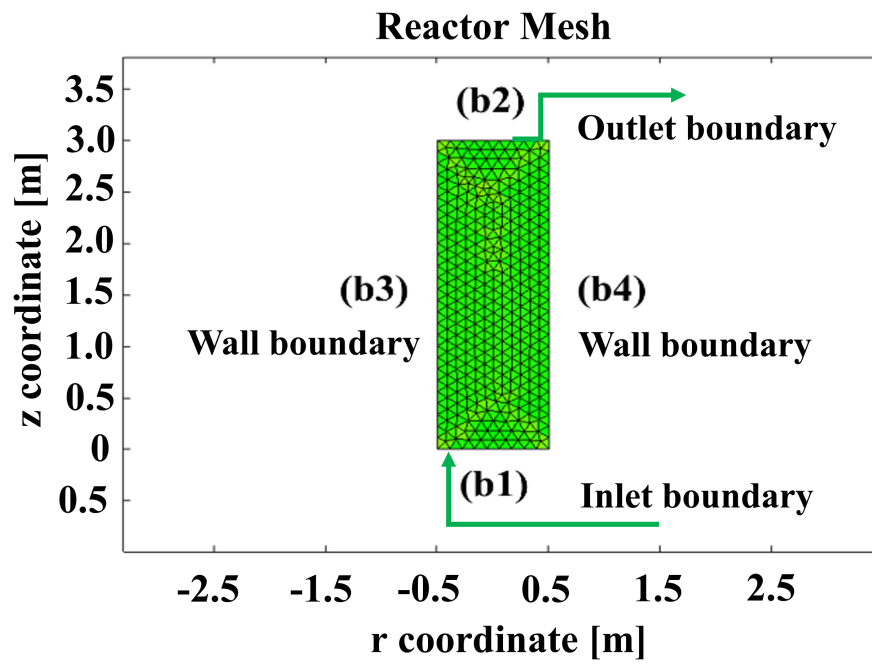


Figure 2.2: Mesh generated for the reactor geometry.

Table 2.1: Reactor, feed, and catalyst data.

Reactor Properties	
Reactor diameter [m]	1
Reactor height [m]	3
Bed porosity, ε_b	0.32
Reference pressure, P_{ref} [bar]	100
Reference temperature, T_{ref} [K]	723.15
Flux of heat removed at reactor walls, Q [kW/m ²]	0, 5, 10, ..., 100
Feed Properties	
Pressure [bar]	100
Temperature [K]	723.15
Feed Flowrate, F [L/min]	50, 100, ..., 1000
N ₂ molar fraction, $y_{\text{N}_2,\text{feed}}$	0.25
H ₂ molar fraction, $y_{\text{H}_2,\text{feed}}$	0.75
NH ₃ molar fraction, $y_{\text{NH}_3,\text{feed}}$	0.0001
N ₂ concentration [mol/m ³]	$y_{\text{N}_2,\text{feed}}P_{\text{ref}}/(RT_{\text{ref}})$
H ₂ concentration [mol/m ³]	$y_{\text{H}_2,\text{feed}}P_{\text{ref}}/(RT_{\text{ref}})$
NH ₃ concentration [mol/m ³]	$y_{\text{NH}_3,\text{feed}}P_{\text{ref}}/(RT_{\text{ref}})$
Catalyst Pellet Properties	
Pellet radius, r_{pe} [mm]	2
Pore radius, r_{pore} [nm]	0.2
Pellet porosity, ε_{pe}	0.40
Density [kg/m ³]	7874
Specific heat [J/(Kg · K)]	440
Thermal conductivity [W/(m · K)]	76.2

Table 2.2: Initial conditions.

Initial Conditions		
Momentum Transport	Heat Transport	Mass Transport
$P_0 = P_{\text{ref},0}$	$T_0 = T_{\text{ref},0}$	$c_{i,0} = c_{i,\text{feed}}$

Table 2.3: Boundary conditions.

Boundary Conditions	Momentum Transport	Heat Transport	Mass Transport
Inlet (b1)	Uniform feed flowrate (F)	Uniform inflow temperature	Fixed inlet concentration
Outlet (b2)	$P = P_{\text{ref}}$	$\mathbf{n} \cdot \mathbf{q}_{\text{conduction}} = 0$	$\mathbf{n} \cdot \mathbf{J}_{\text{diffusion}} = 0$
Thin walls (b3, b4)	$-\mathbf{n} \cdot (\rho \mathbf{v}) = 0$	Finite flux (Q)	$\mathbf{n} \cdot \mathbf{J}_{\text{diffusion}} = 0$

Point probes are assigned to monitor ammonia concentration and temperature fields at specific locations along the flow direction in the reactor, with a particular emphasis on detecting and controlling hot spots. Hot spots pose a significant challenge for conventional instrumentation in real reactors, justifying the development of a high-fidelity transport-reaction model. The probes are strategically positioned at the inlet ($z = 0$ m), outlet ($z = 3$ m), and an additional five points aligned at the center of the reactor ($x = 0.5$ m) along the axial direction ($z = 0.5, 1, 1.5, 2$, and 2.5 m). Spatiotemporal solutions for this ammonia reactor were successfully obtained within a 1000-minute timeframe using the implicit backward differentiation formula (BDF) solver, known for its stability and faster convergence due to applying the backward Euler method. LSTM networks subsequently leverage the time-series dataset collected by the probes to develop a reduced-order model. As outlined in Table 2.1, a simulation window is defined for two manipulated inputs, namely the flux of heat removed and feed flow rate, within which they are uniformly varied,

$$0 < Q < 100 \text{ [kW/m}^2\text{]}, \quad 50 < F < 1000 \text{ [L/min]} \quad (2.23)$$

2.3.2 High-Fidelity Simulations and Spatiotemporal Distribution of Output Variables

This section provides a brief overview of the high-fidelity model’s simulation results, illustrating the system’s complex spatiotemporal behavior. Figures 2.3, 2.4, and 2.5 present the spatial fields of N_2 , H_2 , and NH_3 concentrations, respectively, at two different time instances (30 and 500 minutes). These observations are made under the condition where the inlet flow rate (F) is 500 L/min, and the heat removal flux (Q) is maintained at 50 kW/m². Ad-

ditionally, Figure 2.6 illustrates the temperature field within the reactor, while Figure 2.7 shows the spatial distribution of the ammonia formation rate. To maintain conciseness, we have opted not to display concentration and temperature fields for all potential conditions; however, the trends observed are analyzed.

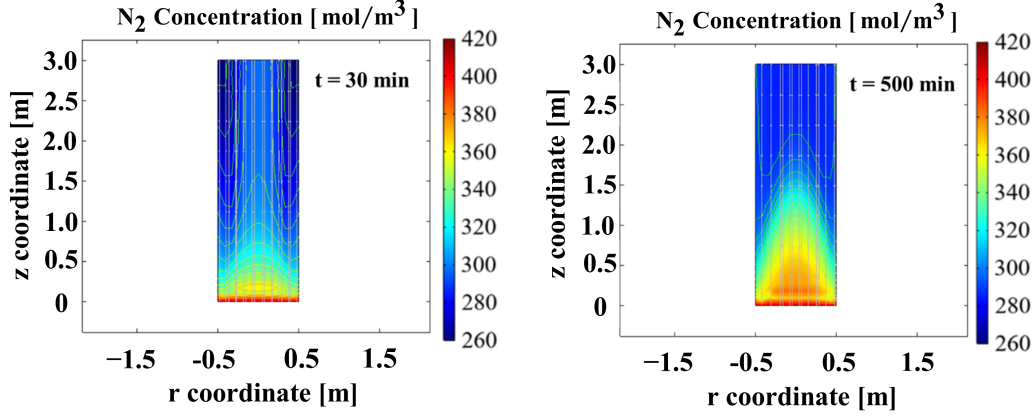


Figure 2.3: N_2 concentration distribution at 30 and 500 min for $F = 500 \text{ L/min}$ and $Q = 50 \text{ kW/m}^2$.

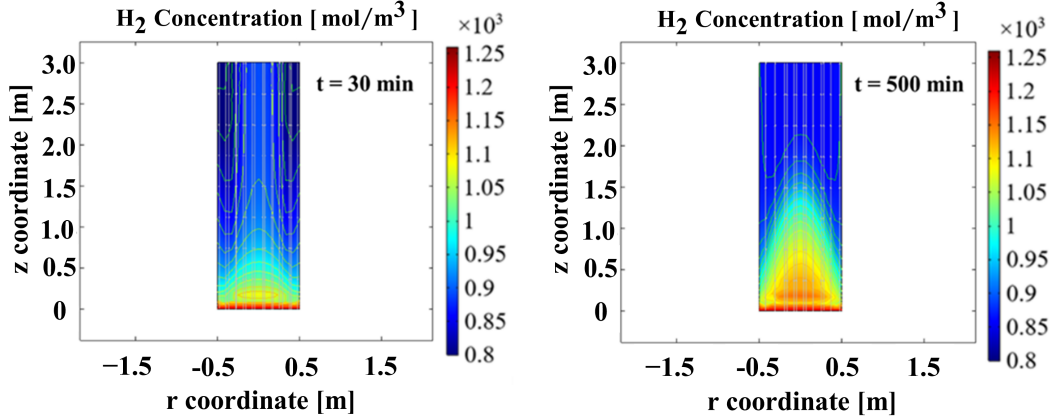


Figure 2.4: H_2 concentration distribution at 30 and 500 min for $F = 500 \text{ L/min}$ and $Q = 50 \text{ kW/m}^2$.

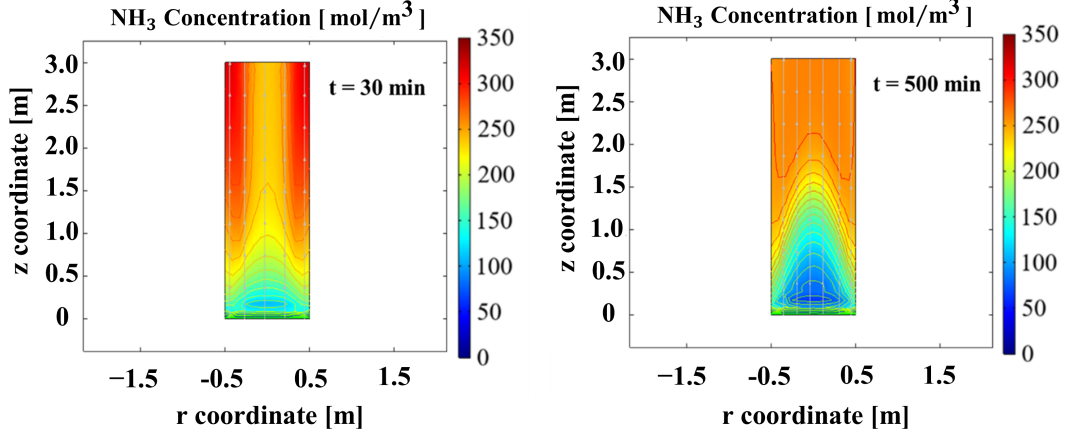


Figure 2.5: NH_3 concentration distribution at 30 and 500 min for $F = 500 \text{ L/min}$ and $Q = 50 \text{ kW/m}^2$.

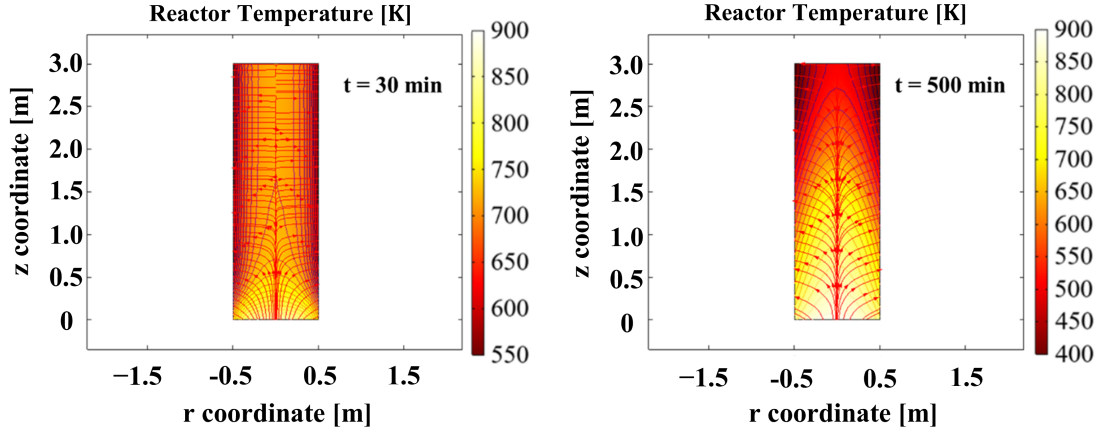


Figure 2.6: Temperature distribution at 30 and 500 min for $F = 500 \text{ L/min}$ and $Q = 50 \text{ kW/m}^2$.

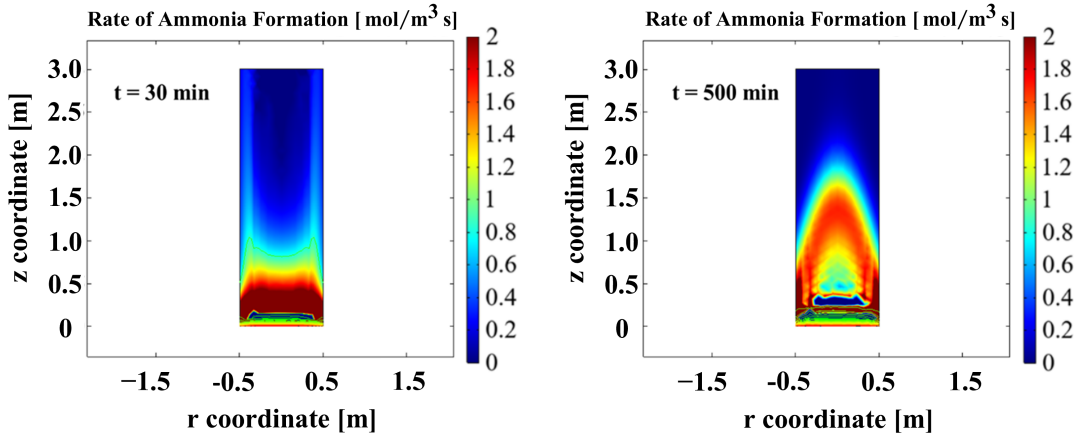


Figure 2.7: Distribution of the ammonia production rate at 30 and 500 min for a $F = 500 \text{ L/min}$ and $Q = 50 \text{ kW/m}^2$.

Figures 2.3-2.7 illustrate intense spatial gradients of temperature and concentrations within the reactor that cannot be accurately predicted by lumped energy and component mass balances. As the gas mixture percolates through the bed, the catalytic reaction ignites at lower regions of the bed, causing the gas to expand, and parabolic fields emerge from the combination of axial dispersion, reaction kinetics, and radial heat conduction. Figures 2.6 and 2.7 show that the rate of ammonia production reaches its maximum for temperatures ranging from 650 to 750 K. Beyond 750 K, the reaction becomes thermodynamically unfavorable due to its exothermic nature, whereas temperatures below 650 K result in kinetic limitations. In the neighborhood slightly above the inlet, where N_2 and H_2 concentrations are high, the temperature reaches its maximum, leading to elevated reaction rates. It is noteworthy to point out that the highest NH_3 concentrations are not located there. Instead, an inverse trend is observed as the gas approaches the reactor outlet. This may appear counterintuitive, as one might anticipate higher ammonia concentrations with higher reaction rates.

The plausible explanation is that axial dispersion occurs more rapidly than NH_3 formation. Once NH_3 is produced on the catalyst surface and diffuses out of the catalyst pellets, it is swiftly carried by the fluid moving axially towards the outlet. At the upper regions, the reaction equilibrium shifts, and the reaction is thermodynamically inhibited by lower temperatures and high ammonia concentrations; hence, the reaction rate is locally lower there, as shown in Figure 2.7. Fast axial dispersion also ensures that reactants are replenished more quickly than they can be consumed. In Figure 2.5, it is initially observed that the NH_3 concentration is significantly higher at the upper lateral points of the reactor. This concentration diminishes after 500 minutes of the reaction, achieving a steady state. The steady state is still characterized by the bell-shaped fields in the lower half of the reactor, while the upper half is relatively more homogenized, except for temperature. The temperature field evolution indicates that the reactor tends to be much colder in the upper regions.

The species concentration, temperature, and reaction rate distributions at different times are presented in the supporting information of published paper (Figures S-1, S-2, S-3, S-4, and S-5) for a feed flow rate of 50 L/min (ten times lower than in the previous case with the

same heat flux at the walls). While reaction kinetics and thermodynamics remain controlling factors, radial heat conduction effects become more pronounced. Although the influence of axial dispersion is observed, pushing ammonia toward the upper sections of the reactor at later times, radial concentration gradients become notably prominent. These scenarios illustrate the interplay between the exothermicity of the reaction, driven by axial dispersion, and heat removal through radial conduction. The ammonia production rate and temperature distributions are closely integrated. Due to the radial heat loss and the establishment of a radial temperature field, optimal reaction rates shift from the lateral regions (colder) towards the lower central portions of the reactor (hotter) as the lateral regions eventually become too cold.

2.3.3 LSTM-Based Model Reduction

The mathematical complexity of the multiscale model renders the FEM solution computationally expensive for predicting process dynamics. While multiscale models are effective, their time constraints make them unsuitable for real-time decision-making and predictive control applications. It is crucial to have a fast-responding model for precise control of the ammonia reactor. RNNs can be an effective intermediary for balancing computational costs and real-time responses in spatiotemporal process systems. LSTM networks, being one of the dominant types of RNNs, exhibit robustness in learning patterns in sequences, especially time-series data. Figure 2.8 illustrates the architecture of an LSTM cell^[42,55,56]. Each LSTM cell comprises input, forget, and output gates connected through "sigmoid (σ)" and "tanh" functions. The input gate updates the cell states with new information, the forget gate regulates the storage of data in the cell states, emulating the short-term memory of the cell, and the output gate determines the next cell state. The interactions between these gates contribute to capturing temporal dynamics and creating a short-term memory that enhances the performance of LSTM networks. Detailed LSTM equations are discussed in the supporting information of the published paper.

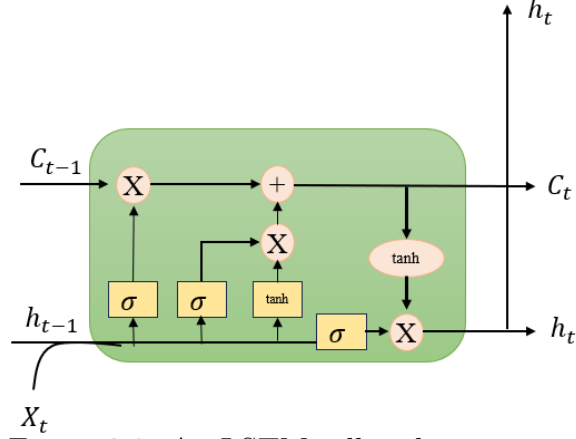


Figure 2.8: An LSTM cell architecture.

This study presents a reduced-order model based on LSTM to streamline the multi-scale model. This surrogate model, renowned for its agility and robustness, yields a time-dependent model that offers sufficient speed and compatibility for real-time MPC applications. The necessary process data is obtained from high-fidelity offline CFD simulations over a wide range of manipulated input values. This data ensemble forms the basis for training, validation, and testing the LSTM-based surrogate model. Despite the advantages of transformers, they are often criticized for requiring substantial training data to achieve optimal performance. On the other hand, one of the key challenges in developing surrogate models for industrial-scale processes is data collection. For large-scale problems with an adequate amount of data, the self-attention mechanism of the transformer demands high computational resources, a well-known obstacle for transformers^[57]. Given the scale of ammonia synthesis in the outlined PBR, collecting a large amount of process data for surrogate model development with transformers proves challenging. Therefore, we chose LSTM networks, which are well-suited for learning from long sequences, given the limitations in data generation. Figure 2.9 concisely illustrates the steps in creating the LSTM-based model. Subsequent sections will delve into the development process of the LSTM-based surrogate model.

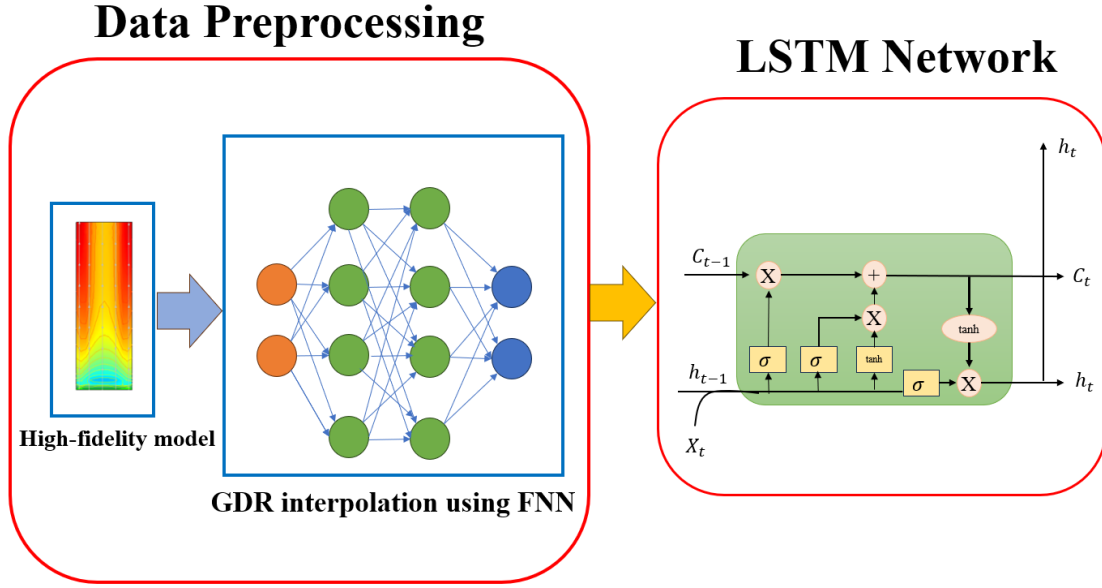


Figure 2.9: LSTM-based model development procedure.

2.3.4 Process Data Ensemble Generation and Analysis

To obtain process data, offline CFD simulations are conducted on the ammonia synthesis reactor using COMSOL Multiphysics across a wide range of system input values. The heat removed (Q) ranges from 0 to 100 kW/m², increasing in increments of 5 kW/m², while the flow rate (F) varies from 50 to 1000 L/min, with increments of 50 L/min. Each simulation is conducted for 1000 minutes to ensure steady state convergence. Consequently, the dataset comprises 420 distinct dynamic simulations. These simulations capture the intricate dynamics of ammonia synthesis in the packed-bed reactor and are used to train the surrogate model.

Figures 2.10, 2.11, and 2.12 illustrate the outlet boundary-averaged ammonia concentration, outlet stream temperature, and ammonia production rate dynamics for flow rates ranging from 400 to 1000 L/min. In these plots, the flux of removed heat at the walls is fixed at 50 kW/m². The notable peaks of the outlet NH₃ concentration are caused by an accumulation of NH₃ inside the reactor before the bulk fluid reaches the outlet. This is expected as ammonia is continuously produced, and the outlet is not reached instantaneously.

As discussed in the previous section and observed in Figures 2.10 and S-3, higher flow rates tend to reduce this transient accumulation at lower parts of the bed. Additionally, Figure 2.11 shows that the outlet temperature initially decreases in all scenarios; however, for higher flow rates (≥ 600 L/min), the exothermic nature of the reaction, combined with axial heat convection, eventually causes the outlet temperature to elevate.

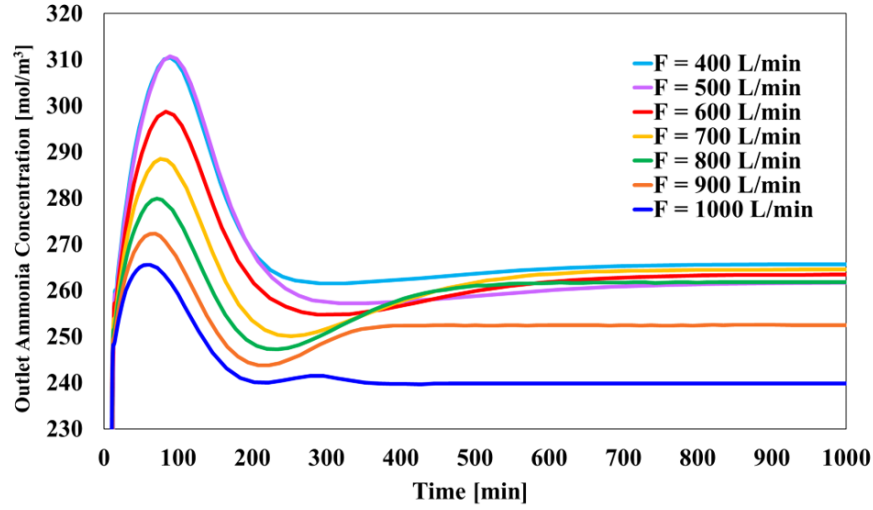


Figure 2.10: Outlet NH_3 concentration dynamics for various feed flowrates.

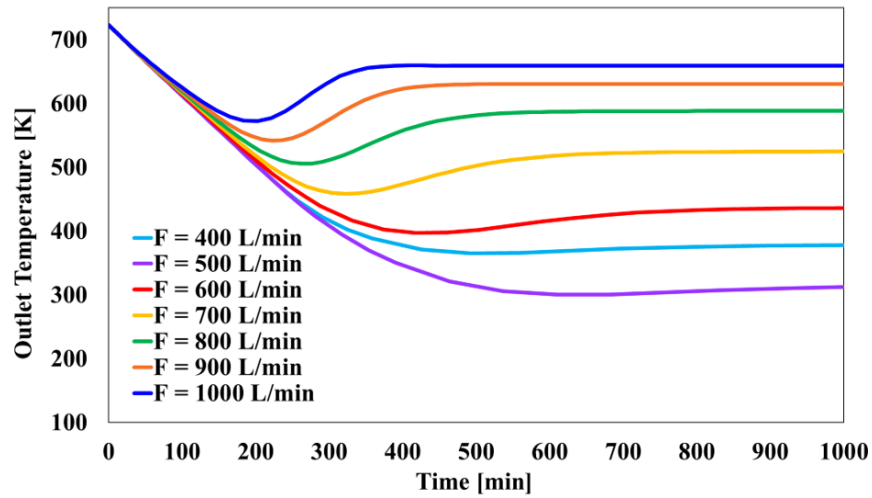


Figure 2.11: Outlet temperature dynamics for various feed flow rates.

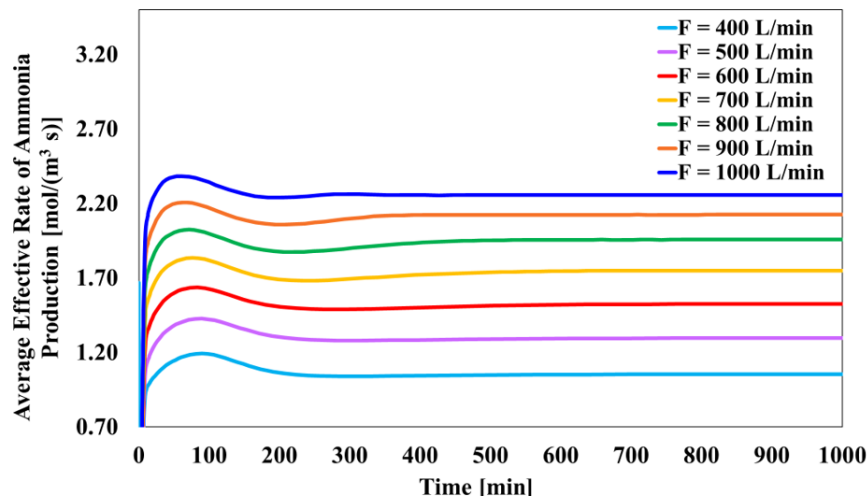


Figure 2.12: Dynamics of the average ammonia production rate for various feed flow rates.

As illustrated in Figure 2.12, the average effective production rate in the catalytic bed increases with the flow rate. In principle, reaction-controlled production rates do not vary with gas velocity (i.e., they are kinetically limited). This suggests that when the flow rate is low, more regions in the bed operate under mass transfer limitations. At lower flow rates, the reaction in the central and upper areas is remarkably suppressed due to lower reactant concentrations and higher ammonia concentrations (see Figures S-1 to S-5). On the other hand, higher gas velocities imply faster transportation of ammonia to the outlet, thereby reducing its residence time and the likelihood of thermodynamic equilibrium in the upper regions.

The increase in average production rate with flow rate can also be explained by the expansion or stretching of the concentration and temperature fields, which activate the upper parts of the reactor, as illustrated in Figure S-6 for a steady flow rate of 1000 L/min. Additional simulation results indicate that internal gradients within the pellets are negligible; in other words, internal diffusion is not a limiting factor. However, as the flow rate increases, the average rate of NH_3 production begins to assume similar values (the relative gaps between the curves are shortened), indicating that fewer regions in the reactor are limited by mass transfer.

Figures 2.13, 2.14, and 2.15 illustrate the overall impacts of heat removal on the outlet ammonia concentration, production rate, and outlet temperature. We again emphasize that

these effects arise from the intricate interplay between thermodynamics and kinetics. For instance, when small amounts of heat are removed, the production rates decrease significantly because the temperature within the reactor tends to rise, leading to a thermodynamic suppression of the reaction, as expected for any exothermic process. It is important to note that temperatures in the lower sections of the reactor are even higher than the outlet temperature. This raises concerns about potential thermal runaway, underscoring the importance of proper heat removal for ensuring the safety and efficiency of the process operation.

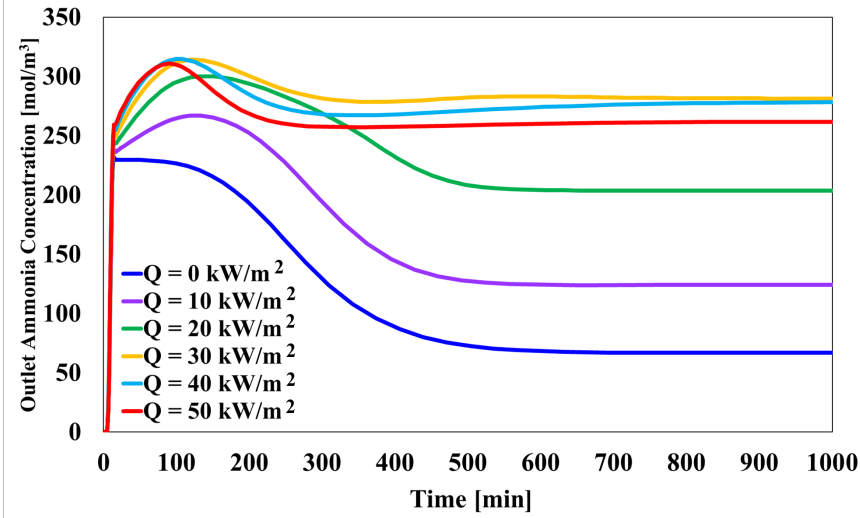


Figure 2.13: Outlet NH_3 concentration dynamics for various heat removal rates.

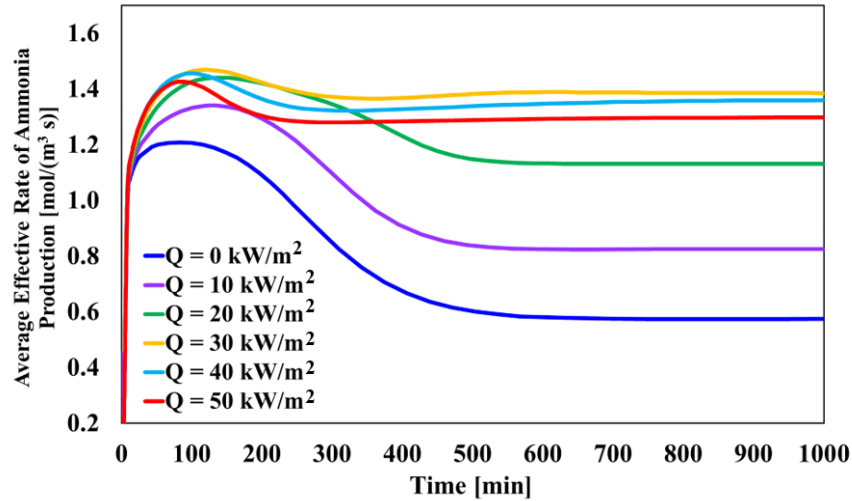


Figure 2.14: Dynamics of the average ammonia production rates for various heat removal rates.

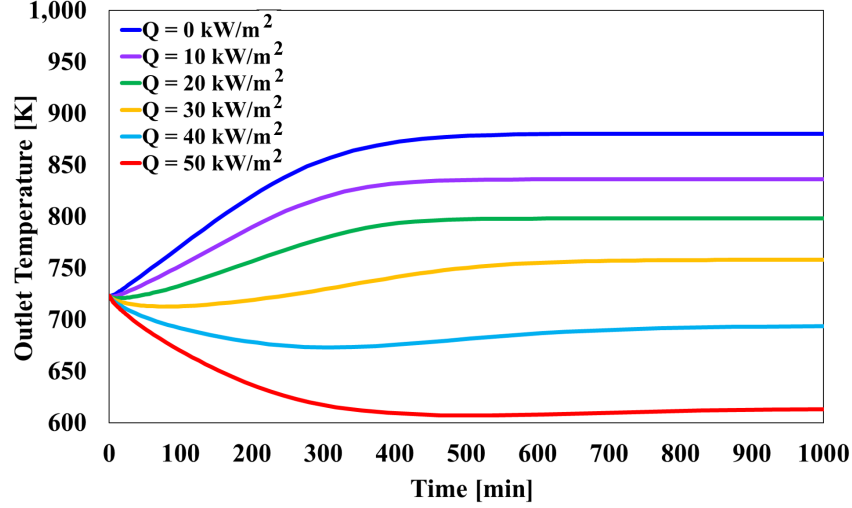


Figure 2.15: Outlet temperature dynamics for various heat removal rates.

The dependability and accuracy of the LSTM-based surrogate model are determined by quantifying the statistical characteristics of the simulation dataset. Despite expecting a simulation dataset of 4.2×10^5 data points with a timestep of one ($dt = 1$), the actual dataset contains only 5×10^4 data points, as the computational demands of CFD simulations impede the FEM solver's ability to maintain a consistent time step sequence, influencing the temporal resolution of the generated results. The irregularities in time-step simulations complicate the training of an effective surrogate model. Consequently, the simulations exhibit a bimodal distribution in process data, as illustrated by the distribution plots for each controlled output in Figure 2.16. The first peak signifies the initial dynamics of the reaction process, while the second peak corresponds to the conditions when the system reaches a steady state. The two distinct patterns of significant relevance introduce considerable bias in LSTM training that can lead to an imprecise surrogate model. This issue arises because the LSTM-based model attempts to capture the sequential patterns present in both distributions simultaneously, diminishing the clarity of each pattern. It is essential to convert this irregular dataset into a regular time-series format to ensure the proper training, validation, and evaluation of the LSTM-based surrogate model. The following sections outline the specialized data preprocessing methods we employed to address this challenge.

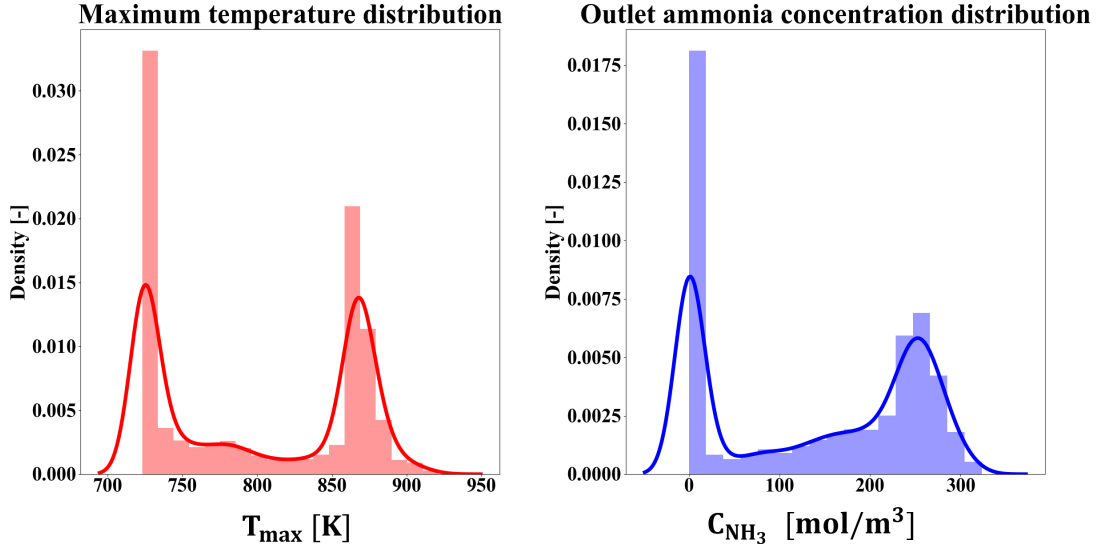


Figure 2.16: Original distribution of the control objectives in the ammonia production reactor.

2.3.5 Gappy Data Regeneration (GDR)

This section focuses on normalizing the bimodal distribution to regenerate a regular time-series dataset with constant time steps. A data regeneration approach is developed based on FNNs (Figure S-9 in the supporting information of the published paper) trained on the simulation dataset, enabling consistent temporal resolution. The GDR architecture consists of seven fully connected layers. To avoid overfitting, we incorporate two dropout layers and employ a combination of "ReLU" and "leaky ReLU" activation functions in the network^[58,59]. The mean squared error (MSE) is chosen as the loss function, and the ADAM optimizer^[60,61] is utilized for training.

To transform the time-series problem into a supervised learning task, we incorporate the time variable (t) as an independent feature in the input map alongside other inputs. Here, $\mathbf{I} = [t, Q, F]$ represents the GDR input vector, while $\mathbf{O} = [T_{\max}, C_{\text{NH}_3, \text{outlet}}]$ forms the GDR output vector. The simulation data is divided into 80% training and 20% validation sets, followed by standardization. Ultimately, the GDR undergoes training for 36 epochs,

implementing an early stopping method. The GDR method is a nonlinear regression model that enables interpolations on offline simulations using constant time steps. Therefore, we conduct open-loop interpolations employing a uniform time step with the trained GDR and generate a high-resolution dataset. This process employs the same input window as the COMSOL simulation. Despite the offline simulations, the regenerated dataset demonstrates regular multivariate time-series process data. All stages of data preprocessing, network implementation, training, and final inferences for data regeneration are carried out using the TensorFlow library in Python.

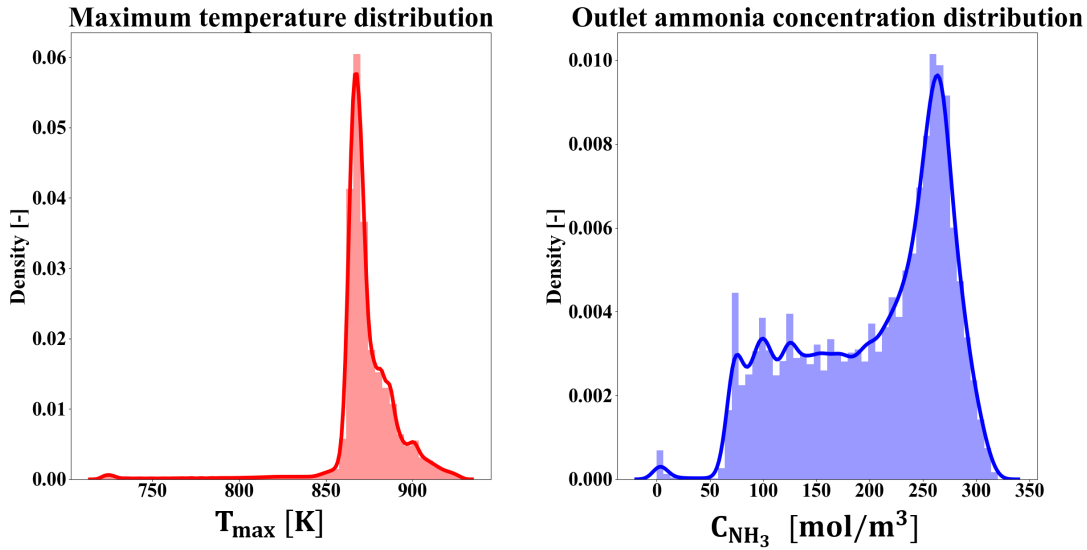


Figure 2.17: Regenerated distributions of the control objectives in the ammonia reactor.

Regularizing process time-series data results in data distributions exhibiting a dominant pattern. As illustrated in Figure 2.17, the bimodal distribution for $T_{\max}$ is normalized, while for $C_{\text{NH}_3, \text{outlet}}$, the dominant peak shows the overall dynamics of $C_{\text{NH}_3, \text{outlet}}$ in the synthesis process. Furthermore, the regenerated dataset ensures a consistent representation of the data distribution. It preserves the integrity of the reactor's physical dynamics, striking a careful balance between standardizing the data and maintaining essential characteristics. Ultimately, the dataset has been expanded to include 5×10^5 time-series data points, effectively capturing the complete dynamics of the ammonia synthesis reactor. This expanded

dataset is well-suited for training the LSTM-based surrogate model.

2.3.6 Min-Max Scaling for Data Normalization

Normalizing the numerical range of data is critical when working with time-series data and LSTM. The min-max scaling technique ensures that every input and output is treated within the same weight range. This helps prevent biases in the LSTM-based model arising from differences in numerical scales. The min-max scaling approach adjusts feature values by utilizing each attribute's minimum and maximum values, ensuring that they fit within a $[0 \ 1]$ range,

$$x_{\text{norm}} = \frac{x - x_{\text{min}}}{x_{\text{max}} - x_{\text{min}}} \quad (2.24)$$

where x_{norm} is the normalized value, x is the original value, x_{max} is the maximum value of the feature, and x_{min} is the minimum value of the feature^[62].

2.3.7 LSTM Training

The LSTM-based model interprets the regenerated dataset as a sequence of independent multivariate time series. Each series denotes the reactor operation, uniquely identified by independent inputs Q and F , which are employed to obtain T_{max} and $C_{\text{NH}_3, \text{outlet}}$. The data undergoes modification before being transformed into time-series sequences, wherein the inputs and outputs of the system are adjusted to deviate from a desired steady state. The deviational manipulated inputs and the desired outputs are described as follows: $u_1 = Q - Q_{\text{ss}}$, $u_2 = F - F_{\text{ss}}$, $y_1 = T_{\text{max}} - T_{\text{max,ss}}$, and $y_2 = C_{\text{NH}_3} - C_{\text{NH}_3, \text{ss}}$, where $Q_{\text{ss}} = 50 \text{ kW/m}^2$, $F_{\text{ss}} = 750 \text{ L/min}$, $T_{\text{max,ss}} = 865.93 \text{ K}$, and $C_{\text{NH}_3, \text{ss}} = 264.72 \text{ mol/m}^3$.

The LSTM network acquires an understanding of the temporal patterns of synthesis dynamics by analyzing previous sequences and forecasting future values based on historical data. Considering the output vector of $y = [y_{(1)}, y_{(2)}, \dots, y_{(k)}, y_{(k+1)}, \dots, y_{(k+\delta)}]$, the LSTM network uses the values of the vector $[y_{(1)}, y_{(2)}, \dots, y_{(k)}]$ as the training history to learn the patterns and predict $[y_{(k+1)}, \dots, y_{(k+\delta)}]$. Hence, k and δ are two principal variables that

must be tuned for better LSTM-based model performance. k is referred to as the memory length, indicating the number of previous nodes or the extent of short-term memory within an LSTM neuron, and δ is the prediction batch size, which denotes the number of future steps to predict with a single inference^[42]. We use $k = 5$ and $\delta = 1$ for optimal LSTM-based surrogate model training.

The independent input features, namely the manipulated inputs of the system, u_1 and u_2 , are integrated with output vectors. Consequently, the final configuration of our proposed parallel multivariate time-series dataset takes the form of $I = [u_{1(1,...,k)}, u_{2(1,...,k)}, y_{1(1,...,k)}, y_{2(1,...,k)}]$. The LSTM-based model architecture comprises five stacked LSTM layers. The first four layers employ hyperbolic tangent activations, while the last layer is dense with linear activation. The initial three LSTM layers capture the sequence inherent in the data, and the ultimate LSTM layer amalgamates these sequences into the final dense layer. The multivariate time-series dataset is partitioned into an 80% training set and a 20% test set. The ADAM optimizer is employed in a gradient descent learning algorithm, and the mean squared error is selected as the cost function for the LSTM network. The LSTM network undergoes training for 30 epochs, implementing an early stopping method to prevent overfitting. The TensorFlow library in Python is employed to implement, train, and evaluate the LSTM network.

2.4 LSTM-Based MPC Architecture

MPC is a constrained optimization-based control method that utilizes a time-discrete (or discretizable) process model to predict the dynamic behavior of the process outputs. MPC systematically calculates the temporal sequence of manipulated inputs within a control horizon that minimizes the cost function of errors between the predictions and setpoint values within a prediction horizon, subject to system constraints^[63]. The cost function is most

simply represented as a sum of quadratic residuals within a prediction horizon,

$$\min_{\mathbf{u}} \sum_{i=k}^{k+L} \|\mathbf{y}_{(i)} - \mathbf{y}_{\text{sp}}\|_{\mathbf{P}}^2 + \|\mathbf{u}_{(i)} - \mathbf{u}_{\text{sp}}\|_{\mathbf{Q}}^2 \quad (2.25)$$

where $\mathbf{y}_{(i)}$ and $\mathbf{u}_{(i)}$ are the vectors of predicted outputs and manipulated inputs at the sampling time t_i , the subscript "sp" denotes setpoint values, and

$$\begin{aligned} \|\mathbf{y}_{(i)} - \mathbf{y}_{\text{sp}}\|_{\mathbf{P}}^2 &= (\mathbf{y}_{(i)} - \mathbf{y}_{\text{sp}})^T \mathbf{P} (\mathbf{y}_{(i)} - \mathbf{y}_{\text{sp}}) \\ \|\mathbf{u}_{(i)} - \mathbf{u}_{\text{sp}}\|_{\mathbf{Q}}^2 &= (\mathbf{u}_{(i)} - \mathbf{u}_{\text{sp}})^T \mathbf{Q} (\mathbf{u}_{(i)} - \mathbf{u}_{\text{sp}}) \end{aligned} \quad (2.26)$$

The weight matrices $\mathbf{P}$ and $\mathbf{Q}$ can be adjusted to penalize the output regulation errors and the manipulated input variations.

The primary goal of the proposed LSTM-based MPC framework is to effectively manage the hot spot temperature of the reactor (T_{max} [K]) and the outlet ammonia concentration (C_{NH_3} [mol/m³]) by optimally regulating the removed heat (Q [kW/m²]) and the inlet flowrate (F [L/min]). Considering the setpoint at a steady state of the system, Equation 2.25 can be reformulated in a deviational form

$$\min_{\mathbf{u}} \sum_{i=k}^{k+L} \|\mathbf{y}'_{(i)}\|_{\mathbf{P}}^2 + \|\mathbf{u}'_{(i)}\|_{\mathbf{Q}}^2 \quad (2.27)$$

where $\mathbf{y}' = [\mathbf{y}'_1 \ \mathbf{y}'_2]^T$, $\mathbf{u}' = [\mathbf{u}'_1 \ \mathbf{u}'_2]$, $\mathbf{y}'_1 = T_{\text{max}} - T_{\text{max,ss}}$, $\mathbf{y}'_2 = C_{\text{NH}_3} - C_{\text{NH}_3,ss}$, $\mathbf{u}'_1 = Q - Q_{\text{ss}}$, $\mathbf{u}'_2 = F - F_{\text{ss}}$, $\|\mathbf{y}'_{(i)}\|_{\mathbf{P}}^2 = \mathbf{y}'_{(i)}^T \mathbf{P} \mathbf{y}'_{(i)}$, and $\|\mathbf{u}'_{(i)}\|_{\mathbf{Q}}^2 = \mathbf{u}'_{(i)}^T \mathbf{Q} \mathbf{u}'_{(i)}$.

The LSTM-based MPC procedure comprises the following steps:

1. At time t_k , the controller evaluates the current states of the variables and makes predictions for times up to t_{k+L} employing the LSTM-based models.
2. Cost function minimization is performed through interior-point calculations with the LSTM-based models, determining optimal control moves for times up to t_{k+L} .
3. The first control move in the sequence is implemented directly on the high-fidelity model, which responds by taking the process variables to a new state.

4. The algorithm then proceeds to the next time step t_{k+1} , updating it as the current time step, reassessing the outputs from the high-fidelity model, revising the setpoints as needed, and redoing the procedure.

In this way, a hybrid and iterative loop is established between both the LSTM-based model (used as the basis for optimization) and the high-fidelity model, which is responsible for the actual implementation of the control moves (Figure 2.18).

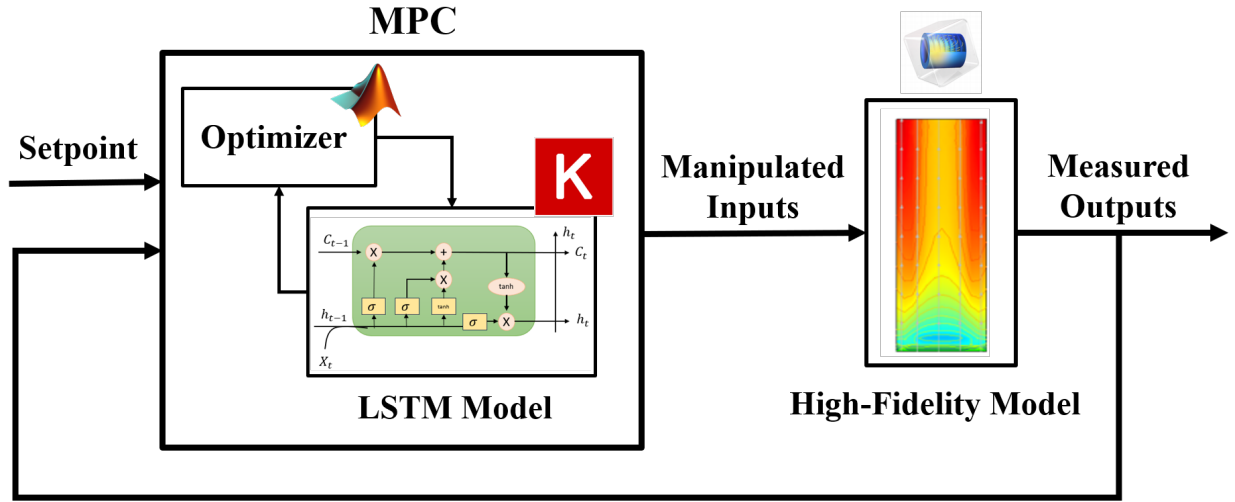


Figure 2.18: Multi-platform computational framework developed to control the ammonia reactor in real-time.

2.5 Results and Discussion

2.5.1 GDR evaluation

Open-loop comparison: GDR vs. high-fidelity CFD simulations

The proposed GDR approach adjusts the resolution of the reactor's simulation to further enhance time-series regularization, where its performance directly impacts the effectiveness of the surrogate model. The mean squared error (MSE) function is utilized as the loss function for the gradient descent-based training of the GDR model. The root mean squared error (RMSE) is also employed to assess the accuracy of the regenerated data in comparison

to the reactor's simulations. This metric ensures unit consistency and effectively identifies significant errors, making it valuable for detecting outliers.

The CFD simulations have demonstrated a bimodal dynamic behavior in both controlled outputs, as referenced in 2.16. The GDR model must capture this bimodal pattern to interpolate and effectively identify the predominant behavior within the process operation. Figure 2.19 illustrates open-loop simulations of the maximum temperature interpolations performed by the GDR compared with the CFD simulations at nine operational regions corresponding to low, moderate, and high flowrates and heat removal rates ($Q = 25, 35$, and 50 kW/m^2 , and $F = 500, 600$, and 800 L/min). The RMSE values for all operational regions reveal that the GDR model excels in interpolations and has adeptly learned the bimodal maximum temperature pattern. A similar figure for the ammonia outlet concentration is presented in the Supporting Information of the published paper (Figure S-7).

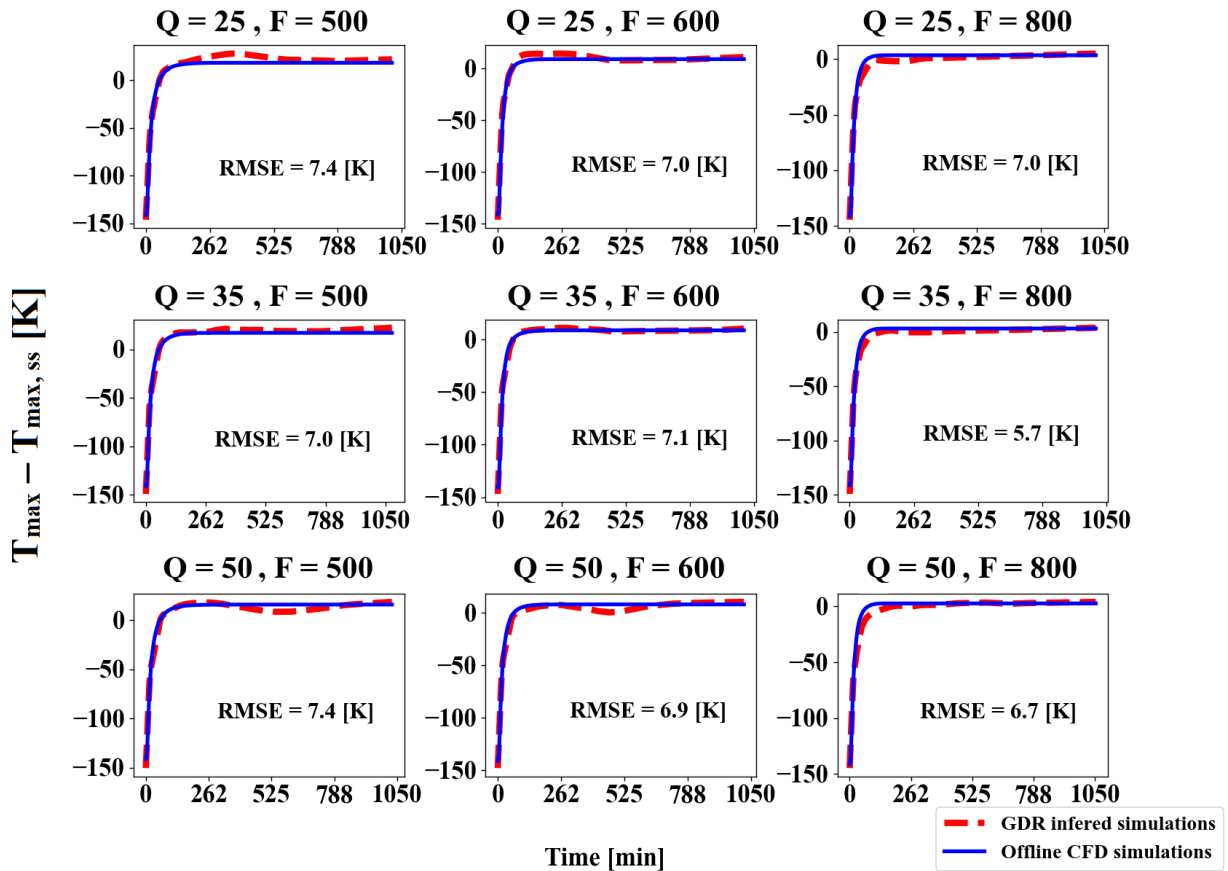


Figure 2.19: Maximum temperature open-loop GDR vs CFD simulations.

It is important to note that errors propagated through open-loop interpolations using the GDR would impact the surrogate model’s performance in closed-loop simulations. Therefore, an accurate GDR facilitates consistent regularization of the time-series data and enables the LSTM-based surrogate model to effectively capture the complex dynamics of the ammonia synthesis.

2.5.2 LSTM surrogate model evaluation

Open-loop simulations: LSTM vs. CFD

The effectiveness of the proposed learning-based MPC in regulating the ammonia synthesis process depends on the performance of the LSTM-based surrogate model in predicting system dynamics. While RMSE is a standard metric for evaluating predictive models^[34], applying RMSE across all parallel multivariate time series might not provide an accurate representation. To ensure the surrogate model’s robustness and accuracy, we evaluate it by computing RMSE for every distinct reactor dynamics. The same segmentation of the process operation conditions for the GDR model’s evaluations is utilized to demonstrate the surrogate model’s performance.

As explained in the previous sections, offline simulations of maximum temperature exhibited a bimodal distribution. The initial peak corresponds to the reactor’s start-up dynamics, reflecting the transient energy balance from the process’s onset towards steady-state conditions. The subsequent peak signified the achievement of these steady-state conditions. The visual representation of the LSTM surrogate model (Figure 2.20) and individual RMSE values for each time-series denote that the GDR method has made the bimodal pattern of the reactor more perceivable for LSTM surrogate model training, leading to optimal performance of the surrogate model in predicting the maximum temperature of the reactor.

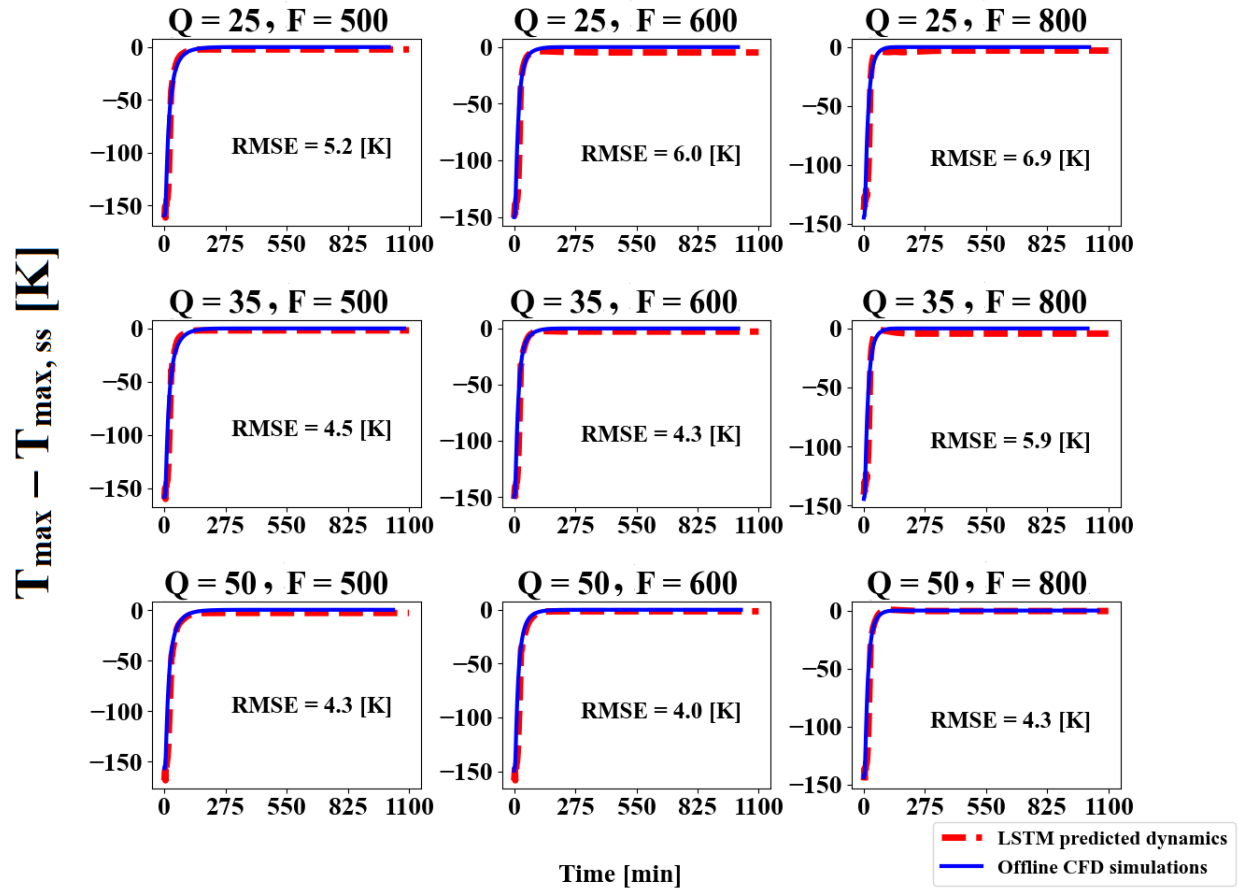


Figure 2.20: Maximum temperature predictions with LSTM surrogate model for nine distinct operation regions.

The outlet ammonia concentration presents more intricate dynamics than the maximum temperature. The initial peak in ammonia concentration is followed by stabilization at a steady state, influenced by the combined effects of external and internal mass transfer in the catalyst pellets. Despite the effective regularization of the time series by GDR networks (Figure S-7), the inherent complexity of the ammonia outlet concentration remains observable in the data distributions. In comparison to the original bimodal distribution (Figure 2.16), the regularized distribution of ammonia outlet concentration (Figure 2.17) exhibits minor peaks, illustrating the transient phases induced by the catalytic reaction. Figure 2.21 illustrates the visual representation of the LSTM-based surrogate model performance compared to the CFD simulations for outlet ammonia concentration under selected operational

conditions

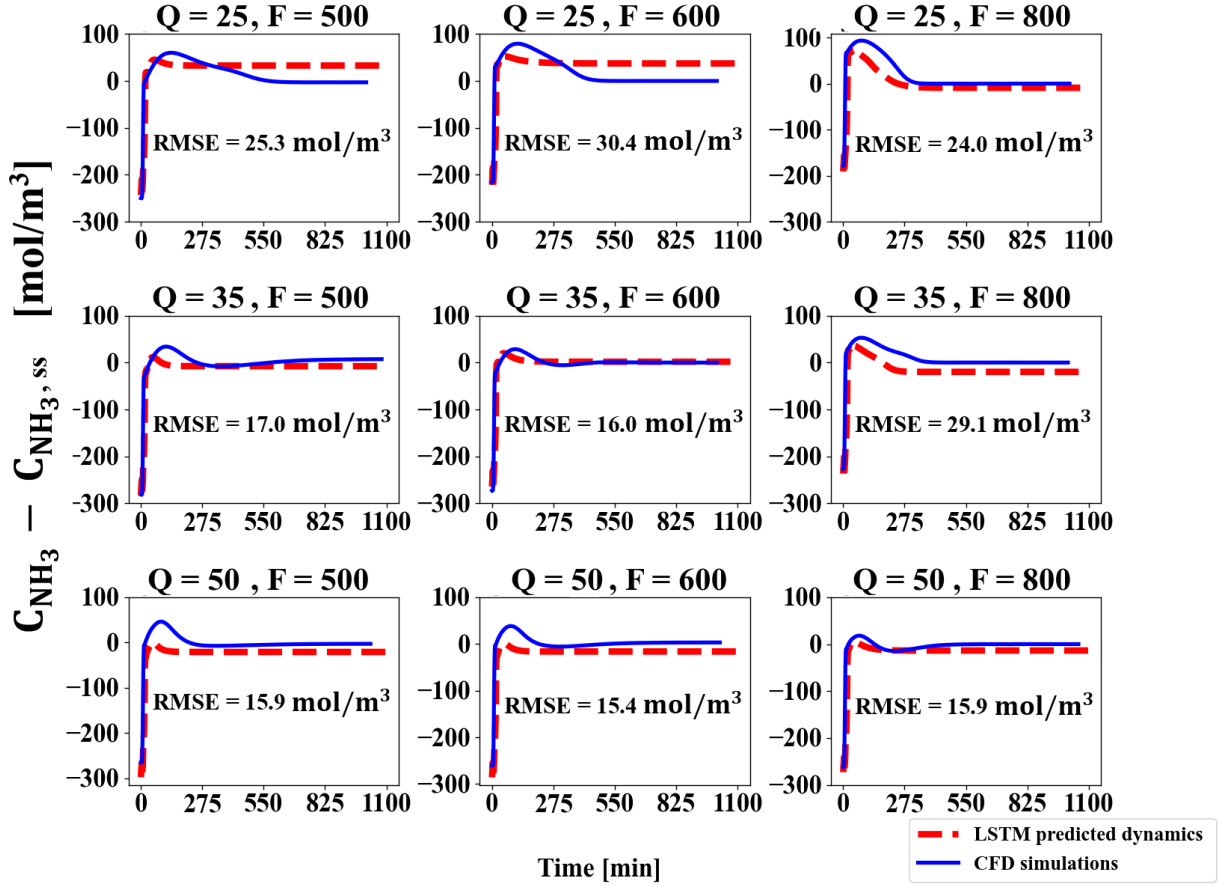


Figure 2.21: Outlet ammonia concentration predictions with LSTM surrogate model for nine distinct operation regions.

2.5.3 LSTM-MPC closed-loop evaluation

The proposed LSTM-MPC framework leverages the fast responses of the surrogate model, thereby resolving the computational bottleneck associated with using complex models for real-time decision-making and control applications. This enables the provision of optimal manipulated inputs at each time step for precise control of system properties. Furthermore, the system's current state at each sampling time is determined by the high-fidelity model, which represents the actual process dynamics. Figure 2.22 shows the normalized closed-loop temporal profiles of the maximum temperature and outlet concentration and the flow rate and removal heat rate obtained by MPC for the sampling time step of 2 minutes and the

control horizon of 10 minutes. As observed, the proposed learning-based MPC architecture effectively regulates the maximum temperature and outlet concentration at the targeted steady state, even in the presence of a mismatch between the LSTM-based model and the high-fidelity COMSOL simulation, which represents the real system dynamics. The input step changes by MPC are reasonable and adhere to the constraints, while the outputs exhibit smooth convergence toward the desired steady state. Minimal offsets are evident due to a minor expected mismatch between the LSTM-based model and high-fidelity model predictions. We also conducted an additional MPC study with a 4-minute sampling time. The closed-loop system's performance under these conditions is similarly efficient, as demonstrated in Figure S-8 of the Supporting Information of the published paper.

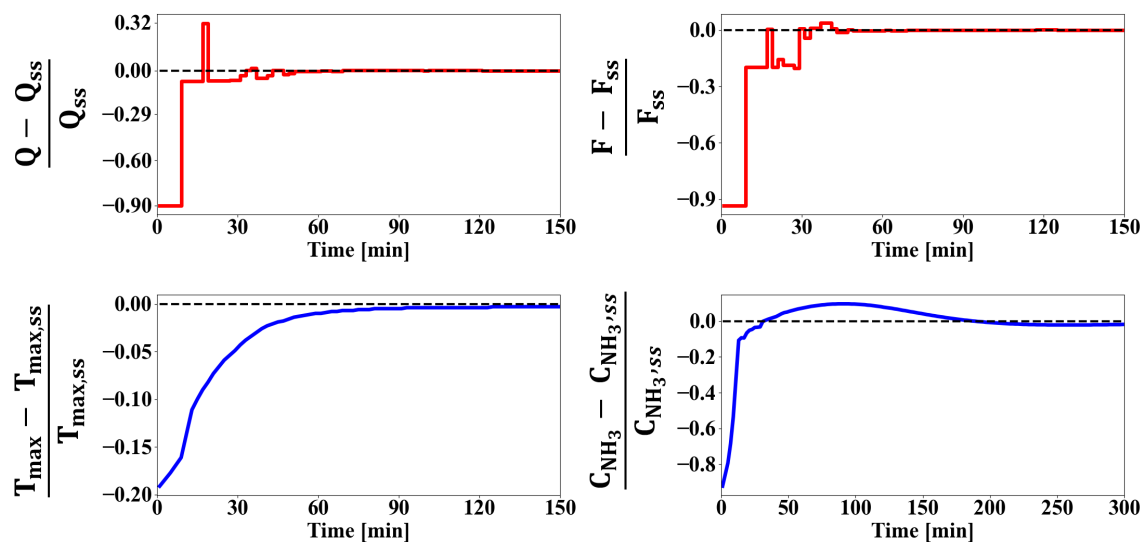


Figure 2.22: Closed-loop temporal profiles of the manipulated input and controlled output variables.

2.6 Conclusion

In this work, we investigated the potential of LSTM-based MPC to address the computational challenges of the optimization-based regulation of an ammonia synthesis reactor.

The high-fidelity multiphysics-multiscale model revealed intricate relationships between the concentration and temperature distributions inside the reactor. The interplay between reaction kinetics and momentum, heat, and mass transport effects was also elucidated by the multiscale-multiphysics nature of the model. While the multiscale model demonstrated strong performance and accuracy, its computational demands were unsuitable for real-time decision-making. The proposed systematic reduced-order modeling approach led to a computationally affordable surrogate model that accurately represents the complex spatiotemporal multiphysics-multiscale dynamics of the synthesis process. Offline simulations for various operating conditions were used to generate the necessary dataset, which is an irregular time series with bimodal distributions. A GDR approach was applied to regularize the dataset method, preparing it for LSTM training by enhancing data distribution and uniformity of the timestep inference. The LSTM-based surrogate model was trained on the regenerated dataset, effectively capturing the dynamics of the process. The resulting LSTM-based model was then employed as the basis for MPC design. The closed-loop performance of the proposed controller was evaluated using the multiscale-multiphysics model, which accurately represents the real system dynamics.

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Chapter 3

Multiscale-Multiphysics Predictive Modeling of Chemical Vapor Deposition Processes for Carbon Nanotube Synthesis

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3.1 Introduction

The synthesis of carbon nanotubes (CNTs) through chemical vapor deposition (CVD) has emerged as a promising technology, extensively studied over the past 30 years^[2-7]. In the CVD process, a gaseous carbon feedstock—typically methane, ethylene, or acetylene—adsorbs onto the surface of iron or nickel nanoparticles and undergoes a series of dissociation reactions to produce elementary carbon species. These carbon species diffuse across the surface

and through the bulk of the catalyst particles, eventually nucleating to form a carbon layer or cap. As additional carbon atoms are supplied to the cap's edge, it grows vertically into hollow nanotubes, lifting off the surface^[8–14]. Nevertheless, vertical growth does not always occur; it typically happens when nucleation density is high and the tubes are supported by adjacent structures. The growth of these nanotubes is influenced by several factors, including the catalyst size, repulsive interactions between adjacent nanotube walls, and the rates of carbon feedstock adsorption, desorption, diffusion, and surface reactions. These factors strongly depend on temperature and underlying atomic-level interactions^[15,16].

Numerous studies have focused on the controlled growth of single and multi-walled nanotubes with increased height, aiming to achieve the desired electronic, mechanical, and textural properties of nanotubes and optimize their structural dimensions. Some research has reported nanotube carpets reaching 1000 μm or more^[17–19]. Water plays a critical role as a synergistic promoter in what is termed "supergrowth", helping to prevent catalyst sintering and selectively oxidizing amorphous carbon species that would otherwise deposit and degrade catalyst activity^[19–23]. In these processes, water can either be added to the feed mixture in trace amounts or generated in situ. While catalyst deactivation typically limits operational life, which lasts for tens of minutes, some studies have reported highly stable catalysts with lifetimes extending to a few hours^[22,24–26]. However, the most significant experimental challenge remains the scalability of the synthetic procedures. Most work is conducted in small reactive environments to maintain higher controllability. Fluidized bed reactors are considered the most economically viable option for large-scale production, as they offer improved management of catalyst utilization and regeneration cycles compared to current small-scale methods for substrate growth.

Despite significant experimental efforts to understand and optimize CNT synthesis processes, predictive growth modeling remains complex and is often oversimplified due to the intricate multiscale nature of the process. This complexity arises from gas-phase transport, high-temperature thermodynamics, reaction kinetics, and surface chemistry. Few studies have successfully integrated multiscale fluid dynamics and surface phenomena into a unified modeling framework^[27–33]. In many cases, modeling studies regress empirical steady state

kinetic data into Langmuir or power rate laws to identify kinetic parameters that best represent the data under conditions where gas transport resistances are negligible^[25,34–43]. While these models are valuable, they are often limited to the specific experimental conditions under which the data were collected, rendering them more descriptive than predictive. Reliable predictive models require a mechanistic approach to gain deeper insights into the effects of key process variables.

Significant contributions in predictive modeling often involve the use of molecular modeling techniques, with Density Functional Theory (DFT) being a widely used method for evaluating potential elementary reactions and the energy barriers associated with transition states on metal catalytic sites^[44–58]. Many studies focus on the sequential dehydrogenation of carbon precursors on these catalytic sites, resulting in the formation of adsorbed carbon atoms that serve as mobile building blocks for nanotubes. Molecular dynamics (MD) is particularly effective for investigating and visualizing the atomic arrangement of nanotubes^[59–63]. It is worth noting that both DFT and MD results often involve simplifications. For example, techniques such as the nudged elastic band (NEB) method rely on idealized conceptual frameworks (e.g., site homogeneity, perfect crystal structures, and static analysis), introducing uncertainties that can propagate and limit predictability at larger scales. Nonetheless, when correctly set up, fundamental models can still provide reliable insights into the dynamics of nanotube growth, particularly at larger scales.

The modeling of CVD processes for nanotube growth has been less extensively explored, whereas the dynamics of atomic deposition for film growth have received more significant attention, encompassing sequential multiscale phenomena such as macroscopic gas transport, Knudsen diffusion in pores, and microscopic atomic adsorption on surfaces. Kinetic Monte Carlo (kMC) methods are widely used to simulate microscopic surface phenomena, while partial differential equations (PDEs) are employed to describe diffusion and fluid transport processes at macroscopic scales^[64–67]. In kMC simulations, the system evolves based on the probabilistic selection of elementary events at each time step, with faster processes more likely to occur. This approach offers a computationally efficient alternative to MD by enabling the simulation of local molecular interactions without relying on mean-field ap-

proximations. The method uses an atomic lattice representation, facilitating the analysis of geometric effects on catalytic surfaces. However, kMC simulations can suffer from slow computational performance when rare events, such as catalyst deactivation, play a significant role, potentially causing the simulation to become trapped in frequent but less critical event cycles. The most straightforward approach to integrating these multiscale models involves solving the kMC and continuum models sequentially, with direct information exchange at specified time intervals^[65]. An alternative method consists of integrating these models with a collocation-based approach, wherein boundary value problems are discretized using orthogonal collocation at each point of the kMC lattice^[68–71]. This approach’s flexibility in defining surface features such as vacancies and defects can lead to more realistic representations of actual surfaces^[72]. Similar multiscale descriptions have been applied to crystallization technologies^[73,74], atomic layer etching^[75], and plasma-enhanced CVD of thin semiconductor silicon films^[76], which are critical in the advanced manufacturing of electronics and solar cells^[77–79]. kMC simulations may become relatively slow and become stuck or blind to rarer (slower) events, such as catalyst-deactivating processes.

In this study, a multiscale modeling framework is developed to predict CNT growth by combining a microscopic surface model informed by DFT/MD energy data from the literature, transition state theory, and microkinetic modeling (MKM) with macroscopic fluid transport equations and mechanistic reaction kinetics. Methods aim to capture the temporal dynamics of species involved in elementary reactions within a reactive ensemble. While kMC resolves these dynamics with spatial resolution by tracking individual events, MKM employs a mean-field approximation, representing the system through a set of coupled differential equations describing the concentrations of surface adsorbates. Although the mean-field assumption sacrifices spatial detail by averaging surface interactions, MKM remains advantageous for gaining system-level insights into surface kinetics over extended time scales. Moreover, its reliance on differential equations facilitates implementation using standard computational software. The study investigates the gas-phase dynamics within an axially oriented CVD reactor, particularly when using a mixed carbon source feed, and the CNT growth dynamics using the surface model, including a mechanistic kinetic analysis.

The primary objective is to validate and extend the multiscale model for predicting CNT growth using a residual Fischer-Tropsch synthesis gas product, which includes methane, ethane, propane, ethylene, propylene, hydrogen, CO, and nitrogen. Multiscale integration is achieved through the parallel computation of macroscale fluid transport and microscale surface kinetics models, executed on separate platforms. Direct communication between these models occurs at each time step, with the fluid transport model providing the local partial pressures of adsorbates to the surface model. The surface model then predicts the net adsorption/desorption rates and the rate of CNT phase formation, which is governed by carbon diffusion within an iron particle.

The remainder of this chapter is structured as follows: Section 2 provides a detailed description of the CVD reactor and process conditions. Section 3 outlines the momentum and mass transport equations, as well as the necessary initial and boundary conditions. Section 4 discusses the reaction network and kinetics in the gas phase, the catalytic surface reaction kinetics for CNT formation, the conversion of reaction rates derived from microkinetic surface modeling into mass flux terms used by transport equations, and the calculation of nanotube height. Section 5 provides an in-depth explanation of the multiscale computational integration of fluid transport and surface kinetics. Finally, Section 6 presents a comprehensive simulation study, experimental validation of the surface microkinetic model, and an assessment of the predictive capabilities of the integrated multiscale-multiphysics model.

3.2 CVD Process Description

The CVD process for CNT fabrication in this study is carried out within a quartz tube or chamber with controlled pressure, temperature, and flow rate. The process involved introducing residual Fischer-Tropsch synthesis gas product at a specific flow rate at one end of the tube, allowing it to flow continuously over a catalytic substrate, and then exiting at the other end, with some systems recycling the gas. Research highlights the economic potential of CNT growth from mixed and less expensive carbon sources^[17,18]. The substrate, supported by a quartz plate, consists of a silica or alumina oxide layer and an active catalytic layer

made of iron, nickel, or another engineered catalyst. According to Everhart et al.^[19], these films are deposited using an ion beam sputter deposition and etching system. The nominal thicknesses of the metal and oxide films are approximately 1 nanometer and several tens of nanometers, respectively, verified through atomic force microscopy profile measurements.

This study replicates the apparatus by considering a cylindrical, axially-oriented reactor characterized by compressible laminar flow, as illustrated in Figure 3.1. The CNT growth exhibits three-dimensional characteristics at both the nanoscale and macroscale. At the macroscale, a thin carbonaceous layer forms at the top of the substrate within the reactor as precursor molecules adsorb onto its surface. However, the fluid dynamics model assumes a uniform substrate height, discarding slight radial surface variations. Furthermore, the macroscopic model simplifies the system by neglecting heterogeneities and spatial variations in the tangential direction. At the nanoscale, the cylindrical morphology of the growing tubes is not explicitly modeled. Instead, vertical growth is inferred through equations governing surface kinetics. The reactor is also assumed to operate isothermally, with the effects of heat transport excluded. This assumption is supported by experimental design principles commonly used in CNT growth studies. Experimental setups are typically configured to maintain a uniform temperature profile, as demonstrated by Everhart et al.^[19], where CNT growth experiments were conducted at constant temperatures with precise thermal control and monitoring. In the reactor system considered in this study, multiple thermocouples positioned along the reactor length enable accurate temperature measurements, and feedstock introduction occurs only after the reactor has reached thermal stabilization. Automatic furnace power adjustments further ensure a consistent temperature profile throughout the reaction. Although minor temperature variations may result from the precision of the thermal controller or the heat generated during the reaction, assuming isothermal conditions provides a reasonable and commonly accepted approximation. Within the reactor, the substrate surface facilitates the initial adsorption of active components, resulting in the formation of carbon nanotubes. The geometric properties of the reactor and substrate, along with key flow parameters, are detailed in Table 3.1.

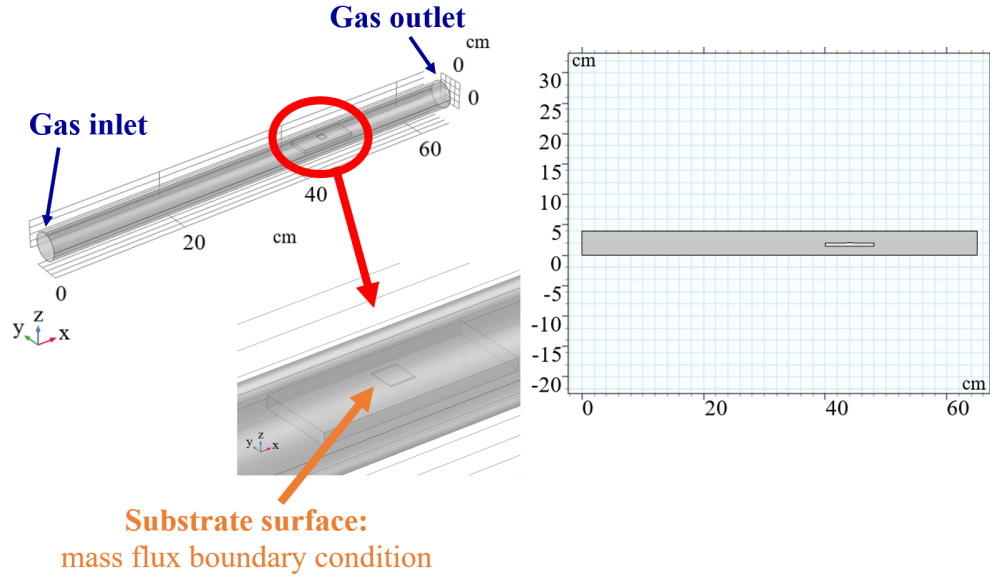


Figure 3.1: The geometry of the CVD reactor used in this study.

Table 3.1: Reactor geometry parameters and feedstock composition.

Parameter	Value
Reactor length	65 cm
Reactor diameter	2 cm
Substrate length	1 cm
Substrate diameter	1 cm
Substrate thickness	0.05 mm
Hydrogen molar fraction in the feed	0.4
Methane molar fraction in the feed	0.3
Ethane molar fraction in the feed	0.08
Ethylene molar fraction in the feed	0.06
Acetylene molar fraction in the feed	0.00
Propane molar fraction in the feed	0.05
Propylene molar fraction in the feed	0.02
CO molar fraction in the feed	0.05
Water molar fraction in the feed	0.00
N ₂ molar fraction in the feed	0.04

3.3 Continuum Transport Model Development

3.3.1 Momentum transport in the gas phase

Momentum conservation for the compressible gas flowing in a laminar regime within the homogeneous CVD reactor is described by coupling the continuity equation:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \quad (3.1)$$

with the Navier-Stokes equation:

$$\rho \frac{\partial \mathbf{v}}{\partial t} + \rho (\mathbf{v} \cdot \nabla) \mathbf{v} = \nabla \cdot \left[-p\mathbf{I} + \mu \left(\nabla \mathbf{v} + (\nabla \mathbf{v})^T \right) - \frac{2}{3}\mu (\nabla \cdot \mathbf{v}) \mathbf{I} \right] \quad (3.2)$$

where t represents time, ρ denotes the fluid density, $\mathbf{v}$ is the velocity field vector, μ is the fluid viscosity, and p represents the gauge pressure, defined as $p = P - P_{\text{ref}}$. No external forces are applied to the gas mixture, and the effective density and viscosity of the fluid mixture are calculated as weighted averages of the densities and viscosities of individual components.

The previous equations establish a compressible gas flow.

3.3.2 Mass transport in the gas phase

Species transport encompasses both diffusion and advection within the bulk gas phase, along with surface reactions occurring on the substrate:

$$\frac{\partial c_i}{\partial t} + \mathbf{v} \cdot \nabla c_i + \nabla \cdot (-D_{i,\text{eff}} \nabla c_i) = \sum R_{\text{reaction},i} \quad (3.3)$$

where c_i represents the volumetric concentration of species i within the reactor, $D_{i,\text{eff}}$ denotes the effective diffusion coefficient of species i in the bulk fluid, and R_i is the volumetric reaction rate for the specific reaction involving species i , with units of $\text{mol}/(\text{m}^3 \cdot \text{s})$. These surface reactions are described as a mass flux boundary condition, with units of $\text{mol}/(\text{m}^2 \cdot \text{s})$, defined by a boundary vector perpendicular to the substrate surface. The effective diffusivities of

the species are calculated using the Fuller correlation and mixing rules^[80,81]:

$$D_{i,\text{mixture}} = \left[\sum_{j \neq i} \frac{\left(\frac{y_j}{1-y_i} \right)}{D_{i,j}} \right]^{-1} \quad (3.4)$$

and

$$D_{i,j} = \frac{10^{-3} T^{1.75} \left(\frac{1}{M_i} + \frac{1}{M_j} \right)}{P \left(\nu_i^{1/3} + \nu_j^{1/3} \right)} \quad (3.5)$$

where $D_{i,\text{mixture}}$ is the diffusivity of species i in the gaseous mixture, y_i is the molar fraction of species i , $D_{i,j}$ represents the binary diffusivity coefficient between species i and j , M_i is the molecular mass of species i , P is the absolute pressure in bars, and ν_i is the molecular volume of species i .

3.3.3 Initial conditions, boundary conditions, and solution strategy for the transport equations

Tables 3.2 and 3.3 present the initial and boundary conditions for the transport equations. The mass transport boundary conditions assume no diffusion except for the inlet and substrate surfaces. A no-slip boundary condition is applied to all boundaries except the inlet and outlet. The mass flux boundary condition on the substrate surface is further discussed in the section on catalytic modeling. The momentum and mass transport equations were solved simultaneously in COMSOL Multiphysics 6.0 using the finite element method (FEM) by including "Laminar Flow" and "Transport of Diluted Species" interfaces, respectively. Regular triangular elements formed a fine mesh that discretized the reactor domain, allowing for the numerical resolution of the PDEs by transforming them into a system of nonlinear algebraic equations. The mechanical properties of the gas mixture were extracted from COMSOL's built-in library. The ideal gas model was employed as an approximate equation of state due to the high-temperature conditions of the process.

Table 3.2: Initial conditions.

Momentum Transport	Mass Transport
$P_0 = P_{\text{ref},0}$	$c_{i,0} = c_{i,\text{feed}}$

Table 3.3: Boundary conditions.

Boundary Condition	Momentum Transport	Mass Transport
Inlet	Uniform feed flow rate	Fixed inlet concentration
Outlet	$P = P_{\text{ref}}$	$\mathbf{n} \cdot \mathbf{J}_{\text{diffusion}} = 0$
External and internal walls	$-\mathbf{n} \cdot (\rho \mathbf{v}) = 0$	$\mathbf{n} \cdot \mathbf{J}_{\text{diffusion}} = 0$

3.4 Multiscale Reaction Model Development

3.4.1 Gas phase reaction network and kinetics

Building on the foundational work of Norinaga and Deutschmann^[82], as well as Sundaram and Froment^[83], on the gas-phase thermal cracking, pyrolysis, and decomposition of light hydrocarbons, we developed a comprehensive reaction network model. This model integrates mass transport with the kinetics of 41 potential reactions involving hydrogen, methane, ethane, ethylene, acetylene, propylene, propyne, and 19 other gas species, as detailed in Table 3.4.

Table 3.4: List of gas phase reactions.

1) $C_3H_6 \rightarrow CH_4 + C_2H_2$	22) $C_2H_5 + H \rightarrow CH_4 + CH_3$
2) $C_3H_6 \rightarrow H + CH_2CHCH_2$	23) $C_2H_6 \rightarrow C_2H_4 + H_2$
3) $C_3H_6 + H \rightarrow C_2H_4 + CH_3$	24) $2C_2H_6 \rightarrow C_3H_8 + CH_4$
4) $C_3H_6 + H \rightarrow CH_3CH_2CH_2$	25) $C_2H_4 + C_2H_6 \rightarrow C_3H_6 + CH_4$
5) $C_3H_6 + CH_3 \rightarrow CH_4 + CH_2CHCH_2$	26) $CH_3 + H_2 \rightarrow CH_4 + H$
6) $C_3H_6 + H \rightarrow H_2 + CH_2CHCH_2$	27) $CH_4 \rightarrow CH_3 + H$
7) $CH_2CHCH_2 \rightarrow CHCHCH_3$	28) $C_2H_4 + CH_3 \rightarrow CH_4 + C_2H_3$
8) $CHCHCH_3 \rightarrow CH_2CHCH_2$	29) $C_2H_3 + H_2 \rightarrow C_2H_4 + H$
9) $CHCHCH_3 \rightarrow C_2H_2 + CH_3$	30) $C_2H_4 + H \rightarrow C_2H_3 + H_2$
10) $C_2H_2 + CH_3 \rightarrow CHCHCH_3$	31) $C_2H_4 + C_2H_5 \rightarrow C_2H_3 + C_2H_6$
11) $CH_3 + CH_2CHCH_2 \rightarrow 1 - \text{Butene}$	32) $C_2H_4 + C_2H_3 \rightarrow 1,3 - \text{Butadiene} + H$
12) $1 - \text{Butene} \rightarrow CH_3 + CH_2CHCH_2$	33) $1,3 - \text{Butadiene} + H \rightarrow C_2H_4 + C_2H_3$
13) $CHCHCH_3 \rightarrow \text{Propyne} + H$	34) $1,3 - \text{Butadiene} \rightarrow C_2H_4 + C_2H_2$
14) $\text{Propyne} + CH_3 \rightarrow CH_4 + C_3H_3$	35) $2C_2H_2 \rightarrow \text{Vinylacetylene}$
15) $\text{Propyne} + H \rightarrow H_2 + C_3H_3$	36) $\text{Vinylacetylene} \rightarrow 2C_2H_2$
16) $\text{Propyne} \rightarrow \text{Propadiene}$	37) $2C_2H_2 \rightarrow \text{Diacetylene}$
17) $\text{Propadiene} \rightarrow \text{Propyne}$	38) $C_2H_2 + C_2H_3 \rightarrow \text{Vinylacetylene} + H$
18) $\text{Propadiene} + CH_3 \rightarrow CH_4 + C_3H_3$	39) $\text{Vinylacetylene} + H \rightarrow C_2H_2 + C_2H_3$
19) $C_3H_3 + C_3H_3 \rightarrow \text{Benzene} + H$	40) $C_2H_2 + \text{Vinylacetylene} \rightarrow \text{Benzene}$
20) $C_3H_3 + CH_2CHCH_2 \rightarrow \text{Benzene} + 2H$	41) $2 \text{ Vinylacetylene} \rightarrow \text{Styrene}$
21) $C_2H_6 + H \rightarrow H_2 + C_2H_5$	

The kinetic model assumes that a general mass action rate law applies:

$$R_{\text{reaction}} = k c_i c_j \quad (3.6)$$

where c_i and c_j are the molar concentrations of reactants i and j , and k denotes the reaction rate constants determined by the Arrhenius equation:

$$k = A T^n \exp\left(\frac{-E_a}{RT}\right) \quad (3.7)$$

Here, the specific values of the kinetic parameters A , n , and activation energies E_a for individual reactions are detailed in the studies by Norinaga and Deutschmann^[82] and Sundaram and Froment^[83]. The reaction network is designed to include complementary forward and reverse processes, ensuring an equilibrated steady state. Figure 3.2 illustrates the reaction mechanism through a network of interdependent connections, where nodes represent species and edges represent their production or consumption relationships. Although reactions involving propane and higher hydrocarbons could influence the overall dynamics in both the gas and surface phases, preliminary computational assessments revealed significant numerical challenges. As a result, these higher hydrocarbon reactions are excluded from the model.

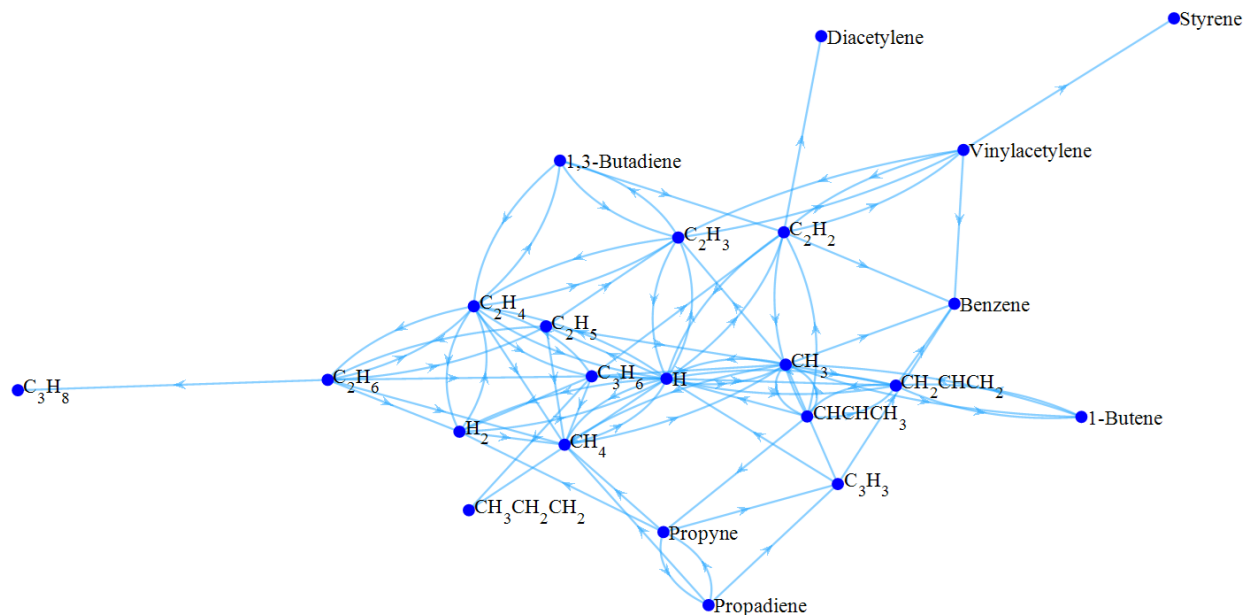


Figure 3.2: Reaction network demonstrating gas species' production and consumption relationships.

3.4.2 Surface model for catalytic growth of carbon nanotubes

The catalytic growth of CNTs is modeled using a combination of mean-field microkinetics and transition state theory^[84–88]. As described by Wagner^[89] and Almkhelfe et al.^[17], the growth follows the vapor-liquid-solid theory. First, carbon precursor molecules adsorb and dissociate into carbon atoms on active catalytic sites. Next, these atoms diffuse through the metal nanoparticle toward the edge of the initially formed CNT cap. Finally, the carbon atoms are systematically incorporated into the CNT structure. This is illustrated in Figure 3.3. Our predictive multiphysics modeling approach begins with hypothesizing the critical surface reactions involving hydrocarbons that lead to the generation of elementary carbon species. These essential reactions include adsorption and desorption processes, surface dehydrogenation steps, and binary adsorbate interactions on undistinguished, homogeneous catalytic iron sites. The geometrical aspects of CNT growth are represented by simply assuming that the spherical metal nanoparticle orients the growth of cylindrical nanotubes. Carbon diffusion represents the final kinetic step in the mechanism and, as such, inherently governs the growth process by acting as either a limiting or limited factor. This model does not account for the chirality or hexagonal lattice structure of CNTs.

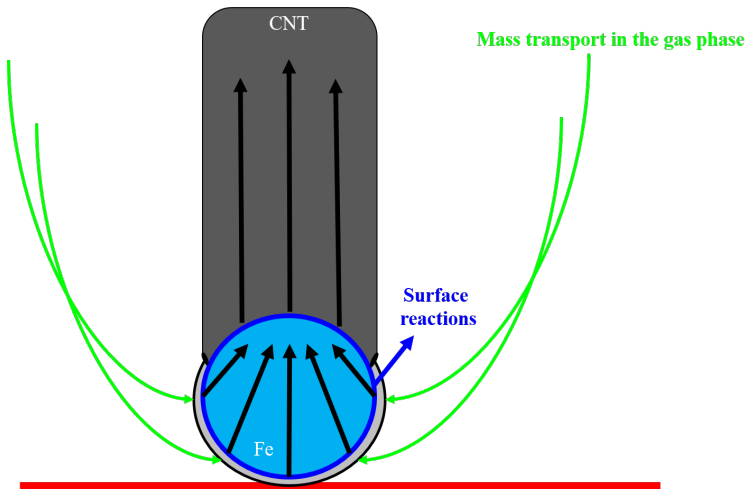


Figure 3.3: Illustration of the CNT growth process. The carbon precursors are transported to the surface of the metal nanoparticles, onto which they dissociate into elementary carbon species, which are direct intermediates of the CNT. The carbon atoms then diffuse towards the edge of the CNT cap, being incorporated into the lattice of the tube in an organized manner.

The model also considers catalytic deactivation through the irreversible formation and deposition of amorphous carbon, which gradually occupies the available catalyst sites. Table 3.5 and Figure 3.4 present the complete surface reaction mechanism and the relationships between adsorbates. These figures denote free catalytic iron sites by the symbol $*$.

Table 3.5: Surface reactions considered in the CNT growth process.

1F) $\text{CH}_4 + 2* \rightarrow \text{CH}_3^* + \text{H}^*$	1R) $\text{CH}_3^* + \text{H}^* \rightarrow \text{CH}_4 + 2*$
2F) $\text{CH}_3^* + * \rightarrow \text{CH}_2^* + \text{H}^*$	2R) $\text{CH}_2^* + \text{H}^* \rightarrow \text{CH}_3^* + *$
3F) $\text{CH}_2^* + * \rightarrow \text{CH}^* + \text{H}^*$	3R) $\text{CH}^* + \text{H}^* \rightarrow \text{CH}_2^* + *$
4F) $\text{C}_2\text{H}_6 + 2* \rightarrow \text{C}_2\text{H}_5^* + \text{H}^*$	4R) $\text{C}_2\text{H}_5^* + \text{H}^* \rightarrow \text{C}_2\text{H}_6 + 2*$
5F) $\text{C}_2\text{H}_5^* + * \rightarrow \text{C}_2\text{H}_4^* + \text{H}^*$	5R) $\text{C}_2\text{H}_4^* + \text{H}^* \rightarrow \text{C}_2\text{H}_5^* + *$
6F) $\text{C}_2\text{H}_4 + * \rightarrow \text{C}_2\text{H}_4^*$	6R) $\text{C}_2\text{H}_4^* \rightarrow \text{C}_2\text{H}_4 + *$
7F) $\text{C}_2\text{H}_4^* + * \rightarrow \text{C}_2\text{H}_3^* + \text{H}^*$	7R) $\text{C}_2\text{H}_3^* + \text{H}^* \rightarrow \text{C}_2\text{H}_4^* + *$
8F) $\text{C}_2\text{H}_3^* + * \rightarrow \text{C}_2\text{H}_2^* + \text{H}^*$	8R) $\text{C}_2\text{H}_2^* + \text{H}^* \rightarrow \text{C}_2\text{H}_3^* + *$
9F) $\text{C}_2\text{H}_2 + * \rightarrow \text{C}_2\text{H}_2^*$	9R) $\text{C}_2\text{H}_2^* \rightarrow \text{C}_2\text{H}_2 + *$
10F) $\text{C}_2\text{H}_2^* + * \rightarrow \text{CH}^* + \text{CH}^*$	10R) $\text{CH}^* + \text{CH}^* \rightarrow \text{C}_2\text{H}_2^* + *$
11F) $\text{C}_2\text{H}_2^* + * \rightarrow \text{C}_2\text{H}^* + \text{H}^*$	11R) $\text{C}_2\text{H}^* + \text{H}^* \rightarrow \text{C}_2\text{H}_2^* + *$
12F) $\text{C}_2\text{H}^* + * \rightarrow \text{CH}^* + \text{C}^*$	12R) $\text{CH}^* + \text{C}^* \rightarrow \text{C}_2\text{H}^* + *$
13F) $\text{CH}^* + * \rightarrow \text{C}^* + \text{H}^*$	13R) $\text{C}^* + \text{H}^* \rightarrow \text{CH}^* + *$
14F) $\text{H}_2 + 2* \rightarrow \text{H}^* + \text{H}^*$	14R) $\text{H}^* + \text{H}^* \rightarrow \text{H}_2 + 2*$
15F) $\text{CO} + * \rightarrow \text{CO}^*$	15R) $\text{CO}^* \rightarrow \text{CO} + *$
16F) $\text{CO}^* + * \rightarrow \text{C}^* + \text{O}^*$	16R) $\text{C}^* + \text{O}^* \rightarrow \text{CO}^* + *$
17F) $\text{CO}^* + \text{H}^* \rightarrow \text{HCO}^* + *$	17R) $\text{HCO}^* + * \rightarrow \text{CO}^* + \text{H}^*$
18F) $\text{HCO}^* + \text{H}^* \rightarrow \text{CH}^* + \text{HO}^*$	18R) $\text{CH}^* + \text{HO}^* \rightarrow \text{HCO}^* + \text{H}^*$
19F) $\text{H}_2\text{O} + 2* \rightarrow \text{HO}^* + \text{H}^*$	19R) $\text{HO}^* + \text{H}^* \rightarrow \text{H}_2\text{O} + 2*$
20F) $\text{HO}^* + * \rightarrow \text{O}^* + \text{H}^*$	20R) $\text{O}^* + \text{H}^* \rightarrow \text{HO}^* + *$
21) $\text{C}^* \rightarrow \text{C}_{\text{amorphous}}$	22) $\text{C}^* \rightarrow \text{Diffusion} \rightarrow \text{CNT}$

0.1 to 0.9. A value of 0.6 was selected, as it yielded the most consistent results. It is important to note that vibrational contributions to the rate constants in Equation 3.10 were excluded, as the vibrational frequencies of the adsorbates and potential transition states could not be determined. The interface area for nucleation and CNT growth is also assumed to be estimated from the radius of the metal nanoparticle, R_p , with the concentration of carbon atoms near the interface approximated as nearly zero. This leads to the conclusion that the primary driving force for subsurface bulk diffusion is governed by the normalized surface concentration of mobile carbon atoms, denoted as θ_C (i.e., surface coverage fraction).

The activation energy barriers for each elementary reaction are derived from various DFT studies on iron nanoclusters or particle facets, specifically those by Li et al.^[47] and Wang et al.^[46]. Chorkendorff and Niemantsverdriet^[88] provide an estimate for the surface site concentration, $N_{(\text{site/area})}$, based on the crystal lattice and bond lengths between atoms on the Fe (111) facet, which is given as $N_{(\text{site/area})} = 1/(14.3 \times 10^{-20}) \text{ site/m}^2$ or $1.161 \times 10^{-5} \text{ mol/m}^2$. Mean-field microkinetic modeling (MKM) involves solving a set of transient ordinary differential equations (ODEs) that establish molecular balances for each adsorbed species in terms of the surface coverage fractions θ_i (not to be confused with the rotational temperature, $\theta_{\text{rot},i}$) and stoichiometric turnover frequencies (TOF). The TOFs are expressed using mass-action laws, with the kinetic factors corresponding to those previously described. The formal mathematical formulation of the MKM is presented as follows:

$$\frac{d\theta_i}{dt} = \sum (\nu_{i,k} \text{ TOF}_k) \quad (3.12)$$

$$\text{TOF} = k_{\text{ads}} P_i \theta_S \quad \text{or} \quad k_{\text{ads}} P_i \theta_S^2 \quad \text{or} \quad k_{\text{surf,des}} \theta_i \theta_j \quad (3.13)$$

$$\sum \theta_i = 1 \quad (3.14)$$

Gas species are incorporated into the surface kinetic model through adsorption. Thus, the TOF for adsorption processes depends on the partial pressure of the adsorbing component on

one vacant site (direct adsorption) or two vacant sites (dissociative adsorption). Surface processes that involve binary reactions depend on the surface coverage fractions of the respective adsorbates. For the solution to be feasible, the sum of all surface coverages must equal 1, or 100% of the available sites. Given the stiffness of this ODE set, using implicit solvers is recommended, particularly the implicit Euler method with backward time discretization.

Table 3.6: Parameters involved in the surface kinetic model.

Parameters	Values	Parameters	Values
$S_{0,\text{methane}}$	$5 \cdot 10^{-6}$	$T_{\text{ref},S,\text{methane}}$	1000 K
$S_{0,\text{ethane}}$	$5 \cdot 10^{-6}$	$T_{\text{ref},S,\text{methane}}$	1000 K
$S_{0,\text{ethylene}}$	$5 \cdot 10^{-4}$	$T_{\text{ref},S,\text{methane}}$	1000 K
$S_{0,\text{acetylene}}$	$5 \cdot 10^{-3}$	$T_{\text{ref},S,\text{methane}}$	1000 K
$S_{0,\text{hydrogen}}$	$1 \cdot 10^{-10}$	$T_{\text{ref},S,\text{methane}}$	500 K
$S_{0,\text{CO}}$	$1 \cdot 10^{-1}$	$T_{\text{ref},S,\text{methane}}$	500 K
$S_{0,\text{water}}$	$1 \cdot 10^{-6}$	$T_{\text{ref},S,\text{methane}}$	500 K
$\theta_{\text{rot},\text{methane}}$	7.5 K	σ_{methane}	1
$\theta_{\text{rot},\text{ethane}}$	10 K	σ_{ethane}	1
$\theta_{\text{rot},\text{ethylene}}$	14 K	σ_{ethylene}	1
$\theta_{\text{rot},\text{acetylene}}$	14.32	$\sigma_{\text{acetylene}}$	1
$\theta_{\text{rot},\text{hydrogen}}$	87.6 K	σ_{hydrogen}	1
$\theta_{\text{rot},\text{CO}}$	2.8	σ_{CO}	1
$\theta_{\text{rot},\text{water}}$	100	σ_{water}	1
R_p	5 nm		

Table 3.7: Kinetic parameters of the elementary surface reactions. Data extracted from^[31] and^[47].

Parameters	Values	Parameters	Values
E _{a,1F}	0.69 eV	E _{a,1R}	1.35 eV
E _{a,2F}	0.24 eV	E _{a,2R}	0.79 eV
E _{a,3F}	0 eV	E _{a,3R}	0.77 eV
E _{a,4F}	0.65 eV	E _{a,4R}	1.23 eV
E _{a,5F}	0.04 eV	E _{a,5R}	1.32 eV
E _{a,6F}	0 eV	E _{a,6R}	0.69 eV
E _{a,7F}	0.22 eV	E _{a,7R}	0.79 eV
E _{a,8F}	0 eV	E _{a,8R}	1.04 eV
E _{a,9F}	0 eV	E _{a,9R}	2.44 eV
E _{a,10F}	1.799 eV	E _{a,10R}	0.92 eV
E _{a,11F}	1.524 eV	E _{a,11R}	0.724 eV
E _{a,12F}	1.829 eV	E _{a,12R}	0.955 eV
E _{a,13F}	0.48 eV	E _{a,13R}	0.93 eV
E _{a,14F}	0.423 eV	E _{a,14R}	1.435 eV
E _{a,15F}	0 eV	E _{a,15R}	0.5 eV
E _{a,16F}	1.17 eV	E _{a,16R}	2.03 eV
E _{a,17F}	0.95 eV	E _{a,17R}	0.23 eV
E _{a,18F}	0.44 eV	E _{a,18R}	0.44 eV
E _{a,19F}	0.92 eV	E _{a,19R}	1.33 eV
E _{a,20F}	0.8 eV	E _{a,20R}	1 eV
k _{0,21F}	$1 \cdot 10^{-8} k_B T/h$	E _{a,21F}	1.05 eV
E _{a,22F(bulk diff)}	1.55 eV		

3.4.3 Conversion of TOF to mass fluxes, determination of growth rate and nanotube carpet height

The net adsorption and desorption rates of gas species on the surface are described by

$$J_{\text{ads,des,i}} = (\text{TOF}_{\text{des,i}} - \text{TOF}_{\text{ads,i}}) N_{(\text{mol/area})} \quad (3.15)$$

where a positive value indicates desorption. Following the methodology proposed by Lebedeva et al.^[31], the growth rate is determined by calculating the bulk diffusion rate at each time step τ according to

$$r_{\text{growth}}(t) = J_{\text{diffusion,C}}(t) N_{(\text{mol/area})} \frac{\Delta R \beta_S}{\gamma_w(2 - \gamma_w)(1 - \beta_S)} \quad (3.16)$$

and

$$\gamma_w = N_w \frac{\Delta R}{R_p(1 - \beta_S)^{1/2}} \quad (3.17)$$

where ΔR represents the distance between the nanotube walls (assumed to be 0.34×10^{-9} m), β_S is the nucleation parameter, γ_w denotes the relative thickness of the nanotube walls, and N_w is the number of nanotube walls ($N_w = 1$ for a single-wall carbon nanotube). The pseudo-steady-state nanotube forest height is tracked by numerically integrating the growth rate from the initial time to the current time step:

$$H_{\text{CNT}}(\tau) = \int_0^\tau r_{\text{growth}}(t) dt \quad (3.18)$$

A trapezoidal integration of the growth rate vector was demonstrated to be more precise in numerically determining the CNT height at each time step.

3.5 Multiscale Integration of Fluid Transport and Surface Kinetics

This study integrates transport phenomena and kinetics through a parallel, real-time connection between a fluid dynamics module (modeled in COMSOL Multiphysics) and a surface reactions module (modeled in MATLAB). Due to time scale disparities between the fluid and surface dynamics and the inherent stiffness of the surface balances, the solvers of the fluid dynamics module in COMSOL alone cannot adequately handle the coupled transport and surface balance equations. This challenge is addressed by delegating the solution of surface balances to a specialized MATLAB solver in two different ways.

In the first approach, the fluid dynamics module collects and vectorizes the partial pressures of hydrocarbons, CO, and water, along with the substrate surface/boundary temperature at each time step. The size of these vectors is determined by the number of spatial nodes discretizing the substrate boundary. These vectors are then passed to the surface kinetics solver, which integrates the surface balances from time 0 to the current time for each vector element. The solver produces a matrix of net rates or net mass fluxes, but only the values at the current time step are returned to the fluid dynamics module. This method efficiently captures the evolution of surface configurations that influence nanotube nucleation while enabling direct monitoring of spatial fields at the main interface.

The second approach involves a more integrated control through MATLAB-COMSOL Livelink, where the surface kinetics solver extracts partial pressures and temperatures at each time step using surface probes defined within the fluid dynamics module. The balances are integrated step by step, with the net mass fluxes calculated at each interval and used to update the surface configuration. The updated surface coverages then serve as initial conditions for subsequent iterations. In this approach, MATLAB controls the time step, and COMSOL restarts the simulation using the latest solution as the initial condition. Unlike the first method, this approach integrates the equations step by step rather than from time 0 to the current time in each call. This method also enables more precise tracking of growth

rates, although it may sacrifice some accuracy with larger time steps. Additionally, data on the dynamics of spatial fields are collected less frequently, as the main COMSOL interface is not continuously active. Figure 3.5 illustrates the iterative exchange of information between the fluid dynamics and surface kinetics modules employed in this multiscale CNT modeling approach.

The MATLAB-COMSOL Livelink framework is utilized in this study to integrate the models. For the numerical solutions, we used the default implicit Backward Differentiation Formula (BDF) with automatic, adaptive time stepping in COMSOL and the ode15s solver for stiff differential equations in MATLAB. The time step used for communication between MATLAB and COMSOL was set to 60 seconds. Within this interval, MATLAB performed adaptive sub-stepping to resolve surface kinetics more precisely. A typical integrated simulation covering 60 minutes of growth required approximately 1.5-2 hours on an average-performance desktop computer with Intel(R) Xeon(R) Gold 5220R CPU @ 2.20GHz 2.19 GHz (2 processors) and 128 GB of usable RAM.

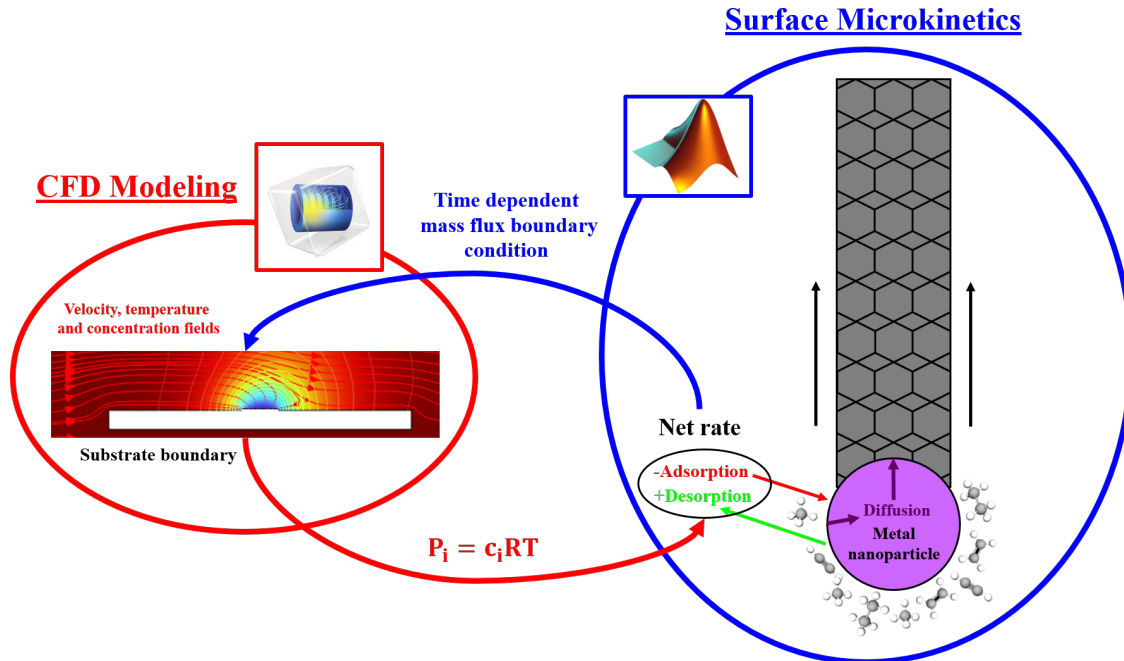


Figure 3.5: Multiscale connection between fluid dynamics (COMSOL) and surface kinetics (MATLAB) modules used to simulate the multiphysics involved in CNT modeling.

3.6 Simulation Results and Discussions

3.6.1 Simulation of the gas phase chemical dynamics

This section presents the dynamic evolution of gas species concentrations and pressures obtained by solving transport and surface kinetic equations. Figures 3.6 and 3.7 illustrate the methane and hydrogen concentration fields at two distinct temporal points—shortly after the onset (5 minutes) and at the end of the growth process. These simulations were conducted under 1000 K temperature and 500 sccm flow rate conditions, using the base feed composition outlined in Table 3.1.

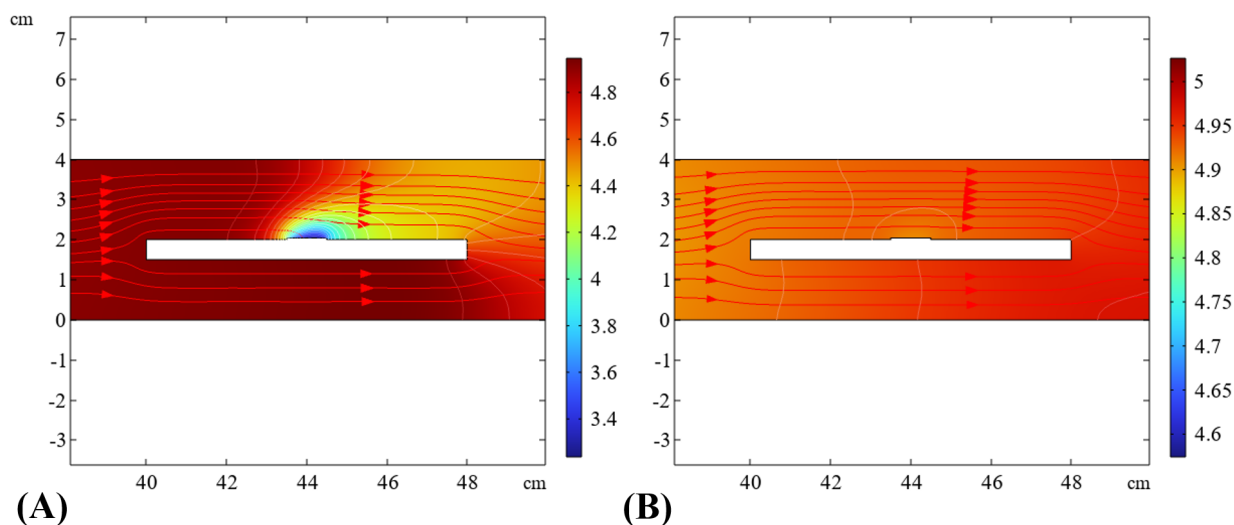


Figure 3.6: Methane concentration field in mol/m^3 at 5 min (A) and 60 min (B) after the start of the CVD.

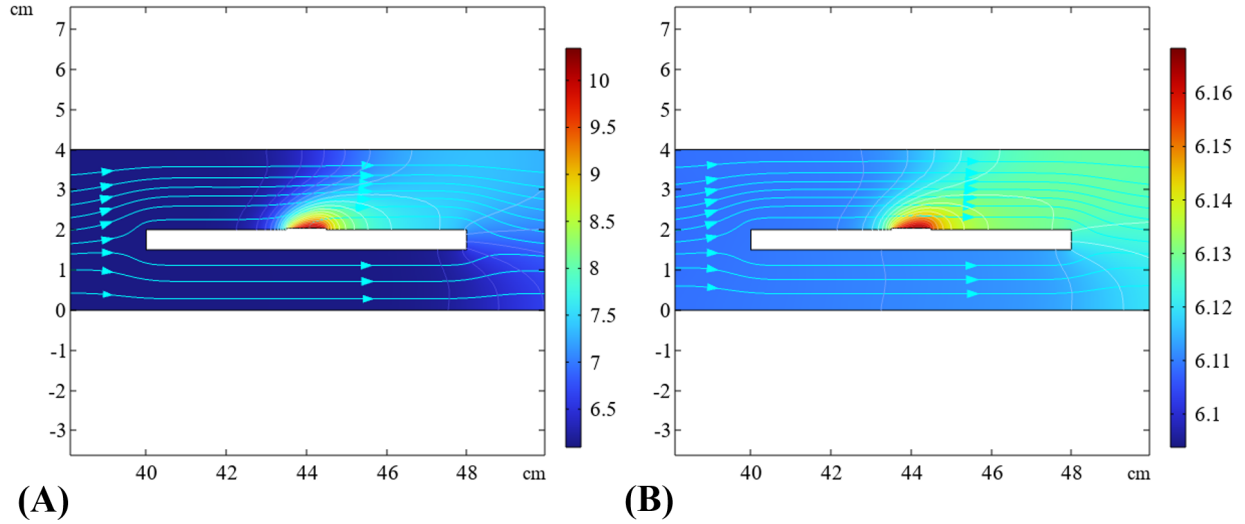


Figure 3.7: Hydrogen concentration field in mol/m^3 at 5 min (A) and 60 min (B) after the start of the CVD.

Initially, the methane concentration near the substrate decreases markedly due to surface reactions. Previous studies have suggested that diffusive limitations of gas species could arise within the tortuous and narrow pathways of the nanotube forest layer^[12,34]. However, analyzing these diffusive limitations through CFD studies poses challenges due to the breakdown of the continuity assumption at this scale and the complexity of reproducing the nanotube forest geometry. Once the catalyst is deactivated and the nanotubes reach their steady-state height, the adsorption and desorption rates decrease to nearly zero, causing the concentration gradients to practically disappear, and the process terminates. Figure 3.8 illustrates the velocity field within the CVD reactor, highlighting an increase in fluid velocity in the region above the substrate support.

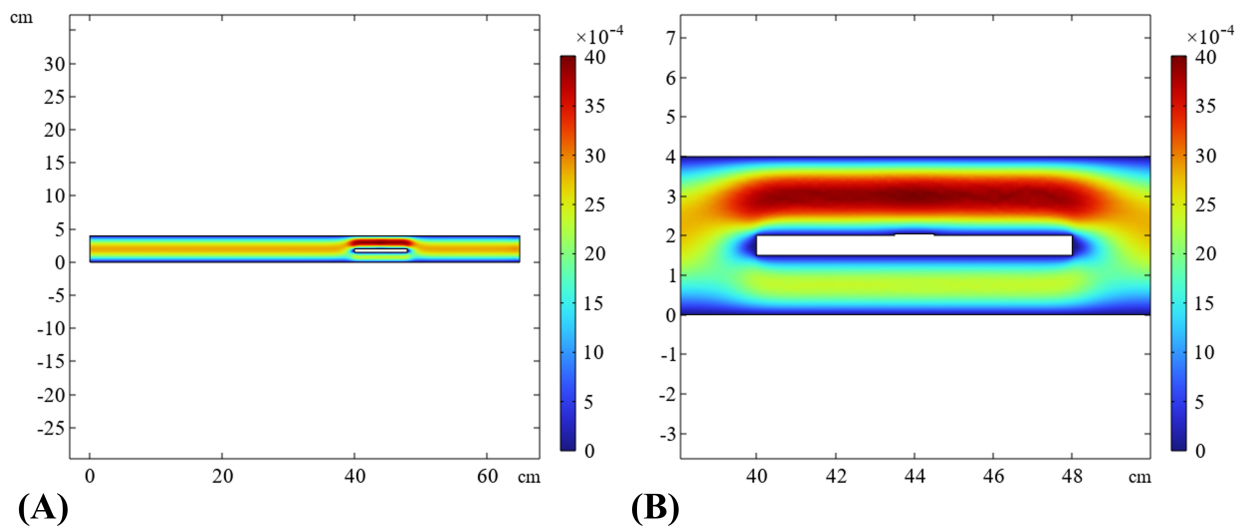


Figure 3.8: Velocity field in m/s for a feed flow rate of 500 sccm, representing: (A) the reactor's whole axial profile and (B) a zoomed look at the supporting plate.

The effects of gas-phase reactions on the partial pressures of various species in the bulk fluid are illustrated in Figures 3.9 and 3.10. These figures focus on a specific location, 2 cm to the left of the substrate surface center, and at the same height.

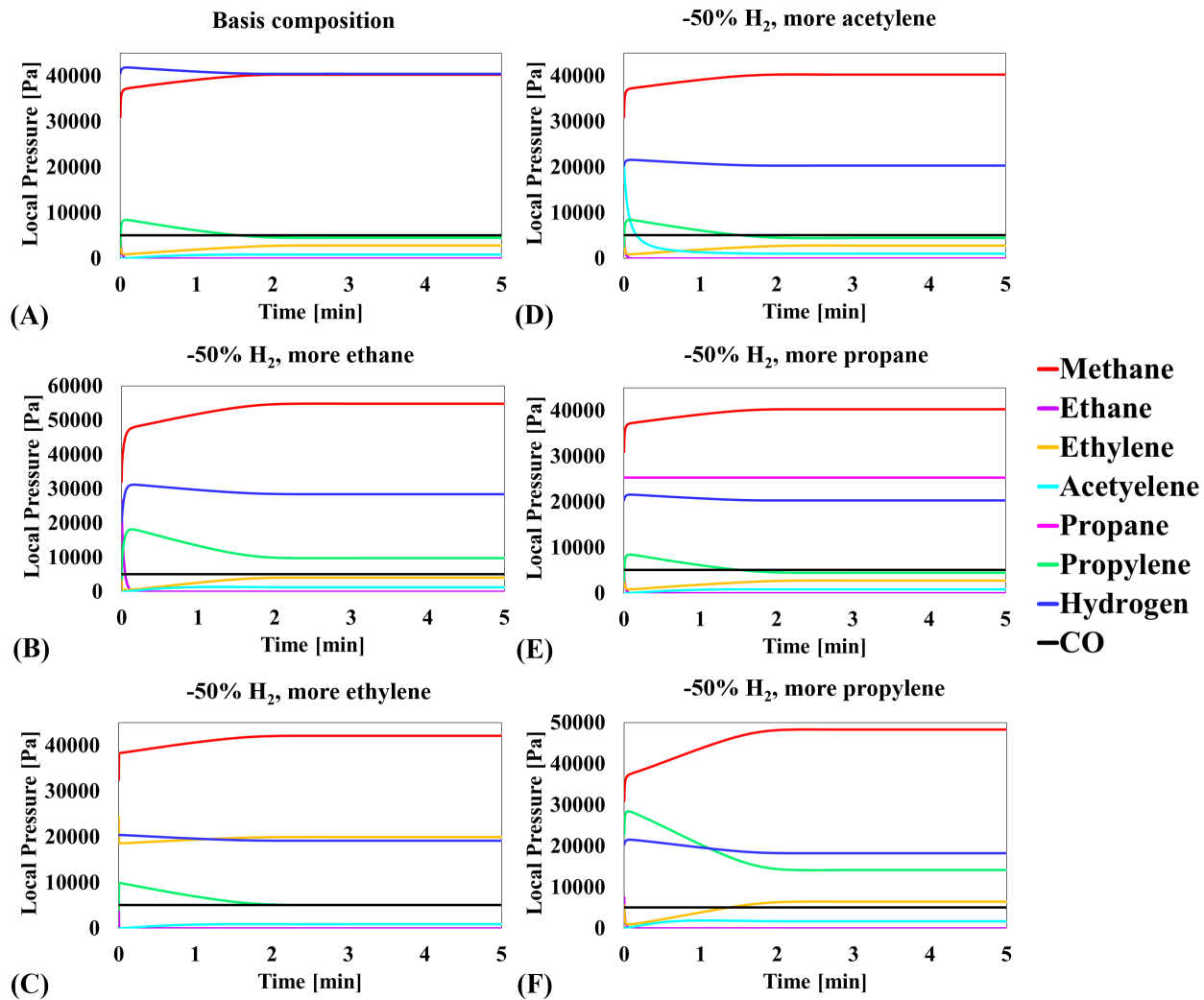


Figure 3.9: Partial pressures of main gas phase components at 1000 K for a feed flow rate of 100 cm. The composition of the feed varied according to the basis composition shown in Table 3.1: (A) Basis composition, 50% less hydrogen with fractions of ethane (B), ethylene (C), acetylene (D), propane (E) and propylene (F) increased in proportionally.

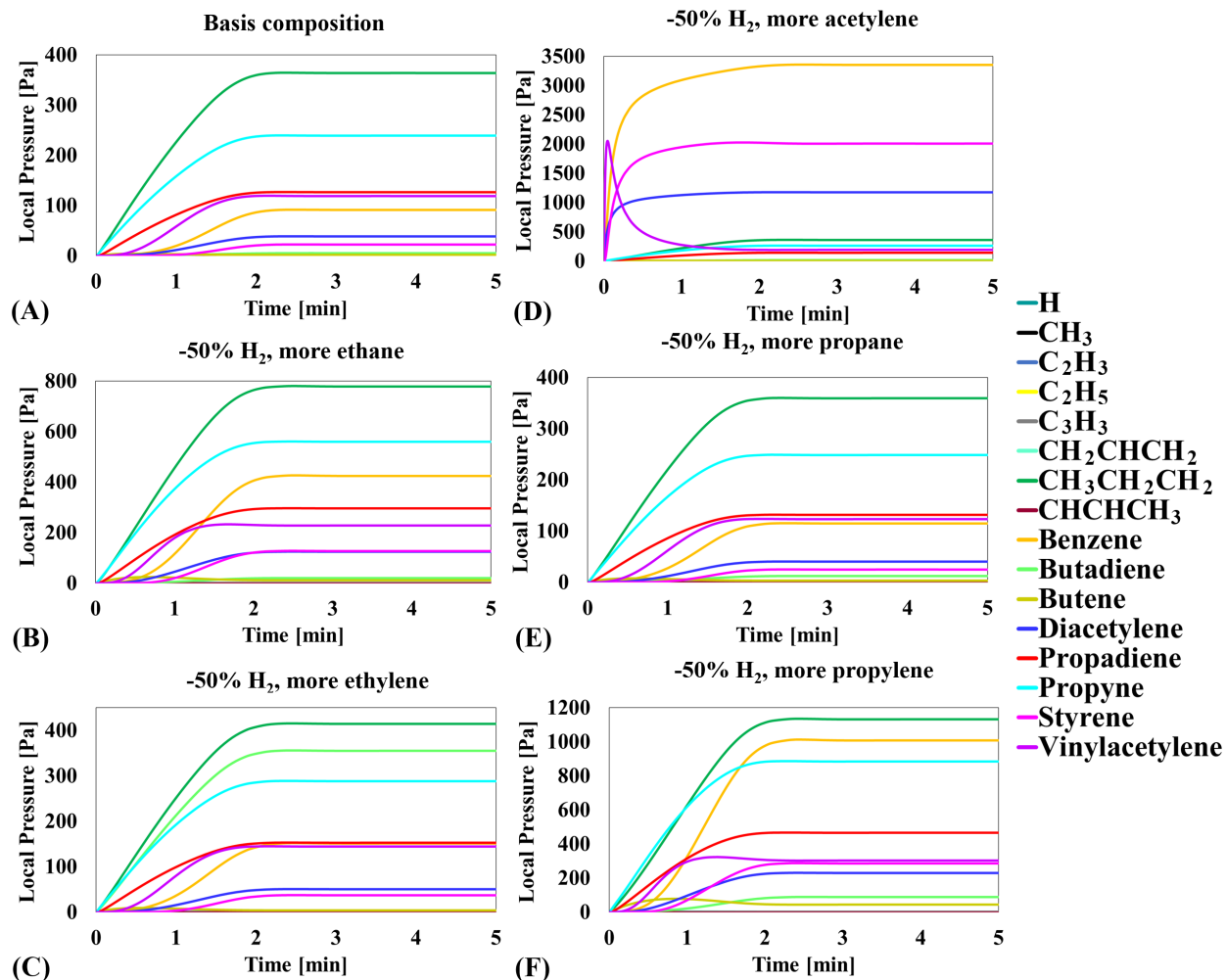


Figure 3.10: Partial pressures of secondary gas phase components at 1000 K for a feed flow rate of 100 sccm. The feed composition varied according to the basis composition shown in Table 3.1: (A) Basis composition, 50% less hydrogen with fractions of ethane (B), ethylene (C), acetylene (D), propane (E), and propylene (F) increased proportionally.

The influence of gas composition was assessed by decreasing the basis concentration of hydrogen while proportionally increasing the concentrations of other hydrocarbons individually. As expected in an axially-oriented reactor, the longer the reactor, the more time gas-phase reactions must develop before reaching the catalytic substrate surface. Not all species are shown, but it can be observed that most intermediate species do not attain elevated pressures at 1000 K. However, the primary species undergo significant changes within five minutes, which, in turn, affects the surface chemistry dynamics. For the baseline composition, ethane

is almost immediately consumed, forming propylene, which is gradually converted into other species. Conversely, ethylene exhibits an opposite trend. Hydrogen and methane remain the dominant components of the gas phase, with hydrogen pressure staying relatively stable under most conditions, except when more ethane is present, which increases its partial pressure. The presence of additional ethylene results in minimal production of other species, except for a slight increase in methane. A higher acetylene concentration appears to generate its dimer (diacetylene), benzene, and styrene. In comparison, higher concentrations of propane inhibit hydrogen production, while increased concentrations of propylene result in the formation of more methane, benzene, and propyne, among other species. The partial pressures of CO and propane coincide, as they are introduced at the same concentration and participate in a few reactions. Notably, CO is not involved in the gas-phase reaction network considered in this study.

3.6.2 Experimental validation of the surface chemistry dynamics

To validate the surface microkinetic model, predicted CNT carpet heights were compared with experimental measurements reported by Everhart et al.^[19]. The feedstock used in the experiments was an industrial gaseous waste mixture from the Fischer-Tropsch synthesis process^[17,18], with the composition specified in Table 3.1. Everhart et al.^[19] monitored the CNT carpet height by sampling the substrate at various growth times under fixed temperatures, generating temporal growth curves that are presented in their study. The experimental setup involved feeding the reactor with the feedstock at 100 sccm, diluted with 1000 sccm of argon. Scanning electron microscopy (SEM) and optical microscopy were employed to measure CNT carpet height. The experimental data were fitted to an exponential decay equation, characterizing the overall process kinetics. Growth termination was attributed to thermokinetic catalyst deactivation.

The surface microkinetic model was solved for 60 minutes using the same partial pressures and temperature conditions considered by Everhart et al.^[19]. The predicted CNT heights were compared with the reported experimental results, as shown in Figure 3.11. The com-

parison indicates consistent agreement between the predicted temporal trends (solid lines) and experimental data (dots). Corresponding growth rates are presented in Figure 3.12. A slight overestimation of CNT height was observed at 650°C, while underestimations occurred at 700 and 800°C. Due to integration sensitivity, uncertainties in growth rate predictions led to amplified errors in predicted heights. Nonetheless, the model, built without empirical fitting, demonstrated satisfactory performance despite these differences.

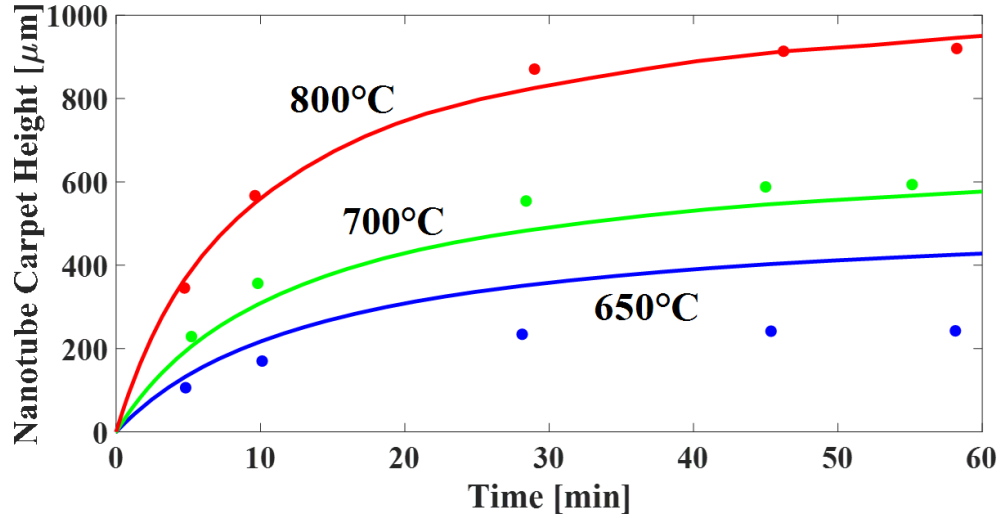


Figure 3.11: A comparison of the evolution of predicted heights (solid lines) with experimental measurements (solid points) provided by Everhart et al.^[19] under the same conditions.

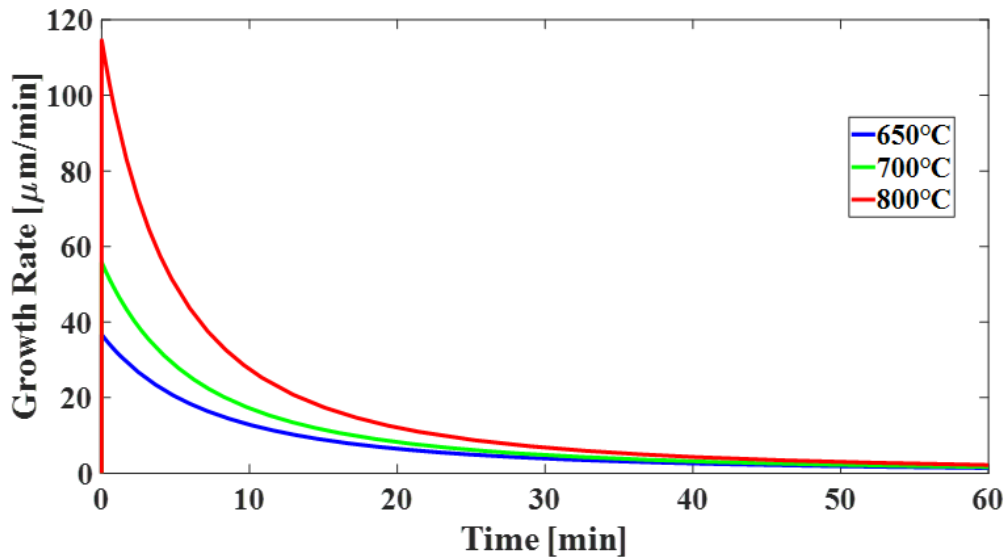


Figure 3.12: Predicted growth rates for the CNT height evolution shown in Figure 3.11.

The influence of catalyst diameter on CNT growth was evaluated by assuming a constant metal nanoparticle radius of 5 nm, following the approach of Lebedeva et al. [30]. In the proposed model, CNT height is determined by the total diffusive flux of carbon atoms reaching the catalyst surface, which depends on the concentration of active catalytic sites rather than the nanoparticle radius itself.

3.6.3 Predicted effects of partial pressures on nanotube carpet height

The model’s predictions for nanotube heights were analyzed across varying partial pressures and temperature ranges. Figure 3.13 illustrates the observed trends within a pressure range of 100 kPa. The results demonstrate that increasing methane pressure and temperature leads to longer nanotube carpets. However, once methane pressure exceeds 40 kPa, the catalytic sites become saturated and deactivated by amorphous carbon, halting further growth.

Acetylene exhibits intriguing behavior, producing carpet heights comparable to those of methane, despite containing twice the number of carbon atoms. Although counterintuitive, this outcome can be attributed to the strength of acetylene’s triple bond, which is difficult to break. High activation energies reported by Wang et al.^[46] for steps 10F, 11F, and 12F in the surface mechanism further support this explanation. The triple bond presents a significant kinetic barrier to the formation of elementary carbon species. This challenge is particularly evident at 800K, 850K, and 900K, where the most abundant surface species is $C_2H_2^*$. At these temperatures, acetylene reaches its maximum activity at relatively low pressures. Although $C_2H_2^*$ is a direct reactive intermediate for CNT formation, increasing the acetylene pressure simultaneously blocks active sites, limiting further CNT growth, as indicated by the decreasing trend in carpet height. This balance between activation and poisoning is a common characteristic in catalytic processes.

Another aspect to consider is poisoning and catalytic deactivation. Not all carbon species generated after acetylene bond dissociation diffuse into the CNT phase. A significant portion forms an amorphous layer that competes with subsurface diffusion and blocks active sites,

inhibiting further adsorption. At higher temperatures, acetylene activation becomes more accessible, resulting in behavior more similar to that of methane, with reduced accumulation of C_2H_2^* on the surface and a more efficient progression toward the formation of carbon species.

Ethylene typically produces shorter CNTs compared to acetylene or methane under most conditions. This difference is attributed to the additional dehydrogenation steps ethylene must undergo before forming C_2H_2^* species. However, at 800 K, ethylene yields significantly taller nanotubes at low pressures, whereas acetylene does not. Analysis of the most abundant surface species shows that, upon ethylene adsorption, C_2H_2^* species occupy no more than 15% of the available sites at this temperature. In contrast, acetylene adsorption nearly saturates the available surface sites.

Furthermore, increasing the temperature, rather than the partial pressure of ethylene, suppresses CNT formation when using ethylene as the feedstock. Ethane, the least reactive hydrocarbon examined for nanotube growth, produces nanotubes with heights two orders of magnitude smaller than those of methane and other hydrocarbons. This outcome stems from ethane’s multiple activation and dehydrogenation steps. Additionally, in the 800–1000 K range, ethane adsorption is more limiting than methane’s, resulting in longer nanotubes at lower temperatures. Surface kinetics analysis using MKM and TST theories suggests that neither hydrogen nor CO significantly affects CNT growth rates at sub-atmospheric pressures. This observation is consistent with the findings of Yadav et al.^[41,42], who reported that methane irreversibly decomposes on ferrocene. However, Lebedeva et al.^[31] demonstrated that high hydrogen pressures (1-1000 bar) shift surface equilibrium by promoting carbon species’ hydrogenation and hydrocarbons’ desorption. This leads to reduced carbon surface coverage and slower CNT growth, which aligns with thermodynamic predictions. Additional kinetic effects are discussed in the following section, acknowledging possible synergistic interactions that are not accounted for in the current model.

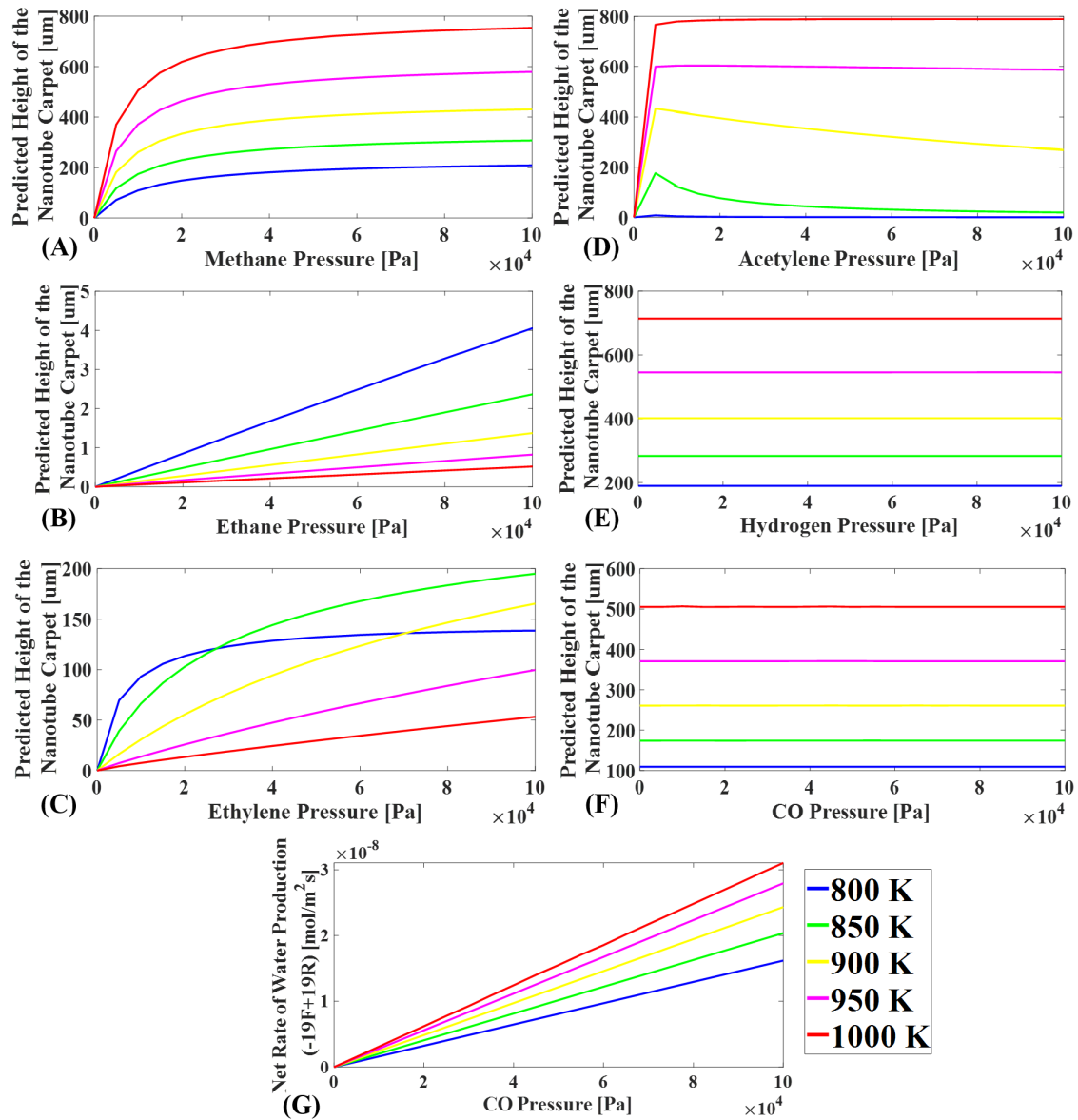


Figure 3.13: The steady state CNT height predicted by the surface chemistry model after 1 hour, assuming no gas-phase transport limitations. The effects of varying the partial pressures of methane (A), ethane (B), ethylene (C), and acetylene (D) are presented, with all other gas components set to a partial pressure of zero. Plots (E) and (F) illustrate the impact of hydrogen and CO partial pressures on CNT growth, with methane held constant at 50 kPa. The bottom plot (G) shows the net flux of water produced at different CO partial pressures when both methane and hydrogen partial pressures are fixed at 10 kPa.

3.6.4 Surface microkinetic simulation data

Surface fractions for all species and turnover frequencies for gas-phase species involved in surface kinetics at two sub-atmospheric partial pressures (1 and 100 kPa) and two temperatures (600 and 900 K) are provided in the supporting information of the published paper. The data captures the temporal dynamics of the system, offering insights into the model’s broader implications. Apart from activated hydrogen, elementary carbon (C^*) and $C_2H_2^*$, the coverage fractions of other species involved in reversible surface processes vary across several orders of magnitude, consistently displaying very low values, ranging from 10^{-7} to 10^{-36} . These values align with the kinetic constants predicted by transition state theory for surface reactions. The surface fractions decrease at higher temperatures as adsorption becomes thermodynamically unfavorable and desorption rates increase. In such conditions, the rapid molecular interactions of adsorbates prevent them from remaining bound to surface sites, except when the binding is irreversible.

Amorphous carbon species are irreversibly bound to the surface sites and are not consumed, leading to a monotonic increase in their surface fraction. This eventually leads to catalyst deactivation, particularly at higher temperatures. $C_2H_2^*$ is one of the most abundant adsorbates at lower temperatures and is a primary contributor to catalyst poisoning. Once formed through reactions 10R, 11R, and 12R (Table 3.5), it is kinetically hindered from dissociation through reactions 10F, 11F, and 12F, resulting in its accumulation. This competition with CH^* dissociation (reaction 13F) further exacerbates surface site saturation. However, the presence of water significantly reduces the coverage of $C_2H_2^*$, even at lower pressures and temperatures, with O^* becoming the most abundant adsorbate in such conditions.

3.6.5 Integrated multiscale simulations

The integration between fluid dynamics and surface reactions was analyzed by examining the effects of varying feed flow rates on CNT growth at two temperatures: 800 and 1000 K. Figures 3.14 and 3.15 show the growth plots corresponding to these temperatures for

flow rates of 250, 500, 1000, and 1500 sccm. Initially, it was assumed that 1% of the basis concentrations were present, with nitrogen as the inert pressure-balancing component. The feed boundary condition was set at time zero according to the basis concentrations. At 800 K, lower flow rates were found to delay surface dynamics, as the fluid had to first travel along the reactor axis to reach the substrate. At this lower temperature, both the kinetics of gas-phase reactions and the catalysis of CNT growth are expected to be reduced, as the elementary reactions exhibit an Arrhenius dependence on temperature. However, a slight decrease in catalytic activity was observed for the flow rates of 250 and 500 sccm, likely due to external transport limitations, compared to the curves for higher flow rates. The curves for the 1000 and 1500 sccm flow rates overlapped, indicating that gas transport was sufficiently rapid to no longer affect surface dynamics. Despite these differences in transport behavior, the growth rates and the resulting CNT carpet heights were nearly identical across all tested flow rates.

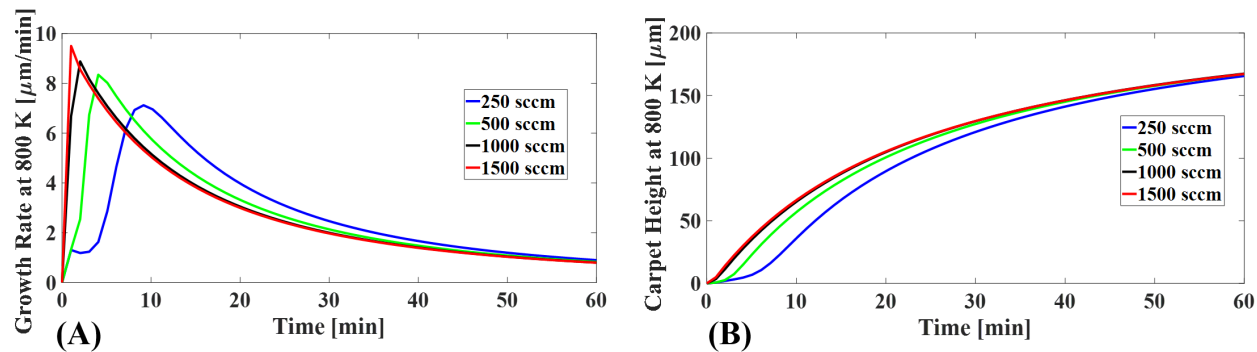


Figure 3.14: Effect of fluid velocity on the growth rate (A) and attained height (B) at 800 K.

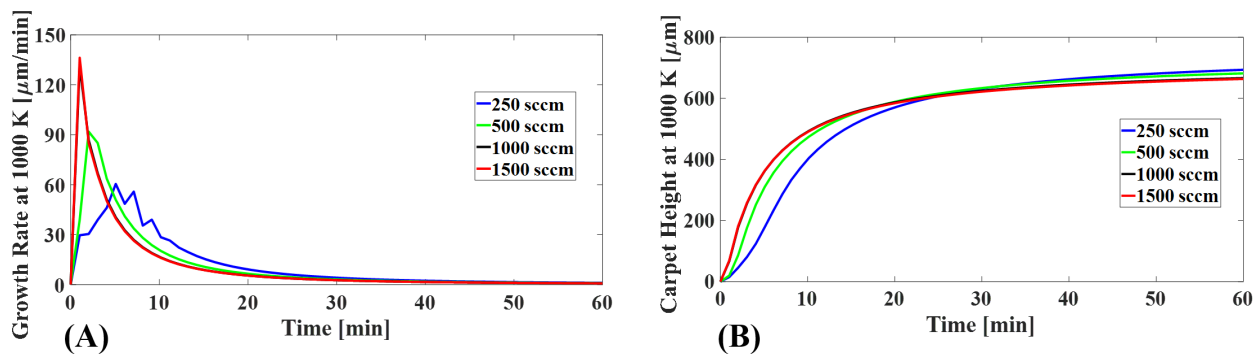


Figure 3.15: Effect of fluid velocity on the growth rate (A) and attained height (B) at 1000 K.

At higher temperatures, the influence of fluid transport becomes more significant as the potential for catalytic activity increases, and surface reactions may no longer be the rate-limiting step in the sequence of processes that contribute to CNT growth. At 1000 K, transport limitations were more pronounced for the flow rates of 250 and 500 sccm, resulting in significantly lower growth rates than those at 1000 and 1500 sccm, particularly in the early stages of the process. However, as discussed in previous sections, catalytic deactivation plays a conflicting role in surface dynamics, even at lower temperatures. Feeding the catalyst with hydrocarbons at higher rates also accelerates the deposition of poisoning carbon species, leading to faster catalyst deactivation. For flow rates of 1000 and 1500 sccm, initial peaks in catalyst activity were higher but dropped sharply after a few minutes due to deactivation. Conversely, lower gas flow rates appeared to support more controlled growth over an extended period, resulting in slightly longer CNTs in this study. If the feed is insufficiently heated and temperature control is absent, the endothermic reactions—acting as volumetric and surface heat sinks—would reduce the reactor temperature, particularly in downstream regions. Given the relatively high activation energies of surface reactions, elevated temperatures are essential for sustaining growth. As reflected in the results, higher temperatures correspond to increased growth rates. However, axial heat transfer from the hot inlet to the cooler outlet would somewhat counteract heat losses, creating a complex interplay between heat transport and thermodynamics. Moreover, elevated temperatures

accelerate catalyst deactivation.

3.7 Conclusion

This chapter presented a multiscale-multiphysics modeling approach for predicting CNT growth from hydrocarbon feedstocks in CVD processes. The study integrated fluid dynamics with reaction kinetics to analyze the complex gas-phase reaction mechanisms occurring when a hydrocarbon mixture—specifically the gas product of Fischer-Tropsch synthesis—flows through a cylindrical reactor. The analysis highlighted the importance of the thermal decomposition of ethane, acetylene, propane, and propylene, as well as the subsequent hydrogenation of smaller carbon radicals, as key reactions in the mechanism. These processes primarily produced methane, with traces of more complex hydrocarbons, such as benzene, also detected. A mechanistic surface model was developed using microkinetics, transition state theory, and DFT data. This surface model effectively predicted trends in CNT growth resulting from the adsorption and dissociation of hydrocarbons. The model was further validated against experimental data. Notably, it indicated that methane had a higher propensity to promote longer nanotube growth and confirmed the apparent inactivity of hydrogen in the growth kinetics at pressures below atmospheric levels. Finally, the fluid and surface dynamics models were integrated, revealing a counterintuitive relationship between lower velocities, sustained growth rates, and CNT height. This finding elucidates the competitive and transient nature of the kinetic interplay between nanotube growth and catalyst deactivation due to the deposition of potentially amorphous carbon phases and the dominance of thermodynamics in determining the steady state heights achieved in the process.

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Chapter 4

Nonlinear Predictive Regulation of an Integrated Green Hydrogen and Ammonia Production System under Time-Varying Renewable Energy Supply

Submitted to Computers and Chemical Engineering. Currently under review.

4.1 Introduction

The growing emphasis on sustainable chemical manufacturing systems has spurred advancements in multifunctional, integrated processes designed to synthesize specialized products^[1-9]. A key strategy to achieve both environmental and economic sustainability in these systems is the seamless integration of chemical manufacturing with renewable energy technologies. Energy-intensive processes, such as those involved in hydrogen and ammonia production, could greatly benefit from integration with solar and wind power systems^[10-14].

Leveraging renewable energy technologies reduces carbon footprints and aligns with global efforts to address climate change and enhance energy sustainability within the chemical industry.

Advancements in photovoltaic technologies, concentrating solar-thermal systems, and modern aerodynamic wind turbine designs have substantially expanded the potential for harnessing solar and wind energy across diverse localities^[15–26]. These innovations have improved the economic viability and operational efficiency of renewable energy systems for both large-scale and small-scale applications^[27–37]. However, integrating renewable energy into chemical manufacturing systems presents a significant challenge due to the inherent intermittency and variability of renewable energy sources, compromising reliability in continuous chemical production. Fluctuations in energy supply can disrupt chemical synthesis processes, affecting product quality and increasing the risk of technical failures. Addressing these issues necessitates implementing intelligent resource management systems and robust power control strategies to ensure stable process operations and consistent production outcomes.

Hydrogen and ammonia are essential commodities with significant roles in various sectors of the global economy. As clean energy carriers, they offer potential alternatives to fossil fuels in the chemical industry, transportation, and electricity generation^[38–41]. Industrial hydrogen production is predominantly achieved through catalytic steam and dry reforming of hydrocarbons, processes that rely on non-renewable resources and emit substantial amounts of carbon monoxide and carbon dioxide^[42–44]. Advancements in technology have introduced greener alternatives for hydrogen production, such as water electrolysis^[45–48] and catalytic bioethanol reforming in heterogeneous reactors^[49–52]. Like traditional hydrocarbon reforming, these processes are thermodynamically constrained and more efficient at elevated temperatures. Water electrolysis, for example, employs proton- or anion-exchange cells to facilitate the transport, diffusion, and reaction of reactants. Among emerging technologies, solid oxide cells with perovskite-like structures have demonstrated superior performance at high operating temperatures^[53,54].

Ammonia, on the other hand, is predominantly synthesized via the Haber-Bosch pro-

cess, which involves catalytic hydrogenation of atmospheric nitrogen under high-pressure conditions^[55,56]. This process relies on air separation technologies, such as cryogenic distillation or adsorption, and requires a purified hydrogen supply. Hydrogen and ammonia are typically co-produced and stored at the same industrial facilities before transportation to end-use locations. While traditionally used as a precursor for fertilizer, ammonia demonstrates significant promise as a viable energy carrier due to its high energy density and the availability of existing infrastructure for its storage and distribution^[40,41,57]. The transition to a hydrogen-ammonia economy could support the development of resilient chemical, energy, and agricultural systems. These systems would benefit from modular production units that dynamically synchronize local production and consumption, thereby enhancing efficiency and optimizing regional resource utilization.

Modular systems offer a scalable and flexible alternative to conventional chemical plants by utilizing standardized functional units designed to meet specific operational objectives. This modularity facilitates upgrades, adaptation, and relocation^[9,58–60], while their compact design enhances physicochemical interactions, minimizes capital costs, reduces environmental impact, and improves safety and resilience. These features also simplify maintenance, making modular systems suitable for rapidly changing demands and small-scale production environments^[61–63]. Integrated modular chemical and energy systems are pivotal in transitioning to a decentralized manufacturing paradigm, reducing reliance on large, centralized infrastructures. This shift enhances energy security and stimulates economic growth, particularly in remote or resource-constrained areas^[64–66]. Several studies have underscored the benefits of modular self-sufficient chemical and renewable energy systems in optimizing economic performance, bolstering resilience, and facilitating the adoption of cleaner energy technologies^[60,67–70]. Integrating modular hydrogen and ammonia production systems further advances sustainable chemical-energy-agriculture frameworks. These systems represent a transformative step toward achieving sustainable and decentralized energy solutions by harnessing renewable-powered electrolysis for green hydrogen production and leveraging ammonia as an easily stored energy carrier.

Under appropriate conditions, renewable energy sources such as solar and wind power can

effectively supply the dynamic energy demands of small-scale hydrogen and ammonia production. However, ensuring efficient and stable operation of such integrated systems requires advanced control and automation strategies to address fluctuations in renewable energy availability. The inherent nonlinearity, complexity, and multiscale nature of these systems, often characterized by interactions across different time scales, necessitate sophisticated methods for control and optimization. Model predictive control (MPC) is a promising approach, as it uses predictive models to anticipate future system states and adjust operational parameters to maintain optimal performance^[71,72]. Its ability to manage multivariable interactions and enforce system constraints makes MPC particularly well-suited to the complexities of integrated renewable energy and chemical production systems^[73–76]. While prior studies have explored ammonia production systems with varying levels of process intensification, such as multifunctional plants, material recycling, and advanced design strategies^[77–82], few have focused on integrating renewable energy sources. Sustainable approaches to water electrolysis have been investigated independently^[83–85], and significant advancements have been achieved in scheduling and techno-economic analyses for wind- and solar-powered ammonia synthesis^[86–88]. However, only a limited number of studies address the integrated dynamics of water electrolysis, ammonia synthesis, and renewable energy systems^[89–92]. This gap is primarily attributed to challenges in mathematical modeling, computational resolution, and ensuring compatibility between different modeling frameworks.

This chapter presents a predictive model for a small-scale chemical system integrating hydrogen production via water electrolysis and ammonia synthesis through the Haber-Bosch process. The model captures the dynamic behavior of concentrations and temperatures within the system, explicitly accounting for the significant energy demands of the nitrogen and hydrogen compressors. To enhance chemical-energy integration, the chemical module is coupled with a renewable energy generation system that utilizes solar and wind power, for which a dynamic model is also developed. A supervised nonlinear model predictive control (NMPC) framework is applied to regulate the chemical module’s operational variables by optimizing energy acquisition under fluctuating renewable energy availability. This strategy minimizes both operational costs and greenhouse gas emissions. The key contributions

of this work are: (1) the development of a dynamic, phenomenological model for the integrated hydrogen and ammonia production system; (2) the chemical-energy integration with a renewable energy module featuring distinct dynamic characteristics; and (3) the design and implementation of a supervised NMPC framework for highly integrated chemical-energy systems undergoing fast operational transitions. By integrating advanced modeling and control techniques, this study offers valuable insights into designing and operating efficient and sustainable chemical-energy systems under dynamic energy supply conditions. The structure of the chapter is as follows: Section II provides a detailed description of the modular hydrogen-ammonia production system model. Section III introduces the renewable energy module model. The NMPC architecture and its design parameters are outlined in Section IV. Finally, Section V presents and analyzes the simulation results.

4.2 Integrated Hydrogen-Ammonia Production Module: Architecture and Process Model

The architecture of the hydrogen-ammonia system is depicted in Figure 4.1. The system employs a one-dimensional solid-oxide anion-exchange water electrolyzer with axial plug flow, operating at high temperatures. The hydrogen generated in the electrolyzer exits with unreacted water, which is completely separated from the hydrogen and recycled. Since the outlet stream of hydrogen from the electrolyzer emerges at high temperatures and low pressures, it undergoes cooling and compression before being fed into the ammonia synthesis reactor, which combines with a compressed stream of pure nitrogen obtained from air separation. Thermodynamic relationships are employed to correlate compressor power with the final outlet pressures and temperatures. The compressed components are introduced into a one-dimensional, axially distributed ammonia synthesis reactor operating at high pressures and moderate temperatures. The reactor's outlet stream is processed through adsorption columns that chemically retain and store ammonia while recycling unreacted nitrogen and hydrogen back to the reactor inlet.

For practical simplification, it is assumed that gas velocities in all connection pipes and process units are uniformly controlled, with negligible pressure losses. The pipes are treated as having no significant dimensional effects on fluid flow. Although viscous forces, pressure gradients, and geometric features can significantly influence the velocity fields, the gas flow is approximated as non-viscous plug flow driven by inertia. While a more accurate flow representation would require solving the Navier-Stokes equations, this is beyond the scope of the current work. The pressure terms in this model primarily pertain to thermodynamics and reaction kinetics rather than fluid dynamics. While thermodynamics, reaction kinetics, and transport phenomena are inherently interconnected through pressure, concentration, and temperature, a degree of decoupling is necessary to simplify the model. These approximations allow the model to remain computationally efficient and solvable while capturing the essential dynamics of the system.

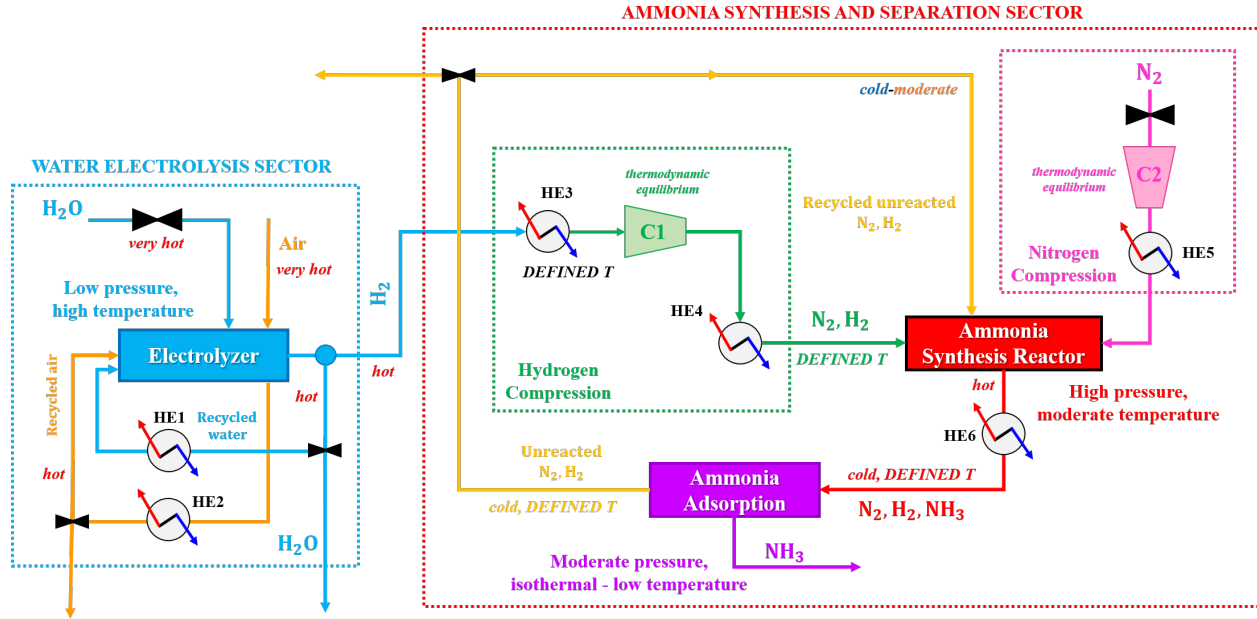


Figure 4.1: Process sheet design of a sustainable hydrogen and ammonia production system.

The multi-column pressure swing adsorption (PSA) system dynamics are described using the Bohart-Adams model to capture time-dependent adsorption, saturation, and desorption cycles. This PSA system ensures that ammonia is efficiently removed from the reactor re-cycle loop. Prior studies, including those by Malmali et al.^[93,94], Lin et al.^[95], and Andres

et al. [96,97], identify MgBr_2 as a potential ammonia adsorbent. Additionally, modern air separation processes commonly utilize PSA systems, though strict safety protocols necessitate the complete exclusion of oxygen from the ammonia synthesis reactor. This requirement ensures that pure nitrogen is consistently supplied to the compressor via a dedicated multi-column PSA system. Consequently, this study does not consider fluctuations in nitrogen concentration at the air separation system outlet.

4.2.1 Water electrolyzer model

The water electrolyzer model integrates transient one-dimensional heat and mass transport equations with nonlinear electrokinetic expressions describing water electrolysis [98–102]. The heat transport equation accounts for both conduction and convection as follows:

$$\sum_i \left(c_i c_{p,i} \right)_{\text{el}} \frac{\partial T_{\text{el}}}{\partial t} + \sum_i \left(c_i c_{p,i} \right)_{\text{el}} v_{g,\text{el}} \frac{\partial T_{\text{el}}}{\partial z} - k_{\text{eff,el}} \frac{\partial^2 T_{\text{el}}}{\partial z^2} = Q_{\text{el}} \quad (4.1)$$

where c_i denotes the concentration of species $i = \text{H}_2\text{O}, \text{H}_2, \text{N}_2, \text{O}_2$, T_{el} represents the temperature distributed along the electrolyzer length, and Q_{el} captures all volumetric heat sources and sinks. The term $k_{\text{eff,el}}$ is the effective thermal conductivity of the gas mixture in the electrolyzer, $v_{g,\text{el}}$ is the nominal axial gas velocity, and $c_{p,i}$ is the specific molar heat capacity of species i , which varies with temperature, as described in the following equations:

$$c_{p,\text{N}_2,\text{el}} = R \left(3.280 + 0.593 \times 10^{-3} T_{\text{el}} + 0.040 \times 10^5 T_{\text{el}}^{-2} \right) \quad (4.2)$$

$$c_{p,\text{O}_2,\text{el}} = R \left(3.639 + 0.506 \times 10^{-3} T_{\text{el}} - 0.227 \times 10^5 T_{\text{el}}^{-2} \right) \quad (4.3)$$

$$c_{p,\text{H}_2,\text{el}} = R \left(3.249 + 0.422 \times 10^{-3} T_{\text{el}} + 0.083 \times 10^5 T_{\text{el}}^{-2} \right) \quad (4.4)$$

$$c_{p,\text{H}_2\text{O},\text{el}} = R \left(3.470 + 1.450 \times 10^{-3} T_{\text{el}} + 0.121 \times 10^5 T_{\text{el}}^{-2} \right) \quad (4.5)$$

The model assumes a distributed temperature profile along the electrolyzer length, while fully accounting for spatial variations in electrode concentrations, thereby avoiding lumped conditions and parameters. The key parameters and constants used in the electrolyzer model

are detailed in Table 5.5. The total heat contribution from bulk sources is expressed by the following equation:

$$Q_{\text{el}} = j^2 R_{\Omega} a_{\text{el}} + \Delta H_{\text{el}} R_{\text{H}_2\text{O},\text{el}} + \frac{Q_{\text{green},\text{el}} + Q_{\text{ext},\text{el}}}{V_{\text{el}}} \quad (4.6)$$

where the first term, $j^2 R_{\Omega} a_{\text{el}}$, represents heat generation due to electrical resistance in the electrolyzer and the second term, $\Delta H_{\text{el}} R_{\text{H}_2\text{O},\text{el}}$, accounts for the thermal energy associated with the electrolysis process, which inherently couples heat and species transport. The third component includes $Q_{\text{green},\text{el}}$ and $Q_{\text{ext},\text{el}}$, which are energy inputs from a green energy module and an external grid, respectively, regulating the operating temperature of the electrolyzer and maintaining system stability.

The transport of species is governed by the Fickian diffusion and advection within the bulk fluid:

$$\left(\frac{\partial c_i}{\partial t} \right)_{\text{el}} + v \left(\frac{\partial c_i}{\partial z} \right)_{\text{el}} - D_{i,\text{el}} \left(\frac{\partial^2 c_i}{\partial z^2} \right)_{\text{el}} = R_{i,\text{el}} \quad (4.7)$$

where the diffusion coefficients for species are assumed to remain constant and the ideal gas law describes the relationship between species concentrations and partial pressures:

$$P_{i,\text{el}} = c_{i,\text{el}} RT_{\text{el}} \quad (4.8)$$

The electrokinetics of the electrolyzer are primarily governed by the Butler-Volmer equation (5.22), which establishes the relationship between the activation overpotential ($\eta_{\text{act},\text{el}}$) and the current density, j :

$$j = j_{0,\text{el}} \left(\exp \left[\frac{\alpha Z_e F \eta_{\text{act},\text{el}}}{RT} \right] - \exp \left[\frac{(1 - \alpha) Z_e F \eta_{\text{act},\text{el}}}{RT} \right] \right) \quad (4.9)$$

This equation captures the rate-limiting electronic transfers and surface interactions at electrode surfaces. The exchange current densities at the anode and cathode (j_0) are determined using the following equations, which depend on the local gas concentrations and reference

parameters^[99]:

$$j_{0,\text{anode}} = \kappa_{\text{anode}} \left(\frac{P_{\text{H}_2}}{P_{\text{el,ref}}} \right)^A \left(\frac{P_{\text{H}_2\text{O}}}{P_{\text{el,ref}}} \right)^B \exp \left(\frac{-E_{\text{a,anode}}}{RT} \right) \quad (4.10)$$

$$j_{0,\text{cathode}} = \kappa_{\text{cathode}} \left(\frac{P_{\text{O}_2}}{P_{\text{el,ref}}} \right)^C \exp \left(\frac{-E_{\text{a,cathode}}}{RT} \right) \quad (4.11)$$

where Faraday's law is used to compute the corresponding reaction rates:

$$R_{\text{i,el}} = \nu_{\text{i}} \frac{j_{\text{a,el}}}{Z_{\text{e}} F} \quad (4.12)$$

The applied voltage in the electrolyzer cell (V_{applied}) is expressed as a sum of the equilibrium voltage (V_{eq}), the activation overpotentials at each electrode (η_{act}), and the ohmic overpotential (η_{ohm}):

$$V_{\text{applied}} = V_{\text{eq}} + \eta_{\text{act,anode}} + \eta_{\text{act,cat}} + \eta_{\text{ohm}} \quad (4.13)$$

where the equilibrium voltage is derived using the Nernst equation:

$$V_{\text{eq}} = V_0 + \frac{RT_{\text{el}}}{Z_{\text{e}} F} \ln \left(\frac{P_{\text{H}_2} P_{\text{O}_2}^{1/2}}{P_{\text{H}_2\text{O}}} \right) \quad (4.14)$$

$$V_0 = \left[1.229 - 0.9 \times 10^{-3} (T_{\text{el}} - T_{\text{ref}}) \right] \quad (4.15)$$

and the ohmic overpotential is calculated by

$$\eta_{\text{ohm}} = j R_{\Omega} \quad (4.16)$$

The current density corresponding to a given applied voltage is obtained by numerically solving the voltage balance equation of 5.26. Tables 5.5, 5.6, and 5.7 summarize the electrolyzer parameters, boundary conditions, and initial/feed conditions, respectively, for modeling heat and mass transport within the system.

Table 4.1: Electrolyzer constants and parameters.

Parameter	Description	Value
$v_{g,el}$	Gas velocity	0.1 [m/s]
R	Ideal gas constant	8.314 [J/mol K]
L_{el}	Length of the electrolyzer	3 [m]
D_{el}	Diameter of the electrolyzer	0.3 [m]
k_{H_2O}	Thermal conductivity of water	105.67×10^{-3} [W/m K]
k_{H_2}	Thermal conductivity of hydrogen	361×10^{-3} [W/m K]
k_{N_2}	Thermal conductivity of nitrogen	51.53×10^{-3} [W/m K]
k_{O_2}	Thermal conductivity of oxygen	48.10×10^{-3} [W/m K]
$k_{eff,el}$	Effective conductivity of mixture	$\sum y_i k_i$
τ_{anode}	Anode thickness	50×10^{-6} [m]
$\tau_{electrolyte}$	Electrolyte thickness	20×10^{-6} [m]
$\tau_{cathode}$	Cathode thickness	500×10^{-6} [m]
σ_{anode}	Anode electrical conductivity	8.4×10^3 [1/ Ω m]
$\sigma_{electrolyte}$	Electrolyte electrical conductivity	$33.4 \times 10^3 \exp(-10.3 \times 10^3/T_{el})$ [1/ Ω m]
$\sigma_{cathode}$	Cathode electrical conductivity	80×10^3 [1/ Ω m]
R_{Ω}	Global electrolyzer resistivity	$\frac{\tau_{anode}}{\sigma_{anode}} + \frac{\tau_{electrolyte}}{\sigma_{electrolyte}} + \frac{\tau_{cathode}}{\sigma_{cathode}}$
ΔH_{el}	Enthalpy of water electrolysis	285.83×10^3 [J/mol]
D_{H_2}	Effective hydrogen diffusivity	2×10^{-5} [m ² /s]
D_{H_2O}	Effective water diffusivity	2×10^{-5} [m ² /s]
D_{N_2}	Effective nitrogen diffusivity	2×10^{-5} [m ² /s]
D_{O_2}	Effective oxygen diffusivity	2×10^{-5} [m ² /s]
α	Charge transfer coefficient	0.5
Z_e	Number of electrons involved in electrolysis	2
F	Faraday's constant	96485.33 [C/mol]
A	Hydrogen exponent coefficient	0.41
B	Water exponent coefficient	0.40
C	Oxygen exponent coefficient	0.3
κ_{anode}	Anode's exchange current density coefficient	3.5×10^6 [A/m ²]
$\kappa_{cathode}$	Cathode's exchange current density coefficient	3.35×10^9 [A/m ²]
$E_{a,anode}$	Anode's activation energy	1.37×10^5 [J/mol]
$E_{a,cathode}$	Cathode's activation energy	1.40×10^5 [J/mol]
a_{anode}	Anode's specific area	1 [m ² /m ³]
$a_{cathode}$	Cathode's specific area	1 [m ² /m ³]
$V_{applied}$	Applied voltage	1.60 [V]
ν_{H_2O}	water stoichiometric coefficient	-1
ν_{H_2}	hydrogen stoichiometric coefficient	1
ν_{O_2}	oxygen stoichiometric coefficient	0.5
r	recycle ratio	0.5

Table 4.2: Electrolyzer boundary conditions.

Boundary Conditions	Expression
Inlet (Heat Transport)	$\frac{\partial T_{\text{el}}}{\partial z} _{z=0} = \frac{\rho c_p v}{k_{\text{eff,el}}} [T_{\text{el}} _{z=0} - (1-r)T_{\text{feed}} - rT_{\text{el}} _{z=L}], r = 0.5$
Inlet (Species Transport)	$\frac{\partial c_i}{\partial z} _{z=0} = \frac{v}{D_i} [c_i _{z=0} - (1-r)c_{i,\text{feed}} - rc_i _{z=L}]$
Outlet (Heat Transport)	$\frac{\partial T_{\text{el}}}{\partial z} = 0$
Outlet (Species Transport)	$\frac{\partial c_i}{\partial z} = 0$

Table 4.3: Initial and feed conditions of the electrolyzer.

Initial Parameters	
$T_{\text{ref},0}$	1073.15 [K]
$P_{\text{ano},0}$	2 [atm]
$P_{\text{cat},0}$	2 [atm]
$y_{\text{H}_2,0}$	0.01
$y_{\text{H}_2\text{O},0}$	0.99
$y_{\text{N}_2,0}$	0.79
$y_{\text{O}_2,0}$	0.21
$c_{i,0}$	$(y_{i,0}P_{\text{el},0})/(RT_{\text{ref},0})$
Initial Conditions	
Heat Transport	Mass Transport
$T_z _{t=0} = T_{\text{ref},0}$	$c_{i,z} _{t=0} = c_{i,0}$
Feed Conditions	
T_{feed}	750 [K]
$P_{i,\text{feed}}$	$y_{i,0}P_{\text{el},0}$

4.2.2 Ammonia synthesis reactor model

The transport phenomena within the ammonia synthesis reactor are modeled analogously to the electrolyzer, treating the reactor as a transient plug-flow process. The heat transport in the reactor is described as follows:

$$\sum_i (c_i c_{p,i})_r \frac{\partial T_r}{\partial t} + \sum_i (c_i c_{p,i})_r v \frac{\partial T_r}{\partial z} - k_{\text{eff},r} \frac{\partial^2 T_r}{\partial z^2} = Q_r \quad (4.17)$$

where T_r represents the reactor temperature profile, v is the fluid velocity, $k_{\text{eff},r}$ is the effective thermal conductivity, and Q_r denotes the net rate of heat to the reactor. The molar-specific heat capacities of the key species involved in the reaction are also expressed by:

$$c_{p,N_2,r} = R(3.280 + 0.593 \times 10^{-3}T_r + 0.040 \times 10^5T_r^{-2}) \quad (4.18)$$

$$c_{p,H_2,r} = R(3.249 + 0.422 \times 10^{-3}T_r + 0.083 \times 10^5T_r^{-2}) \quad (4.19)$$

$$c_{p,NH_3,r} = R(3.578 + 3.020 \times 10^{-3}T_r - 0.186 \times 10^5T_r^{-2}) \quad (4.20)$$

The heat term involves contributions from the heat of reaction and the heat exchanged through the cooling jacket with a thermal regulation fluid:

$$Q_r = \Delta H_r \cdot R_{NH_3} - \frac{U_r A_{\text{lateral}}(T_r - T_{\text{regulation}})}{V_r} \quad (4.21)$$

where $A_{\text{lateral}} = \pi D_r L_r$, $V_r = \pi(D_r/2)^2 L_r$, and the heat of reaction for ammonia synthesis is calculated as follows:

$$\begin{aligned} \Delta H_r = & (0.54526 + 846.609T_r^{-1} + 459.734 \times 10^6T_r^{-3})P_{\text{bar}} \\ & + 5.34685T_r + 0.2525 \times 10^{-3}T_r^2 - 1.69197 \times 10^{-6}T_r^3 + 9157.09 \end{aligned} \quad (4.22)$$

The mass transport in the reactor is described by the following equation:

$$\left(\frac{\partial c_i}{\partial t}\right)_r + v_{g,r} \left(\frac{\partial c_i}{\partial z}\right)_r - D_{i,r} \left(\frac{\partial^2 c_i}{\partial z^2}\right)_r = R_{i,r} \quad (4.23)$$

where c_i denotes the concentration of species i in the reactor, $v_{g,r}$ is the velocity, and $D_{i,r}$ is the diffusivity coefficient. Based on the widely adopted Temkin-Pyzhev model, the reaction rate for ammonia synthesis assumes that the dissociative nitrogen adsorption is the rate-limiting step^[103,104]. The reaction rate is given by:

$$R_{NH_3,r} = k_2 \left[K_{\text{eq}}^2 a_{N_2} \left(\frac{a_{H_2}^3}{a_{NH_3}^2} \right)^{1/2} \left(\frac{a_{NH_3}^2}{a_{N_2}^3} \right)^{1/2} \right] \quad (4.24)$$

where k_2 is the reverse kinetic constant, K_{eq} is the equilibrium constant, $a_i = y_i \phi_i P_r$ represents the activity coefficient of species i , ϕ_i is the fugacity coefficient, $P_r = P_{N_2} + P_{H_2} + P_{NH_3}$ is the reactor pressure, and the partial pressures of species are computed through the ideal gas law, $P_i = c_i RT|_r$. The kinetic and equilibrium constants are computed using the following equations^[104–106]:

$$k_2 = k_0 \exp\left(\frac{-E_a}{R T_r}\right) \quad (4.25)$$

$$\begin{aligned} \log(K_{eq}) = & -2.691122 \log(T_r) - 5.519265 \times 10^{-5} T_r \\ & + 1.848863 \times 10^{-7} T_r^2 + 2001.6 T_r^{-1} + 2.6899 \end{aligned} \quad (4.26)$$

where $k_0 = 8.8490 \times 10^{14}$ kmol/m³h and $E_a = -1.7056 \times 10^5$ J/mol. The fugacity coefficients for the species are also described as follows^[106]:

$$\begin{aligned} \phi_{N_2} = & 0.93431737 + 0.3101804 \times 10^{-3} T_r + 0.295895 \times 10^{-3} P_r \\ & - 0.270729 \times 10^{-6} T_r^2 + 0.4775207 \times 10^{-6} P_r^2 \end{aligned} \quad (4.27)$$

$$\begin{aligned} \phi_{H_2} = & \exp\left[\exp(-3.8402 T_r^{0.125} + 0.541) P_r - \exp(-0.1263 T_r^{0.5} - 15.980) P_r^2\right. \\ & \left.+ 300 \exp(-0.011901 T_r - 5.941) [\exp(-P_r/300) - 1]\right] \end{aligned} \quad (4.28)$$

$$\begin{aligned} \phi_{NH_3} = & 0.1438996 + 0.2028538 \times 10^{-2} T_r - 0.4487672 \times 10^{-3} P_r \\ & - 0.1142945 \times 10^{-5} T_r^2 + 0.2761216 \times 10^{-6} P_r^2 \end{aligned} \quad (4.29)$$

The reactor-specific parameters, including gas velocity, reactor dimensions, thermal conductivity, diffusivity, and heat transfer properties used in this study, are detailed in Table 5.8. Table 5.9 defines the governing boundary conditions for heat and species transport within the reactor, capturing the interactions at the inlet and outlet. Table 5.10 also outlines the initial and feed conditions, including temperature, pressure, species compositions, and nitrogen feed properties.

Table 4.4: Reactor constants and parameters.

Parameter	Description	Value
$v_{g,r}$	Gas velocity	0.1 [m/s]
L_r	Reactor length	3 [m]
D_r	Reactor diameter	0.3 [m]
U_r	Global heat transfer coefficient	35 [W/m ² K]
k_{N_2}	Thermal conductivity of nitrogen	51.53×10^{-3} [W/mK]
k_{H_2}	Thermal conductivity of hydrogen	361×10^{-3} [W/mK]
k_{NH_3}	Thermal conductivity of ammonia	78.22×10^{-3} [W/mK]
$k_{eff,r}$	Effective conductivity of mixture	$\sum y_i k_i$
D_{N_2}	Effective nitrogen diffusivity	2×10^{-5} [m ² /s]
D_{H_2}	Effective hydrogen diffusivity	2×10^{-5} [m ² /s]
D_{NH_3}	Effective ammonia diffusivity	2×10^{-5} [m ² /s]
$T_{regulation}$	Temperature of the regulation fluid	873.15 [K]
r	Recycle ratio	0.5

Table 4.5: Reactor boundary conditions.

Boundary Conditions	Expression
Inlet (Heat Transport)	$\frac{\partial T_r}{\partial z} _{z=0} = \frac{\rho c_p v}{k_{eff,r}} [T_r _{z=0} - (1-r)T_{feed} - rT_r _{z=L}], r = 0.5$
Inlet (Species Transport)	$\frac{\partial c_i}{\partial z} _{z=0} = \frac{v}{D_i} [c_i _{z=0} - (1-r)c_{i,feed} - rc_i _{z=L}]$
Outlet (Heat Transport)	$\frac{\partial T_r}{\partial z} = 0$
Outlet (Species Transport)	$\frac{\partial c_i}{\partial z} = 0$

Table 4.6: Initial and feed conditions of the reactor.

Initial Parameters	
$T_{\text{ref},0}$	723.15 [K]
$P_{\text{r},0}$	10 [bar]
$y_{\text{N}_2,0}$	0.24975
$y_{\text{H}_2,0}$	0.74925
$y_{\text{NH}_3,0}$	0.001
$c_{\text{i},0}$	$y_{\text{i},0}P_{\text{r},0}/RT_{\text{ref},0}$
Initial Conditions	
Heat Transport	Mass Transport
$T_z _{t=0} = T_{\text{ref},0}$	$c_{\text{i},z} _{t=0} = c_{\text{i},0}$
Nitrogen Feed Conditions	
$T_{\text{N}_2,\text{storage}}$	298.15 [K]
$P_{\text{N}_2,\text{feed}}$	1 [bar]

4.2.3 Ammonia PSA Model

The dynamic behavior of the breakthrough curve for an isothermal adsorption process is mathematically described using the Bohart-Adams model^[107,108]:

$$\frac{c_{\text{NH}_3,\text{ads,outlet}}}{c_{\text{NH}_3,\text{ads,inlet}}} = \frac{\exp \left[k_{\text{ads}} c_{\text{NH}_3,\text{ads,inlet}} \left(t - \frac{\varepsilon L}{v} \right) \right]}{\exp \left(\frac{k_{\text{ads}} w_{\text{eq}} L}{v} \right) + \exp \left[k_{\text{ads}} c_{\text{NH}_3,\text{ads,inlet}} \left(t - \frac{\varepsilon L}{v} \right) \right] - 1} \leq 0.01 \quad (4.30)$$

The PSA system periodically shifts the breakthrough curve over time whenever the breakthrough cutoff concentration ratio is reached for a specified gas velocity and inlet ammonia concentration. This approach effectively models the adsorption, saturation, and desorption/regeneration phases in multiple adsorption columns operating simultaneously, ensuring that the outlet ammonia concentration remains below 1% of the inlet concentration at all times. The adsorbent is assumed to interact solely with ammonia, while other gas components are considered non-interactive. For this study, magnesium bromide (MgBr_2) is utilized as the adsorbent, with its properties informed by prior works^[93–97]. The equilibrium adsorp-

tion capacity (w_{eq}) is determined using the Langmuir isotherm [?]:

$$w_{eq} = (1 - \varepsilon) \rho_{ads} w_{max} \frac{K_{eq} c_{NH_3}}{(1 + K_{eq} c_{NH_3})} \quad (4.31)$$

where the maximum adsorption capacity (w_{max}) and equilibrium adsorption constant ($K_{ads,eq}$) are obtained as follows:

$$w_{max} = 0.0541 \exp\left(\frac{1780}{T_{ads}}\right) \quad (4.32)$$

and

$$K_{ads,eq} = K_{ads,eq,ref} \exp\left[\frac{\Delta H_{ads}}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T_{ads}}\right)\right], \quad K_{ads,eq,ref} = K_{ads,eq,ref}|_{P_{ref}} R T_{ref} \quad (4.33)$$

The parameters and constants used in the PSA model are summarized in Table 5.8.

Table 4.7: PSA constants and parameters.

Parameter	Description	Value
k	Adsorption constant	0.0003
ε	Porosity	0.4
L	Adsorption column length	3 [m]
ρ_{ads}	Adsorbent density	3720 [kg/m ³]
ΔH_{ads}	Heat of adsorption	-132900 [J/mol]
$K_{eq,ref} _{P_{ref}}$	Pressure equilibrium constant	$\frac{1.01}{100000}$ [Pa ⁻¹]
T_{ref}	Reference temperature	400 [K]

4.2.4 Heat exchangers

The outlet temperatures of the streams exiting the heat exchangers were defined as follows: $T_{out,HE1,HE2} = 1200$ K, $T_{out,HE3} = 623.15$ K, $T_{out,HE4,HE5} = 723.15$ K, and $T_{out,HE6} = 393.15$ K. While these values were specified for practicality in this analysis, a more detailed design can be performed using the logarithmic mean temperature difference (LMTD) or effectiveness-number of transfer units (NTU) methods to account for heat transfer characteristics and system efficiency.

4.2.5 Compressors

The compressors are essentially modeled using two thermodynamic expressions that describe the isentropic compression of an ideal gas under open flow^[109]. As shown by Equations 5.45 and 5.46, the outlet pressures and temperatures can be predicted straightforwardly from the inlet variables, given the total compressor power applied (W_{comp}). Even though those relations refer to steady-state operation, compressors and heat exchangers exhibit a pseudo-steady state behavior because the inlet variables change over time. The constant η_{comp} represents the non-isentropic efficiency of the compression, which ranges between 0 and 1 and implies a decrease in the output pressure. It is assumed that $\eta_{\text{comp}} = 0.8$ for both nitrogen and hydrogen compressors. The total power applied individually to the nitrogen and hydrogen compressors is given by the sum of a green component coming from the renewable energy module and an external power source component (Equation 5.47). As explained in the next section, the external source component is treated as a manipulable input variable.

$$P_{\text{out}} = P_{\text{in}} \left[\left(\frac{\eta_{\text{comp}} W_{\text{comp}}}{c_p T_{\text{in}}} \right) + 1 \right]^{(c_p/R)} \quad (4.34)$$

$$T_{\text{out}} = T_{\text{in}} + \frac{\left[T_{\text{in}} \left(\frac{P_{\text{out}}}{P_{\text{in}}} \right)^{(R/c_p)} \right] - T_{\text{in}}}{\eta_{\text{comp}}} \quad (4.35)$$

$$W_{\text{comp}} = W_{\text{green,comp}} + W_{\text{ext,comp}} \quad (4.36)$$

4.3 Renewable Energy Module: Structure and Thermokinetic Model Description

The renewable energy module includes wind and solar power units, extensively studied in the literature and widely implemented in practice. However, their integration with chemical process models remains relatively unexplored. Solar energy can be harnessed during daylight

hours and converted directly into electricity using photovoltaic technology, which relies on the photoelectric effect in semiconductor-based panels. Alternatively, concentrating solar-thermal systems utilize mirrors to absorb and concentrate solar radiation, transferring the collected heat to a heat transfer fluid (HTF) that serves as a thermal energy carrier. High-heat-capacity fluids, such as molten salts and specific oils, are commonly used for thermal energy storage and transport in these systems. The overall efficiency of photovoltaic and concentrating solar-thermal technologies ranges from 20% to 40%. However, solar-thermal systems offer the additional advantage of steam generation, which serves as a functional chemical-energy utility, along with the ability to store thermal energy for use during periods of low or no sunlight. This section presents a conceptual model of a small-scale solar-thermal module, incorporating thermophysical properties of molten salt as reported by Yao et al. ^[110]. The temporal variability of solar irradiance—on daily, seasonal, and annual scales—has been well-documented ^[41,111]. Empirical and correlational models that relate solar irradiance to field capacity and time are widely used. However, they often neglect real-time weather conditions such as ambient temperature fluctuations, cloud cover, and precipitation, which can significantly impact heat transfer.

The HTF absorbs heat from the solar field in the proposed model, as illustrated in Figure 5.23. Upon heating, the HTF is stored in a reservoir and subsequently supplies thermal energy to a water evaporator and heat exchanger, producing saturated or superheated steam that drives a turbine. Steam is a critical utility in chemical plants and can be repurposed for various applications. The turbine generates electrical power, which is then supplied to the water electrolyzer or ammonia synthesis reactor. The model assumes negligible heat transfer resistances and losses, with the heat absorbed by the evaporator and heat exchanger directly determined by the enthalpy flow rate of the incoming hot fluid. The cooled HTF is then returned to a secondary reservoir. The mass flow rates of the HTF directed to the evaporator, heat exchanger, and solar field are adjustable, influencing the dynamic hold-up and temperature profiles within the reservoirs.

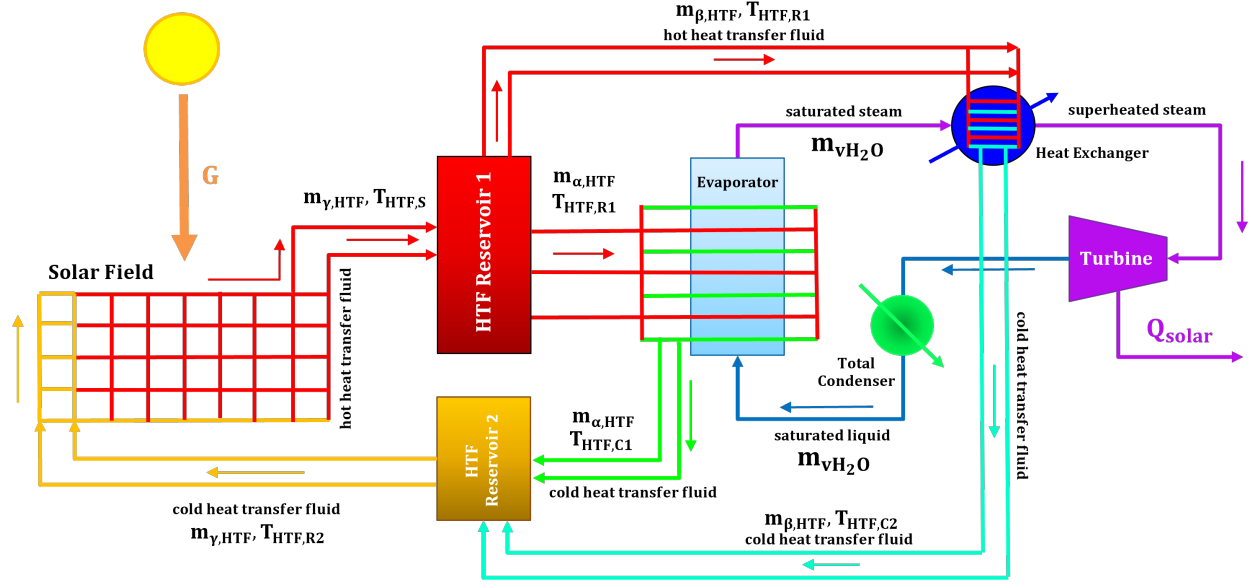


Figure 4.2: Energy transfer scheme in a solar-to-thermal storage system.

4.3.1 Solar energy harvesting

Solar field

The total available solar power depends on time and the effective area of sunlight collection within the field. The correlation provided by Pelay et al.^[111] is utilized to characterize the time-dependent variation of solar irradiance (G) under clear-sky summer conditions:

$$t < 18420 \text{ [s]} : G = 0 \quad (4.37)$$

$$18420 \text{ [s]} < t < 67020 \text{ [s]} : G = -4.985809 \times 10^{-24} t^6 + 1.264474 \times 10^{-18} t^5 \\ - 1.309668 \times 10^{-13} t^4 + 7.086230 \times 10^{-9} t^3 \\ - 2.116637 \times 10^{-4} t^2 + 3.328676 t - 2.10949 \times 10^4 \text{ [W/m}^2\text{]}$$

$$t < 67020 \text{ [s]} : G = 0$$

where heat losses and resistances are neglected, assuming all incident solar energy is fully captured and transferred to the HTF. More details can be found in the studies by Yao et

al.^[110] and Li et al.^[112]. Figure 5.23 shows the ground-level solar irradiance profile throughout a typical summer day under clear-sky conditions, illustrating the time-dependent variation represented by Equation 5.48. The reduced energy balance governing the outlet temperature of the HTF from the solar field is expressed as:

$$T_{\text{HTF,SF}} = T_{\text{R2}} + \frac{G A_{\text{SF}}}{\dot{m}_{\text{HTF},\gamma} c_{\text{p,HTF}}} \quad (4.38)$$

where the definitions and values of the parameters are provided in Table 5.11.

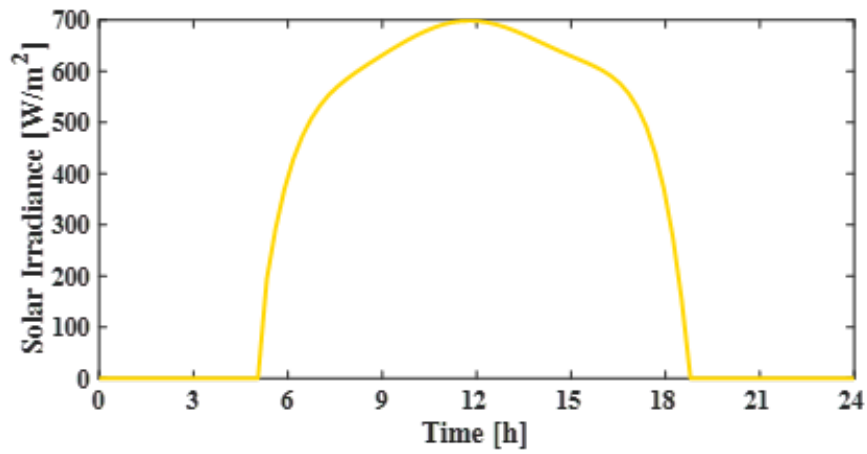


Figure 4.3: Ground solar irradiance under clear sky conditions on a regular summer day.

HTF reservoirs

Several studies, including those by Yao et al.^[110], Pelay et al.^[111], Wei et al.^[113], Yu et al.^[114], and Li et al.^[112], have examined two-reservoir systems for thermodynamic modeling in solar energy capture. These investigations highlight that separating HTF streams based on their thermal properties improves system efficiency while streamlining its design. The governing mass and energy balance equations for the HTF reservoirs are described as follows:

$$\frac{dV_{\text{R1}}}{dt} = \frac{\dot{m}_{\text{HTF},\gamma} - \dot{m}_{\text{HTF},\alpha} - \dot{m}_{\text{HTF},\beta}}{\rho_{\text{HTF}}} \quad (4.39)$$

$$\frac{dV_{\text{R2}}}{dt} = \frac{\dot{m}_{\text{HTF},\alpha} + \dot{m}_{\text{HTF},\beta} - \dot{m}_{\text{HTF},\gamma}}{\rho_{\text{HTF}}} \quad (4.40)$$

$$\frac{dT_{R1}}{dt} = \frac{1}{\rho_{HTF} V_{R1} c_{p,HTF}} \left[\dot{m}_{HTF,\gamma} c_{p,HTF} (T_{HTF,SF} - T_{ref}) - \dot{m}_{HTF,\alpha} c_{p,HTF} (T_{HTF,R1} - T_{ref}) \right. \quad (4.41)$$

$$\begin{aligned} & - \dot{m}_{HTF,\beta} c_{p,HTF} (T_{HTF,R1} - T_{ref}) - h_{conv} A_{R1} (T_{HTF,R1} - T_{air}) \\ & - c_{p,HTF} (T_{HTF,R1} - T_{ref}) (\dot{m}_{HTF,\gamma} - \dot{m}_{HTF,\alpha} - \dot{m}_{HTF,\beta}) \\ & \left. - \sigma \varepsilon A_{R1} (T_{HTF,R1}^4 - T_{air}^4) \right] \end{aligned}$$

$$\frac{dT_{R2}}{dt} = \frac{1}{\rho_{HTF} V_{R2} c_{p,HTF}} \left[\dot{m}_{HTF,\alpha} c_{p,HTF} (T_{HTF,C1} - T_{ref}) + \dot{m}_{HTF,\beta} c_{p,HTF} (T_{HTF,C2} - T_{ref}) \right. \quad (4.42)$$

$$\begin{aligned} & - \dot{m}_{HTF,\gamma} c_{p,HTF} (T_{HTF,R2} - T_{ref}) - h_{conv} A_{R2} (T_{HTF,R2} - T_{air}) \\ & - c_{p,HTF} (T_{HTF,R2} - T_{ref}) (\dot{m}_{HTF,\alpha} + \dot{m}_{HTF,\beta} - \dot{m}_{HTF,\gamma}) \\ & \left. - \sigma \varepsilon A_{R2} (T_{HTF,R2}^4 - T_{air}^4) \right] \end{aligned}$$

where V_{R1} and V_{R2} denote the volumes and T_{R1} and T_{R2} are the temperatures of reservoirs 1 and 2, respectively.

Evaporator

The evaporator functions as both a heat absorber for boiling water and a source of steam generation. It operates at a constant pressure of 10 bar. The boiling temperature is determined using the Antoine equation, and once this temperature is reached, steam production occurs at a rate dictated by the heat transfer process. The evaporator temperature (T_{evap}) never exceeds the boiling temperature used for estimating thermal properties. The evaporator does not exchange heat with the HTF except through convection and radiation to the surrounding environment. A pseudo-entropic energy balance condition ensures that steam generation does not occur if T_{evap} is lower than the HTF temperature from reservoir 1 and the water's boiling temperature. Consequently, heat transfer is inhibited under these conditions, preventing steam formation. The heat balance for the HTF in the evaporator is

expressed as follows:

$$T_{\text{HTF},C1} = T_{\text{HTF},R1} - \frac{\eta_{\text{evap}} \dot{m}_{\text{HTF},\alpha} c_{p,\text{HTF}} (T_{\text{HTF},R1} - T_{\text{evap}})}{\dot{m}_{\text{HTF},\alpha} c_{p,\text{HTF}}} \quad (4.43)$$

$$\begin{aligned} \frac{dT_{\text{evap}}}{dt} = & \frac{1}{\rho_{\text{H}_2\text{O}} V_{\text{evap}} c_{p,\text{H}_2\text{O},\text{liq}}} \left[\dot{m}_{\text{vap},\text{H}_2\text{O}} (\Delta H_{\text{condensate}} - \Delta H_{\text{vap},\text{H}_2\text{O}}) - h_{\text{conv}} A_{\text{evap}} (T_{\text{evap}} - T_{\text{air}}) \right. \\ & \left. + \eta_{\text{evap}} \dot{m}_{\text{HTF},\alpha} c_{p,\text{HTF}} (T_{\text{HTF},R1} - T_{\text{evap}}) - \sigma \varepsilon A_{\text{evap}} (T_{\text{evap}}^4 - T_{\text{air}}^4) \right] \end{aligned} \quad (4.44)$$

where

$$\Delta H_{\text{condensate}} = c_{p,\text{H}_2\text{O},\text{liq}} (T_{\text{exit,cond}} - T_{\text{ref}}) \quad (4.45)$$

and

$$\dot{m}_{\text{vap},\text{H}_2\text{O}} = \frac{\eta_{\text{evap}} \dot{m}_{\text{HTF},\alpha} c_{p,\text{HTF}} (T_{\text{HTF},R1} - T_{\text{evap}})}{\Delta H_{\text{vap},\text{H}_2\text{O}}}, \quad T_{\text{HTF},R1} > T_{\text{evap}} \quad (4.46)$$

Heat exchanger and steam turbine

The steam exiting the evaporator at a fixed temperature undergoes further superheating in a secondary heat exchanger using the HTF. The mathematical model description of this heat exchanger assumes that the HTF stream has a lower heat capacity than the superheated steam, thereby limiting the maximum heat transfer:

$$T_{\text{HTF},C2} = T_{\text{HTF},R1} - \frac{\eta_{\text{hex}} \dot{m}_{\text{HTF},\beta} c_{p,\text{HTF}} (T_{\text{HTF},R1} - T_{\text{evap}})}{\dot{m}_{\text{HTF},\beta} c_{p,\text{HTF}}} \quad (4.47)$$

Although the steam mass flow rate, $\dot{m}_{\text{vap},\text{H}_2\text{O}}$, is lower than that of the HTF, $\dot{m}_{\text{HTF},\beta}$, its enthalpy is significantly higher, resulting in a greater heat capacity. The superheated steam is then directed to a turbine, where it is expanded to generate work from the solar energy system. The steam temperature at the heat exchanger outlet is determined based on the

heat exchanger's efficiency:

$$T_{\text{steam,HE}} = T_{\text{evap}} + \frac{\eta_{\text{hex}} \dot{m}_{\text{HTF},\beta} c_{p,\text{HTF}} (T_{\text{HTF,R1}} - T_{\text{evap}})}{\dot{m}_{\text{vap,H}_2\text{O}} c_{p,\text{gas,H}_2\text{O}}} \quad (4.48)$$

The turbine expansion process is modeled assuming the steam exits at a fixed pressure of 5 bar. The outlet temperature is computed using the isentropic expansion relationship, which describes the entropy change of an ideal gas^[109]:

$$\Delta S = \int_{T_{\text{in}}}^{T_{\text{out}}} \frac{c_{p,\text{H}_2\text{O,gas}}}{T} dT - R \ln \frac{P_{\text{out}}}{P_{\text{in}}} = 0 \quad (4.49)$$

The power generated by the turbine is given by the following equation, which accounts for the turbine efficiency and assumes that steam enthalpy remains nearly constant with pressure:

$$W_{\text{turbine}} = \dot{m}_{\text{vap,H}_2\text{O}} \eta_{\text{turbine}} \int_{T_{\text{in}}}^{T_{\text{out}}} c_{p,\text{H}_2\text{O,gas}} dT \quad (4.50)$$

allowing the use of specific heat at constant pressure:

$$c_{p,\text{H}_2\text{O,gas}} = R (3.470 + 1.450 \times 10^{-3} T + 0.121 \times 10^5 T^{-2}) / \text{MM}_{\text{H}_2\text{O}} [\text{J}/(\text{kg K})] \quad (4.51)$$

After expansion, the steam is fully condensed at constant pressure and returned to the evaporator as saturated liquid water, maintaining a neutral mass balance within the system. Table 5.11 summarizes the key parameters and properties of the solar energy module.

Table 4.8: Parameters of the solar energy system.

Parameter	Description	Value
A_{SF}	Solar field area	5000 [m ²]
$m_{HTF,\alpha}$	Mass flow rate of HTF to evaporator	8 [kg/s]
$m_{HTF,\beta}$	Mass flow rate of HTF to heat exchanger	8 [kg/s]
$m_{HTF,\gamma}$	Mass flow rate of HTF to solar field	16 [kg/s]
ρ_{HTF}	HTF density	2900 [kg/m ³]
$c_{p,HTF}$	HTF specific heat capacity	1443 [J/kg K]
$c_{p,H_2O,liq}$	Specific heat capacity of liquid water	4200 [J/kg K]
A_{R1}	Heat transfer area of reservoir 1	20 [m ²]
A_{R2}	Heat transfer area of reservoir 2	20 [m ²]
A_{evap}	Heat transfer area of evaporator	20 [m ²]
h_{conv}	Air heat transfer coefficient	20 [W/m ² K]
σ	Stefan-Boltzmann constant	5.67×10^{-8} [J/s m ² K ⁴]
ϵ	Air emissivity	0.6
η_{evap}	Evaporator heat transfer efficiency	0.7
η_{hex}	Heat exchanger efficiency	0.7
$\eta_{turbine}$	Turbine efficiency	0.4
MM_{H_2O}	Molar mass of water	$18 \cdot 10^{-3}$ [kg/mol]
T_{ref}	Reference temperature	298.15 [K]
T_{air}	Air temperature	298.15 [K]
$T_{exit,cond}$	Exit temperature from condenser	298.15 [K]
$V_{0,R1}$	Initial volume of reservoir 1	10 [m ³]
$V_{0,R2}$	Initial volume of reservoir 2	10 [m ³]
V_{evap}	Initial volume of evaporator	2 [m ³]
$T_{0,R1}$	Initial temperature of reservoir 1	500 [K]
$T_{0,R2}$	Initial temperature of reservoir 2	400 [K]
T_{evap}	Initial temperature of evaporator	420 [K]

4.3.2 Wind Energy Harvesting

The electricity produced and transmitted from generators of wind turbines are dependent on a very extensive list of electromechanical design factors: the shape, diameter, length, height and number of the blades, the building material of the blades and rotor/shaft themselves, the arrangement of the gear box, the number and positioning of the magnetic poles, the density of the armature coils in the generator, and other derivative phenomena (electromag-

netic inductive effects in the transformer, intensity of the magnetic fluxes, frequency of the alternating currents, etc). The physical description of those factors lay very much outside the scope of this chapter, therefore we employ a convenient correlation provided by Allman et al. [86,87] (Equation 5.65), which directly relates both the blades' height and a forecasted wind velocity ($v_{w,f}$) with output power (W_{wind}) from an indiscriminate wind turbine. We assume that wind velocity (v_w) is a normally distributed random variable that changes at each time step with a constant mean and standard deviation. Typical wind turbines are very large and generate power in the order of hundreds of kilowatts or even megawatts; however, we model a turbine of much smaller size and capacity, compatible with a modular site.

$$v_w = \mathcal{N}(\mu_{\text{wind}}, \sigma_{\text{wind}}^2) \quad (4.52)$$

$$v_{w,f}(t) = v_w(t) \left(\frac{H}{10 [\text{m}]} \right)^{\frac{1}{7}}; \quad (4.53)$$

$$\begin{aligned} & \text{if } v_{w,f}(t) < v_{\text{cut in}}, W_{\text{wind}} = 0 \\ & \text{if } v_{\text{cut in}} < v_{w,f} < v_{\text{cut off}}, W_{\text{wind}} = W_{\text{rated}} \left(\frac{v_{w,f}^3 - v_{\text{cut in}}^3}{v_{\text{rated}}^3 - v_{\text{cut in}}^3} \right) \\ & \text{if } v_{\text{rated}} < v_{w,f} < v_{\text{cut off}}, W_{\text{wind}} = W_{\text{rated}} \\ & \text{if } v_{w,f}(t) > v_{\text{cut off}}, W_{\text{wind}} = 0 \end{aligned} \quad (4.54)$$

Table 4.9: Parameters of the wind energy system.

Parameter	Description	Value
μ_{wind}	mean wind velocity	varied [m/s]
σ_{wind}	deviation of the wind velocity	varied [m/s]
H	height of placement of the turbine blades	10 [m]
$v_{\text{cut in}}$	cut in wind velocity	1 [m/s]
$v_{\text{cut off}}$	cut off wind velocity	5 [m/s]
v_{rated}	rated wind velocity	1.5 [m/s]
W_{rated}	rated wind power capacity	2000 [W]

4.4 System Dynamics Regulation with Model Predictive Control

This study addresses the regulation problem of the integrated H_2 / NH_3 production module using model predictive control (MPC). MPC is a constrained, optimization-based control strategy that utilizes a dynamic model of the process to predict future output behavior over a specified prediction horizon^[71,72]. In regulation, MPC computes a sequence of future control inputs that minimize an objective function, typically defined as deviations between predicted process outputs and desired setpoints. At each time step k , the controller evaluates the system's current state and solves an optimization problem by varying the manipulated inputs to minimize the objective function. This yields an optimal input trajectory over the prediction horizon of length P , spanning time steps $k+1$ to $k+P$. The first control input from the optimized sequence is implemented, after which the horizon shifts forward by a one-time step (a process known as receding horizon control). The controller then updates the system state at $k + 1$, re-evaluates the setpoints, and repeats the optimization procedure. This iterative process enables MPC to continuously regulate the system in real-time, accounting for model predictions and updated measurements at each step.

In this work, the objective function is formulated as the weighted sum of the squared deviations of the controlled state and manipulated input variables from their respective reference values. These deviations are expressed in normalized form as follows:

$$x'_{i,j} = \frac{x_{i,j} - x_{ref,j}}{x_{ref,j}}, \quad u'_{i,j} = \frac{u_{i,j} - u_{ref,j}}{u_{ref,j}} \quad (4.55)$$

where $x'_{i,j}$ and $u'_{i,j}$ represent the relative deviations of the state and input variables, respectively. The MPC's objective is to minimize the cumulative quadratic cost associated with these deviations over a prediction horizon P , as defined in the following equation:

$$\min \sum_{i=k}^{i=k+P} \sum_{j=1}^{j=N_{output}} \|x'_{i,j}\|_{\mathbf{R}}^2 + \sum_{i=k}^{i=k+P} \sum_{j=1}^{j=N_{input}} \|u'_{i,j}\|_{\mathbf{Q}}^2$$

$$\begin{aligned}
\text{subjected to} \quad & W_{\text{green}} = W_{\text{solar}} + W_{\text{wind}} \\
& Q_{\text{green,electro}} = 0.1 W_{\text{green}} \\
& W_{\text{green,N}_2,\text{comp}} = 0.3 W_{\text{green}} \\
& W_{\text{green,H}_2,\text{comp}} = 0.6 W_{\text{green}}
\end{aligned} \tag{4.56}$$

The cost terms are weighted by positive semi-definite matrices $\mathbf{R}$ and $\mathbf{Q}$:

$$\begin{aligned}
||\mathbf{x}'_{i,j}||_{\mathbf{R}}^2 &= (\mathbf{x}'_{i,j})^T \mathbf{R} (\mathbf{x}'_{i,j}) \\
||\mathbf{u}'_{i,j}||_{\mathbf{Q}}^2 &= (\mathbf{u}'_{i,j})^T \mathbf{Q} (\mathbf{u}'_{i,j})
\end{aligned} \tag{4.57}$$

This MPC formulation achieves the regulation objective by penalizing deviations from the desired set points, driving the system toward the reference trajectories by minimizing the normalized quadratic costs.

The manipulated inputs include the energy rates required by the process, which can be supplied by the renewable energy module, as described in the modeling section, or purchased from external sources. Table 4.10 summarizes the selected manipulated inputs, their reference values, and the corresponding open-loop steady-state values of the controlled outputs. The manipulated inputs were bounded within linear constraints to reflect operational limitations: the external heat supplied to the electrolyzer, $Q_{\text{ext,electro,ref}}$, is constrained between 0 and 10,000 W, the electrical power to the nitrogen compressor, $W_{\text{ext,N}_2,\text{comp,ref}}$, range from 0 to 30,000 W, and the electrical power to the hydrogen compressor, $W_{\text{ext,H}_2,\text{comp,ref}}$, is limited between 0 and 50,000 W.

The MPC is configured with a time step of 30 seconds and a prediction horizon of three time steps. The weighting matrices $\mathbf{R}$ and $\mathbf{Q}$ are defined as positive, semi-definite, and diagonal. The underlying constrained dynamic optimization problem is solved using an interior-point algorithm. The inputs are initialized in the closed-loop simulation with a deviation of 30% from their respective reference set points. The control performance of the chemical module is evaluated under constant wind speed fluctuations, modeled as a normal

distribution with a mean of 2 m/s and a standard deviation of 0.5 m/s. All simulations were conducted using MATLAB.

Table 4.10: Steady state values of the input and output variables.

Variable	Description	Steady State Value
$Q_{\text{ext,electro,ref}}$	External heat supplied to the electrolyzer	7500 [W]
$W_{\text{ext,N}_2,\text{comp,ref}}$	Electrical power to the nitrogen compressor	20000 [W]
$W_{\text{ext,H}_2,\text{comp,ref}}$	Electrical power to the hydrogen compressor	50000 [W]
$c_{\text{H}_2,\text{outlet,electro}}$	Hydrogen concentration at the electrolyzer outlet	6.93 [mol/m ³]
$c_{\text{NH}_3,\text{outlet,reactor}}$	Ammonia concentration at the reactor outlet	156.11 [mol/m ³]
$T_{\text{outlet,reactor}}$	Reactor outlet temperature	697.38 [K]

4.5 Results and Discussion

4.5.1 Dynamics of the Renewable Energy Module

The spatial derivatives of the 1D partial differential equations that describe the electrolyzer and ammonia synthesis modules are first discretized by the finite difference method (FDM). The resulting systems of ordinary differential equations, originating from each module, are then combined with the ODEs of the renewable energy module. Explicit Euler strategies are employed to solve the coupled time-dependent ODE system and obtain open-loop dynamics using the method of lines in MATLAB.

Figures 4.4 and 4.5 show the effect of air temperature on the temperature of the reservoirs and the combined renewable energy generated, respectively. Here, the model is solved from 0 to 100,000 seconds to capture periods of sunlight presence and absence. A global verification of the power trends from this system allows the classification of 3 essential periods: (1) low power generation (~ 6000 W), when only the wind is the energy-provider ($t < \sim 6$ h and $t > \sim 21$ h); (2) higher power generation (~ 50000 W), when both solar and wind power modules are active (~ 9 h $< t < \sim 18$ h); (3) transition periods, when the solar power output is sharply increasing or decreasing (~ 6 h $< t < \sim 9$ h and $\sim 18 < t < \sim 21$ h).

Even though convection and radiation through air are considered in the formulation as

heat loss terms, their dynamic contributions are negligible during the day, as the reservoir temperatures are practically the same for 3 different external air temperatures tested (248, 273, and 298 K). However, their effects become noticeable during periods of sunlight absence; with an external air temperature of 248 K, the temperature of the reservoir decreases at a faster rate. As expected, the temperature of the water evaporator must not surpass the boiling temperature of the water; any excess heat transferred by the HTF produces steam that propels the turbine. The peaks on the trends are clearly due to the period of higher solar incidence, while the noise is due to fluctuations in air velocity that directly affect the power generation from the wind turbine.

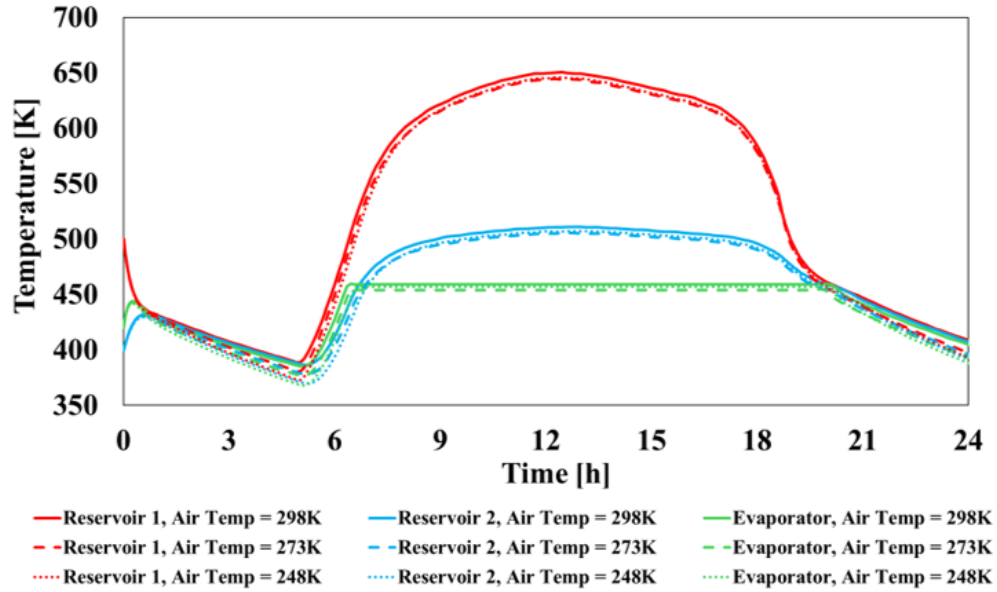


Figure 4.4: Effect of the air temperature on the temperature of the reservoirs, for a mean air velocity of 2 m/s with normal deviation of 0.05 m/s.

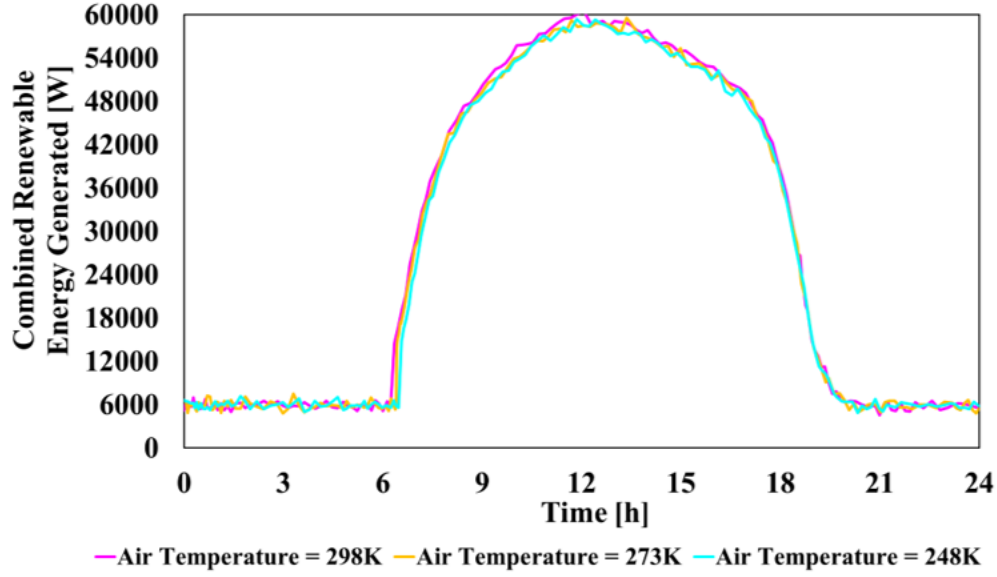


Figure 4.5: Effect of the air temperature on the total energy generated, for a mean air velocity of 2 m/s with normal deviation of 0.05 m/s.

Figures 4.6 and 4.7 display the effect of solar incidence variations in terms of percentage fractions of the value given by the empirical correlation of Equation 5.48. In other words, this can be understood as a pseudo-effect of cloudiness, assuming that Equation 5.48 provides the solar incidence of a regular sunny day. It is verified that solar incidence has a significant impact on the dynamics of the reservoirs; if it is less than 20% of that reported in Equation 5.48 (blue curve in Figure 4.7), the solar module will generate little amounts of steam (and consequently energy generation), despite the evaporator reaching the boiling temperature. Finally, Figures 4.8 and 4.9 show that increases in the mean and normal deviation of the air velocity will naturally cause residual and noisy increases in the combined generated power, although the wind turbine model considers a shutdown for wind velocities higher than the cutoff velocity.

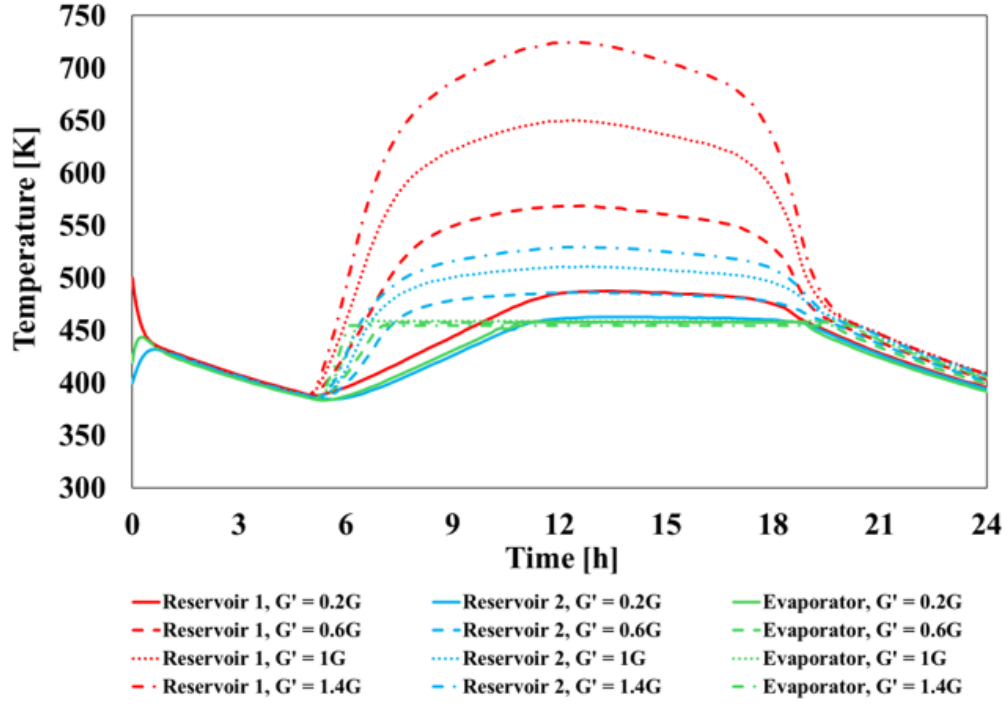


Figure 4.6: Effect of a varying solar irradiance on the temperature of the reservoirs, for a mean air velocity of 2 m/s with normal deviation of 0.05 m/s.

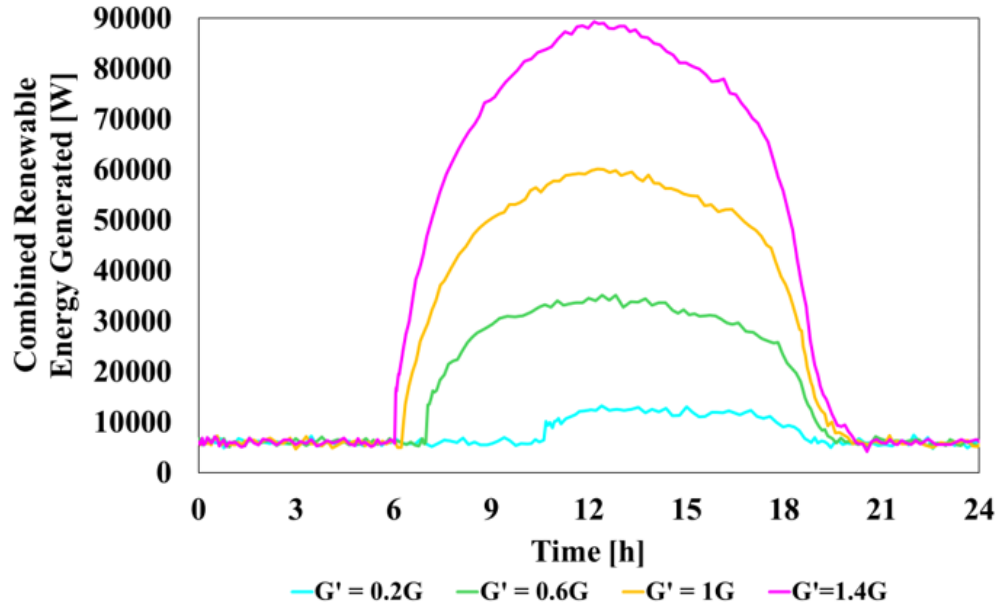


Figure 4.7: Effect of a varying solar irradiance on the total energy generated, for a mean air velocity of 2 m/s with normal deviation of 0.05 m/s.

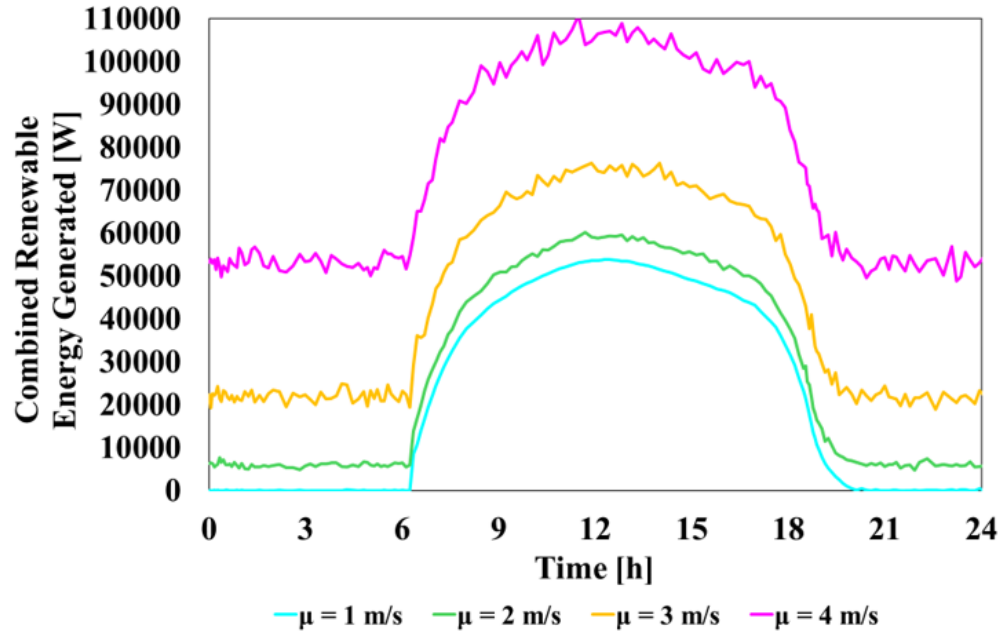


Figure 4.8: Effect of the mean air velocity on the temperature of the reservoirs, for a normal deviation of 0.05 m/s.

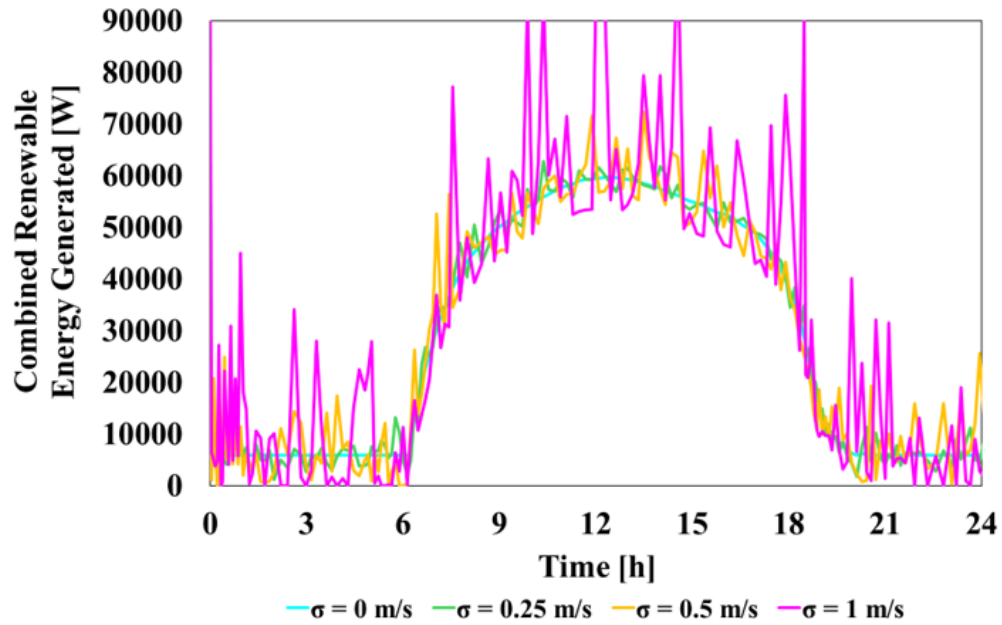


Figure 4.9: Effect of the normal deviation of the air velocity on the total energy generated, for a mean air velocity of 2 m/s.

4.5.2 Open-Loop Dynamic Response of the Chemical Production Module

Figure 4.10 represents the start-up dynamic behavior of outlet variables of the electrolyzer and reactor, when the solar irradiance is maximum for the basis correlation given by^[111], the mean wind velocity of 2 m/s, and its standard deviation of 0.5 m/s. External energy is not introduced in those cases. The first observation is the existence of a time scale separation between the dynamics of the chemical and those of the green energy module; the variables of the former achieve steady state much faster, in the scale of hundreds of seconds, while the dynamics of the latter follow, of course, a scale of hours. The overall response of the chemical module is primarily determined by the reactor, which exhibits slower dynamics than the electrolyzer; however, the ammonia synthesis is limited by the amount of hydrogen produced by the electrolyzer. Nitrogen is expectedly to be responsible for establishing a high pressure in the reactor; in this specific operation, it reaches approximately 155.89 bar at the outlet, according to the ideal gas law. Catalytic ammonia synthesis typically exhibits low productivity rates at pressures below 50 bar.

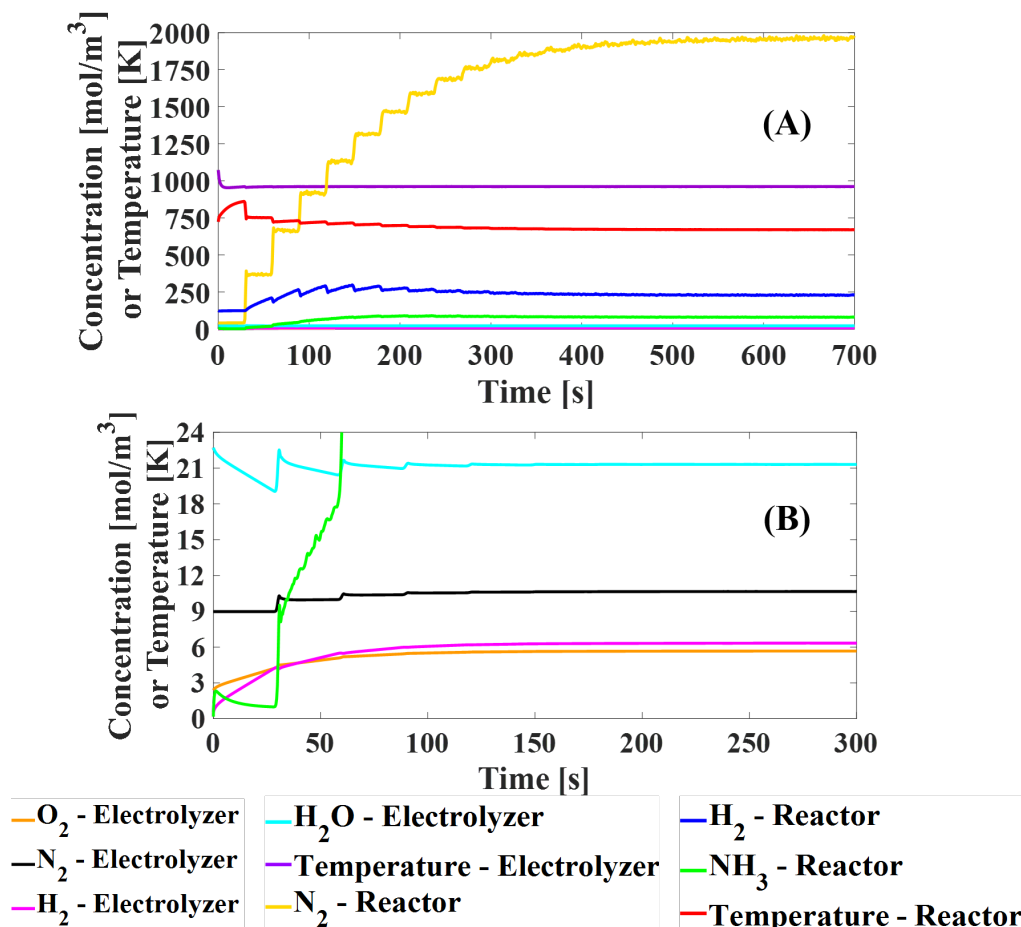


Figure 4.10: Start-up dynamics of the outlet variables of the chemical module subjected to the instantaneous energy available from the green energy module when solar irradiance is maximum.

Another notable feature in the dynamics is the presence of significant oscillatory, step-like behavior in the variables due to the degree of stream recycling adopted in the operation. For this case, 50 % of the outlet streams' flow rates are redirected to the inlets of both units, respectively. The period of oscillation is equivalent to the residence time of the gas, as it axially percolates the units. Figure 4.11 illustrates the dynamics of the system when the recycle ratio is zero, for various power levels applied. The oscillatory dynamics previously observed are not present in this case, and the dynamics are significantly faster. A consequence of stream recycling is a pressure buildup, which favors ammonia synthesis by increasing the concentration of reactants. A temperature decrease is also noticed in comparison to the no-recycle operation. Since ammonia synthesis can be dangerously exothermic and thermo-

dynamically unfavored at higher temperatures, recycling is a cost-effective and advantageous way to self-regulate the temperature in the reactor. The fixed outlet temperatures obtained from the heat exchangers also help stabilize the temperature in the units quickly. Ojo and Camarda^[115] also observed variability and oscillatory patterns in a larger-scale and integrated hydrogen-ammonia plant when step changes in energy consumption were induced. Nevertheless, the dynamics were much slower.

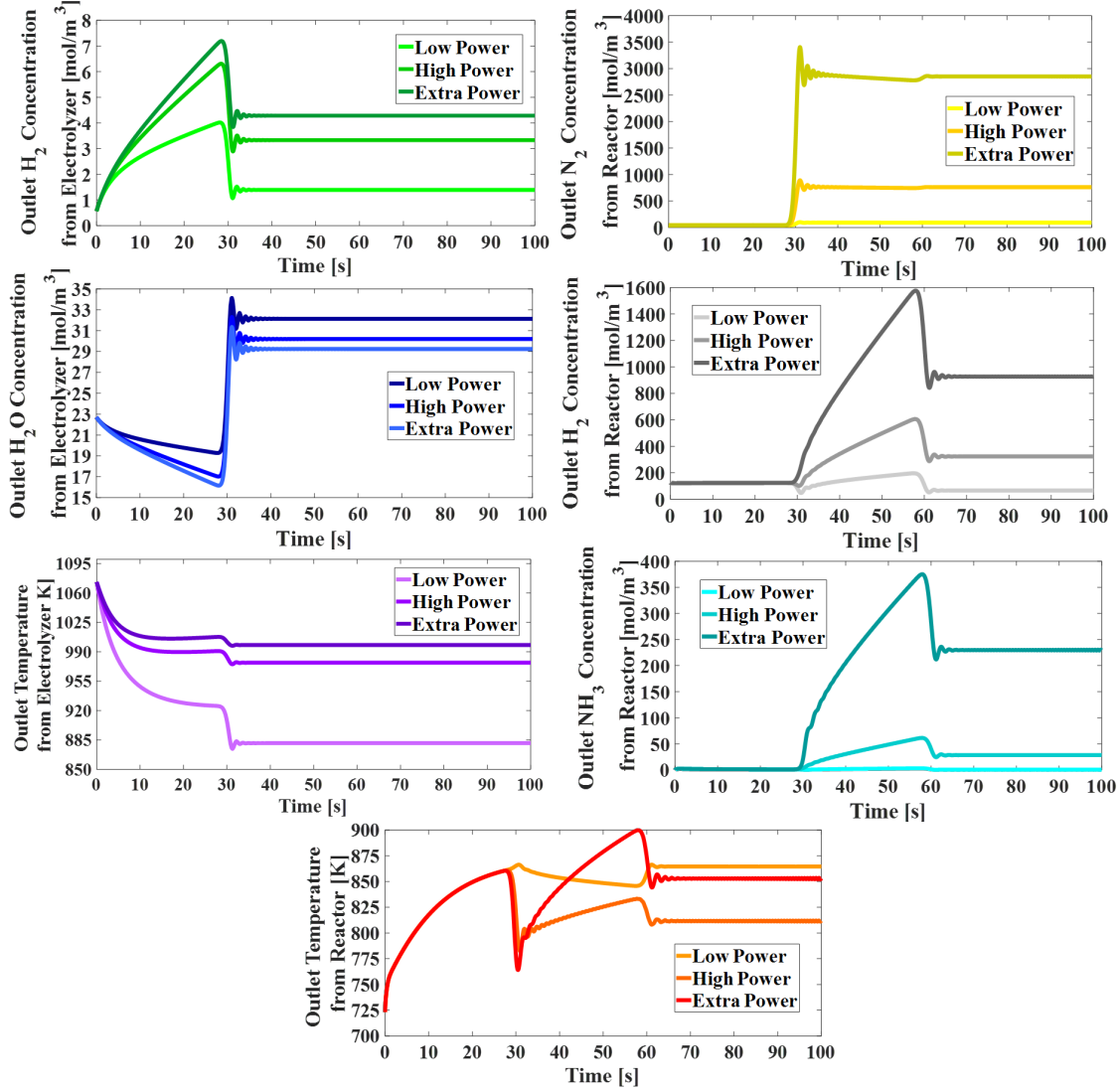


Figure 4.11: Dynamic evolution of the outlet variables when outlet streams are not recycled. In the legends, "low", "high" and "extra power" refer to the following set of values assigned to $W_{H_2,comp}$, $W_{N_2,comp}$ and $Q_{electro}$, respectively, in Watts: [42000, 7000, 4500], [57000, 22000, 10000], [82000, 37000, 12000].

Figure 4.12 points out the importance of compressing the reactants. Given that the model

does not explicitly account for the storage of pressurized hydrogen or nitrogen, nor the direct mixing of gas streams in a single pipe, it is observed that, even with 50% recycling in the reactor, the outlet ammonia concentration would barely reach 2 mol/m^3 at steady state without compression. In comparison with the previous case, that is an approximate 98.6% drop in the outlet ammonia concentration. It is also noted that the absence of compression slows down the dynamics of the reactor variables, particularly the concentrations of nitrogen and ammonia. Compression also has a secondary effect on concentrations through temperature. Since compression simultaneously increases pressure and temperature, the latter needs to be regulated by the heat exchanger before entering the reactor. As a result, the reactant concentrations are significantly altered by adjusting the temperature. Verleysen et al.^[81] conducted a global sensitivity analysis, which indicated that the reactor inlet temperature and hydrogen/nitrogen concentration ratio are the most impactful variables on performance. The study also highlighted the requirement for exceptional control over inlet temperatures. Quintero-Masselski et al.^[116] conducted a sensitivity analysis on the effect of the number of compressors operating sequentially at different pressures and stages, finding that it does not impact hydrogen and nitrogen conversion. However, it does affect investment, maintenance, and electricity consumption costs. In consonance with our design, they concluded that two compressors yielded the optimal structure.

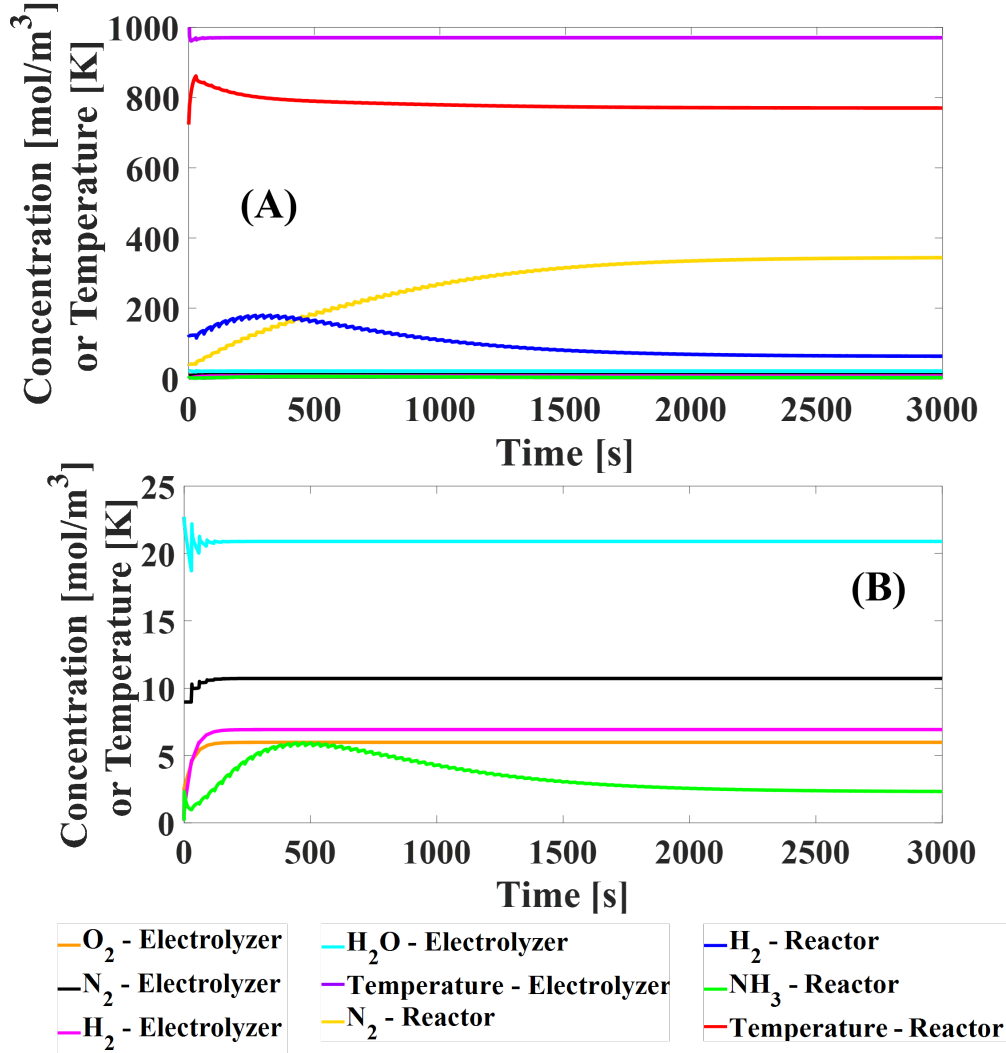


Figure 4.12: Dynamic evolution of outlet variables of the chemical-energy system under the input conditions shown in Table 4.10 without N₂ and H₂ compression.

Due to the time scale disparity and the high nonlinearity of the models, simulating a direct open-loop integration between the modules for more than a few thousand seconds proved extremely computationally demanding. The strategy for assessing complete dynamic trends of outlet concentrations of hydrogen and ammonia over a whole day was to selectively provide the nominal amount of green available at each hour to the chemical module and solve it individually until it attained a steady state. In this approach, daily pseudo-transient production curves were constructed for a gas velocity of 0.05 and 0.1 m/s, as shown in Figure 4.13 for the outlet hydrogen and ammonia leaving the electrolyzer and reactor, respectively. However, information about the start-ups and intermediate dynamics was unfortunately lost.

Figure 4.13 quantitatively reveals the expected higher production during the middle of the day. Curiously, inverse trends are observed for the outlet temperatures of the units when production is higher.

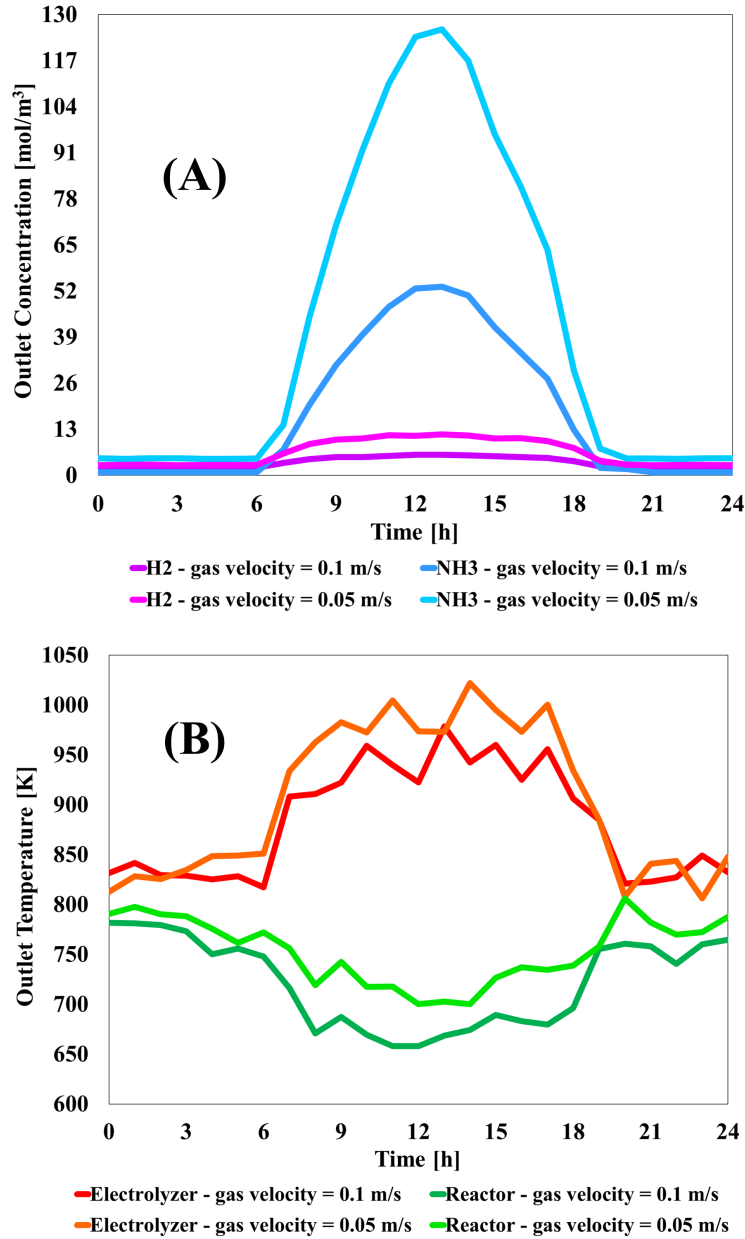


Figure 4.13: Dynamic evolutions of (A) outlet concentrations of hydrogen and ammonia leaving the electrolyzer and reactor, respectively, and (B) outlet temperatures of streams leaving the electrolyzer and reactor under the condition of pseudo-transient integration between the modules over a day.

4.5.3 Closed-Loop Model Predictive Control

The initial investigation with MPC shows that a single central controller can quickly regulate the chemical module when it operates independently from the dynamics of the renewable/green energy; in other words, either when there is no green energy available or there is a significant excess of green energy, such that the total energies required by the chemical units are always lower than the total green energy available. The diagonal elements of the weighting matrices P and Q were set to 10 and 5, respectively, and the minimization algorithm employed was an interior-point method. Figure 4.14 displays the control actions on the inputs, Figure 4.15 presents the closed-loop dynamics of the controlled deviational variables of the electrolyzer, and Figure 4.16 those of the reactor. The controller performs very satisfactorily, leading the states to the desired zero deviation from the set points within a few minutes, with slight oscillations, due to the natural dynamics of the system. The inputs follow a reasonable trajectory and quickly stabilize.

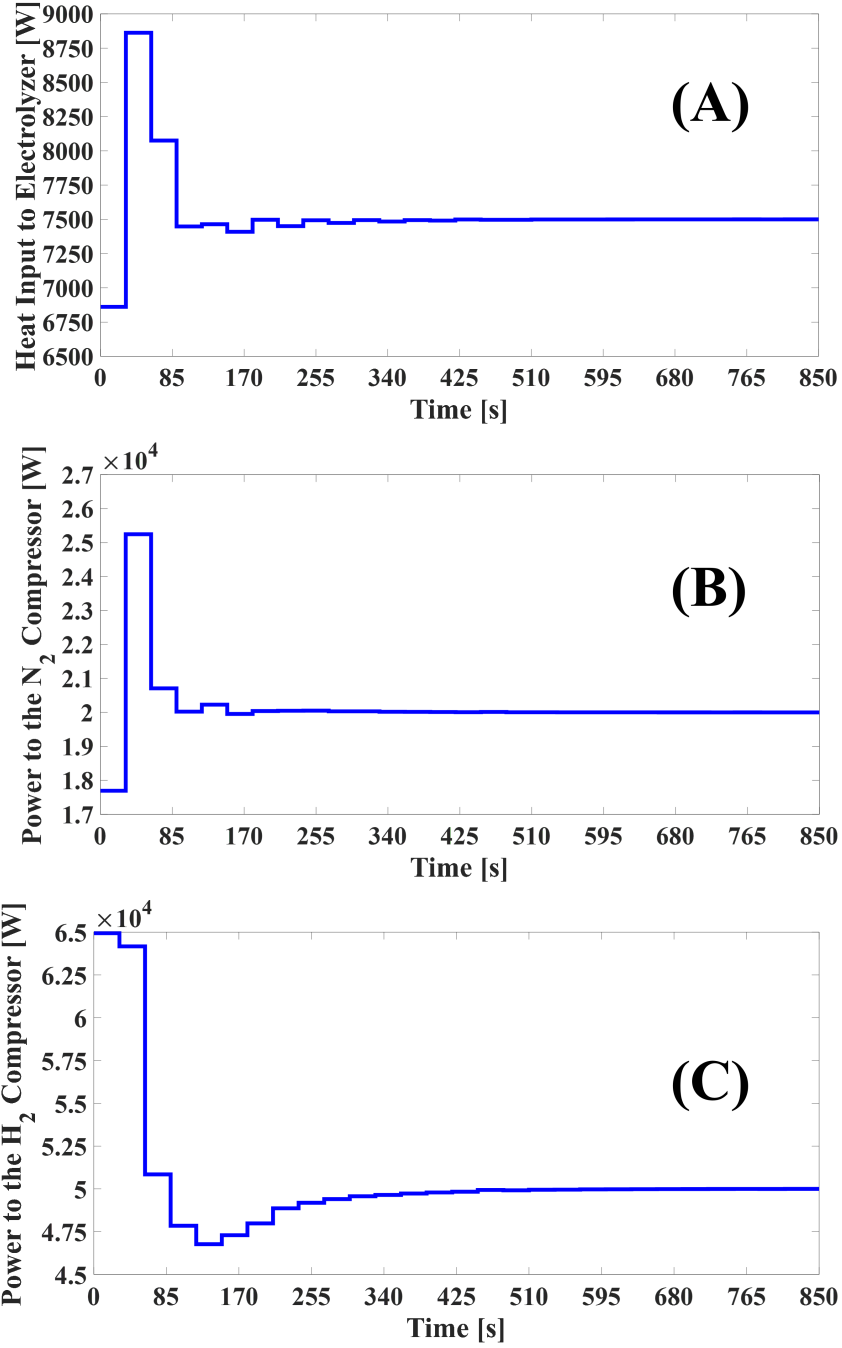


Figure 4.14: Input changes in the regulation problem under the situation of no integration between the chemical and renewable energy modules. $P = \text{diagonal}[10 \ 10 \ 10 \ 10]$, $Q = \text{diagonal}[5 \ 5 \ 5 \ 5]$; minimization algorithm: interior point.

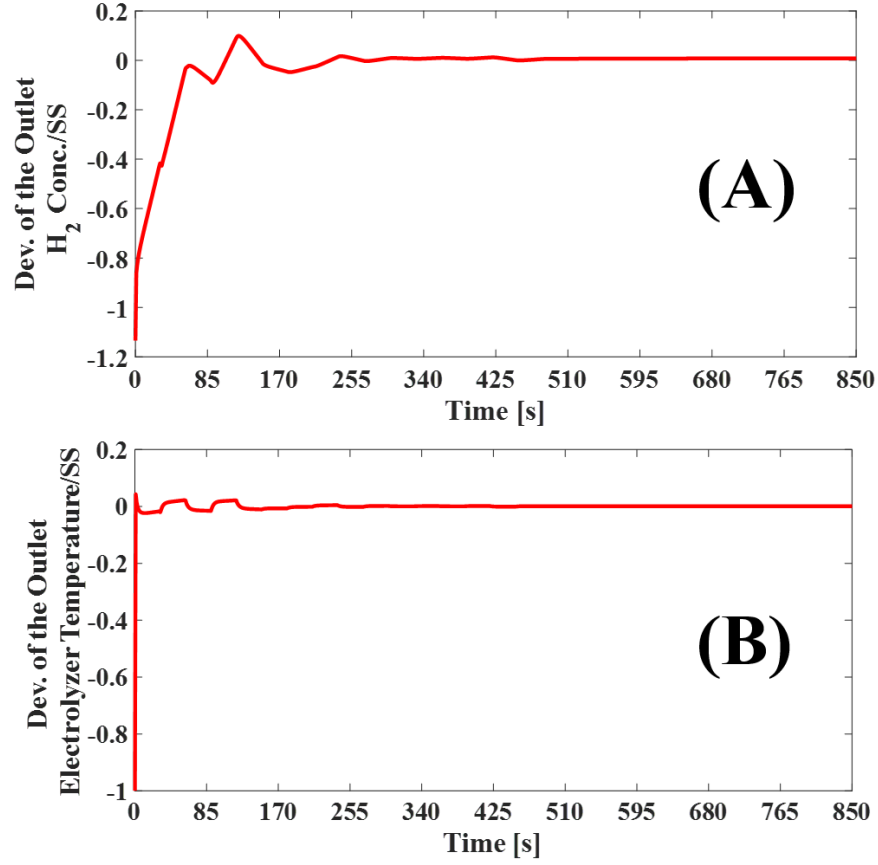


Figure 4.15: Closed-loop dynamics of the deviational outlet hydrogen concentration (A) and temperature (B) from the electrolyzer, under the situation of no integration between the chemical and renewable energy modules. $P = \text{diagonal}[10 \ 10 \ 10 \ 10]$, $Q = \text{diagonal}[5 \ 5 \ 5 \ 5]$; minimization algorithm: interior point.

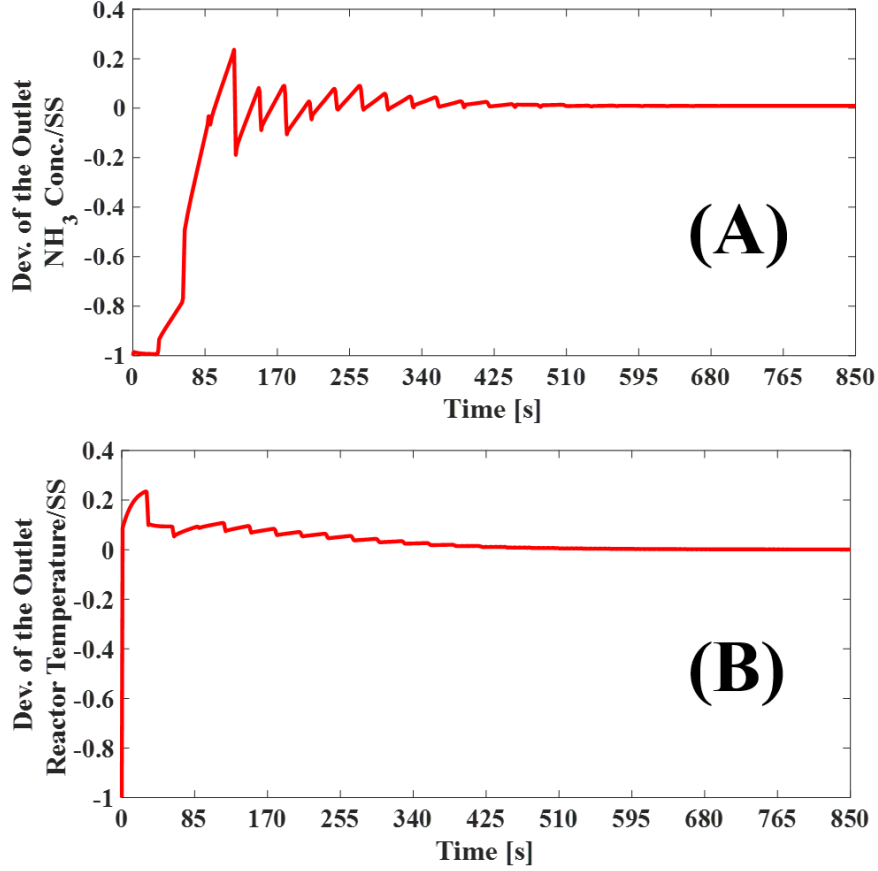


Figure 4.16: Closed-loop dynamics of the deviational outlet ammonia concentration (A) and temperature (B) from the reactor, under the situation of no integration between the chemical and renewable energy modules. $P = \text{diagonal}[10 \ 10 \ 10 \ 10]$, $Q = \text{diagonal}[5 \ 5 \ 5 \ 5]$; minimization algorithm: interior point.

It is noteworthy to emphasize that physically descriptive control studies of similar systems were rarely found in the literature for a compatible comparison. In a notable recent exception, Kong et al.^[92] implemented a nonlinear model predictive control for a multi-bed, inter-staged cooling ammonia synthesis system. Although the authors did not consider direct dynamic integration with water electrolysis or green energy sources, they evaluated the performance of the MPC controller when variations in the load and random fluctuations in the reaction rate were introduced. By manipulating the gas phase output flow rate of the separator, the recycle molar flow rate, and the liquid phase output flow rate, the controller demonstrated stability and flexibility, allowing the states to reach their desired set points within a few minutes. Sun et al.^[91] also developed a comprehensive nonlinear model for green production of hydrogen-ammonia and explored start-up dynamics (by slowly changing inlet variables)

and the effects of step fluctuations in electrical currents. They also considered buffer tanks and reactor recycling. However, they did not observe oscillations in outlet variables such as the ones we report. Buffering dampened the overall system dynamics.

On the other hand, they consistently demonstrate that the water electrolysis subsystem responds more quickly than the reactor. By employing PID controllers, they successfully regulated outlet temperatures and mole fractions. The drawbacks of PID control compared to MPC are the lack of a systematic method for dealing with process constraints and objectives, and the inability to optimize outputs without set points for the inputs. Targeting temperatures with MPC, Zhang et al.^[117] demonstrated desirable closed-loop performance and avoidance of temperature extremities under suitable control design in a purification section of an ammonia process network. Unfortunately, those works do not account for the dynamics of renewable energy generation.

Given the significant time scale separation between the dynamics of the two modules, we investigated the capability of the MPC controller to regulate the chemical module in 3 different periods of instantaneous availability of green energy, as shown in Figure 4.17. Period 1 characterizes a transition period in which the temperatures in the thermal reservoirs are increasing, and so is steam production. Period 2 relates to a period of high green energy availability during the day. Period 3 reflects a low availability of green energy in the evening and night. The fluctuations are again due to normal deviations of the wind velocity.

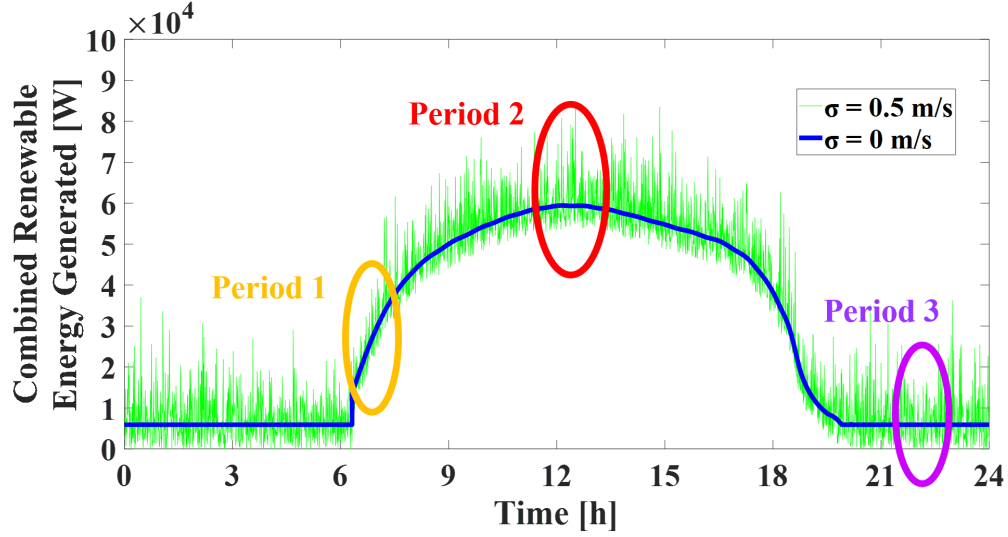


Figure 4.17: Dynamics of the green energy generated for a mean wind velocity of 2 m/s and standard deviations of 0 and 0.5 m/s.

Regulation attempts failed when the optimizer received direct dynamic information from both integrated modules in closed-loop simulations. The conflicting objectives between regulating the states and minimizing the extra energy inputs associated with disturbances from the green energy module led the controller to struggle, particularly in controlling the ammonia concentration leaving the reactor. Even though a much higher weight was consistently placed on the respective element of the P matrix for this variable (implying higher penalty costs in its non-zero deviations), satisfactory performance was not attained. The optimization exhibited significant unresponsiveness (null control moves) to rapid random variations in the renewable power. It became imperative to propose another efficient strategy for the long-term regulation of the chemical module. The plan to address the temporal disparities and numerical issues was to provide the dynamics of the green energy module as supervisory predictive information to the controller after the optimization step is completed for an independent regulation problem, as described earlier. The controller then subtracted the expected or predicted power obtained from the green energy module before applying the control moves to the chemical module. The closed-loop dynamics of the controlled states were exactly as expected from typical regulation, as the controller readjusted the manipulated inputs based on the outputs from the green energy module.

Figure 4.18 displays the control actions on the chosen inputs for period 1, under the

situations of no fluctuations (plots A, B, and C) and normal fluctuations (D, E, and F) in the wind velocity, according to Figure 4.17. The most notable observation is the decline in the amount of extra energy applied to the chemical module as green energy availability increases. In the presence of the usual fluctuations, the descending trend of the additional energy requirement is somewhat masked, but can still be perceived. The adjustments are relatively smooth during the control horizon. Figure 4.19 shows the input moves for period 2. Compared to the first regulation case, significantly less extra power must be distributed to the chemical module to maintain the same operation. Finally, Figure 4.20 presents the input moves during periods of low green energy availability (period 3). The optimal energy requirements are still lower than those in the case of basis regulation.

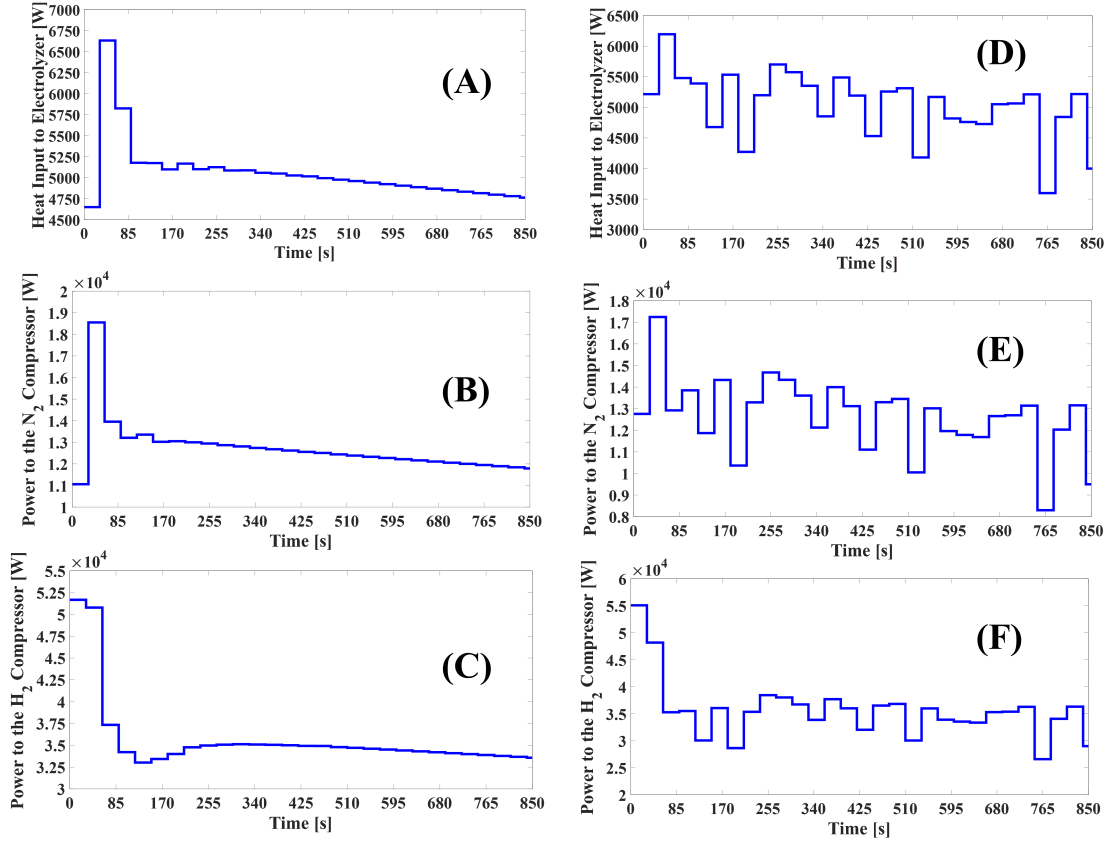


Figure 4.18: Input changes in the regulation problem during a transition period (period 1) of the green energy availability, under a situation of no deviation (A, B, and C) and a normal deviation of 0.5 m/s (D, E, F) in the wind velocity.

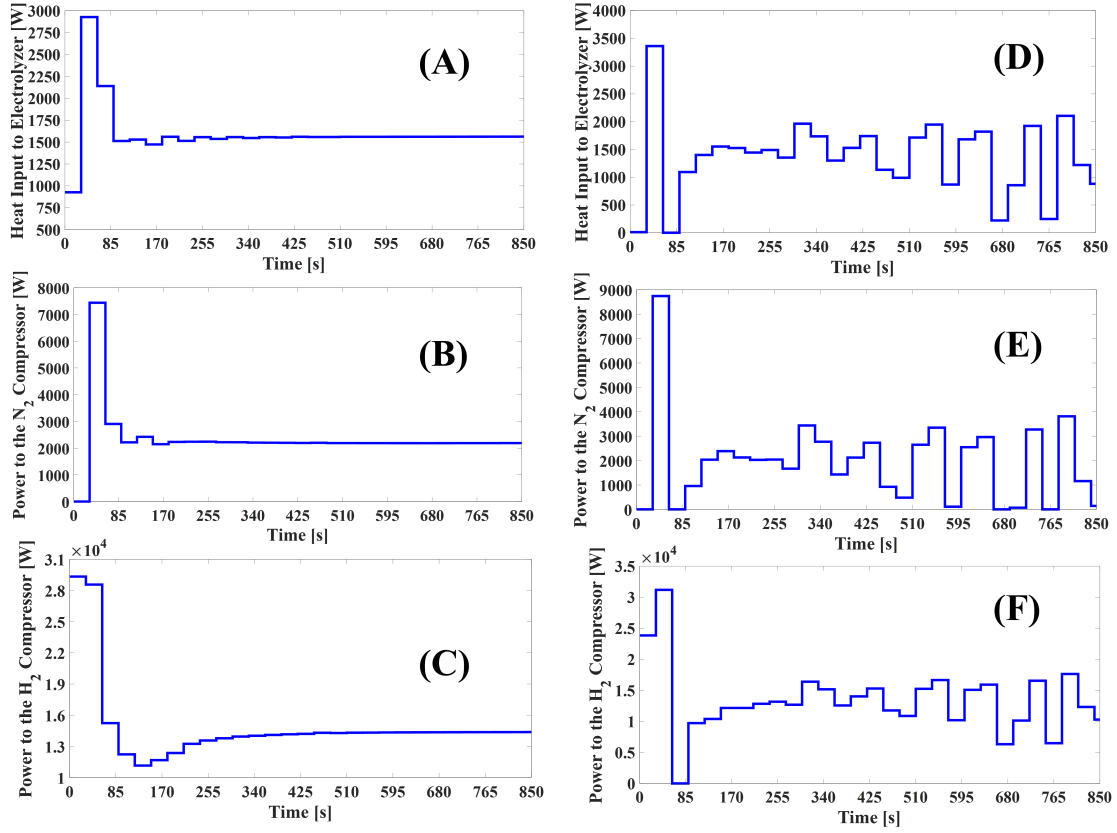


Figure 4.19: Input changes in the regulation problem during a period of high green energy availability (period 2), under a situation of no deviation (A, B, and C) and a normal deviation of 0.5 m/s (D, E, F) in the wind velocity.

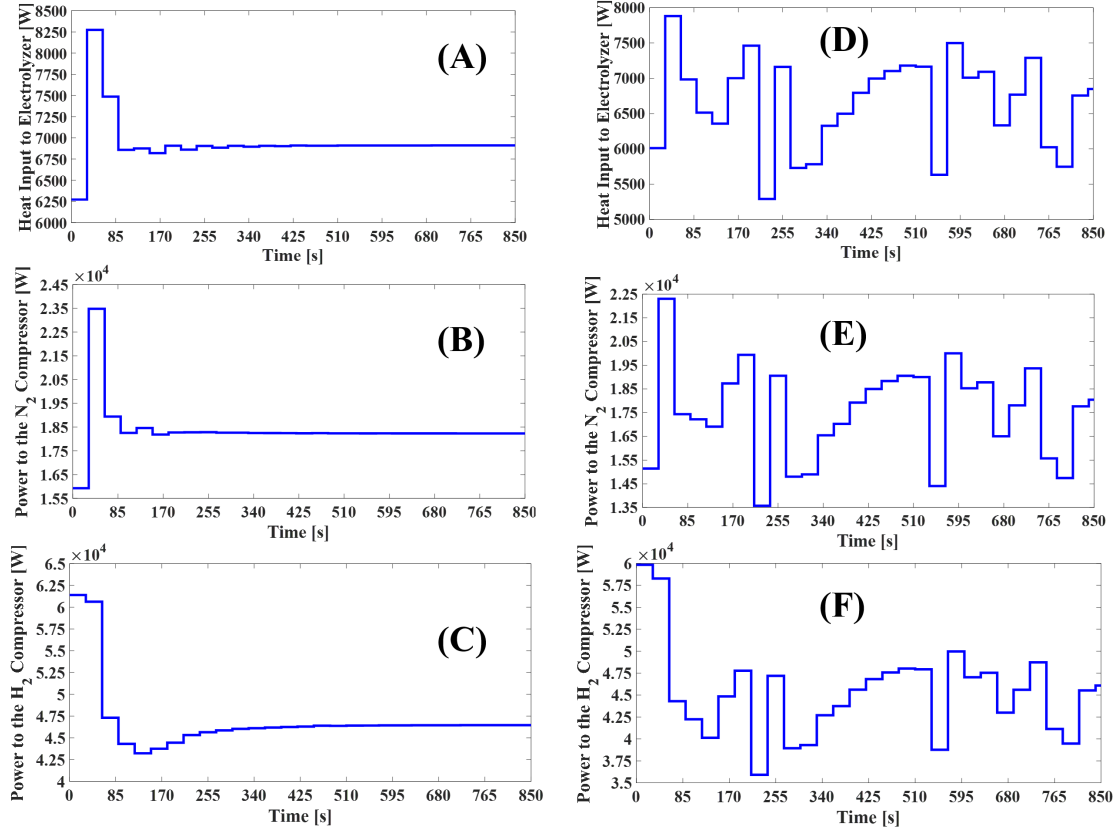


Figure 4.20: Input changes in the regulation problem during a period of low green energy availability (period 3), under a situation of no deviation (A, B, and C) and a normal deviation of 0.5 m/s (D, E, F) in the wind velocity.

4.6 Conclusion

This work proposed and modeled a modular and integrated chemical system for hydrogen and ammonia production with cleaner technologies and sustainable energy. By coupling a water electrolyzer and an ammonia synthesis reactor, we investigated the physical dynamics and energetic demands of the system, verifying that its components are operable with a total power of tens of kilowatts. The chemical system can be paralleled by a green energy-generating system that harnesses renewable energy from the sun and wind through thermal reservoirs and turbines. The green energy module exhibits much slower dynamics, which can partially sustain the chemical module during the day. Depending on the sizing of the solar and wind fields, reasonably sufficient amounts of renewable energy can be harvested.

Economic aspects of both systems were not considered. The regulation of the chemical system was addressed using model predictive control to optimally determine additional energy inputs, enabling the chemical module to achieve a desired set point during periods reflecting the intermittent availability of green energy. By utilizing the dynamics of green energy as a supervisory layer in the controller, it successfully adjusts its movements to stabilize the chemical module. As a last remark, we advise that the combination of the methods of lines with finite difference, employed to solve the PDEs of the model, is not computationally efficient in the context of MPC for this problem. Finite element methods, such as Galerkin projection, are cited in the literature as better and faster alternatives.

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Chapter 5

Resilient Moving Horizon

Optimization of Integrated Green Chemical-Energy Communities under Supply Chain Disruptions

5.1 Introduction

Amid the urgency of climate change and the push for sustainable industrial practices, green hydrogen and ammonia have emerged as key enablers in future multifunctional networks, particularly in the agricultural and power sectors. Due to their complementary thermochemical properties, both compounds serve as valuable chemical commodities and effective energy carriers, paving the way for more integrated and cleaner energy-chemical systems. In such systems, hydrogen is produced via water electrolysis powered by renewable energy sources such as wind or solar. Despite challenges in hydrogen storage and transport—primarily due to its low volumetric energy density—it can be utilized directly in fuel cells or power plants for electricity generation. Ammonia, synthesized from hydrogen and nitrogen, offers a higher energy density and can be stored and transported more readily in liquid form under moderate

pressure. This makes it a practical medium for fuel-to-electricity interconversion. The literature broadly supports the idea that closer integration between producers and consumers in chemical-energy networks enhances resilience to renewable energy intermittency, market fluctuations, feedstock variability, process uncertainties, and supply chain disruptions^[1,2]. Such integration, however, hinges on the availability of robust infrastructure, including pipelines, power lines, and localized production and storage. Modular and distributed chemical systems have been proposed as enabling technologies, offering lower installation and operating costs, as well as enhanced flexibility and adaptability^[1,3].

Several studies have investigated the design and optimization of supply chains for sustainable agriculture and energy systems. Notably, the works of Allman and Daoutidis^[4–6] and Palys et al.^[7–9] have developed supply chain frameworks that integrate wind-powered hydrogen-ammonia plants. Those studies optimized plant locations and ammonia transport logistics to minimize annualized supply chain costs over extended horizons, while incorporating environmental goals, such as reducing CO₂ emissions. Assumptions included fixed production rates and market prices. In a complementary economic assessment, Zhao et al.^[10] evaluated the optimal sizing and deployment of green ammonia production, identifying wind as the most favorable renewable energy source and noting the importance of declining electricity and electrolyzer costs in reducing hydrogen prices. Ong et al.^[11] extended this analysis with a process model covering air separation, NH₃ synthesis, and H₂ recovery from NH₃ decomposition, coupled with economic and CO₂ emission assessments. Peng et al.^[12] developed a stochastic, optimization-based superstructure that considers different process synthesis options for a concentrating solar power plant, which exhibits low (seasonal) and high-frequency (daily) variability. The overall goal was to minimize the levelized cost of electricity and identify the best design. Zhang et al.^[13] propose a multiscale mixed-integer linear programming model that integrates renewable-based fuels and power generation processes into a holistic superstructure, emphasizing the operational constraints and temporal variability of the renewable resources.

Efforts to integrate ammonia production with power systems have also advanced. Edmonds et al.^[14] proposed a coordinated mixed-integer linear programming (MILP) model for

a community microgrid combining renewable generation with a green ammonia plant. The model incorporated dynamic electricity pricing (DLMP), variable ammonia production capacity, and plant operational modes, showing mutual benefits between ammonia economics and grid operations. Ramanujam et al.^[3] optimized microgrid construction to minimize the cost-distance product for power line installations. Their MILP formulation accounted for thousands to millions of time-varying decision variables—ranging from production and inventory levels to power flows—and employed spatial clustering with disaggregation heuristics to enhance traceability. Beerbühl et al.^[15] employed heuristic methods to transform complex, nonconvex mixed-integer problems into solvable convex continuous problems, with a focus on revenue maximization.

Recent contributions to supply chain optimization have highlighted various strategies for enhancing resilience under disruption. Ali and Nakade^[16] proposed a large-scale MILP framework with a multi-multi allocation (MMA) strategy to minimize investment, transportation, and shortage costs in multi-product, multi-echelon networks. Bandejo and Ierapetritou^[17] developed MILP models to optimize raw material distribution and pharmaceutical supply chains under production and transportation capacity limitations, multi-modal routing, and forecasted demand variability. Using robust optimization to mitigate profit loss, Behzadi et al.^[18] addressed rare agricultural disruptions, such as yield shortfalls and harvest delays. Other studies tackled disruptions in distribution infrastructure or supplier availability. Fattahi et al.^[19] presented a stochastic MILP model with a novel resilience metric to optimize facility location and inventory in disrupted distribution environments. Garcia-Herreros et al.^[20] and Jabbarzadeh et al.^[21] focused on facility shutdowns and capacity reductions, incorporating expected costs and reliability into network design. Klibi and Martel^[22] reviewed stochastic programming models for resilient supply networks, emphasizing the need to represent meta-level disruption events. Liu et al.^[23] introduced a bi-objective MILP formulation with NSGA-II to manage ripple effects from supplier-state transitions. Najafi et al.^[24] optimized a four-echelon supply chain for the cooking oil industry in the presence of route failures and facility breakdowns. Beyond traditional frameworks, Kopanos and Pistikopoulos^[25] implemented a rolling horizon approach using multiparametric programming for scheduling

combined heat and power units under demand uncertainty. These contributions underscore the increasing need for computationally tractable optimization methods that integrate resilience metrics, adaptive scheduling, and uncertainty modeling in designing next-generation chemical-energy supply chains.

Despite these advances, many large-scale decision-making studies still avoid deterministic phenomenological models of chemical processes due to the computational burden of simultaneously solving dynamic process simulations and network optimizations. It is typical to exclude fast dynamics and more substantial disturbances or disruptions. However, such factors—including fluctuations in temperature, pressure, reaction rates, maintenance needs, operator errors, and external shocks such as extreme weather or geopolitical events—can significantly alter supply chain performance. These realities underscore the need for resilient strategies encompassing decentralization, diversification, automation, and adaptive scheduling, often supported by real-time monitoring and predictive analytics^[2]. The concept of resilience remains subject to varying definitions across the literature. Gong et al.^[26,27] survey multiple resilience metrics, noting that terms like flexibility and reliability are frequently invoked yet often lack quantifiability. Their proposed metric, adapted from urban infrastructure systems^[28], defines resilience as the ratio of production rates under disruption to those under nominal conditions. They further suggest enhancement strategies such as excess capacity, process parallelization, backup systems, and post-disruption re-optimization.

Some studies have emphasized the integration of process design, control, and scheduling to improve operational resilience. Malcolm et al.^[29] argued that dynamic optimization approaches that co-optimize control and design ensure robust performance under uncertainty. Static design methods, they contend, are insufficient for capturing system information. Mixed-integer dynamic optimization (MIDO) problems have been associated with a range of systems, including non-isothermal reactors^[30,31], batch processes^[32,33], and integrated distillation systems^[34]. The integration of predictive scheduling and control has also been explored using rolling horizon approaches^[35–37]. Bahri et al.^[38] and Flores-Tlacuahuac and Biegler^[39] transformed MIDO problems into MINLP problems via discretization and orthogonal collocation to maintain tractability. Koller et al.^[40] proposed a dynamic opti-

mization framework that decomposes the problem into flexibility and feasibility submodels for uncertain, multi-product systems. Recent advances by Hochhaus et al.^[41] incorporated electricity market signals to schedule a coupled PEM electrolyzer and Haber–Bosch system for demand-side management (DSM), while Obermeier et al.^[42] introduced fatigue-aware scheduling for air separation units under transient operation. While techno-economic metrics have traditionally driven scheduling and supply chain decisions, recent critiques highlight the limitations of purely financial objectives. Jain and Alleyne^[43] advocate for optimization metrics that reflect underlying system dynamics and physical efficiencies. Their proposed exergy-based framework offers an alternative lens for steady-state optimization and control of integrated energy systems.

This work investigates the optimal monthly scheduling and allocation of green energy and ammonia within a chemical-energy community featuring a fixed, modular design. The system integrates the daily dynamics of solar and wind-based energy generation with hydrogen and ammonia production and storage, accounting for consumer demands with stochastic variability as well. Potential disruptions are also modeled as either complete outages or over-production periods in the renewable energy supply, each with defined durations. The work focuses on the dynamic nonlinear optimization of 68 continuous decision variables that represent the synergetic interactions between production modules, warehouses, and consumers within the network. Besides minimizing distribution costs, two community performance metrics were optimized: the supply-to-demand ratio and a Gaussian-based function that quantitatively penalizes both over- and undersupply. The main contributions of the work include: (1) application of integrated phenomenological process models, which are solved within the dynamic optimization framework to enhance realism; (2) utilization of a closed-loop moving horizon optimization; (3) evaluation of multiple objective functions. The rest of this chapter is structured as follows: Section 2 presents the problem formulation, including decision variables, constraints, consumer demands, and objective functions; Section 3 details and discusses the simulation results; Section 4 presents a summary and concluding remarks. Appendix A of the supplementary material provides a detailed model of energy and chemical modules.

5.2 Methods

5.2.1 Problem Description

We address a conceptual and general dynamic optimization problem involving the interactions within a chemical-energy community of seven sites or locations, each having established specific economic entities associated with the production of ammonia, consumption of ammonia, and generation of solar and/or wind power. We assume that the sites are interconnected by appropriate infrastructure or technology that enables the transport of ammonia and energy/electricity as commodities, such that the relative performance of the community with respect to its ability to supply and attend to consumers' demands is maximized at all times. Transportation is not explicitly specified in any possible mode (pressured flow, cylinders, grid lines). Nevertheless, it is associated with decision variables and global cost parameters in the objective function, which will be defined in the next section. Consumers may use ammonia for agricultural, energy, or chemical purposes, which are not directly relevant to the optimization problem itself. However, the specific rates of ammonia demanded by those consumers are key factors in determining the respective performances. Unlike other studies, we do not aim to find optimal locations for installing chemical plants or modules; a resilient community design is predetermined.

Figure 5.1 represents the community with the discriminated entities. Entities located on the same site are spatially close to each other. Thus, shorter distances are associated with the transportation of commodities between them. Table 5.2 shows the distance between the economic entities in each site. Green or renewable energy generation modules (REM) can exploit solar power (yellow triangles) and wind power (green squares). The green energy generation modules operate dynamically, according to variations in the different sites' solar irradiance and wind velocity. Modular chemical plants (CHEM, represented as red circles) produce green hydrogen and ammonia. The chemical modules comprise a solid oxide water electrolyzer connected to an ammonia synthesis reactor modeled as axial plug flow units. Detailed modeling of the renewable energy and chemical modules is presented in the supple-

mentary information. Pure nitrogen is ideally mixed with hydrogen and separated from the outlet stream of the water electrolyzer. The reactants are pressurized before entering the ammonia synthesis reactor. A complete separation of the components in the outlet stream of the reactor (ammonia, non-reacted nitrogen, and hydrogen) is assumed.

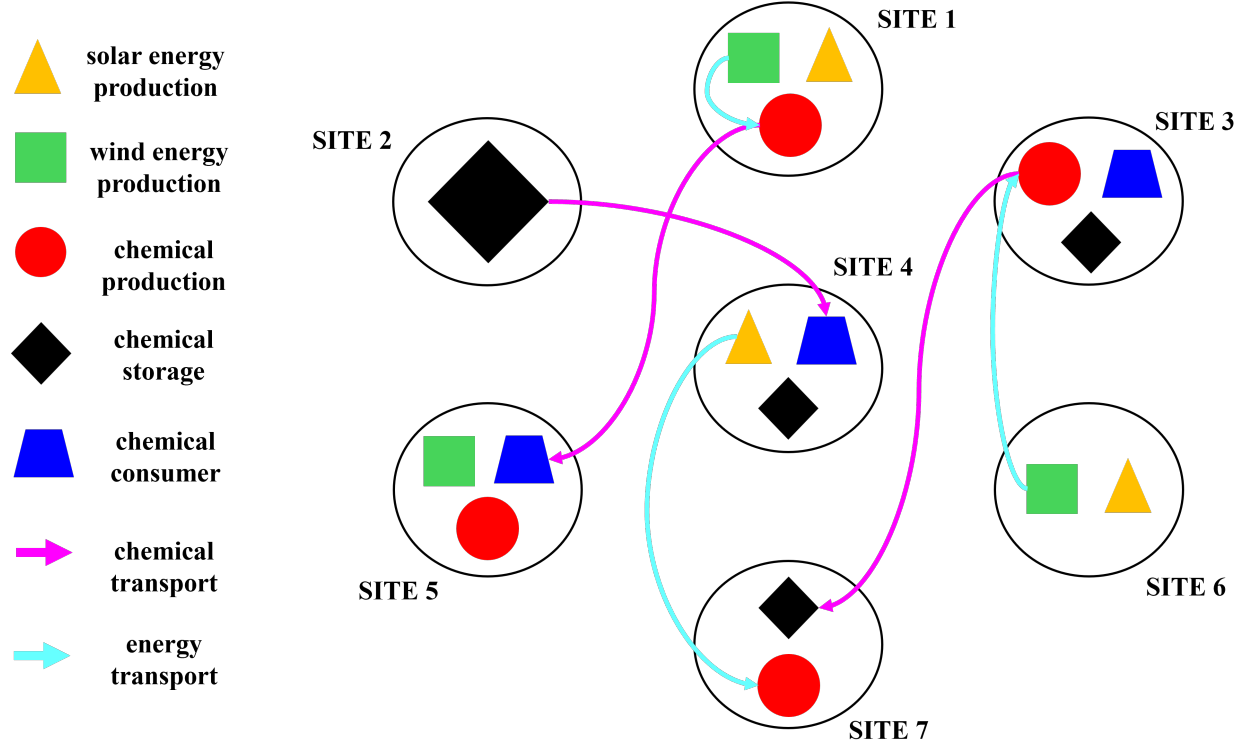


Figure 5.1: Design of the targeted chemical-energy community, highlighting a few chemical-energy supply connections.

Table 5.1: Sites configurations in the community network.

Site	Solar Power	Wind Power	Chemical Module	Chemical Storage	Consumer
1	✓	✓	✓	×	×
2	×	×	×	✓	×
3	×	×	✓	✓	✓
4	✓	×	×	✓	✓
5	×	✓	✓	×	✓
6	✓	✓	×	×	×
7	×	×	✓	✓	×

Table 5.2: Distance $d_{i,j}$ or $d_{j,i}$ between the entities in the community in kilometers.

j/i	1	2	3	4	5	6	7
1	10	20	20	20	30	30	40
2	20	10	30	20	20	40	30
3	20	30	10	20	40	20	30
4	20	20	20	10	20	20	20
5	40	20	40	20	10	30	20
6	30	40	20	20	30	10	20
7	40	30	30	20	20	20	10

It is also assumed that the intrinsic phenomenological dynamics of the chemical modules are much faster than any other interaction in the system. Therefore, the modeling of the chemical modules does not explicitly consider time as a variable in the constitutive physical equations. However, the chemical modules exhibit a pseudo-transient behavior, as the varying power outputs from the REMs directly supply the nitrogen and hydrogen compressors of the CHEMs in different proportions, thereby helping to maintain the temperatures of the electrolyzers. The constant energetic supply physically characterizes the chemical-energy integration between the modules to a limited, yet considerable extent. Extra energy can also be acquired from the grid within a defined boundary. The electrolyzer and compressors are considered the only energy-demanding units of the chemical module, and other specific energetic requirements are disregarded in this study for practical simplicity. The consumers (CONS) are represented as blue trapezoids in the community map. Each is assumed to have a distinct varying demand rate for ammonia, which is mathematically described in Section 2.3. Warehouses or storage units (STO, black diamonds) are also featured in the system to ensure the safe containment of excess production and a more efficient and resilient inventory management of ammonia. Hydrogen storage is not contemplated in this study.

5.2.2 Decision Variables

The decision variables for this work refer to how ammonia production and green energy generation can be distributed or transported to the consumers, warehouses, or chemical modules in the supply chain. They are categorized into two classes: energy decision variables

(EDVs) and chemical decision variables (CDVs). Decision groups EDV 1, CDV 1, and CDV 2 constitute fractions of the total commodity produced (ammonia or electrical power), which can be optimally and continuously varied between 0 and 1. Decision groups EDV 2, EDV 3, EDV 4, and CDV 3 consist of normalized power or flow rates and are also only permitted to assume continuous values within defined bounds. Therefore, the problem can be more easily treated with nonlinear nonconvex programming only and does not involve mixed-integer, unlike most works in the field. The detailed description of each decision group is given below. In total, there are 68 decision variables.

- EDV 1 = $\phi_{\text{RE},k,\text{prod},i}$, fraction of the energy generated by the renewable energy module at site k and transferred to the chemical production module at site i .
- EDV 2 = $Q_{\text{EE},\text{electro},i}$, energy acquired by external sources and used as volumetric heat input to the electrolyzer of the chemical production module at site i .
- EDV 3 = $W_{\text{EE},\text{comp},\text{N}_2,i}$, power acquired by external sources and applied to the nitrogen compressor of the chemical production module at site i .
- EDV 4 = $W_{\text{EE},\text{comp},\text{H}_2,i}$, power acquired by external sources and applied to the hydrogen compressor of the chemical production module at site i .
- CDV 1 = $\alpha_{\text{prod},i,\text{cons},j}$, fraction of the molar flow rate of ammonia produced by the chemical production module at site i and transferred to the consumer at site j .
- CDV 2 = $\beta_{\text{prod},i,\text{sto},n}$, fraction of the molar flow rate of ammonia produced by the chemical production module at site i and transferred to storage at site n .
- CDV 3 = $F_{\text{sto},n,\text{cons},j}$, flow rate of ammonia transferred from storage at site n to consumer at site j .

Logical linear constraints involving the decision variables are given by Equations 5.1 and 5.2, as well as Inequality 5.3. Equation 5.1 is a global distribution balance of the power generated by the renewable energy modules. Similarly, Equation 5.2 represents a

distribution balance of the ammonia produced by each chemical module. The distribution fractions must, of course, sum to 1. Inequality 5.3 states that the total amount of ammonia extracted from the storage units in a time step must be smaller than the current storage level. That restriction avoids the storage levels from assuming numerically negative values.

$$\sum_{i=1,3,5,7} \phi_{k,i} = 1 \quad (5.1)$$

$$\sum_{j=3,4,5} \alpha_{\text{prod},i,\text{cons},j} + \sum_{n=2,3,4,7} \beta_{\text{prod},i,\text{sto},n} = 1 \quad (5.2)$$

$$\sum_{j=3,4,5} F_{\text{sto},n,\text{cons},j} \cdot \Delta t \leq N_{\text{NH}_3,\text{sto},n}; \quad (5.3)$$

where $N_{\text{NH}_3,\text{sto},n}$ is the current amount of ammonia stored at site n.

Table 5.3: Lower and upper bounds of the decision variables.

Decision Variable	Lower Bound	Upper Bound
$\phi_{\text{RE},k,\text{prod},i}$	0	1
$Q_{\text{EE},\text{electro},i}$	0 W	1 kW
$W_{\text{EE},\text{comp-N}_2,i}$	0 W	5 kW
$W_{\text{EE},\text{comp-H}_2,i}$	0 W	5 kW
$\alpha_{\text{prod},i,\text{cons},j}$	0	1
$\beta_{\text{prod},i,\text{sto},n}$	0	1
$F_{\text{sto},n,\text{cons},j}$	0 mol/s	0.01 mol/s

5.2.3 Consumer Demands

The consumers' demands for ammonia are allowed to vary within the evaluation period of the supply chain. The variability is introduced as random Gaussian factors " γ_{rand} " that range between 0 and 1 and are combined to a nominal expected demand rates for ammonia, which therefore also adds uncertainty to the final demand expectations, as expressed in Equations 5.4-5.6. Figure 5.2 illustrates the unsteady behavior of the consumer demands, which is further included in the dynamic optimization problem as a parameter of the community

performance metric.

$$f_{\text{demand},3}(t)[\text{mol/s}] = 0.01 \cdot (0.8 + 0.4 \cdot \gamma_{\text{rand},3}) \quad (5.4)$$

$$f_{\text{demand},4}(t)[\text{mol/s}] = 0.007 \cdot (0.9 + 0.2 \cdot \gamma_{\text{rand},4}) \quad (5.5)$$

$$f_{\text{demand},5}(t)[\text{mol/s}] = 0.015 \cdot (0.85 + 0.30 \cdot \gamma_{\text{rand},5}) \quad (5.6)$$

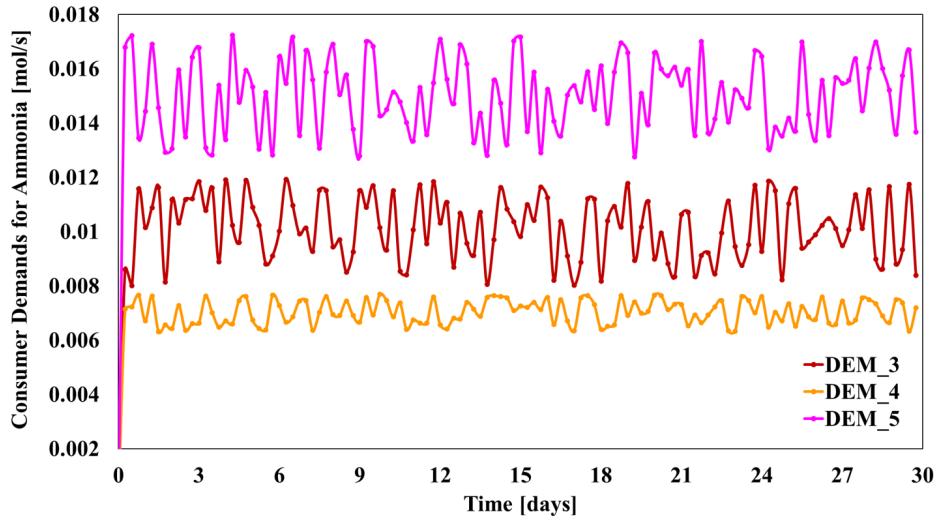


Figure 5.2: Normal variability of the consumer demands over the period of a month.

5.2.4 Green Energy Generation and Disruptions

Disruptions are implemented as over-generation and under-generation of renewable energy, or even its total interruption or absence from the chemical-energy supply chain in the community. It is essential to reemphasize that the renewable energy modules are connected to the chemical modules, which utilize the energy to power the nitrogen and hydrogen compressors and water electrolyzers. Figure 5.3 presents the obtained dynamics of the green energy generated by the modules (W_{RE}) over a month, including disruptions and natural daily oscillations due to the solar irradiance patterns and wind velocity variations. The peaks refer

to the maximum solar irradiance attained daily around noon. It is first verified that the modules' output energy ranges from tens to hundreds of kilowatts. REM1 undergoes one period of disruption: a complete shutdown between days 9 and 12, resulting in no energy generation. Similarly, REM4 also experiences a complete shutdown between days 25 and 30. REM5, which relies exclusively on wind power, experiences an interruption between days 2 and 7 and slightly higher-than-normal generation in the period between days 18 and 21. Finally, the REM6, the largest in capacity, exhibits higher-than-normal energy levels between days 2 and 8 and is completely interrupted between days 14 and 19. In this work, excess green energy generation is not economically discriminated and not considered to be sold to the grid: the chemical modules are subjected to the green energy dynamics and always receive 100% of the total green energy generated.

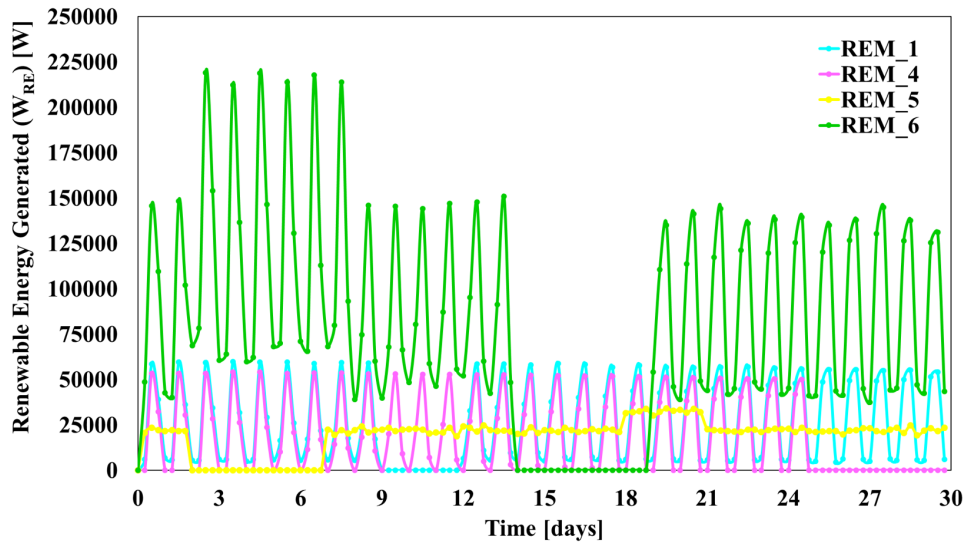


Figure 5.3: Dynamics of the green energy modules over the period of a month.

5.2.5 Community Performance Oriented to the Consumers

The chemical production modules or warehouses can directly supply the consumers with a total supply rate given by Equation 5.7. We qualitatively define performance (PER) as the ability of the community to manage its resources, adapt its supply chain, and meet consumers' demands for ammonia at all times, particularly during temporary disruptive events.

$$f_{\text{supply},j}(t) = \sum_i \alpha_{\text{prod},i,\text{cons},j} \cdot F_{\text{prod},i} + \sum_n F_{\text{sto},n,\text{cons},j} \quad (5.7)$$

Quantitatively, we propose investigating performance using two metrics. The first (PER_1) is the simple ratio between the total supply rate and total demand rate, as shown in Equation 5.8. This metric fails if the demand rates are zero and there is no maximum.

$$\text{PER}_{1,\text{cons},j}(t) = \frac{f_{\text{supply},j}(t)}{f_{\text{demand},j}(t)} \quad (5.8)$$

The second metric (PER_2), presented in Equation 5.9, is expressed through a continuous Gaussian function with a single maximum value of 1 when the total supply rate $f_{\text{supply},j}(t)$ is equal to the demand rate $f_{\text{demand},j}(t)$, and values between 0 and 1 if the supply rates are different than the demand rates, given that the demand rates are not exactly zero. Under that definition, the performance displays the characteristic bell shape with a maximum value at the demand rates, as shown in Figure 5.4. Considering that supply rates larger than demand rates imply waste or incorrect delivery of the product, the function definition penalizes these mistakes with performance values smaller than 1. The full width quarter maximum of the performance curves (or their inflection points) is achieved when the supply rates are equal to 50% and 150% of the demand rates, to avoid a significant non-zero performance when the supply rates are zero, and approximately zero performance when the supply rates are twice the demand rates.

$$\text{PER}_{2,\text{cons},j}(t) = \exp \left[- \left(\frac{2\sqrt{2 \ln 2}}{f_{\text{demand},j}(t)} \right)^2 \cdot [f_{\text{supply},j}(t) - f_{\text{demand},j}(t)]^2 \right] \quad (5.9)$$

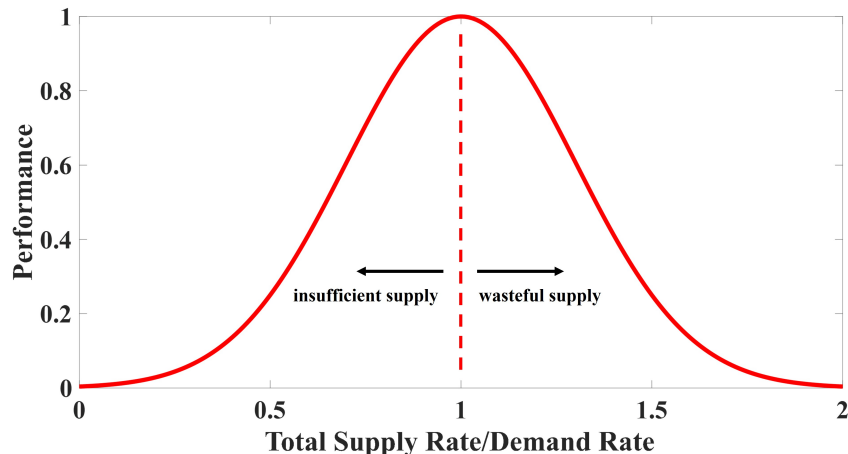


Figure 5.4: Behavior of the Gaussian performance.

5.2.6 Community Optimization

The objective function can account for different economic goals: minimizing the relative costs of the distribution of green energy, extra energy, and ammonia, with respect to the relative distances between the economic entities in the supply chain (as in Equation 5.10) or maximizing the consumer-oriented performances (as in Equation 5.11). This general approach on the optimization serves a conceptual framework for scheduling of modular chemical-energy systems. The quadratic forms of the performance terms in Equation 5.11 induce the optimizer to minimize the deviations of the individual performances from reference values χ , which reflect the maximum values expected from the performances. Both ψ and χ are therefore inductive parameters for performance maximization. Since obtaining performance values equal to 1 is ideal, χ values are fixed at 1. Parameters ψ_j were fixed at an equal value of 10 [\$/s] to assess the behavior of the supply chain.

$$\begin{aligned}
f_{\text{obj,dist}} = & \sum_k c_{\text{RE}} \cdot W_{\text{RE},k} \sum_i (d_{k,i} \cdot \phi_{\text{RE},k,\text{prod},i}) + \\
& + \sum_i c_{\text{EE}} \cdot (Q_{\text{EE},\text{electro},i} + W_{\text{EE},\text{comp.N}_2,i} + W_{\text{EE},\text{comp.H}_2,i}) + \\
& + \sum_i c_{\text{prod,cons}} \cdot F_i \cdot \sum_j (d_{i,j} \cdot \alpha_{\text{prod},i,\text{cons},j}) + \sum_i c_{\text{prod,sto}} \cdot F_i \cdot \sum_n (d_{i,n} \cdot \beta_{\text{prod},i,\text{sto},n}) + \\
& + \sum_n \sum_j c_{\text{sto,cons}} \cdot d_{n,j} \cdot F_{\text{sto},n,\text{cons},j}
\end{aligned} \tag{5.10}$$

$$f_{\text{obj,perf}} = \sum_j \psi_j (\text{PER}_{\text{cons},j} - \chi_j)^2 \tag{5.11}$$

Table 5.4 presents the parameters associated with the relative costs of the community interactions. Our optimization algorithm works as follows: at time step t , it evaluates the current values of the outputs of the system. Still at time step t , it performs a cost function evaluation by systematically changing the decision variables and assessing their effect on the forecasted trajectories of the community outputs (renewable energy generated, hydrogen and ammonia production rates, and consumer-oriented performances) for a future predictive horizon of length τ . The algorithm, therefore, utilizes the input-output relationships of the community models to obtain and return predictions of the outputs that minimize the accumulated costs, as defined by a particular objective function, over the entire horizon (Equation 5.12). The algorithm then applies the optimal input sequence found in the optimization stage, effectively proceeds to the next time step $t + \tau$, and sets it as the current state. In this manner, this scheduling algorithm operates in a manner equivalent to those used in model predictive control. Finally, at the new time step, it reassesses the outputs and redoes the procedures. The minimization step was conducted in MATLAB, employing the "fmincon" function and the interior-point algorithm (IPA). The time step used in the computations was set to 6 hours, and the length of the prediction horizon was maintained at 1 time step.

$$\begin{aligned}
& \text{objective} = \min \sum_t^{t+\tau} f_{\text{obj}} \\
& \text{subjected to } W_{\text{RE},j} \text{ and } f_{\text{demand},j} \\
& \text{and constraints defined in section 2.2.}
\end{aligned} \tag{5.12}$$

Table 5.4: Global costs involved in the distribution of energy and ammonia.

Fixed Cost	Value
c_{RE}	10 [\$/ (km · kWh)]
c_{EE}	0.079 [\$/kWh]
$c_{\text{prod,cons}}$	$3.63 \cdot 10^{-7}$ [\$/ (km · mol)]
$c_{\text{prod,sto}}$	$1.82 \cdot 10^{-7}$ [\$/ (km · mol)]
$c_{\text{sto,cons}}$	$4.36 \cdot 10^{-7}$ [\$/ (km · mol)]

5.3 Results and Discussion

5.3.1 Community Optimization under Distribution Costs Only

In this scenario, the objective function does not include the ratio and Gaussian performance metrics. Figure 5.5 shows the optimizer decisions on variables EDV1, which are related to the distribution of the renewable energy. In the legends, the subscript "phi_ki" denotes the variable $\phi_{\text{RE},k,\text{prod},i}$. It is noticed that, most of the time, REM1 and REM5 have most of their energy directed to the nearest chemical modules or those on the same site. REM4, located equally distant from all the other sites, does not show any distribution preference and provides 25% of the energy generated to each chemical module. REM 6 also tends to send most of its energy to the closest chemical modules, located at sites 3 and 7. During the disruption of energy surplus at REM6 (days 2-8), REM5 is not generating energy, and CHEM5 receives the least energy. During the total interruption of green energy generation at REM6 between days 14 and 19, apparent changes arise in $\phi_{\text{RE},6,\text{prod},1}$ and $\phi_{\text{RE},6,\text{prod},5}$, however, they are not effective during the disruption. In the next few days, they will have a residual effect on the chemical production of modules CHEM1 and CHEM5. Compared to periods

before the disruption, those modules receive slightly more energy from the reestablished REM6.

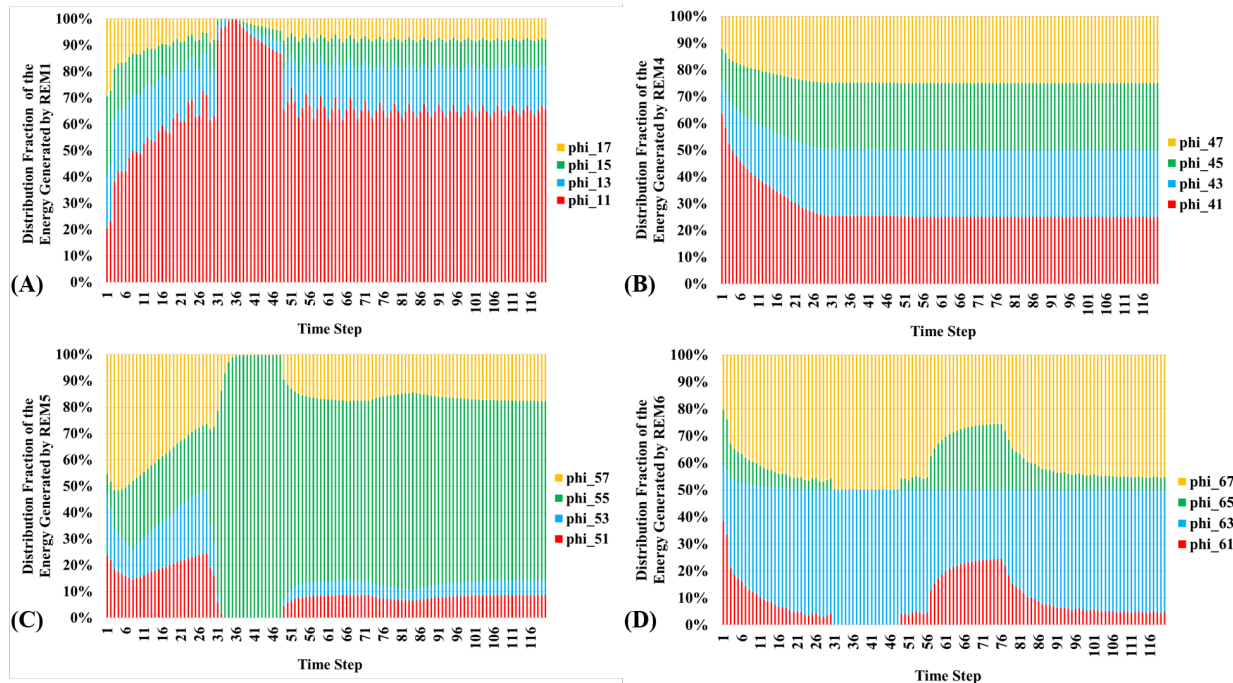


Figure 5.5: Distribution of the renewable energy generated by REM1 (A), REM4 (B), REM5 (C) and REM6 (D).

Figure 5.6 displays the amount of extra energy (EDV 2-4) acquired by the CHEM1. Since distances do not affect the additional energy distribution for the chemical modules (due to their universal availability) and there are no cost distinctions, the trends obtained for the other chemical modules are the same as those for CHEM1. The optimizer gradually sends more energy to the CHEMs until the maximum values permitted by the constraints are attained, then maintains this level for the rest of the schedule. Contextually, those extra energy decisions are considered disadvantageous or counterproductive because they did not exhibit any sensible dynamic relation or response that would balance the current outputs from the REMs and ultimately result in the overproduction of hydrogen or ammonia. If the upper bounds are doubled or even tripled, further investigations proved that the optimizer still tends to stabilize the EDV 2-4 at the maximum constrained values. This suggests that the total cost of the extra energy distribution is negligible during the dynamic optimization,

or the optimization is faulty or insensitive to those variables; the latter situation could only be remedied artificially by upscaling the costs.

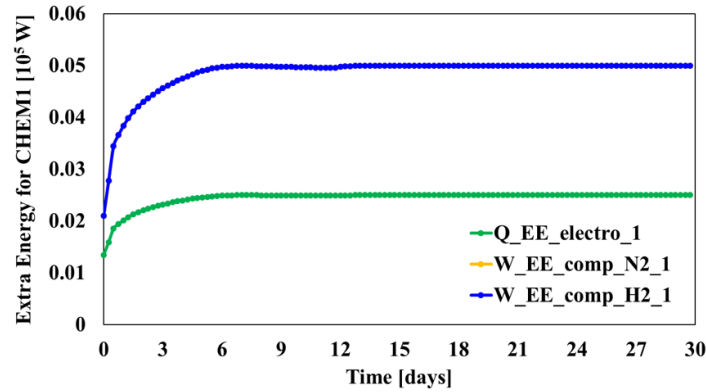


Figure 5.6: Extra energy acquired by the chemical modules.

Figure 5.7 presents the hydrogen production by the water electrolyzers and ammonia production by the Haber-Bosch reactors of each chemical module. The hydrogen produced was found to be the same by all modules, because the water electrolyzers are subjected to the same feed conditions and receive the same extra energy inputs. As expected, CHEM3 and CHEM7 output the largest amounts of ammonia, because their compressors receive the largest amount of green energy from REM6. During days 14 and 19, ammonia production drops significantly due to the shutdown of REM6, and CHEM1 is responsible for the largest ammonia production.

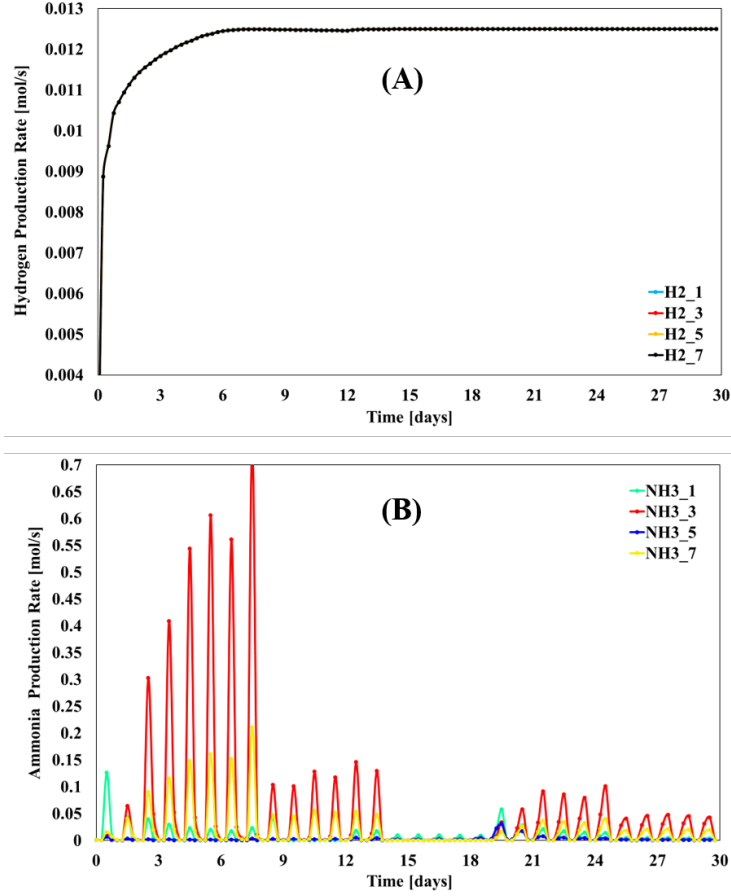


Figure 5.7: Hydrogen (A) and ammonia (B) produced at each chemical module.

Counterintuitive trends are observed in the distribution of ammonia from the chemical modules, as shown in Figure 5.8. Before day 12, CHEM1 gradually sent most of its production to STO7, even though it was the farthest relative entity. At day 12, the distribution fractions to other entities suddenly increase, likely as a predicted response to the interruption of REM6 in the subsequent time steps. CHEM3 also favors warehouses, particularly STO4 and STO7, but distributes a significant fraction of its production to CONS5, and smaller fractions to the other consumers. Additionally, CHEM3 is more evidently influenced by the production surplus during days 2-8, by systematically increasing $\beta_{\text{prod},3,\text{sto},4}$ and $\beta_{\text{prod},3,\text{sto},7}$. CHEM5 and CHEM7 end up distributing their production equally between the warehouses and consumers, regardless of distances. CHEM5 and CHEM7 are responsible for attending to the consumers, with overproduction being sent to the warehouses.

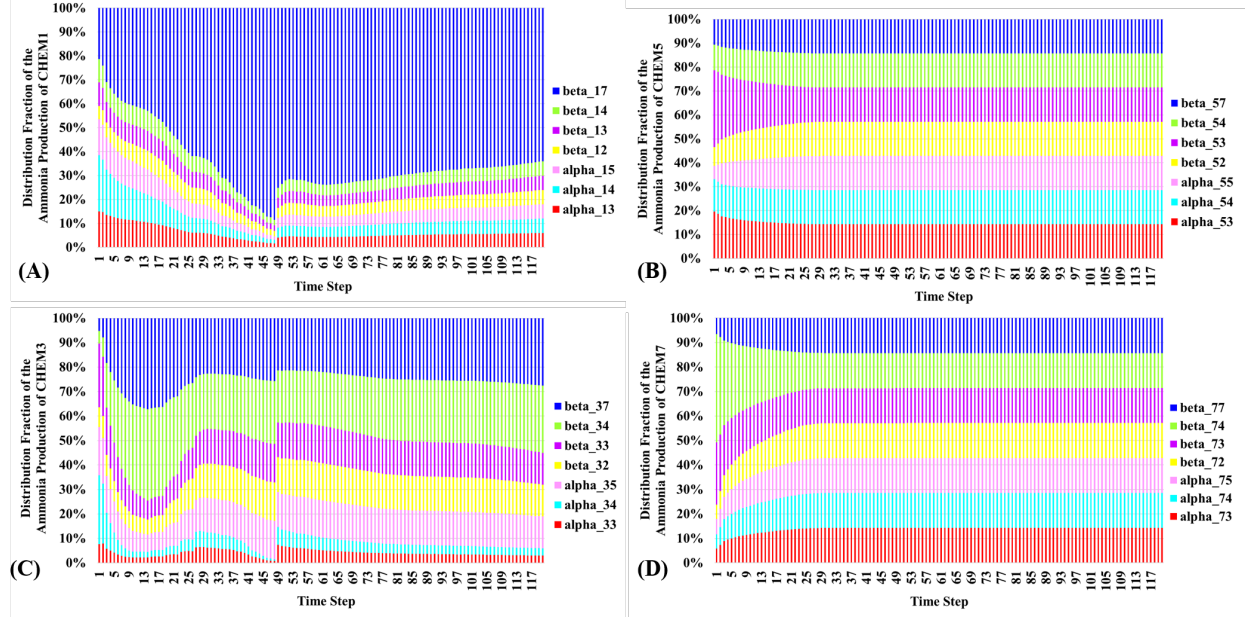


Figure 5.8: Distribution of ammonia from the chemical modules.

Figure 5.9 displays the amount of ammonia in mols stored at the warehouses, and Figure 5.10 shows the amount of ammonia withdrawn from them and distributed equally to each consumer over the schedule. In the first quarter of the schedule, storage levels increase sharply due to the overproduction of CHEM3 and CHEM7, with STO4 and STO7 keeping the majority of the production. The overproduction leads the optimizer to maintain constant ammonia withdrawals from the storage units. Between days 8-14, storage levels also decrease as energy generation and ammonia production levels decrease. And during the substantial disruption at REM6 between days 14-19, storage levels of STO3 and STO7 unsurprisingly decrease again, this time more sharply, due to diminished production and steady withdrawals. An unsteady second-half schedule is observed for STO2 and STO3. Their levels remain practically at the constrained minimum after day 15, indicating that those warehouses readily distribute most of the ammonia they receive to consumers, as evidenced by daily spikes in the withdrawn flow rates.

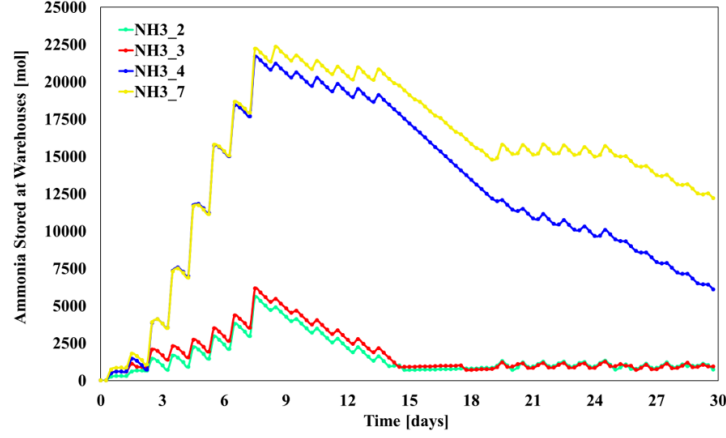


Figure 5.9: Ammonia storage levels.

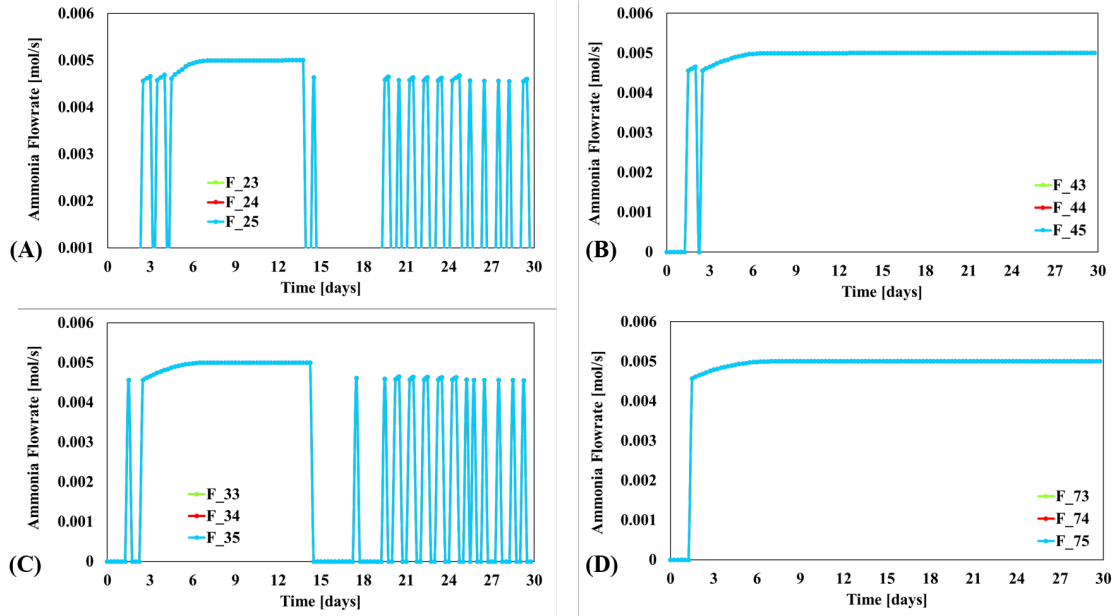


Figure 5.10: Distribution of ammonia from storage units.

Figure 5.11 presents the performance metrics of the community, even though they were not explicitly considered in the optimization. It is verified that the consumer's demands are met in excess, the supply rates being significantly higher than the demand rates. The excessive supply rates induce the Gaussian performances to be lower than 1 in the first half of the schedule; nevertheless, an improvement is verified in the second half, with supply/demand ratios much closer to 1.

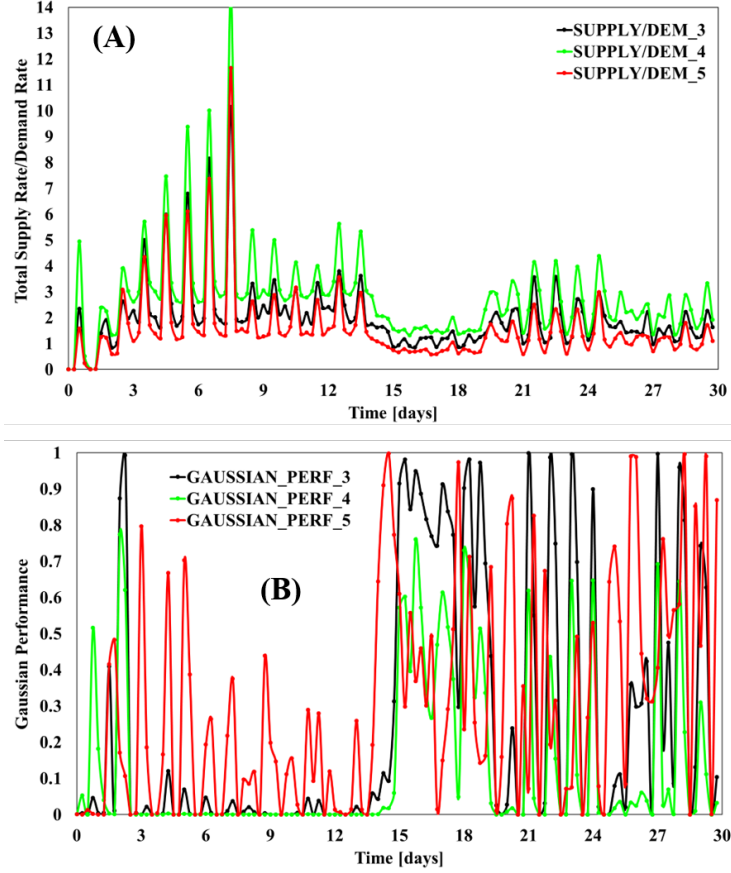


Figure 5.11: Overall performance of the community in attending its consumers.

5.3.2 Community Optimization under Performance Objectives Only

Figure 5.12 presents the distribution of the renewable energy, as done in the previous case. In this scenario, since distance-related cost factors are not considered, it takes less than 6 days for all REMs to decide to equally send the energy generated to the chemical modules. Interestingly, the result was the same for both performance metrics. Given the initial conditions, which generally influenced most of the initial dynamics of the modules, CHEM1 receives a higher proportion of the total energy generated by REM4 and REM6. Production by CHEM3 is now compared to that of CHEM1 and CHEM5. The extra energy acquisition trends were the same as the previous situation, which may indicate the optimizer is biased regarding those variables. Figure 5.13 presents each chemical module's daily production of hydrogen and ammonia. Again, the individual productions were virtually the same for both

metrics, since they relied on similar energy supply trends.

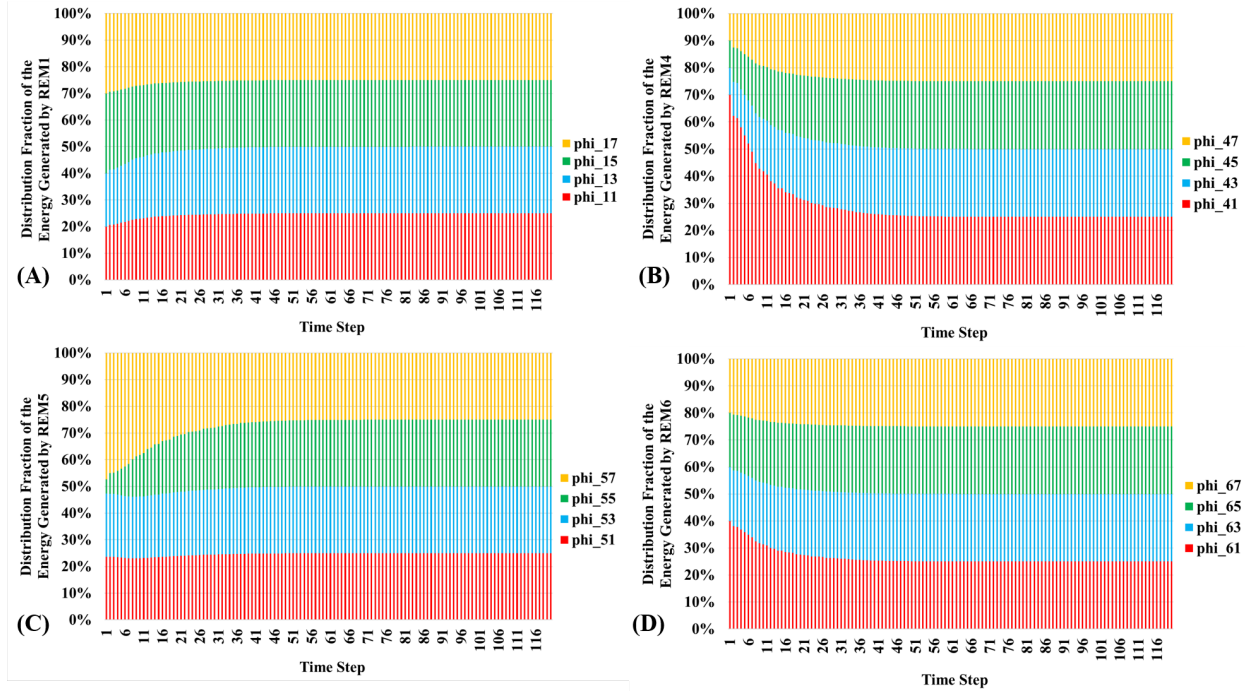


Figure 5.12: Distribution of the renewable energy generated by REM1 (A), REM4 (B), REM5 (C) and REM6 (D).

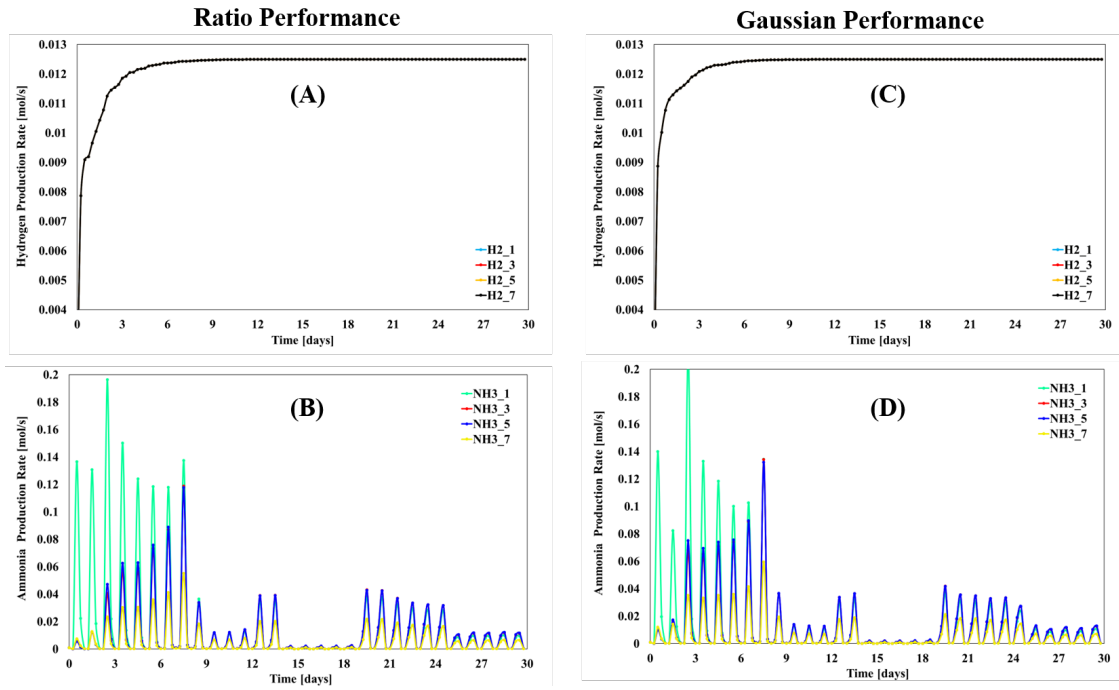


Figure 5.13: Hydrogen (A) and ammonia (B) produced at each chemical module.

The ammonia distribution variables are shown in Figures 5.14 (for the ratio performance)

and 5.15 (for the Gaussian performance). For both performance metrics, the optimization seems to converge to similar values for $\alpha_{\text{prod},1,\text{cons},j}$ and $\alpha_{\text{prod},3,\text{cons},j}$, which make the trend differences quite subtle. Apart from initial dynamics, all the consumers together obtain no more than 35% of the production from CHEM1 directly, for both metrics, whereas for the ratio performance metric, CONS5 (the most demanding) is favored. For the Gaussian performance, $\alpha_{\text{prod},1,\text{cons},j}$ are more slightly more similar. Yet, STO7 is majorly favored by CHEM1. CHEM3 also transports most of its production to STO4 and STO7 for both metrics; CONS5 is the only consumer that directly receives more than 5% of CHEM3's total production. The distribution trends associated with CHEM5 and CHEM7 are quite distinct for both performance metrics. The ratio metric maintains a predominantly conservative distribution of output to storage units, while the Gaussian metric facilitates more significant transfers directly to consumers, particularly CONS5. An apparent shift in the trends of CHEM5 and CHEM7 occurs after the shutdown of REM6, when the ratio metric was employed, which resulted from a sudden decrease of $\alpha_{\text{prod},5,\text{cons},5}$ and $\alpha_{\text{prod},7,\text{cons},5}$.

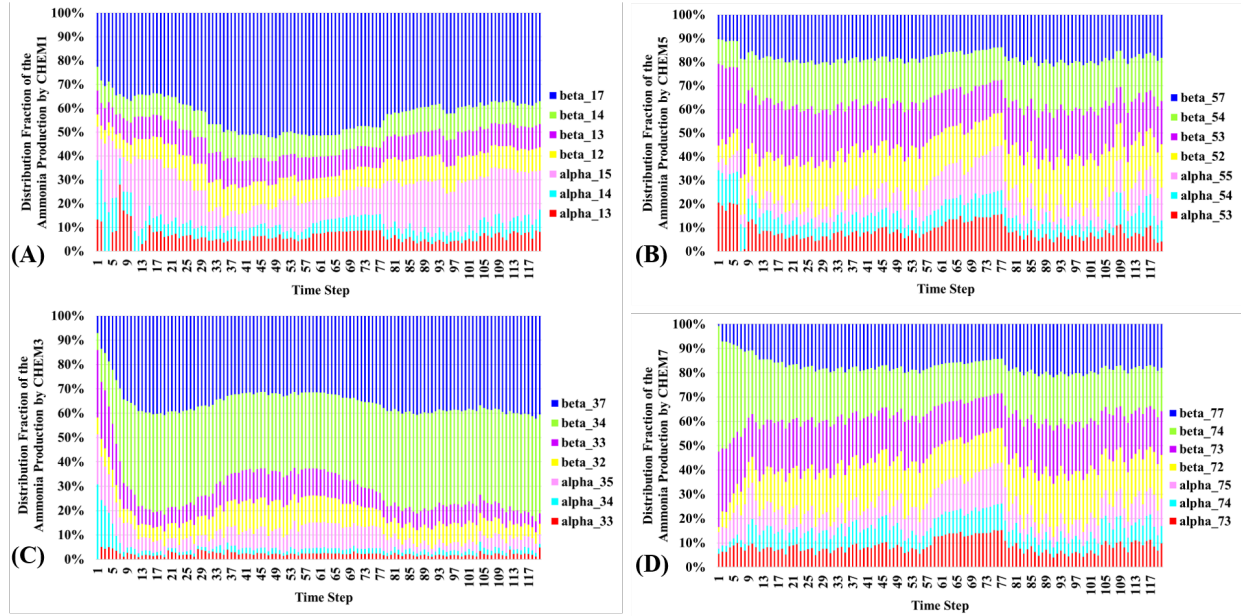


Figure 5.14: Distribution of ammonia from the chemical modules employing the ratio performance metric.

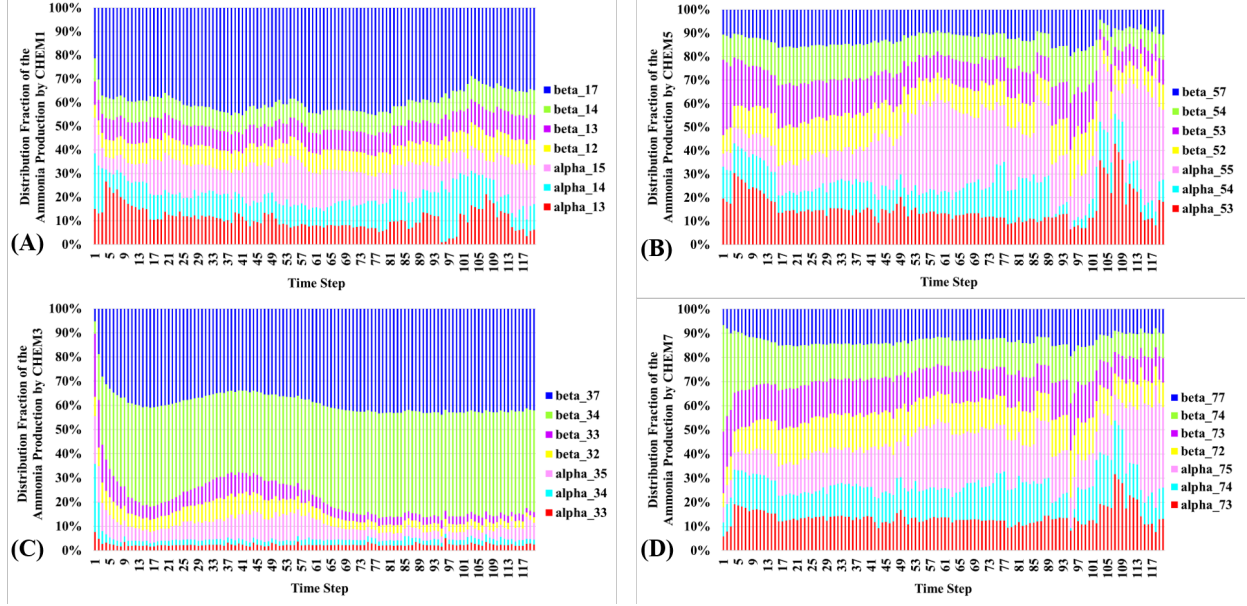


Figure 5.15: Distribution of ammonia from the chemical modules employing the Gaussian performance metric.

Figure 5.16, Figure 5.17, and Figure 5.18 display the storage levels and the ammonia flowrates for both performance metrics. As expected from the previous observations, the warehouses achieve higher levels of performance with the ratio, with STO7 being the most resourced. STO2, STO3, and STO4 again stay marginally close to the minimum storage level during the second half of the schedule. Curiously, STO7 levels also eventually decrease to minimum levels with the Gaussian performance metric, implying that the consumers are either oversupplied when that metric is used or undersupplied when the ratio metric is used.

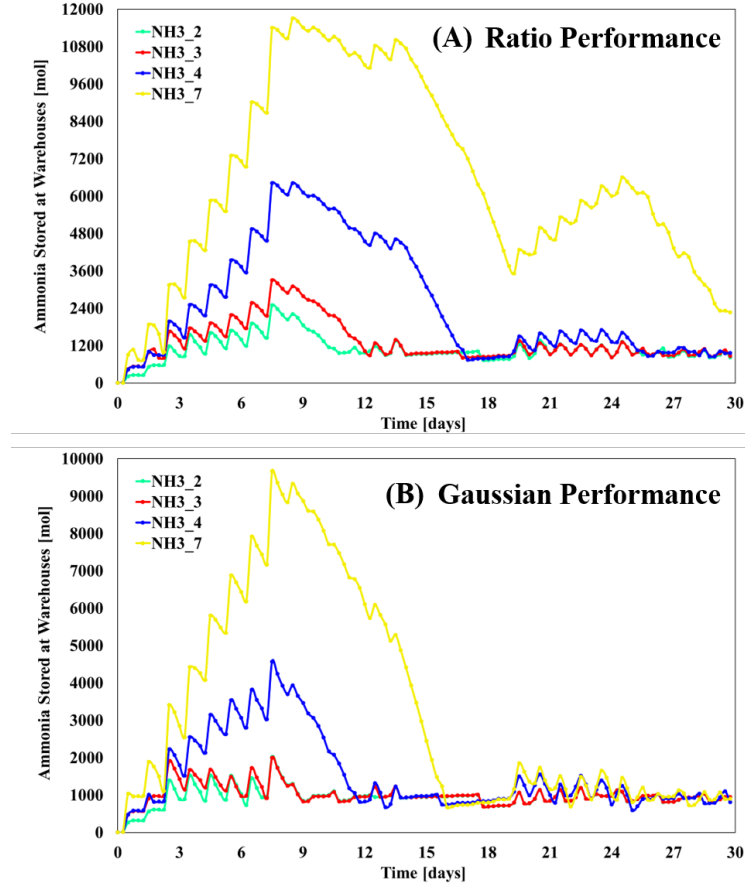


Figure 5.16: Ammonia storage levels.

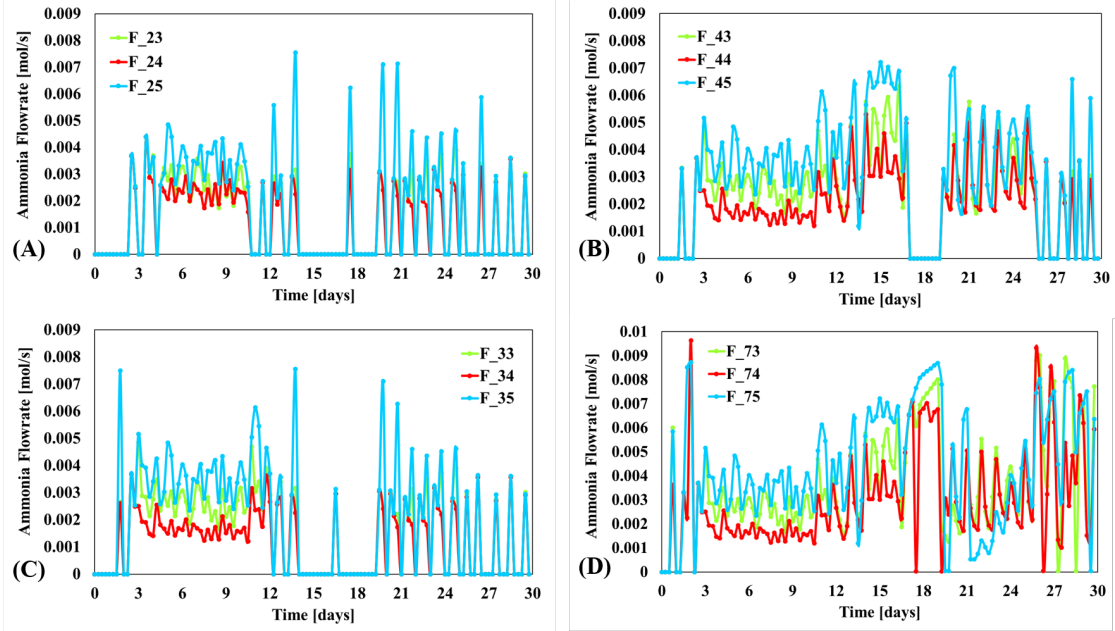


Figure 5.17: Distribution of ammonia from storage units employing the ratio performance.

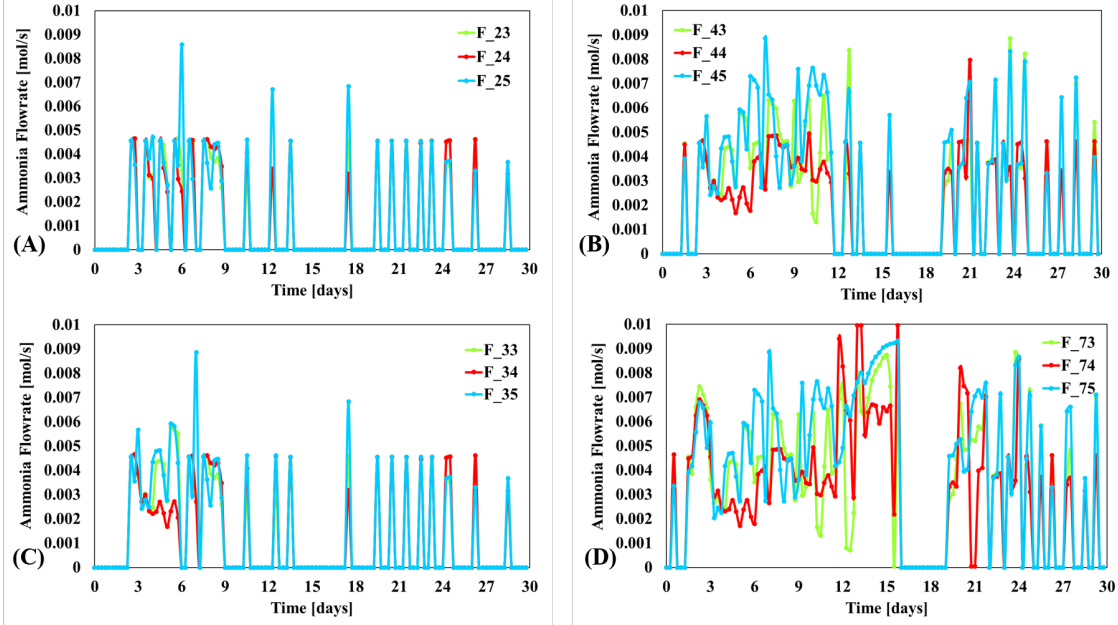


Figure 5.18: Distribution of ammonia from storage units employing the Gaussian performance.

The performance metrics are presented in Figures 5.19 and 5.20. The optimizer struggles to keep the Gaussian performance at values close to 1, due to oversupply to the consumers, except during the interruption of REM6. Still, the supply-demand ratio achieved when the Gaussian performance is used is very similar to that when the ratio is optimized as the metric.

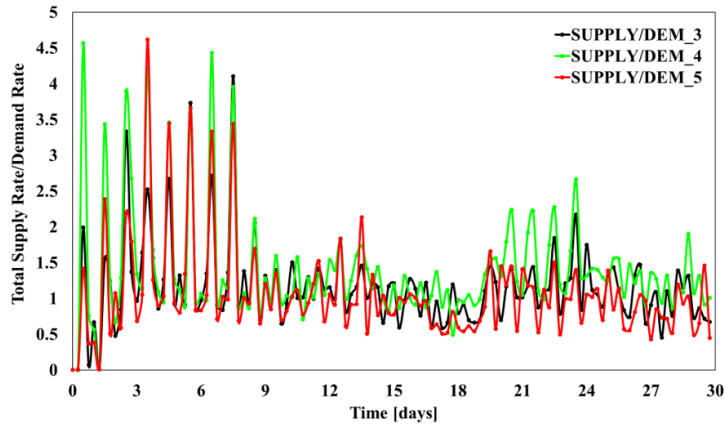


Figure 5.19: Ratio performance attained.

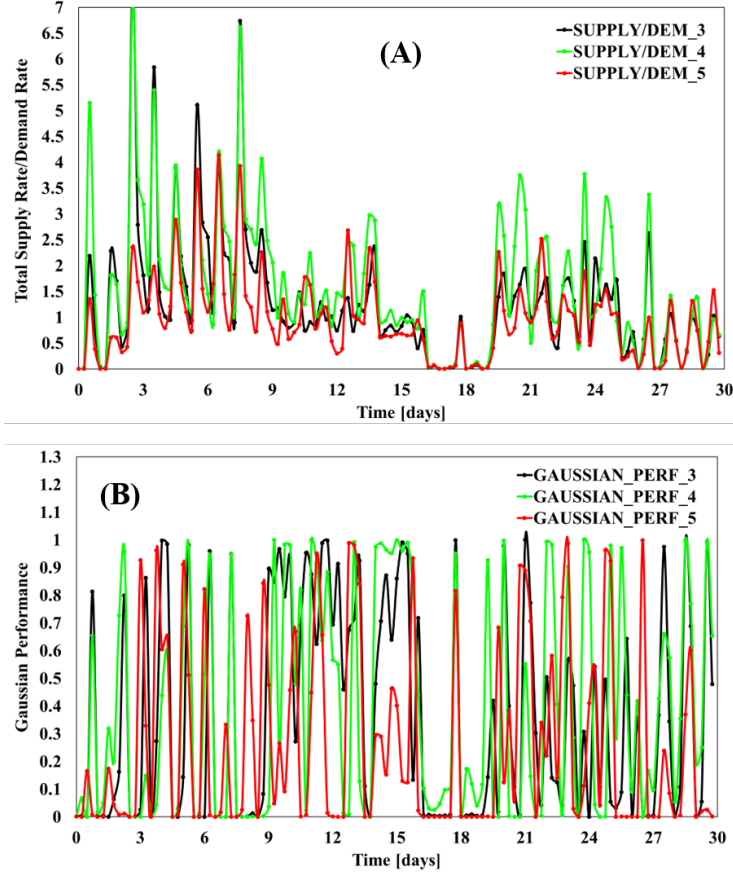


Figure 5.20: Gaussian performance attained.

5.4 Conclusion

An investigation into the monthly dynamic schedule of a chemical-energy community was conducted using a moving horizon approach in MATLAB. The community consisted of hydrogen and ammonia production modules supplied by renewable energy generation modules, which needed to meet the varying demands of consumers for ammonia at all times, particularly during disruptions. The disruptions were implemented through periods of complete shutdowns of the renewable energy generation modules or unusual energy overgeneration, both with defined durations. Two community performance metrics were evaluated: a simple supply-demand ratio and a Gaussian function that mathematically penalized both over- and undersupply to each consumer according to their demand. Since all green energy generated in the community was thoroughly utilized for ammonia production, warehouses were present

to buffer any undesired economic interactions between production modules and consumers, and to store excessive ammonia production. A horizon of 6 hours was used during the simulations for more efficient computational performance. Generally, the dynamics of decision variables were notably influenced by the initial conditions during the first days of the schedule. An apparent state of struggle of the algorithms to deal with overgeneration of energy, overproduction, and distribution of ammonia, even under restrictive optimization conditions, caused the performance metrics to deviate from the ideal expectation of unit supply/demand ratios. Both metrics displayed very similar results when the objective function was purely minimizing performance costs.

Nevertheless, they were surprisingly closer to the unit during a massive disruption that reduced the total energy generated. The decision variables and community models were thus more sensitive to the outputs of the renewable energy modules than to other entities, highlighting that the placement and operation of these energy modules should be considered in conjunction with a prior assessment of typical consumer needs to avoid economic excesses. Suppose it is decided that a resilient infrastructure must possess multiple energy generation entities. In that case, we believe that the community can become more resilient by incorporating extra energy sales into the grid.

5.5 Phenomenological Model of the Chemical Modules

Figure 5.21 presents the general structure of a chemical module. A water electrolyzer is employed to produce green hydrogen, which is assumed to be completely separated from the outlet stream. The hydrogen produced is then compressed and combined with compressed nitrogen in the Haber-Bosch reactor. The molar flow rate of ammonia obtained at the reactor outlet is the main output variable of the chemical modules.

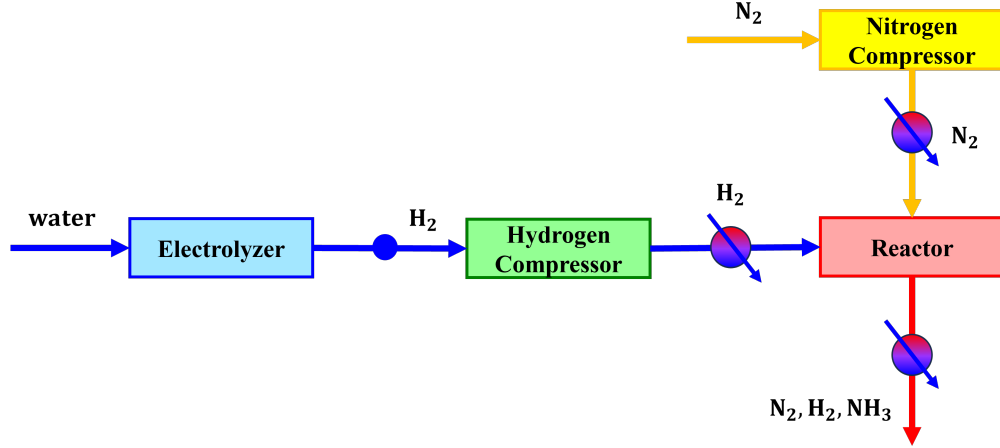


Figure 5.21: Design of the chemical modules.

5.5.1 Water Electrolyzer Model

The water electrolyzer is modeled as a transient 1-dimensional plug-flow unit, with energy and molar conservation balances coupled to an electrokinetic description of the water electrolysis reaction^[44–46]. The energy balance assumes the form of the Equation 5.13, where $F_{i,\text{electro}}$ is the molar flowrate of species i ($i = \text{H}_2\text{O}, \text{H}_2, \text{N}_2, \text{O}_2$), T_{electro} is a single temperature variable distributed along the volume of the electrolyzer V_{electro} , $c_{p,i}$ is the specific molar heat of species i . The electrodes are not considered to be lumped in the computation of the flowrates. Table 5.5 presents the values of all the parameters employed in the electrolyzer model.

$$\frac{dT_{\text{electro}}}{dV_{\text{electro}}} = \frac{\sum Q}{\sum (F_{i,\text{electro}} \cdot C_{p,i})} \quad (5.13)$$

The specific molar heat of the species applied to the electrolyzer is given by:

$$C_{P,\text{N}_2}|_{\text{electro}} = R \cdot (3.280 + 0.593 \cdot 10^{-3} \cdot T_{\text{electro}} + 0.040 \cdot 10^5 \cdot T_{\text{electro}}^{-2}) \text{ [J/(mol} \cdot \text{K)]} \quad (5.14)$$

$$C_{P,\text{O}_2}|_{\text{electro}} = R \cdot (3.639 + 0.506 \cdot 10^{-3} \cdot T_{\text{electro}} - 0.227 \cdot 10^5 \cdot T_{\text{electro}}^{-2}) \text{ [J/(mol} \cdot \text{K)]} \quad (5.15)$$

$$C_{P,H_2}|_{\text{electro}} = R \cdot (3.249 + 0.422 \cdot 10^{-3} \cdot T_{\text{electro}} + 0.083 \cdot 10^5 \cdot T_{\text{electro}}^{-2}) \text{ [J/(mol} \cdot \text{K)]} \quad (5.16)$$

$$C_{P,H_2O}|_{\text{electro}} = R \cdot (3.470 + 1.450 \cdot 10^{-3} \cdot T_{\text{electro}} + 0.121 \cdot 10^5 \cdot T_{\text{electro}}^{-2}) \text{ [J/(mol} \cdot \text{K)]} \quad (5.17)$$

A bulk heat source, caused by electrical resistance, and a bulk heat sink, generated by electrolysis, are both considered, as shown in Equation 5.18, coupling heat and species transports even more deeply. Two heat sources, $Q_{\text{green,electro}}$ and $Q_{\text{ext,electro}}$, originating from the green energy module and the external grid, are added to the equation as energy inputs to maintain the electrolyzer at a reasonable operating temperature.

$$\sum Q = \Delta H_{\text{electrolysis}} \cdot R_{H_2O,\text{electro}} + j^2 R_{\Omega} a_{\text{electrode}} + \frac{Q_{\text{green,electro}} + Q_{\text{ext,electro}}}{V_{\text{electrolyzer}}} \quad (5.18)$$

$$R_{\Omega} = \left(\frac{\tau_{\text{anode}}}{\sigma_{\text{anode}}} + \frac{\tau_{\text{electrolyte}}}{\sigma_{\text{electrolyte}}} + \frac{\tau_{\text{cathode}}}{\sigma_{\text{cathode}}} \right) \quad (5.19)$$

The molar species balance (Equation 5.20) considers axial transport in the unit. In this model, gas mixtures and species are assumed to be ideal. Therefore, the ideal gas law relates the concentrations with the partial pressures ($P_{i,\text{electro}}$) according to Equation 5.21.

$$\frac{dF_{i,\text{electro}}}{dV_{\text{electro}}} = R_{i,\text{electro}} \quad (5.20)$$

$$P_i|_{\text{electro}} = c_i R T|_{\text{electro}} \quad (5.21)$$

The primary model used to describe electrokinetics is given by the Butler-Volmer Equation (5.22), which relates the activation overpotential/loss ($\eta_{\text{act,electrode}}$) in an electrode with the current density (j), also generally referring to the rate-determining electronic transfers and surface interactions in the electrolyzer cell. The exchange current densities in both cathode and anode ($j_{0,\text{cathode}}, j_{0,\text{anode}}$) are empirically estimated through Equations 5.23 and 5.24, which are concentration dependent on a reference condition^[45]. The actual rates are given

by Faraday's law (Equation 5.25).

$$j = j_{0,\text{electrode}} \cdot \left\{ \exp \left(\frac{\alpha Z_e F \eta_{\text{act,electrode}}}{RT} \right) - \exp \left[\frac{(1 - \alpha) Z_e F \eta_{\text{act,electrode}}}{RT} \right] \right\} \quad (5.22)$$

$$j_{0,\text{anode}} = \left(\frac{P_{\text{H}_2}}{P_{\text{electro,ref}}} \right)^A \left(\frac{P_{\text{H}_2\text{O}}}{P_{\text{electro,ref}}} \right)^B \cdot \kappa_{\text{anode}} \cdot \exp \left(\frac{-E_{\text{a,anode}}}{RT} \right) \quad (5.23)$$

$$j_{0,\text{cathode}} = \left(\frac{P_{\text{O}_2}}{P_{\text{electro,ref}}} \right)^C \cdot \kappa_{\text{cathode}} \cdot \exp \left(\frac{-E_{\text{a,cathode}}}{RT} \right) \quad (5.24)$$

$$R_i|_{\text{electro}} = \nu_i \frac{j \cdot a_{\text{electrode}}}{Z_e F} \quad (5.25)$$

The applied voltage in the cell (V_{applied}) relates to the activation overpotentials in each electrode ($\eta_{\text{act,electrode}}$) according to the voltage balance in Equation 5.26. The equilibrium voltage (V_{eq}) is given by Nernst equation (Equation 5.27), while the ohmic overpotential (η_{ohm}) is given by Equation 5.29. The current density in the cell for a nominal applied voltage is calculated by numerically solving the voltage balance with the Newton-Raphson method.

$$V_{\text{applied}} = V_{\text{eq}} + \eta_{\text{act,anode}} + \eta_{\text{act,cat}} + \eta_{\text{ohm}} \quad (5.26)$$

$$V_{\text{eq}} = V_0 + \left(\frac{RT_{\text{electro}}}{Z_e F} \right) \ln \left(\frac{P_{\text{H}_2} P_{\text{O}_2}^{1/2}}{P_{\text{H}_2\text{O}}} \right) \quad (5.27)$$

$$V_0 = [1.229 - 0.9 \cdot 10^{-3} \cdot (T_{\text{electro}} - T_{\text{ref}})][V] \quad (5.28)$$

$$\eta_{\text{ohm}} = j \cdot R_{\Omega} \quad (5.29)$$

Table 5.5: Electrolyzer constants and parameters.

Parameter	Description	Value
v	gas velocity	0.1 [m/s]
R	ideal gas constant	8.314 [J/(mol · K)]
L_{electro}	length of the electrolyzer	3 [m]
D_{electro}	diameter of the electrolyzer	0.3 [m]
$k_{\text{H}_2\text{O}}$	thermal conductivity of water	$105.67 \cdot 10^{-3}$ [W/(mK)]
k_{H_2}	thermal conductivity of hydrogen	$361 \cdot 10^{-3}$ [W/(mK)]
k_{N_2}	thermal conductivity of nitrogen	$51.53 \cdot 10^{-3}$ [W/(mK)]
k_{O_2}	thermal conductivity of oxygen	$48.10 \cdot 10^{-3}$ [W/(mK)]
$k_{\text{eff,electro}}$	effective conductivity of mixture	$\sum y_i k_i$
τ_{anode}	anode thickness	$50 \cdot 10^{-6}$ [m]
$\tau_{\text{electrolyte}}$	electrolyte thickness	$20 \cdot 10^{-6}$ [m]
τ_{cathode}	cathode thickness	$500 \cdot 10^{-6}$ [m]
σ_{anode}	anode electrical conductivity	$8.4 \cdot 10^3$ [1/(Ω m)]
$\sigma_{\text{electrolyte}}$	electrolyte electrical conductivity	$33.4 \cdot 10^3 \cdot \exp(-10.3 \cdot 10^3 / T_{\text{electro}})$ [1/(Ω m)]
σ_{cathode}	cathode electrical conductivity	$80 \cdot 10^3$ [1/(Ω m)]
R_{Ω}	global electrolyzer resistivity	Equation 5.19
$\Delta H_{\text{electrolysis}}$	enthalpy of water electrolysis	$285.83 \cdot 10^3$ [J/mol]]
D_{H_2}	effective hydrogen diffusivity	$2 \cdot 10^{-5}$ [m ² /s]
$D_{\text{H}_2\text{O}}$	effective water diffusivity	$2 \cdot 10^{-5}$ [m ² /s]
D_{N_2}	effective nitrogen diffusivity	$2 \cdot 10^{-5}$ [m ² /s]
D_{O_2}	effective oxygen diffusivity	$2 \cdot 10^{-5}$ [m ² /s]
α	charge transfer coefficient	0.5
Z_e	number of electrons involved in electrolysis	2
F	Faraday's constant	96485.33 [C/mol]
A	hydrogen exponent coefficient	0.41
B	water exponent coefficient	0.40
C	oxygen exponent coefficient	0.3
κ_{anode}	anode's exchange current density coefficient	$3.5 \cdot 10^6$ [A/m ²]
κ_{cathode}	cathode's exchange current density coefficient	$3.35 \cdot 10^9$ [A/m ²]
$E_{\text{a,anode}}$	anode's activation energy	$1.37 \cdot 10^5$ [J/mol]]
$E_{\text{a,cathode}}$	cathode's activation energy	$1.40 \cdot 10^5$ [J/mol]]
a_{anode}	anode's specific area	1 [m ² /m ³]
a_{cathode}	cathode's specific area	1 [m ² /m ³]
V_{applied}	applied voltage	1.60 [V]
$\nu_{\text{H}_2\text{O}}$	water stoichiometric coefficient	-1
ν_{H_2}	hydrogen stoichiometric coefficient	1
ν_{O_2}	oxygen stoichiometric coefficient	1/2
r	recycle ratio	0.5

Table 5.6: Electrolyzer boundary conditions.

Boundary Conditions	Expression
Inlet - Heat Transport	$-\frac{\partial T_{\text{electro}}}{\partial z} _{z=0} = \frac{\rho c_p v}{k_{\text{eff,electro}}} [T_{\text{electro}} _{z=0} - (1-r)T_{\text{feed}} - rT_{\text{electro}} _{z=L}], r = 0.5$
Inlet - Species Transport	$\frac{\partial c_i}{\partial z} _{z=0} = \frac{v}{D_i} [c_i _{z=0} - (1-r)c_{i,\text{feed}} - rc_i _{z=L}]$
Outlet - Heat Transport	$\frac{\partial T_{\text{electro}}}{\partial z} = 0$
Outlet - Species Transport	$\frac{\partial c_i}{\partial z} = 0$

Table 5.7: Initial and feed conditions of the electrolyzer.

Initial Parameters	
$T_{\text{ref},0}$	1073.15 [K]
$P_{\text{ano},0}$	2 [atm]
$P_{\text{cat},0}$	2 [atm]
$y_{\text{H}_2,0}$	0.01
$y_{\text{H}_2\text{O},0}$	0.99
$y_{\text{N}_2,0}$	0.79
$y_{\text{O}_2,0}$	0.21
$c_{i,0}$	$(y_{i,0}P_{\text{electro},0})/(RT_{\text{ref},0})$
Initial Conditions	
Heat Transport	Mass Transport
$T_z _{t=0} = T_{\text{ref},0}$	$c_{i,z} _{t=0} = c_{i,0}$
Feed Conditions	
T_{feed}	750 [K]
$P_{i,\text{feed}}$	$y_{i,0}P_{\text{electrode},0}$

5.5.2 Ammonia Synthesis Reactor Model

The model of the ammonia synthesis reactor is expressed similarly to the description in the electrolyzer (a plug-flow unit). Equations and 5.30 present the energy balance in the reactor.

$$\frac{dT_{\text{reactor}}}{dV_{\text{reactor}}} = \frac{\sum Q}{\sum (F_{i,\text{reactor}} \cdot C_{p,i})} \quad (5.30)$$

The specific molar heat of the species applied to the reactor is given by:

$$C_{P,N_2}|_{\text{reactor}} = R \cdot (3.280 + 0.593 \cdot 10^{-3} \cdot T_{\text{reactor}} + 0.040 \cdot 10^5 \cdot T_{\text{reactor}}^{-2}) \text{ [J/(mol} \cdot \text{K)]} \quad (5.31)$$

$$C_{P,H_2}|_{\text{reactor}} = R \cdot (3.249 + 0.422 \cdot 10^{-3} \cdot T_{\text{reactor}} + 0.083 \cdot 10^5 \cdot T_{\text{reactor}}^{-2}) \text{ [J/(mol} \cdot \text{K)]} \quad (5.32)$$

$$C_{P,NH_3}|_{\text{reactor}} = R \cdot (3.578 + 3.020 \cdot 10^{-3} \cdot T_{\text{reactor}} - 0.186 \cdot 10^5 \cdot T_{\text{reactor}}^{-2}) \text{ [J/(mol} \cdot \text{K)]} \quad (5.33)$$

The volumetric heat terms include the heat of reaction and the heat exchanged in a cooling jacket with a thermal regulation fluid:

$$\begin{aligned} \sum Q &= \Delta H_{\text{reactor}} \cdot R_{NH_3} - \frac{U_{\text{reactor}} A_{\text{lateral}} (T_{\text{reactor}} - T_{\text{regulation}})}{V_{\text{reactor}}}, \\ A_{\text{lateral}} &= \pi D_{\text{reactor}} L_{\text{reactor}}; \quad V_{\text{reactor}} = \pi (D_{\text{reactor}}/2)^2 L_{\text{reactor}} \end{aligned} \quad (5.34)$$

$$\begin{aligned} \Delta H_{\text{reactor}} [\text{cal/mol}_{NH_3}] &= (0.54526 + 846.609 \cdot T_{\text{reactor}}^{-1} + 459.734 \cdot 10^6 \cdot T_{\text{reactor}}^{-3}) \cdot P_{\text{bar}} + \\ &+ 5.34685 \cdot T_{\text{reactor}} + 0.2525 \cdot 10^{-3} \cdot T_{\text{reactor}}^2 - 1.69197 \cdot 10^{-6} \cdot T^3 + 9157.09 \end{aligned} \quad (5.35)$$

Equation 5.36 expresses the molar species conservation in the reactor. The work of Temkin and Pyzhev provides the most widespread reaction rate law used to predict NH_3 synthesis (Equation 5.37), assuming that N_2 dissociative adsorption is the rate-limiting elementary reaction^[47,48]. In Equation 5.37, a_i denotes the activity coefficient of species i , ϕ_i is the fugacity coefficient of species i .

$$\frac{dF_{i,\text{reactor}}}{dV_{\text{reactor}}} = R_{i,\text{reactor}} \quad (5.36)$$

$$R_{NH_3}|_{\text{reactor}} = k_2 \left[K_{\text{eq}}^2 \cdot a_{N_2} \cdot \left(\frac{a_{H_2}^3}{a_{NH_3}^2} \right)^{1/2} \cdot \left(\frac{a_{NH_3}^2}{a_{H_2}^3} \right)^{1/2} \right] \quad (5.37)$$

$$a_i = y_i \phi_i P_{\text{reactor}}; \quad P_{\text{reactor}} = P_{\text{N}_2} + P_{\text{H}_2} + P_{\text{NH}_3} \quad (5.38)$$

$$P_i|_{\text{reactor}} = c_i RT|_{\text{reactor}} \quad (5.39)$$

The reverse kinetic constant k_2 and the equilibrium constant K_{eq} are determined by Equations 5.40 and 5.41, respectively^[48–50].

$$k_2 = k_0 \cdot \exp\left(\frac{-E_a}{RT_{\text{reactor}}}\right); \quad k_0 = 8.8490 \cdot 10^{14} \left[\frac{\text{kmol}}{\text{m}^3 \cdot \text{h}}\right]; \quad E_a = -1.7056 \cdot 10^5 \left[\frac{\text{J}}{\text{mol}}\right] \quad (5.40)$$

$$\begin{aligned} \log(K_{\text{eq}}) = & -2.691122 \cdot \log(T_{\text{reactor}}) - 5.519265 \cdot 10^{-5} \cdot T_{\text{reactor}} \\ & + 1.848863 \cdot 10^{-7} \cdot T_{\text{reactor}}^2 + 2001.6 \cdot T_{\text{reactor}}^{-1} + 2.6899 \end{aligned} \quad (5.41)$$

The correlated fugacity coefficients are given by Equations 5.42–5.44:

$$\begin{aligned} \phi_{\text{N}_2} = & 0.93431737 + 0.3101804 \cdot 10^{-3} \cdot T_{\text{reactor}} + 0.295895 \cdot 10^{-3} \cdot P_{\text{reactor}}[\text{bar}] + \\ & -0.270729 \cdot 10^{-6} \cdot T_{\text{reactor}}^2 + 0.4775207 \cdot 10^{-6} \cdot (P_{\text{reactor}}[\text{bar}])^2 \end{aligned} \quad (5.42)$$

$$\begin{aligned} \phi_{\text{H}_2} = & \exp\{\exp(-3.8402 \cdot T_{\text{reactor}}^{0.125} + 0.541) \cdot P_{\text{reactor}}[\text{bar}] - \exp(-0.1263 \cdot T_{\text{reactor}}^{0.5} \\ & - 15.980) \cdot (P_{\text{reactor}}[\text{bar}])^2 + 300 \cdot \exp(-0.011901 \cdot T_{\text{reactor}} - 5.941) \cdot [\exp(-P_{\text{reactor}}[\text{bar}]/300) - 1]\} \end{aligned} \quad (5.43)$$

$$\begin{aligned} \phi_{\text{NH}_3} = & 0.1438996 + 0.2028538 \cdot 10^{-2} \cdot T_{\text{reactor}} - 0.4487672 \cdot 10^{-3} \cdot P_{\text{reactor}}[\text{bar}] + \\ & -0.1142945 \cdot 10^{-5} \cdot T_{\text{reactor}}^2 + 0.2761216 \cdot 10^{-6} (P_{\text{reactor}}[\text{bar}])^2 \end{aligned} \quad (5.44)$$

Table 5.8: Reactor constants and parameters.

Parameter	Description	Value
v	gas velocity	0.1 [m/s]
L_{reactor}	reactor length	3 [m]
D_{reactor}	reactor diameter	0.3 [m]
U_{reactor}	global heat transfer coefficient	35 [W/(m ² K)]
k_{N_2}	thermal conductivity of nitrogen	$51.53 \cdot 10^{-3}$ [W/(mK)]
k_{H_2}	thermal conductivity of hydrogen	$361 \cdot 10^{-3}$ [W/(mK)]
k_{NH_3}	thermal conductivity of ammonia	$78.22 \cdot 10^{-3}$ [W/(mK)]
$k_{\text{eff,reactor}}$	effective conductivity of mixture	$\sum y_i k_i$
D_{N_2}	effective nitrogen diffusivity	$2 \cdot 10^{-5}$ [m ² /s]
D_{H_2}	effective hydrogen diffusivity	$2 \cdot 10^{-5}$ [m ² /s]
D_{NH_3}	effective ammonia diffusivity	$2 \cdot 10^{-5}$ [m ² /s]
$T_{\text{regulation}}$	temperature of the regulation fluid	873.15 K]
r	recycle ratio	0.5

Table 5.9: Reactor boundary conditions.

Boundary Conditions	Expression
Inlet - Heat Transport	$\frac{\partial T_{\text{reactor}}}{\partial z} _{z=0} = \frac{\rho c_p v}{k_{\text{eff,reactor}}} [T_{\text{reactor}} _{z=0} - (1-r)T_{\text{feed}} - rT_{\text{reactor}} _{z=L}], r = 0.5$
Inlet - Species Transport	$\frac{\partial c_i}{\partial z} _{z=0} = \frac{v}{D_i} [c_i _{z=0} - (1-r)c_{i,\text{feed}} - rc_i _{z=L}]$
Outlet - Heat Transport	$\frac{\partial T_{\text{reactor}}}{\partial z} = 0$
Outlet - Species Transport	$\frac{\partial c_i}{\partial z} = 0$

Table 5.10: Initial and feed conditions of the reactor.

Initial Parameters	
$T_{\text{ref},0}$	723.15 [K]
$P_{\text{reactor},0}$	10 [bar]
$y_{\text{N}_2,0}$	0.24975
$y_{\text{H}_2,0}$	0.74925
$y_{\text{NH}_3,0}$	0.001
$c_{i,0}$	$(y_{i,0}P_{\text{reactor},0})/(RT_{\text{ref},0})$
Initial Conditions	
Heat Transport	Mass Transport
$T_z _{t=0} = T_{\text{ref},0}$	$c_{i,z} _{t=0} = c_{i,0}$
Nitrogen Feed Conditions	
$T_{\text{N}_2,\text{storage}}$	298.15 [K]
$P_{\text{N}_2,\text{feed}}$	1 [bar]

5.5.3 Heat Exchangers

For the sake of practicality, the temperatures of the streams leaving the heat exchangers were specified at $T_{\text{outlet,HE1,HE2}} = 1200\text{K}$, $T_{\text{outlet,HE3}} = 623.15\text{K}$, $T_{\text{outlet,HE4,HE5}} = 723.15\text{K}$ and $T_{\text{outlet,HE6}} = 393.15\text{K}$. A more rigorous design analysis can be further developed using logarithmic mean temperature difference or NTU methods.

5.5.4 Compressors

The compressors are essentially modeled using two thermodynamic expressions that describe the isentropic compression of an ideal gas under open flow^[51]. As shown by Equations 5.45 and 5.46, the outlet pressures and temperatures can be predicted straightforwardly from the inlet variables, given the total compressor power applied (W_{comp}). Even though those relations refer to steady-state operation, compressors and heat exchangers exhibit a pseudo-steady-state behavior because the inlet variables change in time. The constant η_{comp} represents the non-isentropic compression efficiency, which ranges between 0 and 1 and implies a decrease in the output pressure. It is assumed that $\eta_{\text{comp}} = 0.8$ for both nitrogen and hydrogen compressors. The total power applied individually to the nitrogen and

hydrogen compressors is given by the sum of a green component coming from the renewable energy module and an external power source component (Equation 5.47). The external source component is treated as a manipulable decision variable.

$$P_{\text{out}} = P_{\text{in}} \left[\left(\frac{\eta_{\text{comp}} W_{\text{comp}}}{c_p T_{\text{in}}} \right) + 1 \right]^{(c_p/R)} \quad (5.45)$$

$$T_{\text{out}} = T_{\text{in}} + \frac{\left[T_{\text{in}} \left(\frac{P_{\text{out}}}{P_{\text{in}}} \right)^{(R/c_p)} \right] - T_{\text{in}}}{\eta_{\text{comp}}} \quad (5.46)$$

$$W_{\text{comp}} = W_{\text{green,comp}} + W_{\text{ext,comp}} \quad (5.47)$$

5.6 Phenomenological Model of the Green Energy Modules

This module discusses the dynamic model of wind and solar power components, which have been widely studied and applied, though their coupling with chemical-transport models remains underexplored. Solar energy can be converted into electricity through photovoltaic panels, which utilize the photoelectric effect, or by concentrating solar-thermal technologies that concentrate solar heat to transfer it to a fluid, such as molten salts, for energy storage and transport. Both technologies have similar global efficiencies (20% to 40%), but solar-thermal systems offer the additional benefits of steam production and energy storage during periods without sunlight. This work develops a simple model for a small-scale solar-thermal system using properties of molten salt, incorporating the temporal variance of solar irradiance^[52–54]. In this model, molten salt (the heat transfer fluid, HTF) receives heat from the solar field, is stored in a reservoir, and serves as a heat source for a water evaporator that generates steam to drive a turbine. The system is illustrated in Figure 5.22. The turbine produces electrical power, which can be used in water electrolysis or ammonia synthesis. The system assumes no heat transfer losses, and the mass flows of the heat transfer fluid are

adjustable to control the dynamic temperature and hold-up of the reservoirs.

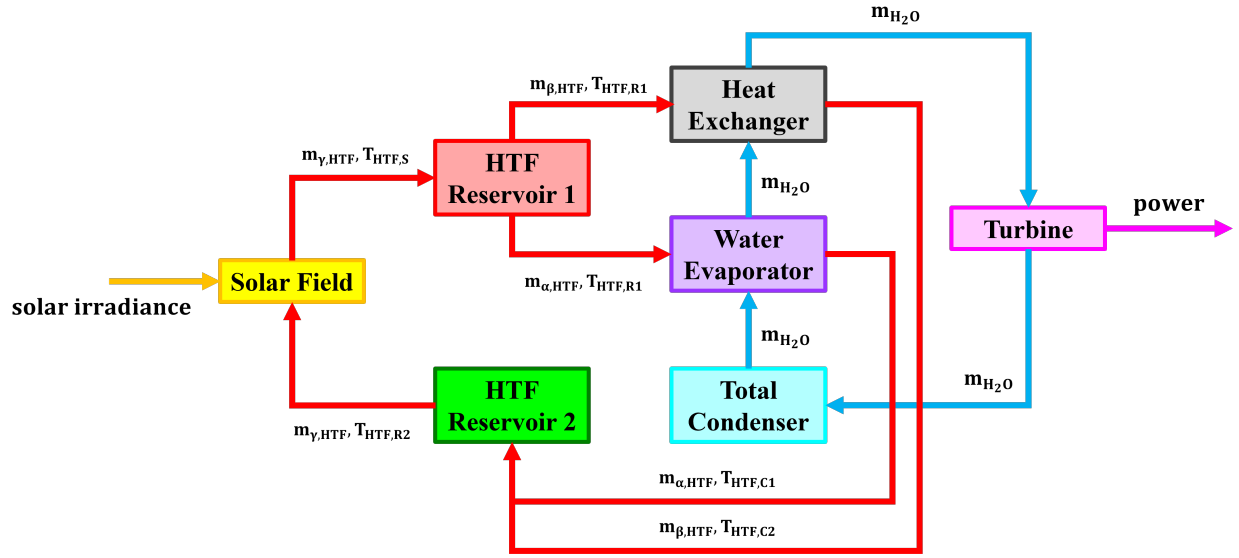


Figure 5.22: Design of the renewable energy modules.

5.6.1 Solar Energy Harvesting

Solar Field

The total solar power is a function of time and the area of the solar field. The dynamics of the solar irradiance (G) in a regular sunny summer day (Equation 5.48) is provided by a correlation regressed by Pelay et al.^[53]. For the sake of practical simplicity, heat losses and resistances are neglected. For a more comprehensive description, we indicate the works of Yao et al.^[52] and Li et al.^[55].

$$\begin{aligned}
& \text{if } t < 18420 \text{ [s]}, G = 0 \text{ [W/m}^2\text{]} \\
& \text{if } 18420 \text{ [s]} < t < 67020 \text{ [s]}, \\
& G = -4.985809 \cdot 10^{-24} t^6 + 1.264474 \cdot 10^{-18} t^5 - 1.309668 \cdot 10^{-13} t^4 + 7.086230 \cdot 10^{-9} t^3 \\
& \quad - 2.116637 \cdot 10^{-4} t^2 + 3.328676 t - 2.10949 \cdot 10^4 \text{ [W/m}^2\text{]} \\
& \text{if } t < 67020 \text{ [s]}, G = 0 \text{ [W/m}^2\text{]}
\end{aligned} \tag{5.48}$$

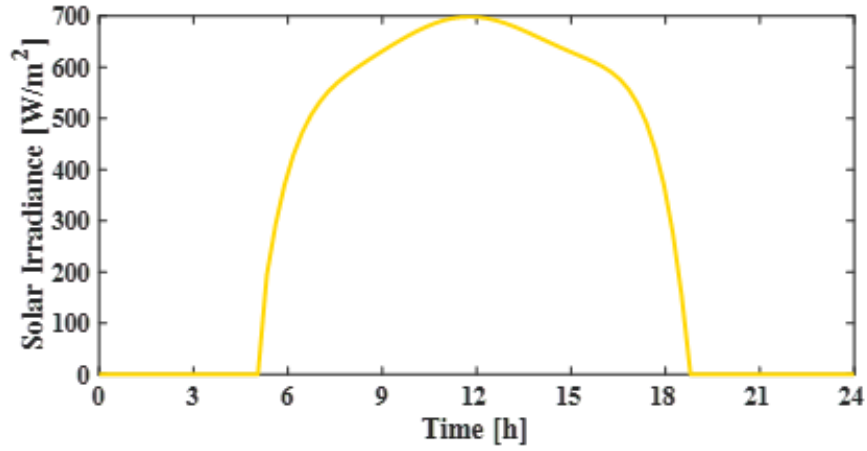


Figure 5.23: Ground solar irradiance under clear sky conditions on a regular summer day.

The reduced energy balance that determines the exiting temperature of the HTF from the solar field is shown by Equation 5.49. The parameters involved in the equations of this section are discriminated in Table 5.11.

$$T_{\text{HTF,SF}} = T_{\text{HTR,R2}} + \frac{G \cdot A_{\text{SF}}}{\dot{m}_{\text{HTF},\gamma} \cdot c_{p,\text{HTF}}} \tag{5.49}$$

Heat Transfer Fluid Reservoirs

Multiple-reservoir thermo-solar systems are suggested by the work of Yao. et al.^[52], Pelay et al.^[53], Wei et al.^[56], Yu et al.^[57] and Li et al.^[55]. They demonstrate that separating HTF streams with different thermal qualities from different system sectors yields a higher overall efficiency and facilitates easier mathematical resolution. The mass and energy balances that

describe the dynamics of the volumes ($V_{\text{HTR},\text{R1}}, V_{\text{HTR},\text{R2}}$) and homogeneous temperatures ($T_{\text{HTR},\text{R1}}, T_{\text{HTR},\text{R2}}$) of reservoirs 1 and 2, respectively, are shown below:

$$\frac{dV_{\text{HTR},\text{R1}}}{dt} = \frac{m_{\text{HTF},\gamma} \dot{m} - m_{\text{HTF},\alpha} \dot{m} - m_{\text{HTF},\beta} \dot{m}}{\rho_{\text{HTF}}} \quad (5.50)$$

$$\begin{aligned} \frac{dT_{\text{HTR},\text{R1}}}{dt} = & \left[m_{\text{HTF},\gamma} \dot{m} c_{p,\text{HTF}} (T_{\text{HTF},\text{SF}} - T_{\text{ref}}) - m_{\text{HTF},\alpha} \dot{m} c_{p,\text{HTF}} (T_{\text{HTF},\text{R1}} - T_{\text{ref}}) + \right. \\ & - m_{\text{HTF},\beta} \dot{m} c_{p,\text{HTF}} (T_{\text{HTF},\text{R1}} - T_{\text{ref}}) - h_{\text{conv}} A_{\text{R1}} (T_{\text{HTF},\text{R1}} - T_{\text{air}}) + \\ & \left. - \sigma \varepsilon A_{\text{R1}} (T_{\text{HTF},\text{R1}}^4 - T_{\text{air}}^4) - \rho_{\text{HTF}} c_{p,\text{HTF}} (T_{\text{HTF},\text{R1}} - T_{\text{ref}}) \frac{dV_{\text{HTR},\text{R1}}}{dt} \right] \frac{1}{(\rho_{\text{HTF}} V_{\text{HTR},\text{R1}} c_{p,\text{HTF}})} \end{aligned} \quad (5.51)$$

$$\frac{dV_{\text{HTR},\text{R2}}}{dt} = \frac{m_{\text{HTF},\alpha} \dot{m} + m_{\text{HTF},\beta} \dot{m} - m_{\text{HTF},\gamma} \dot{m}}{\rho_{\text{HTF}}} \quad (5.52)$$

$$\begin{aligned} \frac{dT_{\text{HTR},\text{R2}}}{dt} = & \left[m_{\text{HTF},\alpha} \dot{m} c_{p,\text{HTF}} (T_{\text{HTF},\text{C1}} - T_{\text{ref}}) + m_{\text{HTF},\beta} \dot{m} c_{p,\text{HTF}} (T_{\text{HTF},\text{C2}} - T_{\text{ref}}) + \right. \\ & - m_{\text{HTF},\gamma} \dot{m} c_{p,\text{HTF}} (T_{\text{HTF},\text{R2}} - T_{\text{ref}}) - h_{\text{conv}} A_{\text{R2}} (T_{\text{HTF},\text{R2}} - T_{\text{air}}) + \\ & \left. - \sigma \varepsilon A_{\text{R2}} (T_{\text{HTF},\text{R2}}^4 - T_{\text{air}}^4) - \rho_{\text{HTF}} c_{p,\text{HTF}} (T_{\text{HTF},\text{R2}} - T_{\text{ref}}) \frac{dV_{\text{HTR},\text{R2}}}{dt} \right] \frac{1}{(\rho_{\text{HTF}} V_{\text{HTR},\text{R2}} c_{p,\text{HTF}})} \end{aligned} \quad (5.53)$$

Evaporator

The evaporator acts as the steam source, operating at a constant defined pressure of 10 bars. Steam production occurs as soon as the boiling point is reached, according to the Antoine equation and the heat transfer rate. The temperature in the evaporator (T_{evap}) is maintained at the boiling point by logical, pseudo-entropic constants. Therefore, the thermal properties of the steam are conditioned by this temperature. The evaporator does not lose heat to the HTF, except by convection and environmental radiation. No steam generation happens if the evaporator temperature is lower than both the temperature of the HTF coming from

reservoir 1 and the boiling temperature of the water.

$$T_{\text{HTF},C1} = T_{\text{HTF},R1} - \frac{(\eta_{\text{evap}}) \dot{m}_{\text{HTF},\alpha} c_{p,\text{HTF}} (T_{\text{HTF},R1} - T_{\text{evap}})}{\dot{m}_{\text{HTF},\alpha} c_{p,\text{HTF}}} \quad (5.54)$$

$$\begin{aligned} \frac{dT_{\text{evap}}}{dt} = & \left[\dot{m}_{\text{vap},\text{H}_2\text{O}} (\Delta H_{\text{condensate}} - \Delta H_{\text{vap},\text{H}_2\text{O}}) + (\eta_{\text{evap}}) \dot{m}_{\text{HTF},\alpha} c_{p,\text{HTF}} (T_{\text{HTF},R1} - T_{\text{evap}}) + \right. \\ & \left. - h_{\text{conv}} A_{\text{evap}} (T_{\text{evap}} - T_{\text{air}}) - \sigma \varepsilon A_{\text{evap}} (T_{\text{evap}}^4 - T_{\text{air}}^4) \right] \frac{1}{(\rho_{\text{H}_2\text{O}} V_{\text{evap}} c_{p,\text{H}_2\text{O},\text{liq}})} \end{aligned} \quad (5.55)$$

$$\Delta H_{\text{condensate}} = c_{p,\text{H}_2\text{O},\text{liq}} \cdot (T_{\text{exit,cond}} - T_{\text{ref}}) \quad (5.56)$$

$$\dot{m}_{\text{vap},\text{H}_2\text{O}} = \frac{(\eta_{\text{evap}}) \dot{m}_{\text{HTF},\alpha} c_{p,\text{HTF}} (T_{\text{HTF},R1} - T_{\text{evap}})}{\Delta H_{\text{vap},\text{H}_2\text{O}}}, \text{ if } T_{\text{HTF},R1} > T_{\text{evap}} \quad (5.57)$$

Heat Exchanger and Steam Turbine

The steam exiting the evaporator is superheated in a heat exchanger with the HTF. It is assumed that the HTF stream has a lower heat capacity than that of superheated steam; thus, HTF determines the maximum amount of heat that can be transferred. Even though $\dot{m}_{\text{vap},\text{H}_2\text{O}}$ is smaller than $\dot{m}_{\text{HTF},\beta}$, its enthalpy is multiple times higher than that of the HTF, therefore, its heat capacity is higher as well.

$$T_{\text{HTF},C2} = T_{\text{HTF},R1} - \frac{(\eta_{\text{hex}}) \dot{m}_{\text{HTF},\beta} c_{p,\text{HTF}} (T_{\text{HTF},R1} - T_{\text{evap}})}{\dot{m}_{\text{HTF},\beta} c_{p,\text{HTF}}} \quad (5.58)$$

$$T_{\text{steam,HE}} = T_{\text{evap}} + \frac{(\eta_{\text{hex}}) \dot{m}_{\text{HTF},\beta} c_{p,\text{HTF}} (T_{\text{HTF},R1} - T_{\text{evap}})}{\dot{m}_{\text{vap},\text{H}_2\text{O}} c_{p,\text{gas},\text{H}_2\text{O}}} \quad (5.59)$$

A steam turbine is responsible for generating the output work or power from the solar energy system. Given the heat exchanger efficiency (η_{hex}), the steam temperature leaving the heat exchanger is readily found. Fixing the outlet steam pressure of the turbine at 5 bar,

its outlet temperature can be determined by assuming an isentropic expansion of an ideal gas according to Equation 5.60 for the isentropic expansion of an ideal gas^[51].

$$\Delta S = \int_{T_{\text{in}}}^{T_{\text{out}}} \frac{c_{p,\text{H}_2\text{O,gas}}}{T} dT - R \ln \frac{P_{\text{out}}}{P_{\text{in}}} = 0 \quad (5.60)$$

The isentropic enthalpy change (i.e., isentropic power generated) is then found (Equation 5.61) and adjusted by the turbine efficiency. The steam is condensed at constant pressure and returned to the evaporator as saturated liquid water. The effective mass balance of water in the evaporator is therefore neutral. Parameters and properties of this solar energy module are given in Table 5.11.

$$W_{\text{turbine}} = m_{\text{vap,H}_2\text{O}} \cdot \eta_{\text{turbine}} \cdot \int_{T_{\text{in}}}^{T_{\text{out}}} c_{p,\text{H}_2\text{O,gas}} dT \quad (5.61)$$

$$c_{p,\text{H}_2\text{O,gas}} = (1/\text{MM}_{\text{H}_2\text{O}}) \cdot R \cdot (3.470 + 1.450 \cdot 10^{-3} T + 0.121 \cdot 10^5 T^{-2}) [\text{J}/(\text{kg K})] \quad (5.62)$$

Table 5.11: Parameters of the solar energy system.

Parameter	Description	Value
A_{SF}	solar field area	5000 [m ²]
$m_{HTF,\alpha}$	mass flow rate of HTF sent to evaporator	8 [kg/s]
$m_{HTF,\beta}$	mass flow rate of HTF sent to heat exchanger	8 [kg/s]
$m_{HTF,\gamma}$	mass flow rate of HTF sent to solar field	16 [kg/s]
ρ_{HTF}	density of the HTF	2900 [kg/m ³]
$c_{p,HTF}$	specific heat of the HTF	1443 [J/(kg · K)]
$c_{p,H_2O,liq}$	specific heat of liquid water	4200 [J/(kg · K)]
A_{R1}	heat transfer area of the reservoir 1	20 [m ²]
A_{R2}	heat transfer area of the reservoir 2	20 [m ²]
A_{evap}	heat transfer area of the evaporator	20 [m ²]
h_{conv}	heat transfer coefficient of air	20 [W/(m ² · K)]
σ	Stefan-Boltzmann constant	$5.67 \cdot 10^{-8}$ [J/(s · m ² · K ⁴)]
ϵ	air emissivity	0.6
η_{evap}	global heat transfer efficiency in the evaporator	0.7
η_{hex}	global heat transfer efficiency in the heat exchanger	0.7
$\eta_{turbine}$	global turbine efficiency	0.4
T_{ref}	reference temperature	298.15 [K]
T_{air}	air temperature	298.15 [K]
$T_{exit,cond}$	exit temperature from total condenser	298.15 [K]
$V_{0,HTR,R1}$	initial volume of the reservoir 1	10 [m ³]
$V_{0,HTR,R2}$	initial volume of the reservoir 2	10 [m ³]
V_{evap}	initial volume of the evaporator	2 [m ³]
$T_{0,HTR,R1}$	initial temperature of the reservoir 1	500 [K]
$T_{0,HTR,R2}$	initial temperature of the reservoir 2	400 [K]
T_{evap}	initial temperature of the evaporator	420 [K]

5.6.2 Wind Energy Harvesting

The electricity produced by modular wind turbines are assumed to follow the correlation provided by Allman et al.^[5,6] (Equation 5.65), which directly relates both the blades' height and a forecasted wind velocity ($v_{w,f}$) with output power (W_{wind}) from an indiscriminate wind turbine. We assume that wind velocity (v_w) is a normal random variable changing at each time step with constant mean and standard deviation.

$$v_w = \mathcal{N}(\mu_{\text{wind}}, \sigma_{\text{wind}}^2) \quad (5.63)$$

$$v_{w,f}(t) = v_w(t) \left(\frac{H}{10 \text{ [m]}} \right)^{\frac{1}{7}}; \quad (5.64)$$

$$\begin{aligned} & \text{if } v_{w,f}(t) < v_{\text{cut in}}, \quad W_{\text{wind}} = 0 \\ & \text{if } v_{\text{cut in}} < v_{w,f} < v_{\text{cut off}}, \quad W_{\text{wind}} = W_{\text{rated}} \left(\frac{v_{w,f}^3 - v_{\text{cut in}}^3}{v_{\text{rated}}^3 - v_{\text{cut in}}^3} \right) \\ & \text{if } v_{\text{rated}} < v_{w,f} < v_{\text{cut off}}, \quad W_{\text{wind}} = W_{\text{rated}} \\ & \text{if } v_{w,f}(t) > v_{\text{cut off}}, \quad W_{\text{wind}} = 0 \end{aligned} \quad (5.65)$$

Table 5.12: Parameters of the wind energy system.

Parameter	Description	Value
μ_{wind}	mean wind velocity	varied [m/s]
σ_{wind}	deviation of the wind velocity	varied [m/s]
H	height of placement of the turbine blades	10 [m]
$v_{\text{cut in}}$	cut in wind velocity	1 [m/s]
$v_{\text{cut off}}$	cut off wind velocity	5 [m/s]
v_{rated}	rated wind velocity	1.5 [m/s]
W_{rated}	rated wind power capacity	2000 [W]

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Chapter 6

High Fidelity Modeling of Other Advanced Processes

6.1 Fluidized and Particulate Systems

Fluidized or particulate systems are characterized by a dispersed and insoluble phase (small solid particles, liquid droplets, or gas bubbles) interacting with a moving fluid under gravitational forces. Physical formulations that mathematically track the dynamic trajectories and boundaries of the discrete particles are possible. Still, they are highly computationally burdensome, rendering the simulation prohibitive for most large-scale real-time applications. Nonlinear, non-equilibrated, and non-homogeneous physical-chemical phenomena such as pyrolysis, oxidation, gasification, agglomeration, shrinking, segregation, and attrition may all occur, making it even more challenging to gain dynamic operational data about the process. Furthermore, accurate experimental measurements are, unfortunately, equally complicated to obtain.

In a review, Alobaid et al. ^[1] provide a broad overview of the modeling of fluidized systems. They evaluated and discussed the capabilities of the mixture, two-fluid, hybrid, and discrete-colliding particle models (soft and hard-sphere) applied to chemical-energy processes. The dynamic behavior of multiphase fluidized systems is more efficiently approximated by dis-

persed field approaches, such as the Euler-Euler model. A volume field function (ϕ) describes the local average volume fraction of the dispersed phase in the continuous phase, which is both interpenetrable. The field function then varies continuously between 0 (pure continuous phase) and 1 (pure dispersed phase)^[2]. In other words, the fluid and dispersed phases can exist simultaneously in space and time in dispersed multiphase flow models. Turbulence is the regular flow regime in fluidized systems. To capture motion fluctuations, the instantaneous velocity and other quantities are decomposed and approximated by time-averaged quantities, as conveniently describes the Reynolds-Average Navier-Stokes (RANS) model. In practice, the RANS model is solvable when turbulence variables, namely the kinetic energy (κ) and dissipation rate (ϵ), are introduced and combined with the momentum transport equations through stress tensors in the continuous fluid (τ_c) and dispersed phase (τ_d).

6.1.1 Theory and Methods

To predict the transport of both phases across the fluidized domain, the momentum conservation of the continuous phase is solved:

$$\rho_c \frac{\partial \mathbf{v}_c}{\partial t} + \rho_c (\mathbf{v}_c \cdot \nabla) \mathbf{v}_c = \nabla \cdot [-p\mathbf{I} + \tau_c] + \rho_c \mathbf{g} + \mathbf{F}_{m,c} + \mathbf{F}_c + \frac{m_{dc}}{\phi_c} (\mathbf{v}_{int} - \mathbf{v}_c) \quad (6.1)$$

$$\tau_c = (\mu_m + \mu_T)(\nabla \mathbf{v}_c + (\nabla \mathbf{v}_c)^T) - \frac{2}{3}(\nabla \cdot \mathbf{v}_c)\mathbf{I} - \frac{2}{3}\rho_c k\mathbf{I} \quad (6.2)$$

Along with the momentum conservation of the dispersed phase:

$$\rho_d \frac{\partial \mathbf{v}_d}{\partial t} + \rho_d (\mathbf{v}_d \cdot \nabla) \mathbf{v}_d = \nabla \cdot [-p\mathbf{I} + \tau_d] - \frac{\nabla p_s}{\phi_d} + \rho_d \mathbf{g} + \frac{\mathbf{F}_{m,d}}{\phi_d} + \mathbf{F}_d - \frac{m_{dc}}{\phi_d} (\mathbf{v}_{int} - \mathbf{v}_d) \quad (6.3)$$

$$\tau_d = (\mu_m + \mu_T)(\nabla \mathbf{v}_d + (\nabla \mathbf{v}_d)^T) - \frac{2}{3}(\nabla \cdot \mathbf{v}_d)\mathbf{I} - \frac{2}{3}\rho_d k\mathbf{I} \quad (6.4)$$

Additional conservation equations are coupled to determine the volume fractions of each phase:

$$\frac{\partial \phi_d}{\partial t} + \nabla \cdot (\phi_d \mathbf{v}_d) - \nabla \cdot (D_{m,d} \nabla \phi_d) = -\frac{m_{dc}}{\phi_d}; \quad (6.5)$$

$$\nabla \cdot (\phi_c \mathbf{v}_c + \phi_d \mathbf{v}_d) = \frac{m_{dc}}{\phi_d} \left(\frac{1}{\rho_c} - \frac{1}{\rho_d} \right) \quad (6.6)$$

$$\phi_c = 1 - \phi_d \quad (6.7)$$

$$\phi = \phi_d \rho_d + \phi_c \rho_c \quad (6.8)$$

The kappa-epsilon (κ - ε) turbulence model (Equations 6.9 and 6.10) is commonly employed to simulate mean-flow characteristics under turbulent conditions. Phase-specific turbulence variables may be defined; however, the complexity multiplies accordingly, which may cause numerical and computational difficulties.

$$\frac{\partial \kappa}{\partial t} + \rho(\mathbf{v}_m \cdot \nabla) \kappa = \nabla \cdot \left[\left(\mu_m + \frac{\mu_T}{\sigma_k} \right) \nabla \kappa \right] + P_k - \rho \varepsilon \quad (6.9)$$

$$\rho \frac{\partial \varepsilon}{\partial t} + \rho(\mathbf{v}_m \cdot \nabla) \varepsilon = \nabla \cdot \left[\left(\mu_m + \frac{\mu_T}{\sigma_k} \right) \nabla \varepsilon \right] + C_{\varepsilon,1} \frac{\varepsilon}{k} P_k - C_{\varepsilon,2} \rho \frac{\varepsilon^2}{k} \quad (6.10)$$

$$P_k = \mu_T \left[\nabla \mathbf{v}_m : \left(\nabla \mathbf{v}_m + (\nabla \mathbf{v}_m)^T - \frac{2}{3} (\nabla \cdot \mathbf{v}_m) \mathbf{I} \right) \right] - \frac{2}{3} \rho k (\nabla \cdot \mathbf{v}_m) \quad (6.11)$$

$$\mu_T = \rho C_\mu \frac{k^2}{\varepsilon} \quad (6.12)$$

In its simplest form, the κ - ε model also necessitates the definition of an average mixture viscosity and velocity (Equations 6.13 and 6.15).

$$\mu_m = \mu_c \left(1 - \frac{\phi_d}{\phi_{d,\max}} \right) \left[-2.5\phi_{d,\max} \left(\frac{\mu_d + 0.4\mu_c}{\mu_d + \mu_c} \right) \right] \quad (6.13)$$

$$D_{m,d} = \frac{\mu_T}{\rho\sigma_T} \quad (6.14)$$

$$\mathbf{v}_m = \frac{\phi_d \rho_d \mathbf{v}_d + \phi_c \rho_c \mathbf{v}_c}{\phi_d \rho_d + \phi_c \rho_c} \quad (6.15)$$

Table 6.1 presents typical values of the parameters of the κ - ϵ model, which have been optimized for the most fluidization cases.

Table 6.1: Parameters of the κ - ϵ model.

Parameter	Value
$C_{\epsilon,1}$	1.44
$C_{\epsilon,2}$	1.92
C_μ	0.09
σ_κ	1
σ_ϵ	1.30
κ_V	0.41
B	5.2
σ_T	0.35

The two phases exchange momentum through drag forces (F_d), and fortunately, the Euler-Euler formulation is flexible enough to accommodate different drag models. The Schiller-Naumann (Equation 6.16) is a general drag model for diluted flows, valid for dispersed, rigid spheres when $Re_p < 2.5 \cdot 10^5$.

$$C_d = \frac{24}{Re_p} \cdot (1 + 0.15 Re_p^{0.687}), \text{ for } Re_p < 1000 \quad (6.16)$$

$$C_d = 0.44, \text{ for } Re_p > 1000$$

The Hadamard-Rybczynski model (Equation 6.17) is appropriate for diluted flows at low Reynolds numbers.

$$C_d = \frac{24}{\text{Re}_p} \cdot \left(\frac{1 + \frac{2}{3} \frac{\mu_c}{\mu_d}}{1 + \frac{\mu_c}{\mu_d}} \right) \quad (6.17)$$

The Haider-Levenspiel model (Equation 6.18) describes diluted non-spherical solid particles for low and moderate particle Reynolds numbers. The drag coefficient follows the Schiller-Naumann model, but includes empirical correlations of particle sphericity (S_p).

$$C_d = \frac{24}{\text{Re}_p} \cdot \left[1 + A(S_p) \cdot \text{Re}_p^{B(S_p)} \right] + \frac{C(S_p)}{\left(1 + \frac{D(S_p)}{\text{Re}_p} \right)} \quad (6.18)$$

The Gidaspow model (Equation 6.19) describes the drag force coefficient (β) for dense dispersed phase flows (i.e., solid particles in gas) for all concentrations of the dispersed solid, including high concentrations.

$$\begin{aligned} \beta &= \frac{3\phi_c\phi_d\rho_c C_d}{4d_p} \cdot \mathbf{v}_{\text{slip}} \cdot \phi^{2.65}, \text{ for } \phi_c > 0.8 \\ \beta &= 150 \cdot \left(\frac{\mu_c\phi_d^2}{\phi_c d_p^2} \right) + 1.75 \left(\frac{\phi_d\rho_c}{d_p} \right) |\mathbf{v}_{\text{slip}}|, \text{ for } \phi_c < 0.8 \end{aligned} \quad (6.19)$$

Finally, a solid pressure (p_s) model is required for fluid-solid mixtures where $\rho_d \gg \rho_c$, for example, solid particles in gas flow. The solid pressure captures particle interactions due to collisions and friction between them. Models like the Gidaspow and Ettehadieh (Equations 6.21 and 6.22, respectively) implement a gradient diffusion-based assumption to account for solid pressure, in which the empirical function $-G(\phi_d)$ is treated as the modulus of elasticity or powder modulus.

$$\nabla p_s = -G(\phi_d) \nabla \phi_d \quad (6.20)$$

$$G(\phi_d)|_{\text{Gidaspow}} = 10^{(-10.5\phi_d+9)} \quad (6.21)$$

$$G(\phi_d)|_{\text{Ettehadieh}} = 10^{(-10.46\phi_d+6.577)} \quad (6.22)$$

6.1.2 Simulation Results

The Euler-Euler model is evaluated by simulating a fluidized-bed reactor (FBR) that produces high-quality silicon particles used in solar cell manufacturing. The Gidaspow drag and solid pressure models were chosen since solid-gas fluidization occurs in the reactor. The fluid is composed of a hot mixture of silane, which decomposes into hydrogen and silicon vapor, as it flows from the bottom to the top boundary in a 2D domain. The silicon vapor nucleates and crystallizes to form fine particles, while the latter is scavenged by larger particles. Figures 6.1 and 6.2 show the dynamic evolution of solid volume fraction (or porosity) in the first few seconds. Initially, a porous bed (porosity = 0.5) of silicon seed particles with an average particle size of 100 μm is located at the bottom. The inlet gas velocity is 0.1 m/s. As the system displays bubbling and slurry flow regimes, the solid is dispersed by the gas, and the bed quickly reaches a new steady-state with almost five times its original height and consequently one-fifth of its original porosity. The behavior would not be the same for solid particles of different sizes: the minimum fluidization velocity tends to be much smaller for smaller particles, and they may even be carried out of the reactor, depending on the gas velocity.

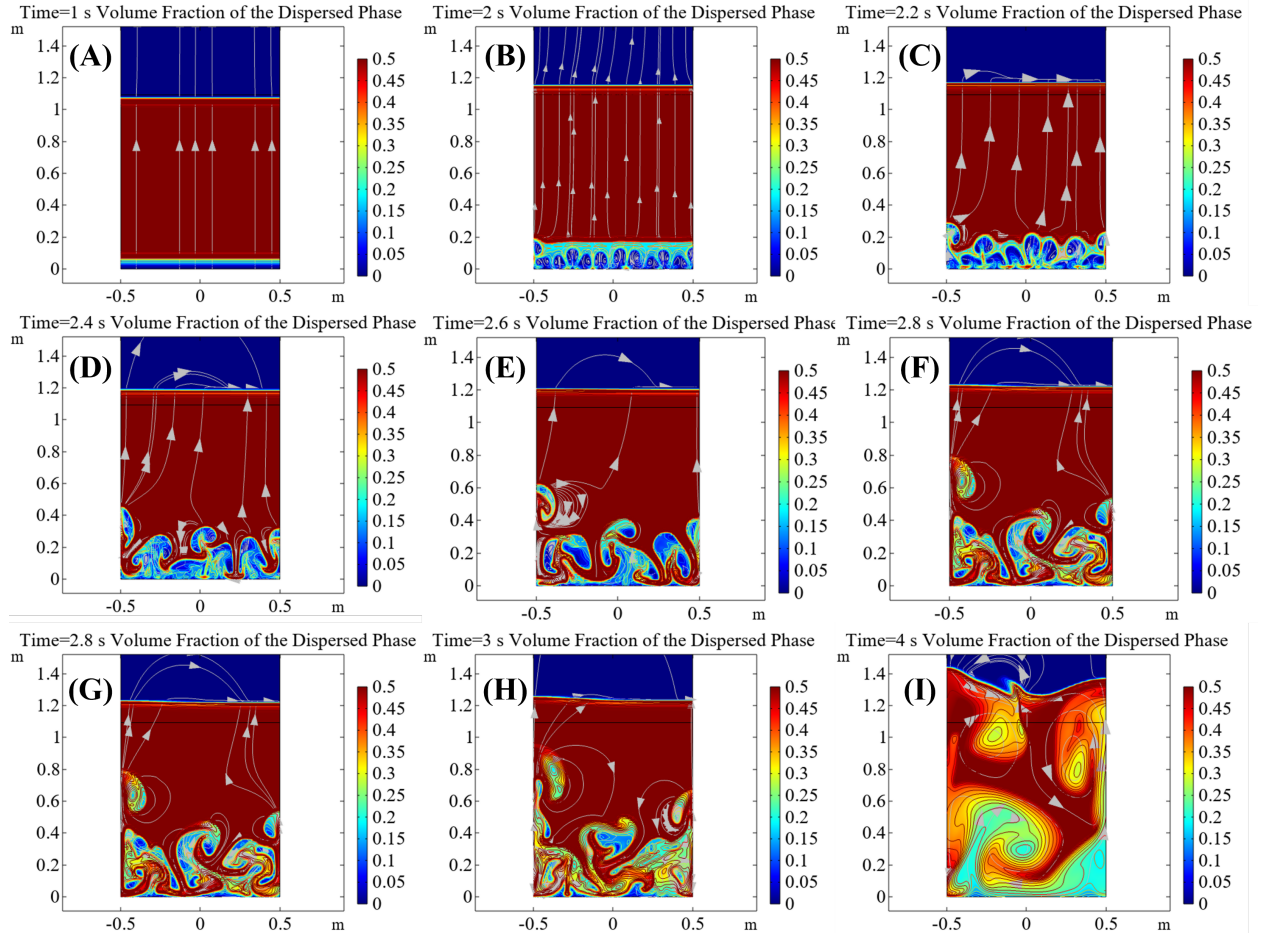


Figure 6.1: Initial dynamic evolution of the solid volume fraction in a FBR at times equal to (A) 1 s, (B) 2 s, (C) 2.2 s, (D) 2.4 s (E) 2.6 s.

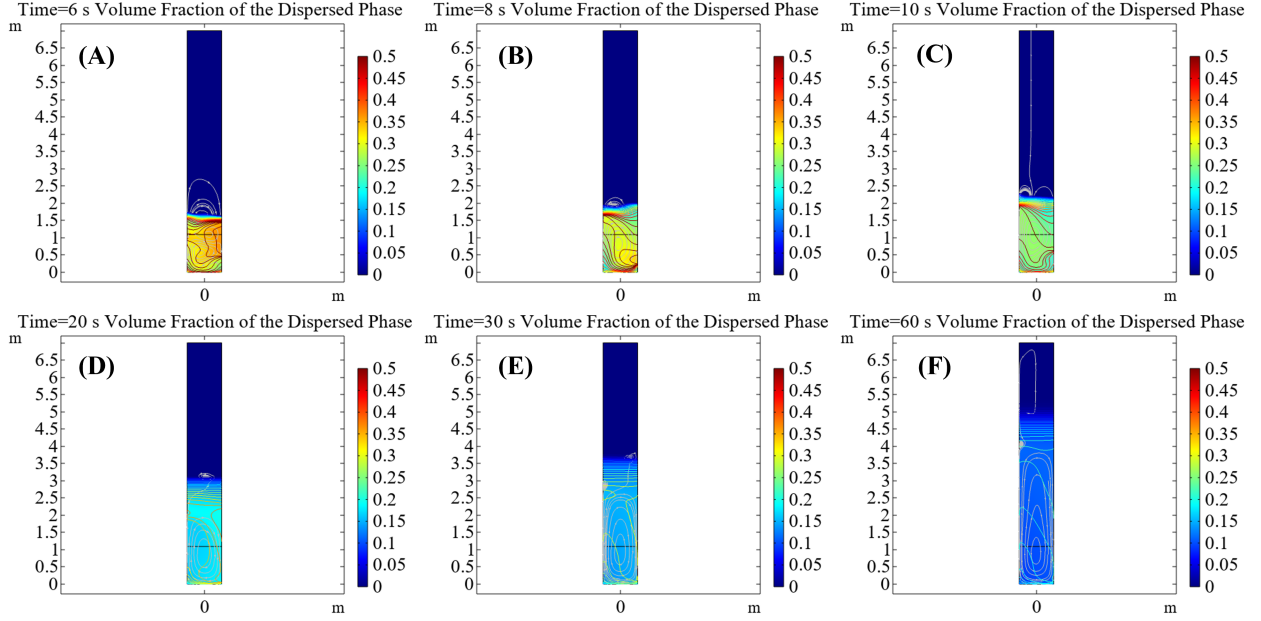


Figure 6.2: Later dynamic evolution of the solid volume fraction in a FBR.

6.2 Conceptual Digital Twin Modeling of a Bioreactor

Digital twins (DT) are virtual computational models representing real objects and processes. They ideally replicate the geometry, physical properties, and essential phenomena occurring in the object, simulating it in real time or faster. It is expected that the simulated and real objects should have identical outputs. Even though uncertainties and discrepancies between the model and the real object exist, they can be studied and minimized to a satisfactory level, such that the model provides accurate insights and reliable predictions of the behavior of the real object. This project proposed the development of a digital twin model for a bioreactor. A bioreactor is a vessel or container where certain chemicals are biologically metabolized into useful industrial products, such as ethanol, through batch or fed-batch operations. The equipment comprises multiple phases: a liquid culture medium, air or oxygen, solid organic matter (cell colonies), and other solid apparatus for mixing (impeller, blades) and sensing.

6.2.1 Sugar Fermentation Kinetics and Ethanol Production

Under oxidizing conditions, yeast cells can utilize sugar (through fermentation and oxidation) and ethanol (through oxidation) to continuously grow in the bioreactor. Air is injected into the bioreactor to provide oxygen, which is transferred from the air bubbles to the bulk of the liquid phase and dissolved. Essential variables of the process are the concentration of biomass, sugar, ethanol, dissolved oxygen, and specific activities of free enzymes involved in the fermentation of sugar, oxidation of sugar, and oxidation of ethanol. Kinetic information about the three processes is given by Di Serio et al. [3,4]. The bioreaction rates depend on the local concentrations of biomass, dissolved oxygen, sugar, and ethanol, as well as the specific enzyme activities.

Sugar fermentation:

$$r_{\text{sug,ferm}} \left[\frac{\text{kg}_{\text{bio}}}{\text{m}^3\text{s}} \right] = \zeta_{\text{sug,ferm}} \cdot \eta_{\text{ferm}} \quad (6.23)$$

$$\zeta_{\text{sug,ferm}} = \mu_{\text{max,ferm}} \cdot a_{\text{enz,ferm}} \cdot \left(\frac{c_{\text{sug}}}{K_{\text{sug,ferm}} + c_{\text{sug}}} \right) c_{\text{bio}} \quad (6.24)$$

$$\eta_{\text{sug,ferm}} = \frac{\zeta_{\text{sug,ferm}}}{\max(\zeta_{\text{sug,ferm}}, \zeta_{\text{sug,ox}}, \zeta_{\text{eth,ferm}})} \quad (6.25)$$

Sugar oxidation:

$$r_{\text{sug,ox}} \left[\frac{\text{kg}_{\text{bio}}}{\text{m}^3\text{s}} \right] = \zeta_{\text{sug,ox}} \cdot \eta_{\text{sug,ox}} \quad (6.26)$$

$$\zeta_{\text{sug,ox}} = \mu_{\text{max,sug,ox}} \cdot a_{\text{enz,sug,ox}} \cdot \left(\frac{c_{\text{sug}}}{K_{\text{sug,ox}} + c_{\text{sug}}} \right) \cdot \left(\frac{c_{\text{O}_2}}{K_{\text{O}_2} + c_{\text{O}_2}} \right) c_{\text{bio}} \quad (6.27)$$

$$\eta_{\text{sug,ox}} = \frac{\zeta_{\text{sug,ox}}}{\max(\zeta_{\text{sug,ferm}}, \zeta_{\text{sug,ox}}, \zeta_{\text{eth,ferm}})} \quad (6.28)$$

Ethanol oxidation:

$$r_{\text{eth,ox}} \left[\frac{\text{kg}_{\text{bio}}}{\text{m}^3 \text{S}} \right] = \zeta_{\text{eth,ox}} \cdot \eta_{\text{eth,ox}} \quad (6.29)$$

$$\zeta_{\text{eth,ox}} = \mu_{\text{max,eth,ox}} \cdot a_{\text{enz,eth,ox}} \cdot \left(\frac{c_{\text{eth}}}{K_{\text{eth,ox}} + c_{\text{eth}}} \right) \cdot \left(\frac{c_{\text{O}_2}}{K_{\text{O}_2} + c_{\text{O}_2}} \right) c_{\text{bio}} \quad (6.30)$$

$$\eta_{\text{eth,ox}} = \frac{\zeta_{\text{eth,ox}}}{\max(\zeta_{\text{sug,ferm}}, \zeta_{\text{sug,ox}}, \zeta_{\text{eth,ferm}})} \quad (6.31)$$

Rate of change of the enzyme activities:

$$\frac{da_{\text{enz,ferm}}}{dt} = (\mu_{\text{max,ferm}} + \beta) \cdot \left[1 - \varepsilon + \varepsilon \lambda_{\text{sug,ferm}} \left(\frac{c_{\text{sug}}}{K_{\text{sug,ferm}} + c_{\text{sug}}} \right) \right] - \left(\beta + \sum_i r_i \right) a_{\text{enz,ferm}} \quad (6.32)$$

$$\lambda_{\text{sug,ferm}} = \frac{\zeta_{\text{sug,ferm}}}{\sum_i \zeta_i} \quad (6.33)$$

$$\frac{da_{\text{enz,sug,ox}}}{dt} = (\mu_{\text{max,sug,ox}} + \beta) \cdot \left[1 - \varepsilon + \varepsilon \lambda_{\text{sug,ox}} \left(\frac{c_{\text{sug}}}{K_{\text{sug,ox}} + c_{\text{sug}}} \right) \right] - \left(\beta + \sum_i r_i \right) a_{\text{enz,sug,ox}} \quad (6.34)$$

$$\lambda_{\text{sug,ox}} = \frac{\zeta_{\text{sug,ox}}}{\sum_i \zeta_i} \quad (6.35)$$

$$\frac{da_{\text{enz,eth,ox}}}{dt} = (\mu_{\text{max,eth,ox}} + \beta) \cdot \left[1 - \varepsilon + \varepsilon \lambda_{\text{eth,ox}} \left(\frac{c_{\text{eth}}}{K_{\text{eth,ox}} + c_{\text{eth}}} \right) \right] - \left(\beta + \sum_i r_i \right) a_{\text{enz,eth,ox}} \quad (6.36)$$

$$\lambda_{\text{eth,ox}} = \frac{\zeta_{\text{eth,ox}}}{\sum_i \zeta_i} \quad (6.37)$$

Table 6.2: Kinetic parameters, stoichiometric coefficients, and yields of the bioreactions.

Parameter	Value	Parameter	Value	Parameter	Value
ϕ_{ferm}	$0.41 \frac{\text{kg}_{\text{eth,produced}}}{\text{kg}_{\text{sug,consumed}}}$	$\phi_{\text{sug,ox}}$	$0.52 \frac{\text{kg}_{\text{O}_2,\text{consumed}}}{\text{kg}_{\text{sug,consumed}}}$	$\phi_{\text{eth,ox}}$	$1.067 \frac{\text{kg}_{\text{O}_2,\text{consumed}}}{\text{kg}_{\text{eth,consumed}}}$
Y_{ferm}	$0.15 \frac{\text{kg}_{\text{bio,produced}}}{\text{kg}_{\text{sug,consumed}}}$	$Y_{\text{sug,ox}}$	$0.50 \frac{\text{kg}_{\text{bio,produced}}}{\text{kg}_{\text{sug,consumed}}}$	$Y_{\text{eth,ox}}$	$0.74 \frac{\text{kg}_{\text{bio,produced}}}{\text{kg}_{\text{eth,consumed}}}$
$\mu_{\text{max,ferm}}$	$1.25 \cdot 10^{-4} \text{s}^{-1}$	$\mu_{\text{max,sug,ox}}$	$9.1667 \cdot 10^{-5} \text{s}^{-1}$	$\mu_{\text{max,eth,ox}}$	$5.5556 \cdot 10^{-5} \text{s}^{-1}$
$K_{\text{sug,ferm}}$	$1 \frac{\text{kg}}{\text{m}^3}$	$K_{\text{sug,ox}}$	$1 \cdot 10^{-3} \frac{\text{kg}}{\text{m}^3}$	$K_{\text{eth,ox}}$	$0.08 \frac{\text{kg}}{\text{m}^3}$
β	$5.5556 \cdot 10^{-5} \text{s}^{-1}$	ε	0.909	K_{O_2}	$4.6 \cdot 10^{-5} \frac{\text{kg}}{\text{m}^3}$

6.2.2 Reactor Geometry

The main geometric features of the bioreactor are displayed in Table 6.3. The bioreactor is a modular cylindrical tank designed for liquid reactive media, equipped with sensors and connected to an autonomous controller. The manipulated variables are the impeller rotation rate, heating jacket power, cooling water flow rate, and air inflow. The controlled variables are temperature, dissolved oxygen concentration, and pH. Figure 6.3 shows a picture of the real bioreactor. The impeller is attached to 2 sets of 6 rectangular radial blades near the vessel's bottom and middle.

Table 6.3: Geometric features of the bioreactor

Parameter	Value
Vessel height	32.5 cm
Vessel diameter	18 cm
Impeller diameter	11.9 mm
Blade width	15.5 mm
Blade height	18 mm
Blade support diameter	31 mm
Blade support thickness	18 mm
Relative height of blade set 1 from bottom	5.5 cm
Relative height of blade set 2 from bottom	14.5 cm



Figure 6.3: Picture of the real bioreactor.

6.2.3 COMSOL Digital Twin

The digital twin created in COMSOL is a 3-dimensional model that attempts to represent the geometry (Figure 6.3) and physical behavior of the real bioreactor in the most incredible detail possible. The main outputs from a real bioreactor would be the liquid velocity, temperature, and species concentrations at each point of the bioreactor. Therefore, to describe and predict the real system with high fidelity and account for the multiphase fluid interac-

tions, the model considers conservation of momentum, energy, and mass of the aqueous and air phases. Solid organic phases are disregarded.

The continuity and Navier-Stokes equations (Equation 6.38 and 6.39) for the liquid are coupled and modified to incorporate the presence of different phases with volume field fractions ($\phi_{\text{liq}}, \phi_{\text{gas}}$), similarly to the approach described in the previous section.

$$\rho_{\text{liq}} \cdot (\nabla \cdot \mathbf{v}_{\text{liq}}) = 0 \quad (6.38)$$

$$\rho_{\text{liq}} \frac{\partial \mathbf{v}_{\text{liq}}}{\partial t} + \rho_{\text{liq}} (\mathbf{v}_{\text{liq}} \cdot \nabla) \mathbf{v}_{\text{liq}} = \nabla [-p\mathbf{I} + \mathbf{K}] + \phi_{\text{liq}} \rho_{\text{liq}} \mathbf{g} \quad (6.39)$$

$$\mathbf{K} = (\mu_{\text{liq}} + \mu_T) \cdot [\nabla \mathbf{v}_{\text{liq}} + (\nabla \mathbf{v}_{\text{liq}})^T] \quad (6.40)$$

Air is introduced through an inlet boundary in the inferior part of the moving domain. The conservation balance for air takes the form of Equation 6.41, where $\dot{m}_{\text{gl}}$ is the mass transfer rate from the gas to the liquid. The mass transfer rate typically depends on the interfacial area between the two phases and occurs when a gas dissolves into a liquid. To determine the interfacial region, it is necessary to solve for both the bubble number density (i.e., the number of bubbles per unit volume) and the phase volume fraction. Interphase effects such as surface tension, buoyancy, and transport across phase boundaries can be treated as additional sources and sinks. The interfacial model was assumed to be a homogeneous flow when there is no relative velocity (no slip) between the phases; in other words, the bubbles always follow the liquid phase.

$$\rho_{\text{gas}} \frac{\partial \phi_{\text{gas}}}{\partial t} + \nabla \cdot (\rho_{\text{gas}} \phi_{\text{gas}} \mathbf{v}_{\text{gas}}) = -\dot{m}_{\text{gl}} \quad (6.41)$$

$$\mathbf{v}_{\text{gas}} = \mathbf{v}_{\text{liq}} + \mathbf{v}_{\text{slip}} - \frac{D_{\text{gc}}}{\phi_{\text{gas}}} \nabla \phi_{\text{gas}} \quad (6.42)$$

$$D_{gc} = \frac{\mu_T}{\rho_{liq}\sigma_T} \quad (6.43)$$

Turbulence was handled by the RANS/ $\kappa - \varepsilon$ model:

$$\rho_{liq} \frac{\partial \kappa}{\partial t} + \rho_{liq} (\mathbf{v}_{liq} \cdot \nabla) \kappa = \nabla \cdot \left[\left(\mu_{liq} + \frac{\mu_T}{\sigma_k} \right) \nabla \kappa \right] + P_k - \rho_{liq} \varepsilon + S_\kappa \quad (6.44)$$

$$\rho_{liq} \frac{\partial \varepsilon}{\partial t} + \rho (\mathbf{v}_m \cdot \nabla) \varepsilon = \nabla \cdot \left[\left(\mu_m + \frac{\mu_T}{\sigma_k} \right) \nabla \varepsilon \right] + C_{\varepsilon,1} \frac{\varepsilon}{k} P_k - C_{\varepsilon,2} \rho_{liq} \frac{\varepsilon^2}{k} + C_\varepsilon S_\kappa \frac{\kappa}{\varepsilon} \quad (6.45)$$

$$P_k = \mu_T \left[\nabla \mathbf{v}_{liq} : \left(\nabla \mathbf{v}_{liq} + (\nabla \mathbf{v}_{liq})^T \right) \right] \quad (6.46)$$

$$\mu_T = \rho_{liq} C_\mu \frac{\kappa^2}{\varepsilon} \quad (6.47)$$

$$S_\kappa = -C_\kappa \phi_{gas} \nabla p \cdot \mathbf{v}_{slip} \quad (6.48)$$

Only the properties of liquid water were employed to obtain a solution for the heat transport (Equation 6.49), and a homogenized thermal domain was assumed. Since convection by fluid motion is the major contributor to heat transfer, uncoupled solutions for the liquid velocity field are first attempted to alleviate computational demands.

$$\rho_{liq} c_{p,liq} \frac{\partial T}{\partial t} + \rho_{liq} c_{p,liq} \mathbf{v}_{liq} \cdot \nabla T + \nabla \cdot (-k_{eff} \nabla T) = \dot{Q} \quad (6.49)$$

Figure 6.4 shows the replicated COMSOL model and the mesh applied to solve the conservation equations. The solutions were approximated by the Finite Element Method (FEM). All internal wall boundaries were assumed to be no-slip. In a few simulations, the external lateral walls of the bioreactor DT were exposed to constant heat fluxes to emulate a heating jacket.

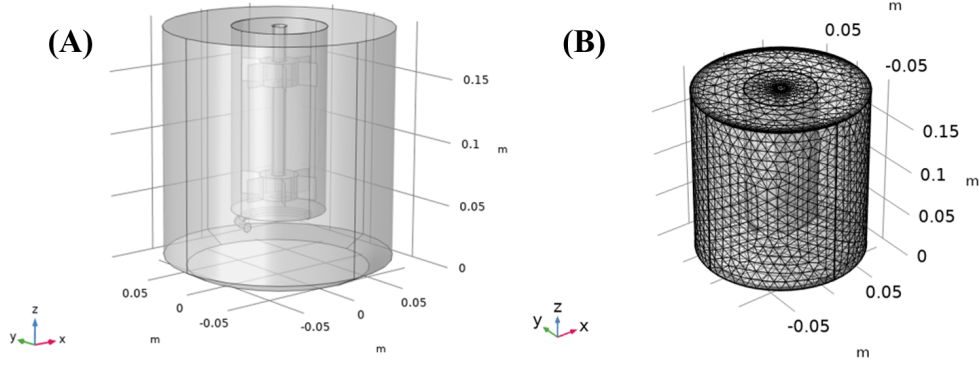


Figure 6.4: (A) Replicated bioreactor model; (B) Meshed model.

6.2.4 MATLAB Digital Twin

Spatial homogenization is the most significant assumption of the MATLAB digital twin. It assumes that the output variables do not depend significantly on space, so it neglects the geometry of the bioreactor and other physical features or phenomena that encompass spatial variations. A differential energy balance was formulated for a homogenized medium, considering the fluxes from a heating jacket and volumetric thermal exchanges with humid air.

$$\rho_{\text{liq}} V_{\text{liq}} c_{p,\text{liq}} \frac{dT}{dt} = -UA_{\text{lat}} (T - T_{\text{amb}}) - \rho_{\text{air}} \nu_{\text{air}} \Delta H_{\text{air}} \quad (6.50)$$

$$\Delta H_{\text{air}} = \int_{T_{\text{in}}}^T (c_{p,\text{dry air}} + w_{\text{hum}} \cdot c_{p,\text{water vapor}}) dT + w_{\text{hum}} \cdot \Delta H_{\text{water vapor}} \quad (6.51)$$

w_{hum} is the absolute humidity of the air, which is given as a function of the relative humidity ϕ_{hum} :

$$w_{\text{hum}} = 0.622 \cdot \frac{P_{\text{vap}}}{P - P_{\text{vap}}}; P_{\text{vap}} = \phi_{\text{hum}} \cdot P_{\text{sat}} \quad (6.52)$$

$$P_{\text{sat}} = 1000 \cdot \exp \left(16.3872 - \frac{3885.70}{T + 230.170} \right) [\text{Pa}] \quad (6.53)$$

6.2.5 Study of the Hydrodynamics and Heat Transfer in a Bioreactor

Experiments were conducted to study the thermo-hydrodynamics of the bioreactor as a function of agitation rate, airflow and heat input rate (the manipulated variables of the equipment). Agitation/rotation rates of 50, 100 and 200 RPM and air flow rates of 5 and 10 L/min were evaluated. The experiments involved heating water in the bioreactor to 50°C at a constant agitation rate and allowing it to undergo natural cooling under varying mixing agitation rates and air flow rates. Temporal temperature data were measured by a sensor in the reactor and contrasted with the COMSOL and MATLAB digital twin models.

6.2.6 Simulation Results

A steady-state numerical solution with the COMSOL DT was achieved after 60 seconds for the three components of the liquid velocity field in a situation with no air flow and a rotation rate of 50 RPM. The field is represented in Figure 6.5. It displays a regular rotating field that resembles an altered Taylor-Couette flow. The x and y components have similar magnitudes and change orientation, establishing the rotating pattern observed. A transient solution of the velocity field in the bioreactor was obtained for 15 seconds of simulation when air was injected at a rate of 5 L/min. The velocity field components are shown in Figure 6.6. It is observed that the combination of a rotating bulk mass of water and an air bubble system creates a highly turbulent and mixed system. Good mixing is, in fact, a desired feature in reactors because it reduces spatial variations in temperature and concentration. In other words, a high degree of mixing homogenizes the output variables across space and validates this assumption for a more easily computable model, such as the MATLAB model. That very complex velocity field exhibits a pseudo-steady state with continuous fluctuations. An extended solution for longer periods was not attempted, due to convergence problems and significant computational demand.

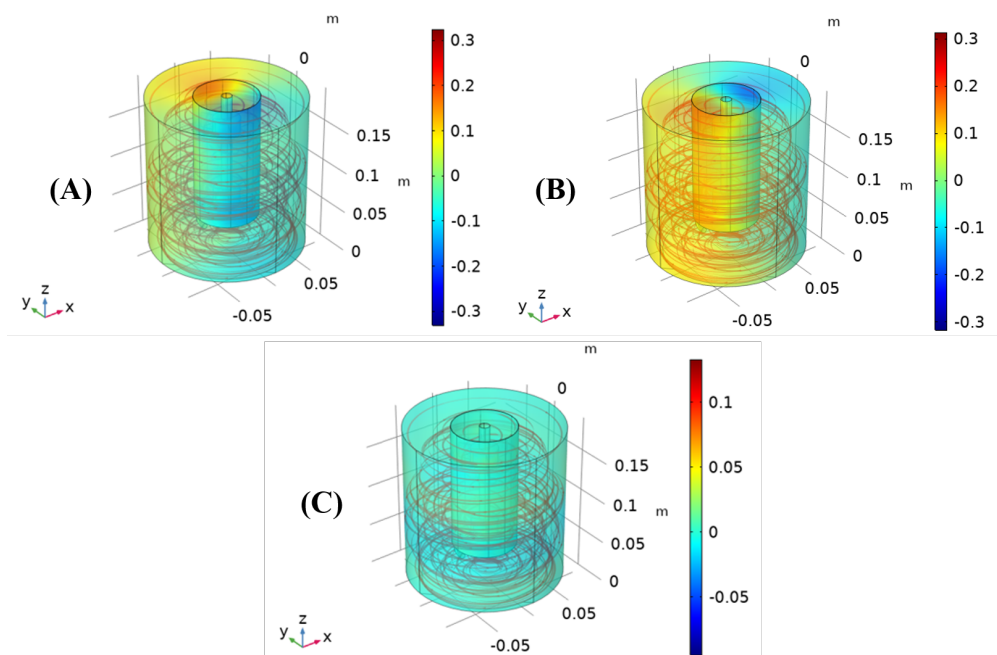


Figure 6.5: Component of the liquid velocity field in the (A) x, (B) y, and (C) z directions when no air is injected and an agitation rate of 50 RPM is applied.

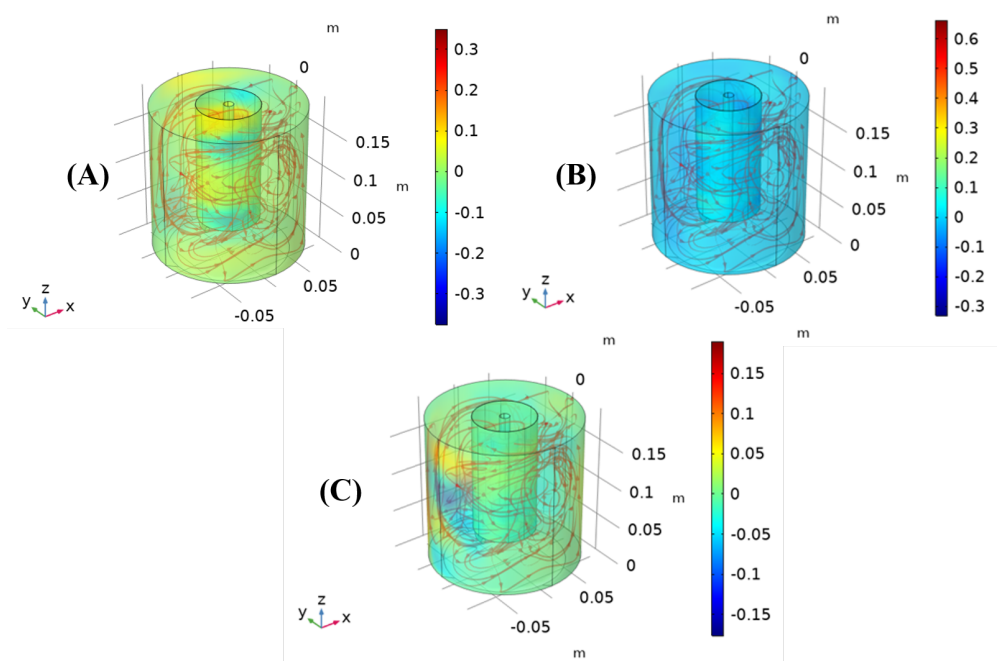


Figure 6.6: Component of the liquid velocity field in the (A) x, (B) y, and (C) z directions when air is injected with a flow rate of 5 L/min and an agitation rate of 50 RPM is applied.

The dynamics of the average reactor temperature predicted by the COMSOL DT was validated with an experiment using an impeller rotation of 100 RPM. Figure 6.7 shows a

satisfactory agreement between the model and experiments. Further simulations with the COMSOL DT for different lateral heat fluxes predict that the reactor is thermally homogeneous throughout all domains (Figure 6.8). Axial temperature gradients become noticeable only when a heat flux exceeding 1500 W/m^2 is applied, resulting in a higher temperature at the bottom of the reactor.

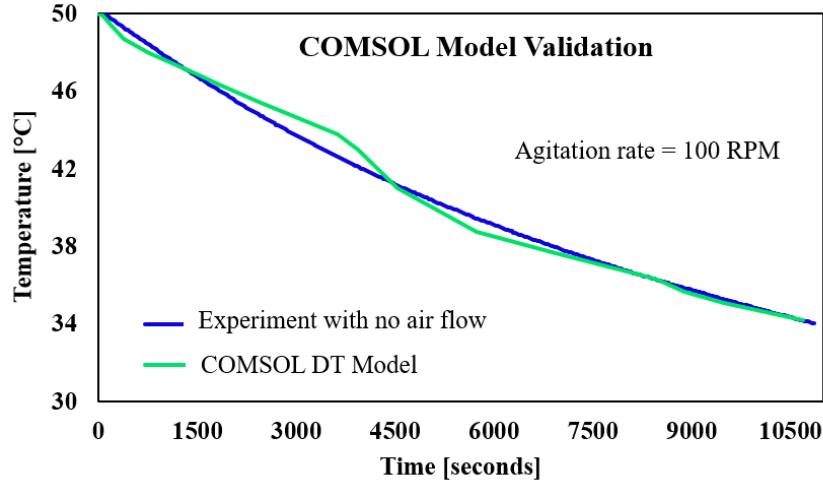


Figure 6.7: Validation of the average temperature predicted by the COMSOL DT model.

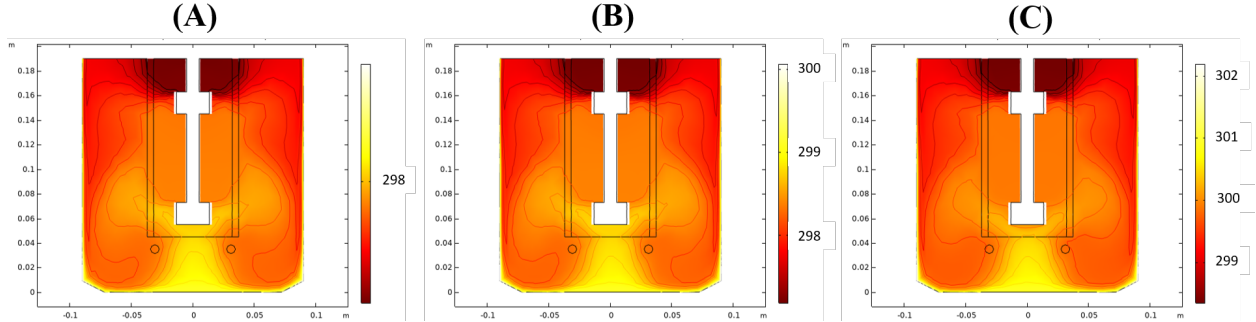


Figure 6.8: Predictions of the temperature field with the COMSOL DT model for an agitation rate of 50 RPM and lateral heat fluxes of (A) 1000 W/m^2 , (B) 1500 W/m^2 , and (C) 2000 W/m^2 .

The temperature dynamics obtained experimentally and by the MATLAB model are contrasted in Figure 6.9. The applied rotation rates of the impeller seem to have little to no effect on the temperature temporal evolution comparatively, meaning that the slowest rotation tested (50 RPM) is enough to make heat convection by fluid motion and heat

diffusion in the wall of the bioreactor much faster than external convection, which is the limiting transport process. As expected, a higher air flow rate leads to a faster temperature decrease. Heat removal by air bubbles is a somewhat complex phenomenon, and it is treated in the MATLAB DT model as a heat sink. Nevertheless, it is noted that the excellent agreement between experimental data and model estimates is readily applicable for real-time prediction, optimization, and control.

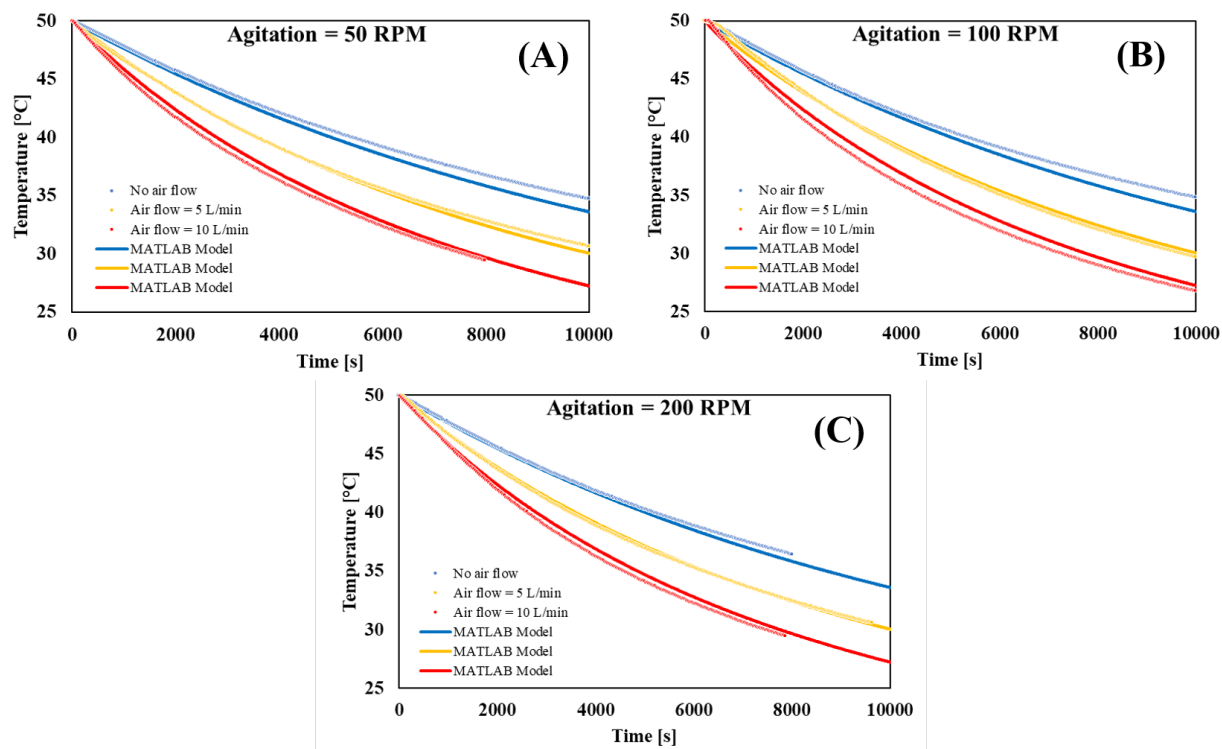


Figure 6.9: Comparison between the MATLAB DT and experimental data for different agitation rates.

6.3 Additive Manufacturing

Additive Manufacturing, also known as 3D printing, is a technology that creates three-dimensional objects by building them layer by layer from digital models. Unlike traditional manufacturing methods, which often involve cutting or molding materials, 3D printing enables greater precision, customization, and efficiency. It works with various materials, including plastics, metals, and biological substances, making it applicable in healthcare, aerospace,

and automotive industries. For those reasons, it has been considered a smart engineering method for product design and production, enabling innovative constructions and reducing material waste.

3D printing utilizes a wide range of liquid materials, each chosen based on its rheological properties and the intended application of the final product. Common materials include thermoplastics, such as PLA (polylactic acid) and ABS (acrylonitrile butadiene styrene), which are popular due to their ease of use and affordability. Resin and viscoelastic polymeric materials are employed when flexible and smoother components are needed in stereolithography. For more durable or functional parts, materials such as nylon, PETG, and polycarbonate can be used. In industrial and engineering applications, metal powders like stainless steel, titanium, and aluminum enable the production of strong, heat-resistant components. Emerging biomaterials and food-grade substances are also expanding the possibilities of 3D printing in fields such as medicine and the culinary arts.

6.3.1 Study of PDMS Printing

This project developed a model that simulates the incompressible viscous flow of PDMS, which is a common printing non-Newtonian material, whose apparent viscosity is characterized by the power law (Equation 6.54) or the Herschel-Bulkley-Papanastasiou equation. The power law is a function of the shear rate ($\dot{\gamma}$), fluid consistency (m), and flow index (n). The higher the fluid consistency, the more viscous the material appears. If $0 < n < 1$, the fluid exhibits shear thinning effects, while if $n > 1$, it has shear thickening effects. For this example, $m = 1000 \text{ Pa} \cdot \text{s}$ and $n = 0.1$.

$$\mu = m \left(\frac{\dot{\gamma}}{\dot{\gamma}_{\text{ref}}} \right)^{(n-1)} \quad (6.54)$$

$$\dot{\gamma} = \max \left(\sqrt{2\mathbf{S} : \mathbf{S}}, \dot{\gamma}_{\text{min}} \right) \quad (6.55)$$

$$S = \frac{1}{2} [\nabla \mathbf{v} + (\nabla \mathbf{v})^T] \quad (6.56)$$

The material ought to print a straight line on a flat surface, according to Figure 6.10. It represents a small syringe with a conical needle filled with the printing fluid, placed inside a block initially containing air. The geometric dimensions of the domains are shown in Table 6.4. The material is fed from the top boundary of the syringe at a pressure of 200 kPa. The outlet boundary is located at the rightmost corner of the block. The surface onto which the material is printed is a sliding conveyor belt at a constant relative velocity of 20 mm/s.

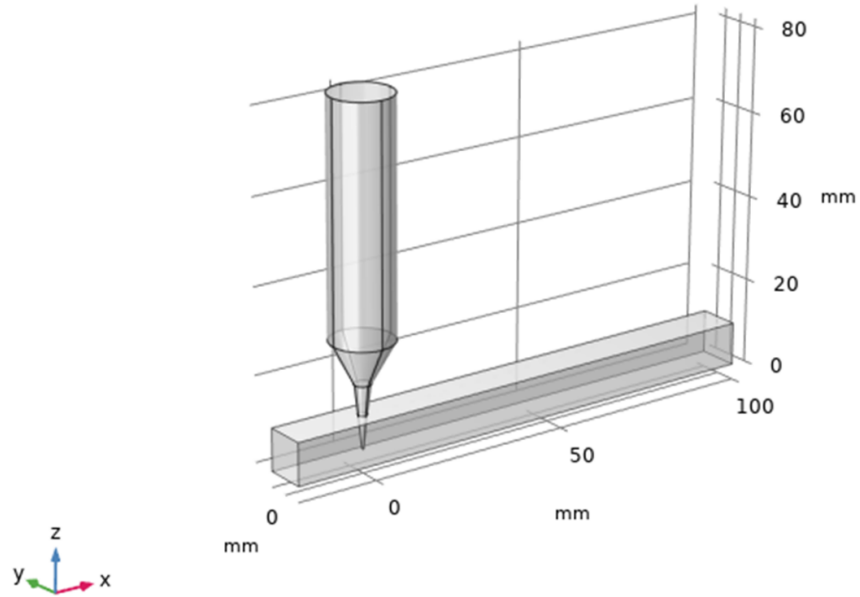


Figure 6.10: Geometry of the 3D printing device.

Table 6.4: Geometric features of the 3D printing device.

Parameter	Value
Internal syringe diameter	14.6 mm
Syringe height	55 mm
Internal needle base diameter	4 mm
Internal needle tip diameter	0.41 mm
Needle height	15 mm
Air block width	10 mm
Air block length	120 mm

6.3.2 The Level Set and Phase Field Methods

The model therefore contemplates the 2-phase flow of air and printing fluid, both governed by the continuity equation (Eq. 6.57) and a single Navier-Stokes equation (Equation 6.58); $\mathbf{v}$ is the spatial-temporal velocity field.

$$\frac{\partial \mathbf{v}}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \quad (6.57)$$

$$\rho \frac{\partial \mathbf{v}}{\partial t} + \rho (\mathbf{v} \cdot \nabla) \mathbf{v} = \mathbf{v} [-p\mathbf{I} + \mathbf{K}] + \mathbf{F} \quad (6.58)$$

$$\mathbf{K} = \mu \cdot [\nabla \mathbf{v} + (\nabla \mathbf{v})^T] + \frac{2}{3} \mu (\nabla \cdot \mathbf{v}) \mathbf{I} \quad (6.59)$$

To track the moving interface between phases, two approaches are tested: the level set and phase field methods. In field-based methods, a free liquid surface is represented as an isosurface of the level set or phase field functions, representing ϕ . The free liquid surface corresponds to the phase boundary between the liquid, gas, and solid parts and is defined on a fixed mesh. The level set function smoothly assumes values between 0 and 1 in mixed and interfacial regions, and in pure bulk regions of the fluid phases, it assumes either 0 or 1 values. Similarly, the phase field variable varies between -1 and 1 in mixed or interfacial regions and assumes either -1 or 1 in pure bulk regions. The level set and phase field functions are both advected by the velocity field computed by the Navier-Stokes equation.

The level set formulation includes a transport equation to the model (Equation 6.60) that ultimately provides the volume fraction of the phases in the domains; γ_{ls} is the reinitialization parameter (set to 1) and ϵ_{ls} is the interface thickness controlling parameter. A large thickness smears out the shape of the free surface. The problem becomes easier to solve, but accuracy in the shape of the free surface is lost. A small value of ϵ_{ls} yields a compact representation of the surface but requires a corresponding resolution of the mesh. There is no point in setting a value much smaller than the mesh element size, since the interface then becomes ragged and unresolved surface tension forces might cause spurious velocities.

$$\frac{\partial \phi}{\partial t} + \mathbf{v} \cdot \nabla \phi = \gamma_{\text{ls}} \nabla \cdot \left[\epsilon_{\text{ls}} \nabla \phi - \phi(1 - \phi) \frac{\nabla \phi}{|\nabla \phi|} \right] \quad (6.60)$$

The effective density and viscosity employed by the Navier-Stokes equation are volume-averaged by the volume field variable:

$$\rho = \rho_1 + (\rho_2 - \rho_1)\phi \quad (6.61)$$

$$\mu = \mu_1 + (\mu_2 - \mu_1)\phi \quad (6.62)$$

Surface tension forces between the fluids and the walls are also considered through the $\mathbf{F}$ term in the Navier-Stokes equation. The surface tension is represented by σ . The Navier slip boundary condition is designated at the interface with solid walls.

$$\mathbf{F} = \mathbf{F}_{\text{surface tension}} = \sigma \delta \kappa \mathbf{n}_{\text{int}} + \delta \nabla_s \sigma \quad (6.63)$$

$$\kappa = -\nabla \cdot \mathbf{n}_{\text{int}} \quad (6.64)$$

$$\nabla_s = \left(\mathbf{I} - \mathbf{n}_{\text{int}} \mathbf{n}_{\text{int}}^T \right) \nabla \quad (6.65)$$

The PDE governing the phase field variable is the Cahn-Hilliard equation (Equation 6.66). It adds a particular parameter, a source of external free energy ψ , which is minimized to determine the position of the interface. The interface thickness γ_{pf} is the product of a mobility tuning parameter (χ) and ϵ_{pf}^2 . The mobility tuning parameter determines the timescale of the Cahn-Hilliard diffusion and governs the diffusion-related timescale for the interface.

$$\frac{\partial \phi}{\partial t} + \mathbf{v} \cdot \nabla \phi = \nabla \cdot \left(\frac{\gamma_{\text{pf}} \lambda}{\epsilon_{\text{pf}}^2} \nabla \psi \right) \quad (6.66)$$

$$\psi = -\nabla \cdot \epsilon_{\text{pf}}^2 \nabla \phi + (\phi^2 - 1) \phi + \frac{\epsilon_{\text{pf}}^2}{\lambda} \frac{\partial f}{\partial \phi} \quad (6.67)$$

Interfacial forces are accounted for differently with the phase field approach:

$$\mathbf{F} = \mathbf{F}_{\text{surface tension}} = \left(\frac{\lambda}{\epsilon_{\text{pf}}^2} \psi - \frac{\partial f}{\partial \phi} \right) \quad (6.68)$$

6.3.3 Simulation Results

Level Set Approach

Figure 6.11 shows the volume fraction and isosurface of the multiphase air-PDMS mixture predicted by the level set model. The most noticeable effect is the lack of consistency in the printed material, which spreads and fills the spaces like a highly mixed, aerated, and dense fluid bound by the walls of the air domain. Figure 6.12 shows that the pressure gradients are only substantial at the tip of the needle. The physical presence of the needle creates a stagnant layer of air between faster flowing layers.

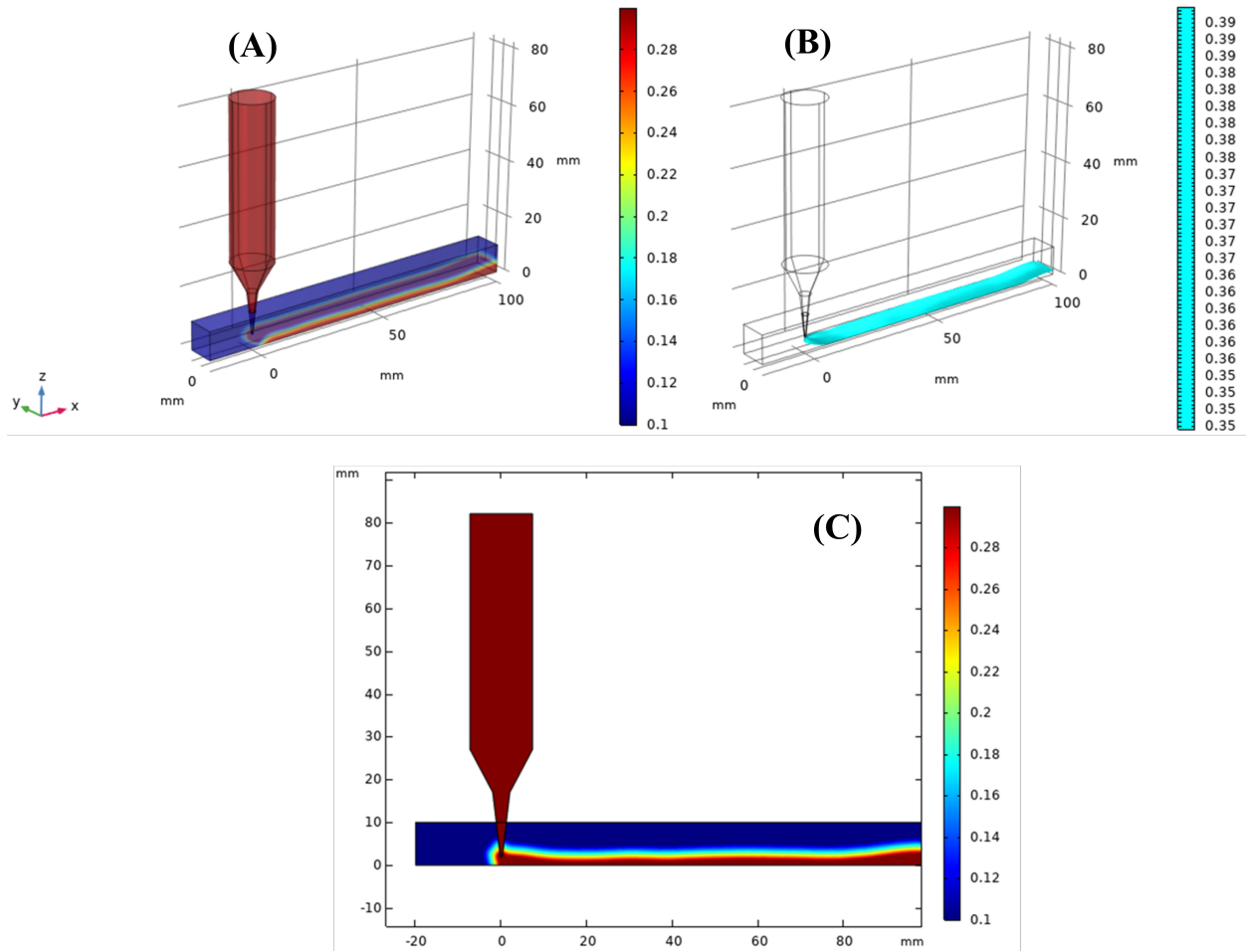


Figure 6.11: (A) Volume fraction of printed material; (B) isosurface of the printed line, and (C) cross-sectional view of the volume fraction along the xz plane at $y = 0$ and time equal to 10 seconds, for an applied absolute inlet pressure of 200 kPa.

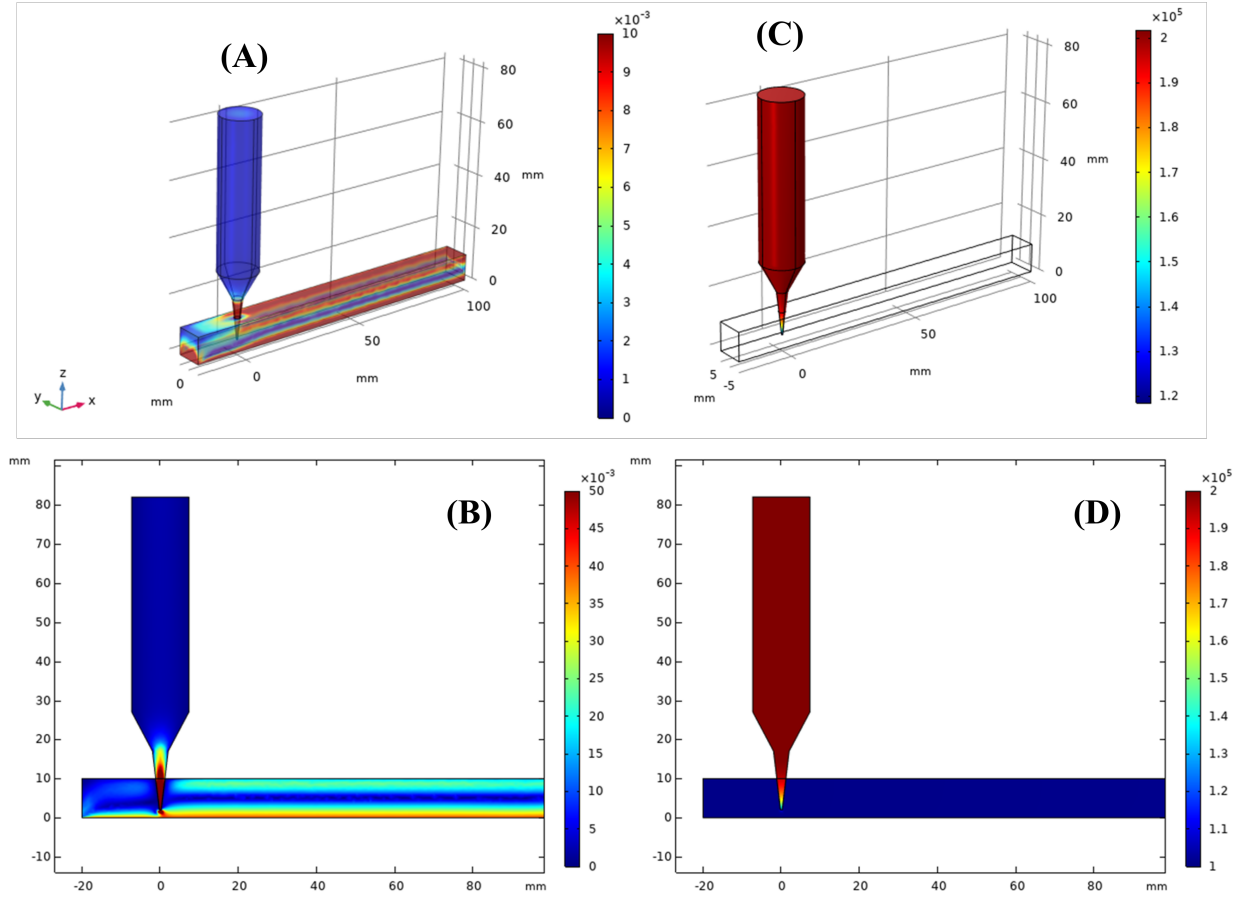


Figure 6.12: (A) Velocity field [m/s] in the whole 3D domain, (B) cross sectional view of the velocity field [m/s] along the xz plane at $y = 0$ and time equal to 10 seconds; (C) pressure field [Pa] in the whole 3D domain; (D) cross sectional view of the pressure field [Pa] along the xz plane at $y = 0$ and time equal to 10 seconds.

Phase Field Approach

The results obtained using the phase field approach under the same conditions differed significantly from those obtained with the previous method. As shown in Figure 6.13, there is not much spreading; a high degree of phase separation allowed a more homogeneous deposition of the PDMS. This phase separation can be attributed to weaker interfacial forces or lower wettability, which favor pure phase interactions and minimize fluid-structure interactions.

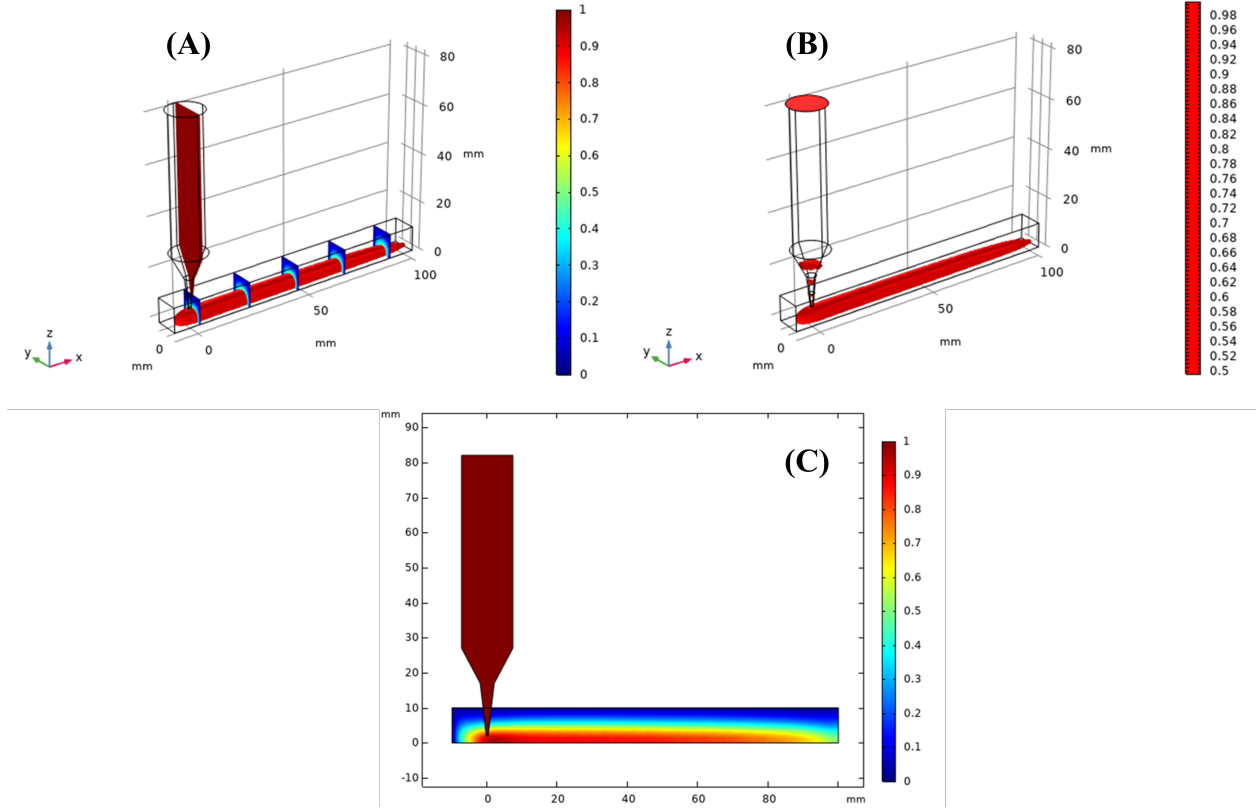


Figure 6.13: (A) Volume fraction of printed material; (B) isosurface of the printed line, and (C) cross-sectional view of the volume fraction along the xz plane at $y = 0$ and time equal to 10 seconds, for an applied absolute inlet pressure of 200 kPa.

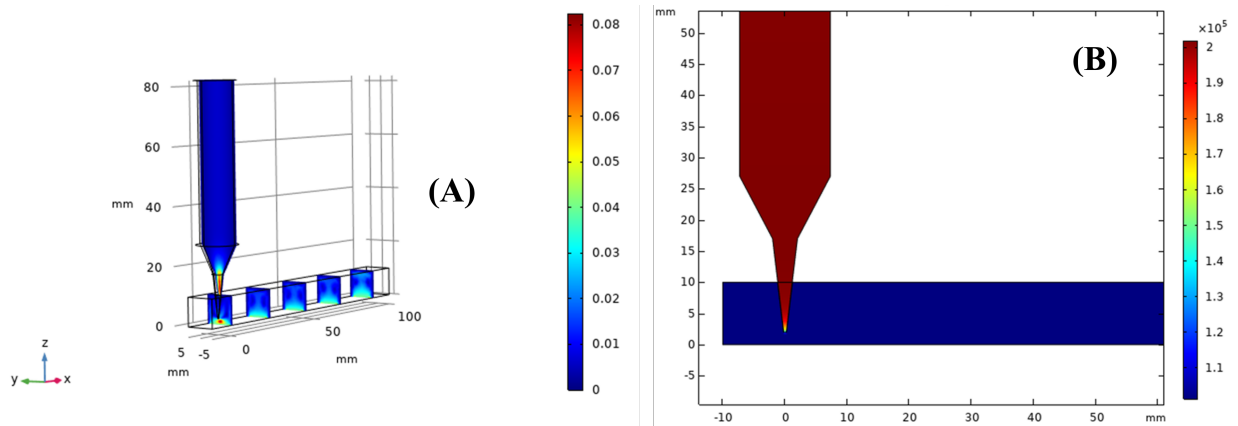


Figure 6.14: (A) Velocity field [m/s] in the whole 3D domain, (B) cross sectional view of the velocity field [m/s] along the xz plane at $y = 0$ and time equal to 10 seconds; (C) pressure field [Pa] in the whole 3D domain; (D) cross sectional view of the pressure field [Pa] along the xz plane at $y = 0$ and time equal to 10 seconds.

6.4 Water Electrolysis and Fuel Cells

Water electrolyzers and hydrogen fuel cells are unique equipment designed for electrochemical reactions. They can be the same device working in opposite modes. This also implies that they can operate reversibly^[5,6]. They are exciting for sustainable manufacturing systems because they are clean and direct chemical-electricity converters, therefore devices inherently intensified by their material chemistry. This operational versatility justifies their suitability in polygenerative systems, whether for hydrogen conversion or production^[7–11]. In the context of zero-carbon emission technologies, water is the substance that yields the cleanest H_2 (and O_2). Nevertheless, splitting the water molecule is quite energy-demanding; it is thermodynamically favored at temperatures as high as 750 K or higher.

As its name suggests, a fuel cell is a solid container in which an active fuel (hydrogen) is electrocatalytically oxidized by air or pure oxygen. This reaction is split into two half-reactions occurring in separate electrodes (anode and cathode), connected by a third material, an electrolyte. It is a membrane that allows the diffusion of specific ions from one electrode to the other, which completes the stoichiometric chemical balance of both semi-reactions. A fourth material must also be present in the cell: a current collector. In fuel cell mode, the current collector captures the electrons released by the fuel oxidative adsorption on the anode and conducts them to an external circuit that ends at the air electrode (cathode), where air reduction occurs. Thus, electricity is produced. In an electrolysis cell, the opposite happens, and the denominations of the electrodes swap: water molecules are broken. At the same time, intermediate species are reduced by electrons from the circuit (electrolysis), producing smaller fuel (H_2) molecules.

The high-performance cells that gained prominence in material and fuel engineering possess ceramic solid oxide electrolytes with a perovskite-like structure. The electrodes are composite metal oxides; therefore, the short form "solid oxide cells" (SOCs) is generally applied. Some solid oxide membranes transport oxygen anions from one electrode to the other (oxygen exchange), while others transmit protonic species (proton exchange). Proton exchange membrane cells have an intrinsic operational advantage over oxygen-exchange: water

and hydrogen flow in different electrodes, so there is no fuel dilution; further separation is unnecessary. This material-driven intensification is unique to proton exchange cells.

Most modeling studies on dynamic and control-oriented investigations of sustainable fuel cell/electrolyzer operation adopted a lumped or quasi-multidimensional approach. The primary goal is to control cell stack temperature, as it significantly impacts their functionality and durability. Huang et al.^[12] denoted some challenges regarding solid oxide cell control: decoupling very nonlinear interdependencies between the variables, applying nonlinear MPC, controlling temperature gradients, and real-time monitoring. Motylinski et al.^[13] aimed to integrate grid wind electricity balancing service with the operation of reversible solid oxide cells. They showed safe compatibility and accurate strategies for switching modes without infringing thermal limits. Botta et al.^[14] developed a control strategy to minimize temperature variation in a reversible solid oxide cell stack subjected to intermittent electrical power sources. They manipulated only the flow rate of fuel and air and employed PID controllers that assured stable operation. Chatrattanawet et al.^[15] had a similar objective, but created a multivariate linear model predictive controller for a SOFC stack instead, varying the current density, inlet composition, and temperature. Kandukuri et al.^[16] tested a non-isothermal operation of SOFC with a gain scheduling controller and achieved good control performance over a wide range of voltages. Kandepu et al.^[17] developed a controller for a SOFC integrated with a gas turbine, indicating that lumped models can be aggregated to approximate the distributed nature of essential variables of solid oxide cells. Zheng et al.^[8] is a rare case of a dynamic study of mode switching in reversible solid oxide cells using a distributed model. They applied a step change in voltage and showed that the dynamic response is primarily dominated by electrochemical and heat transport processes, with the latter being significantly slower.

CFD studies on solid oxide fuel cells and electrolyzers are relatively popular, although rarely transient. Tseronis et al.^[18] conducted parametric simulations in 2D porous electrodes using COMSOL and verified that heat transport dynamics respond much slower to changes in current density than charge and mass transport. Only axial gradients were observed in the temperature or concentration distributions. Zhang et al.^[19] tested different electrochemical

kinetic models in planar cells and detected similar fields. Russner et al.^[20] neglected gradients perpendicular to the axial flow and analyzed the influence of anode/electrolyte-supported cells, and the reactants flow regime. Compared to counter-flow, co-flow results in smaller temperature gradients, which are localized in the center of the cell. Wang et al.^[21] also observed central temperature gradients in planar reversible solid oxide cells.

Sayadian et al.^[22] evaluated the effects of non-dimensional parameters (Sherwood, Peclet, Reynolds, Darcy, and Damkohler) on output power density and concluded that lowering Re in the electrodes helped increase the performance of SOFC. Conversely, decreasing Darcy's number, which measures the permeability of the porous electrodes, reduces the power density. Grondin et al.^[23] was the only work in the literature that systematically explored substituting the traditional electrokinetic description of cathodic interactions in an electrolyzer with an artificial and analytical neural network model. They then coupled the neural network model with CFD and demonstrated that it could be utilized in multiscale modeling to provide coherent gradients and predictions. Uriz et al.^[24] studied the fluid dynamics of ethanol steam reforming in a rather innovative reactor: 3-dimensional catalytic wall microchannels with a square shape. Their results indicate that the low characteristic channel dimension leads to an almost isothermal flow and effective temperature control, thereby preserving high hydrogen yields.

6.4.1 Modeling Electrochemical Processes

The surface electrochemistry in solid oxide cells differs somewhat from that in other catalytic processes. Essentially, the active sites in both electrodes are located at triple-phase regions or boundaries (TPB), which are constituted by the gas molecules and the surfaces of the ion-conductive and electron-conductive phases^[25]. Therefore, the electrodes must have mixed-conducting properties, which justifies their composite nature. For macroscale predictions, the primary model used to describe electrokinetics in all electrolyzers and fuel cells is the highly nonlinear Butler-Volmer equation (Equation 6.69). It relates the activation overpotential/loss in an electrode to the current density, which controls the rate of elec-

trochemical conversion in the cell. Under external diffusion limitations, when the surface concentrations of the species are smaller than the bulk concentrations, modified forms of the Butler-Volmer Equation (resembling Equation 6.70) may be employed by models that do not directly contemplate transport equations.

$$j = j_{0,\text{electrode}} \cdot \left\{ \exp \left(\frac{\alpha z F \eta_{\text{act},\text{electrode}}}{RT} \right) - \exp \left[\frac{(1 - \alpha) z F \eta_{\text{act},\text{electrode}}}{RT} \right] \right\} \quad (6.69)$$

$$j = j_{0,\text{electrode}} \cdot \left\{ \frac{c_{\text{react,TPB}}}{c_{\text{react}}} \exp \left(\frac{\alpha z F \eta_{\text{act},\text{electrode}}}{RT} \right) - \frac{c_{\text{prod,TPB}}}{c_{\text{prod}}} \exp \left[\frac{(1 - \alpha) z F \eta_{\text{act},\text{electrode}}}{RT} \right] \right\} \quad (6.70)$$

The exchange current density in both cathode and anode ($j_{0,\text{electrode}}$) can be empirically estimated using Equation 6.71 (independent of reactants concentrations) or Equations 6.72 and 6.73 (concentration dependent on a reference condition)^[26]. The actual rates are given by Equation 6.74.

$$j_{0,\text{electrode}} = \left(\frac{RT}{zF} \right) \cdot k_{\text{electrode}} \cdot \exp \left(\frac{-E_{\text{a},\text{electrode}}}{RT} \right) \quad (6.71)$$

$$j_{0,\text{anode}} = \left(\frac{P_{\text{H}_2}}{P_{\text{H}_2,\text{ref}}} \right)^A \left(\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2\text{O},\text{ref}}} \right)^B \cdot k_{\text{anode}} \cdot \exp \left(\frac{-E_{\text{a},\text{anode}}}{RT} \right) \quad (6.72)$$

$$j_{0,\text{anode}} = \left(\frac{P_{\text{O}_2}}{P_{\text{O}_2,\text{ref}}} \right)^C \cdot k_{\text{cathode}} \cdot \exp \left(\frac{-E_{\text{a},\text{cathode}}}{RT} \right) \quad (6.73)$$

$$R_{\text{electro},i} = \nu_i \frac{jA}{zF} \quad (6.74)$$

The activation overpotentials in each electrode ($\eta_{\text{act},\text{electrode}}$) in Equation 6.69 relate to the applied voltage in the cell, according to the balance in Equation 6.75. Thus, to determine the current density in the cell for a specific voltage, Equations 6.69 and 6.75 must be numerically solved together. To calculate the equilibrium (or open-circuit) voltage, the Nernst equation

is applied (Equation 6.76). An expression for the ohmic overpotential/loss (Equation 6.78) also becomes necessary. It is common to find works that convert Equation 6.69 to an inverse hyperbolic sine function to obtain an explicit expression for the activation potentials as a function of the current density. Some studies also advise about the inclusion of another term in the voltage balance, the concentration overpotential/loss (η_{conc}), for situations when mass transfer is limiting.

$$V_{\text{applied}} = V_{\text{eq}} + \eta_{\text{act,anode}} + \eta_{\text{act,cat}} + \eta_{\text{ohm}} \quad (6.75)$$

$$V_{\text{eq}} = V_0 + \left(\frac{RT}{zF} \right) \ln \left(\frac{P_{\text{H}_2} P_{\text{O}_2}^{1/2}}{P_{\text{H}_2\text{O}}} \right) \quad (6.76)$$

$$V_0[\text{V}] = [1.229 - 0.9 \cdot 10^{-3} \cdot (T - T_{\text{ref}})] \quad (6.77)$$

$$\eta_{\text{ohm}} = j \cdot \text{resistance} = j \cdot \left(\frac{\tau_{\text{anode}}}{\sigma_{\text{anode}}} + \frac{\tau_{\text{electrolyte}}}{\sigma_{\text{electrolyte}}} + \frac{\tau_{\text{cathode}}}{\sigma_{\text{cathode}}} \right) \quad (6.78)$$

A higher-fidelity phenomenological electrokinetic model can be devised by coupling the momentum, energy and mass conservation with charge conservation/Ohm's Law (Equation 6.79); the subscript ζ denotes an electronic or ionic species, σ is the conductivity, and ϕ is the electronic/ionic potential driving charge motion.

$$\frac{\partial \rho_{\zeta}}{\partial t} + \nabla \cdot (-\sigma_{\zeta} \nabla \phi_{\zeta}) - \sum R_{\zeta} = 0 \quad (6.79)$$

6.4.2 Simulation Results

Fuel Cell Mode

A three-dimensional solid oxide microcell represented in Figure 6.15) was simulated on COMSOL at the stationary state and fuel conversion mode. Coupled partial differential equations describing mass, momentum, energy and charge transport were solved by the finite element

method (FEM). Average material properties for the cells were defined, and a countercurrent flow regime was established in both electrodes. The reference pressure was set at 1 atm. The inlet fuel is constituted by 80% H_2 and 20% H_2O at 800°C , with a flow rate of 10^{-8} kg/s. A net voltage of 0.1 V is applied. Under those same conditions, simulations were also conducted for a stack of 9 identical microcells.

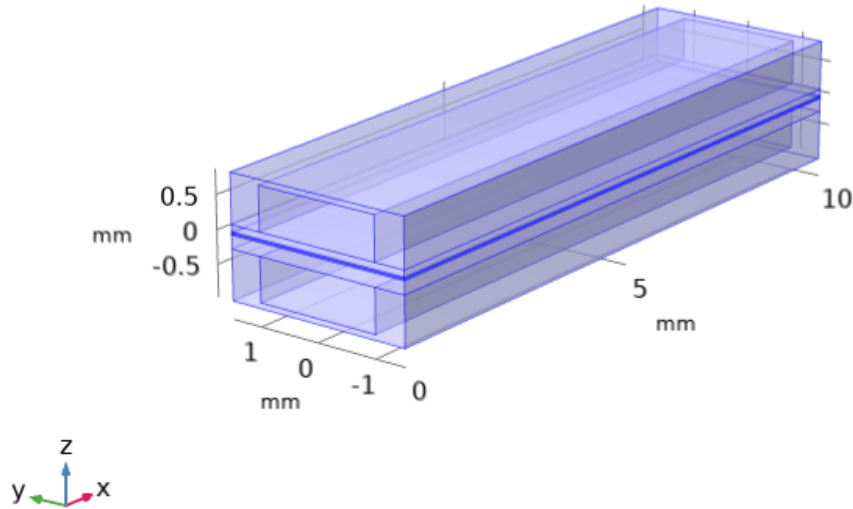


Figure 6.15: Geometry of the solid oxide microcell.

Figure 6.16 shows the mole fraction profiles of H_2 , H_2O , and O_2 inside the fuel cell. A parabolic distribution along the cell length is observed; the H_2 mole fraction decreases from 0.8 at the inlet region to 0.65 at the outlet, while the H_2O mole fraction increases proportionally. In the air gas channel, the O_2 mole fraction decreases to approximately 0.12 at the outlet.

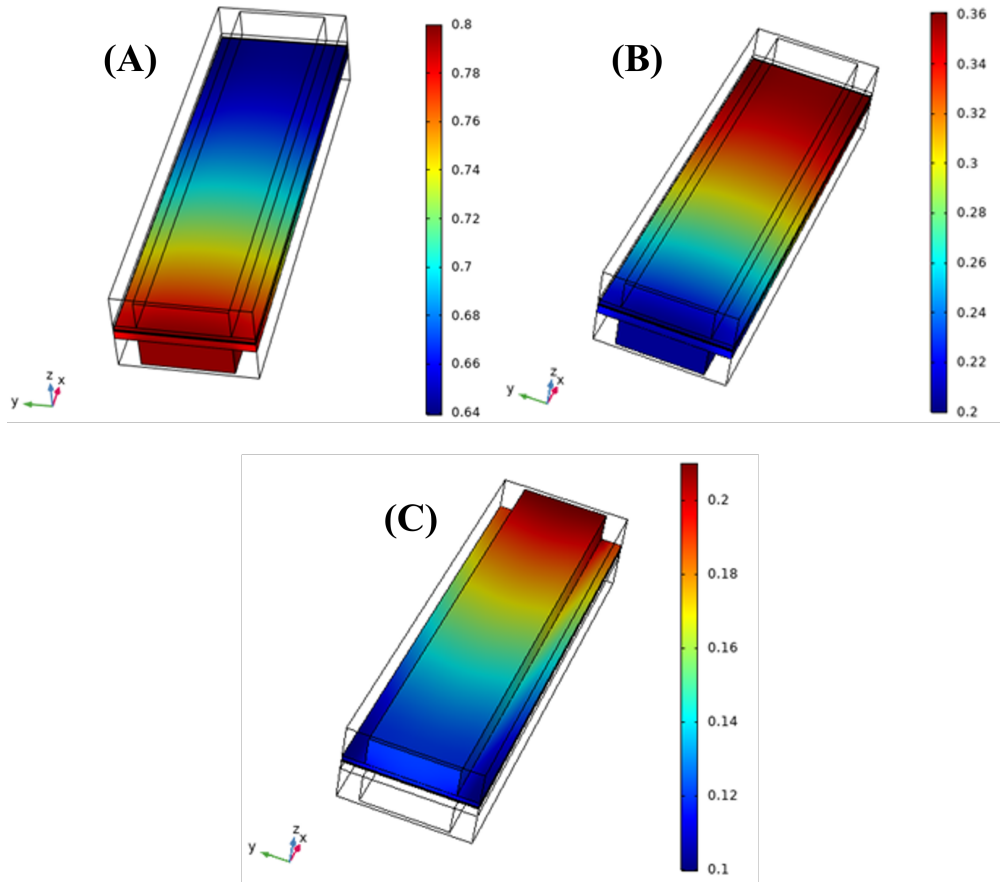


Figure 6.16: Molar fractions of (A) hydrogen, (B) water, and (C) oxygen.

The temperature distribution in the cell, presented by Figure 6.17, shows a slight gradient at the air inlet. The electrodes and electrolyte are at a slightly higher temperature because of the heat released by the electrochemical reactions. Overall, the combined effects of heat generation and convection result in small thermal gradients within the cell; however, the convection rate to the environment is higher, which causes the cell to be colder than the streams fed into it. The average temperature, current density, and cell power were 1009.2 K, 5035.7 A/m², and 503.57 W/m². The overpotentials in the fuel and air electrodes were 0.1648 and -0.6121 V, respectively.

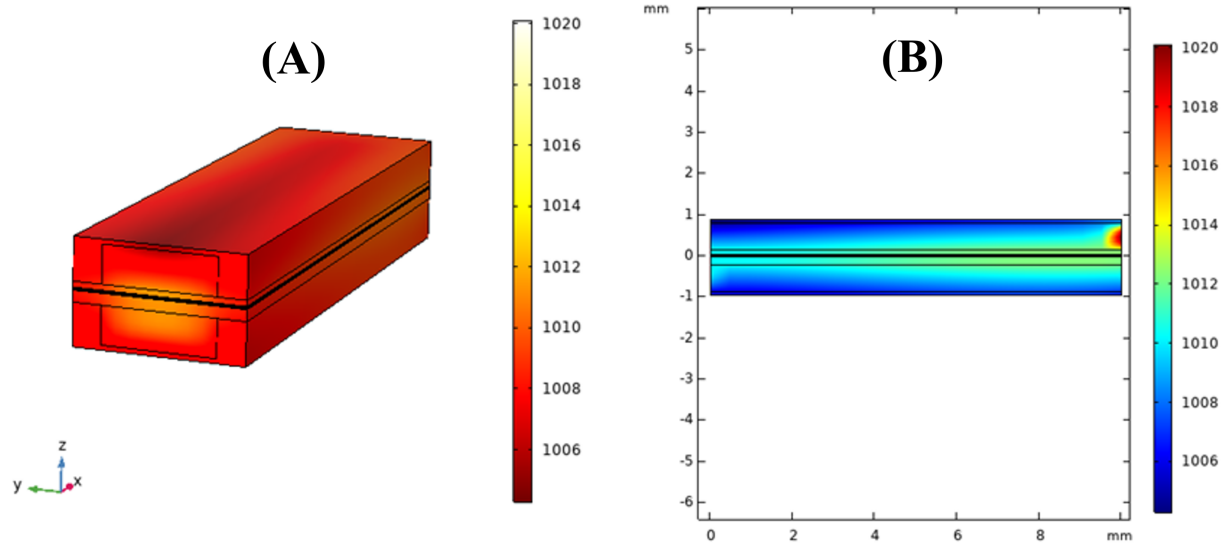


Figure 6.17: (A) Temperature distribution in the cell. (B) Temperature distribution in the cell along the cell length (plane xz).

The results for the stack of SOFC were significantly different, as shown by Figures 6.18 and 6.19. For the same applied voltage (0.1 V), comparisons with the single SOFC unit reveal that the steady-state average temperature of the stack (1466.3 K) is considerably higher, and the fuel utilization is lower in each cell that constitutes the stack. Since the internal contacting area of the cells is no longer exposed for heat convection with the environment, the heat released ends up increasing the average stack temperature. Consequently, an exothermic equilibrium process, such as H_2 oxidation, is thermodynamically disfavored, leading to lower H_2 conversion. Additionally, thermal degradation can compromise the performance of individual cells. Those observations open possibilities for thermal management and optimization studies on SOFC stacks.

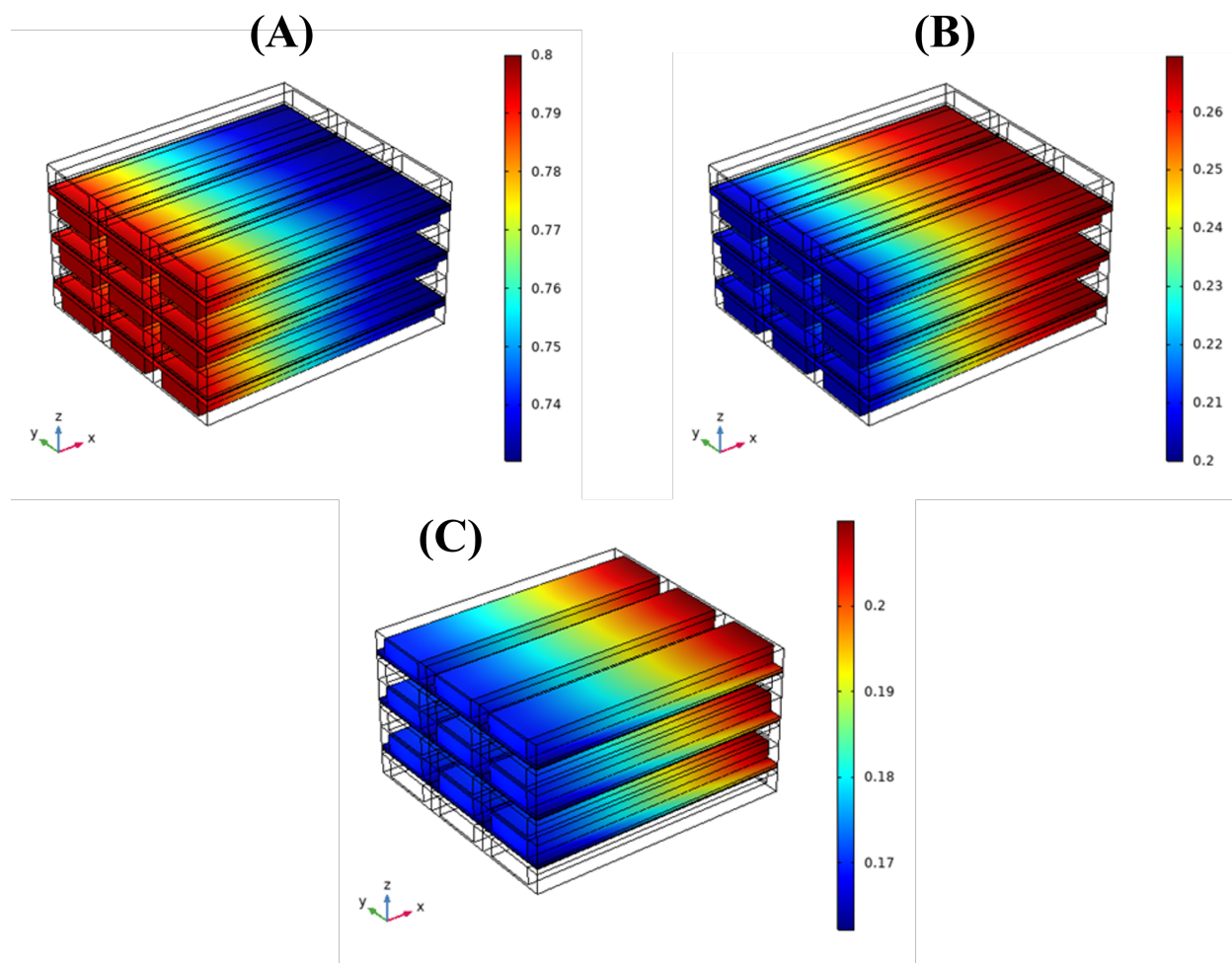


Figure 6.18: Molar fractions of (A) hydrogen, (B) water, and (C) oxygen in the solid oxide cell stack.

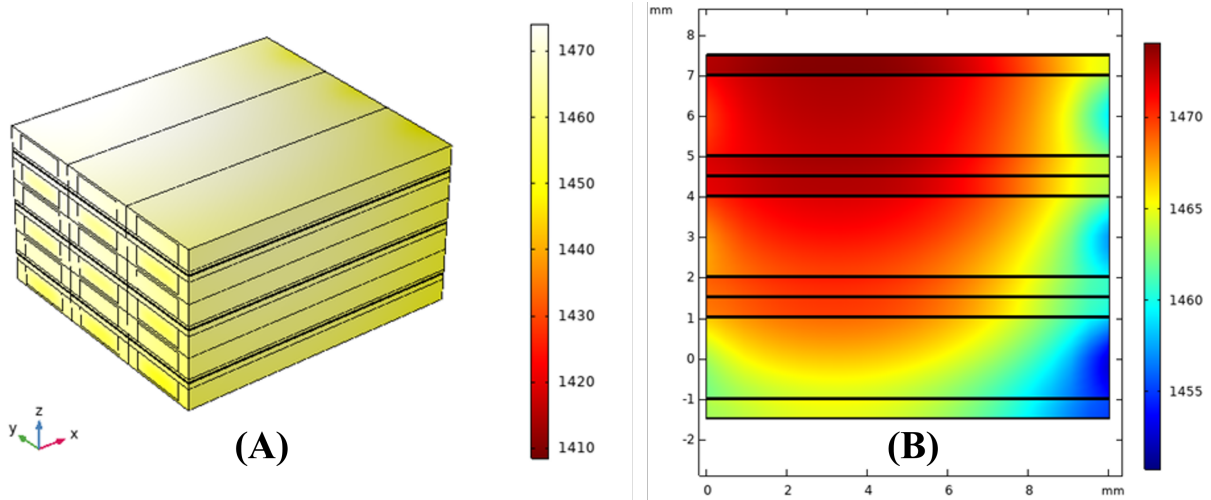


Figure 6.19: (A) Temperature distribution in the solid oxide cell stack. (B) Temperature distribution in the cell along the cell length (plane xz).

Electrolysis Mode

In electrolysis mode, the applied voltage must be lower than the equilibrium voltage of the reaction, so a voltage of -1.3 was necessary to get the simulation to run. As seen in Figure 6.20, the H_2 mole fraction increases from 0.1 to approximately 0.58 at the outlet region, while the O_2 mole fraction goes up to 0.28.

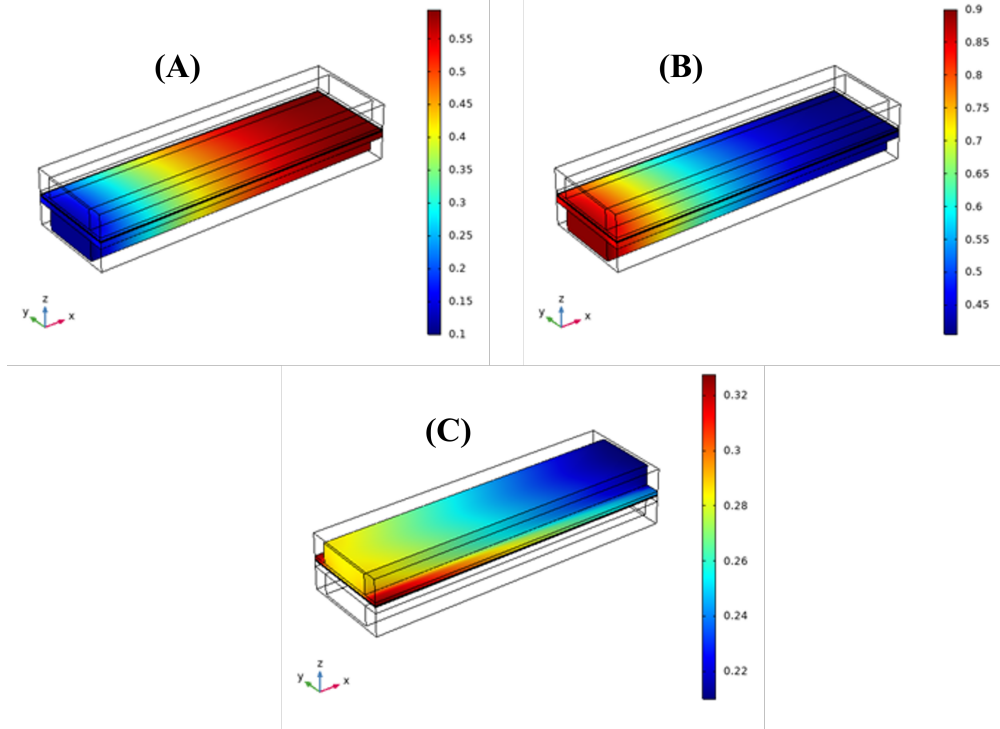


Figure 6.20: Molar fractions of (A) hydrogen, (B) water, and (C) oxygen.

The temperature in the cell (Figure 6.21) is much lower than the inlet temperature of the fluids, due to heat absorption by the reaction and external convection. Except for the inlet regions, there are no significant thermal gradients inside the cell. The average temperature, current density, and cell power of the cell were 463.66 K, 4950.3 A/m², and 6435.3 W/m². The overpotentials in the water and air electrodes were -0.0146 and 0.0314 V, respectively.

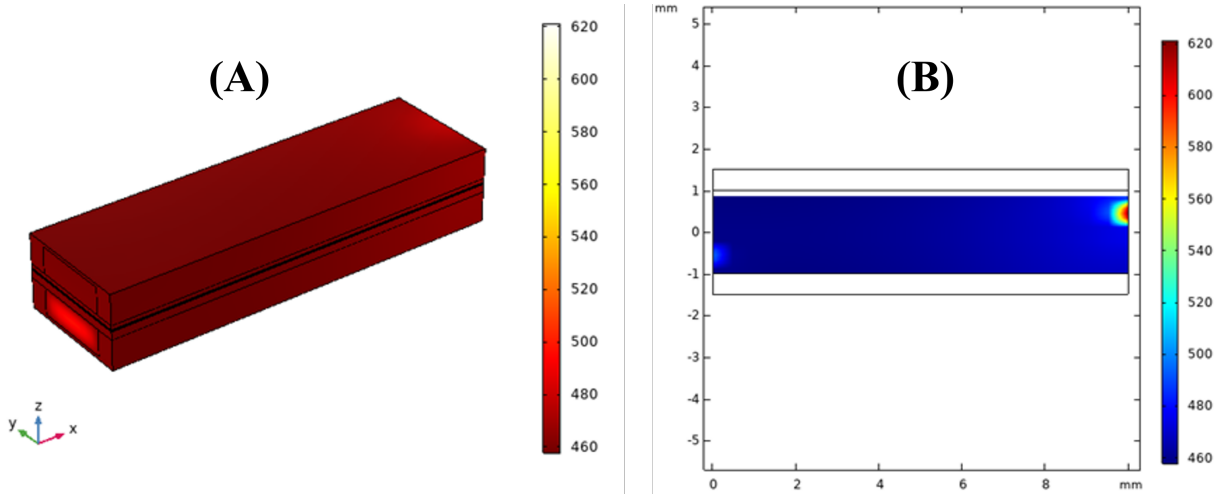


Figure 6.21: (A) Temperature distribution in the cell. (B) Temperature distribution in the cell along the cell length (plane xz).

When a stack of SOEC was constructed, the unavailability of internal area for heat convection with the external environment makes the average temperature of the stack increase to 685.44 K. Since water electrolysis is an endothermic equilibrated process and thermodynamically favored at higher temperatures, higher H_2O conversion to H_2 and O_2 was achieved.

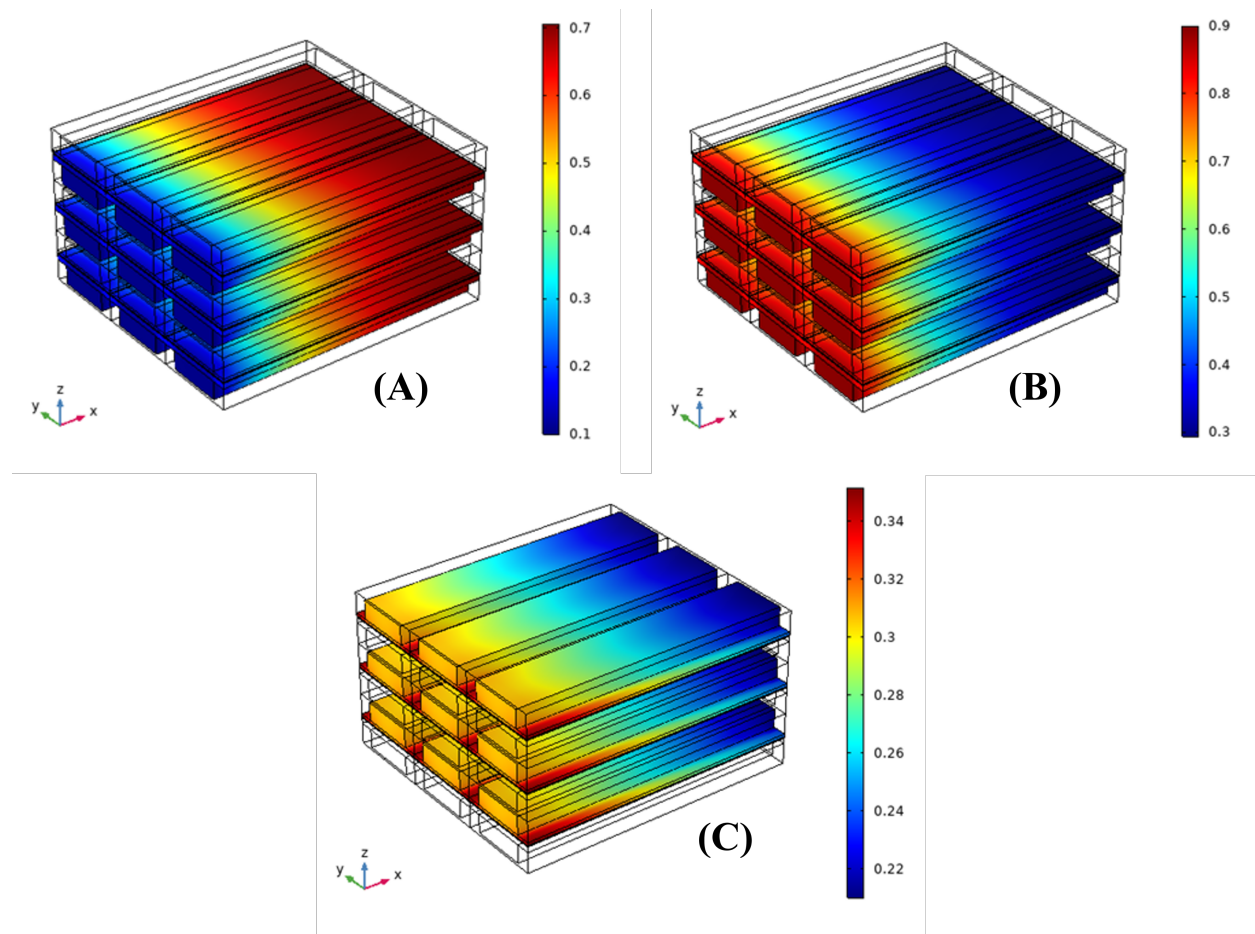


Figure 6.22: Molar fractions of (A) hydrogen, (B) water, and (C) oxygen in the solid oxide cell stack.

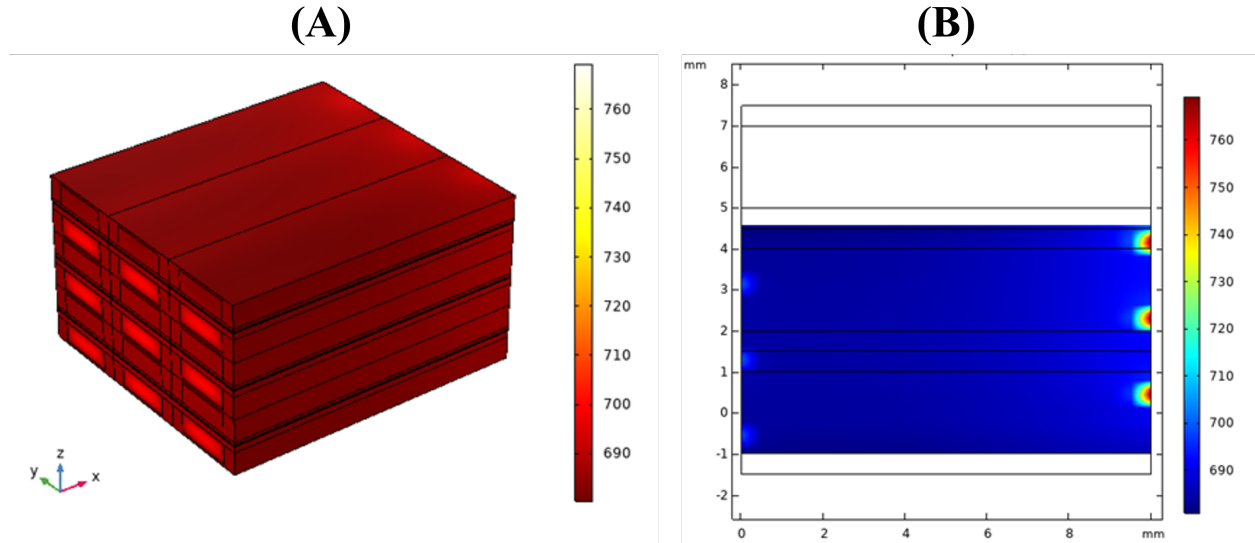


Figure 6.23: (A) Temperature distribution in the solid oxide cell stack. (B) Temperature distribution in the cell along the cell length (plane xz).

A 3D proton-exchange ceramic electrolysis cell with a different geometry (Figure 6.24) was also tested on COMSOL. Figure 6.25 shows the H_2O and H_2 concentrations and temperature fields in such a device cell under a typical countercurrent operation. The electrolyte is very thin, $10\ \mu\text{m}$. A current density of $400\ \text{mA}/\text{cm}^2$ is being applied between the bottom surface of the hydrogen electrode and the electrolyte. The local current density is calculated using the Butler-Volmer equation. The cell exhibits significant axial gradients across the electrodes; complex interactions between charge and mass conservation dictate the transport. Steam diluted in air is fed through the top right boundary (where the concentration is higher), while hydrogen is carried by argon in the bottom electrode in the opposite direction, leaving at the bottom right boundary (also where its concentration is higher). Other flow configurations are possible and certainly affect the cell performance.

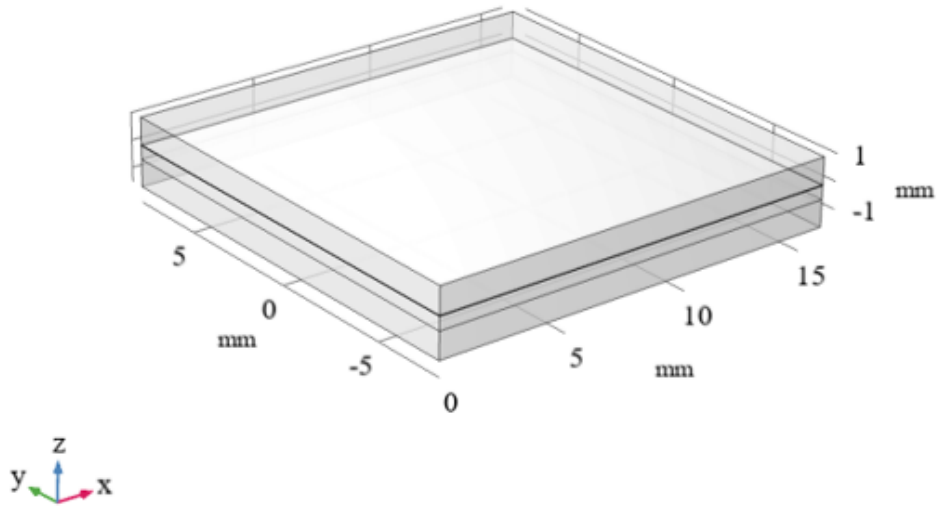


Figure 6.24: Geometry for a proton-exchange ceramic electrolysis cell.

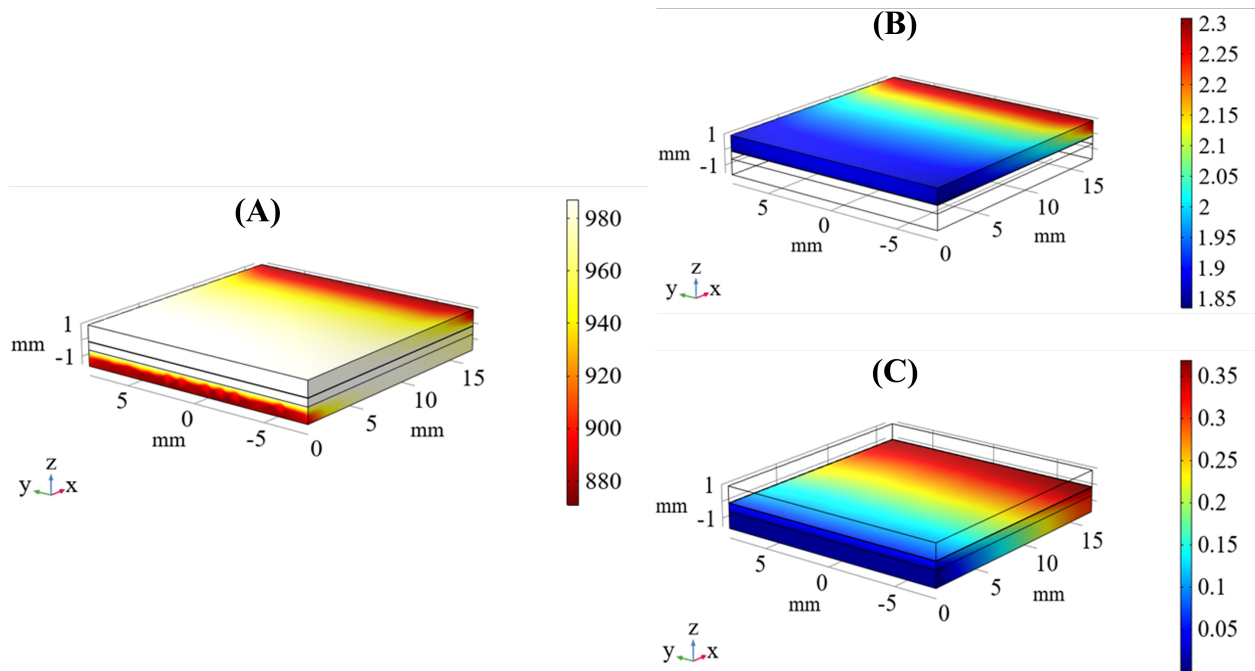


Figure 6.25: (A) Temperature field, (B) H_2O concentration field and (C) H_2 concentration field in a proton-exchange electrolysis cell under countercurrent operation.

6.5 Integrated Ammonia Systems

6.5.1 Ammonia Synthesis in Intensified Reactors

Multidimensional fluid dynamic studies of ammonia systems are very uncommon. Mirvakili et al. ^[27] are an exception, who treated a three-bed industrial ammonia reactor at steady-state with the radial-axial flow and inter-stage coolers. Their predictions of the outlet concentrations and temperature were validated by experimental data and showed good agreement. However, the lack of CFD studies on ammonia, particularly transient, was a motivation to contribute to this topic. In a 2D study, it is demonstrated that complex dynamic evolutions occur within an industrial reactor due to interactions between reaction kinetics, thermodynamics, radial and axial transport, resulting in significant changes in the fields.

Figure 6.26 shows the entire geometry of a conceptual and intensified model for an inter-stage cooling reactor with 4 beds, inspired by the design of real TOPSOE S-300 converters. The reactor's total height is 10 meters and its width is 3 meters. The feed is initially divided into 4 streams at the top of the reactor: 2 colder ones used as cooling fluids in intermediate heat exchangers and 2 hotter streams that descend through the center of the reactor. Those hotter streams are redirected to the left and right set of beds by ascending through lateral regions of the reactor, entering the beds at slits located at the top of the upper beds. During the lateral ascension, they are mixed with the feed streams that have warmed up in the heat exchanger. The flow in the porous beds is axial-radial, which has been associated with less transport limitations than purely axial flows. The reactive gas heats up in the upper beds due to the exothermicity of the synthesis, so it is cooled in the upper heat exchangers and sent to another set of lower beds to push conversion towards thermodynamic limitations. In this design, the gas is therefore circulated so that autothermal interactions internally intensify the heat transfer.

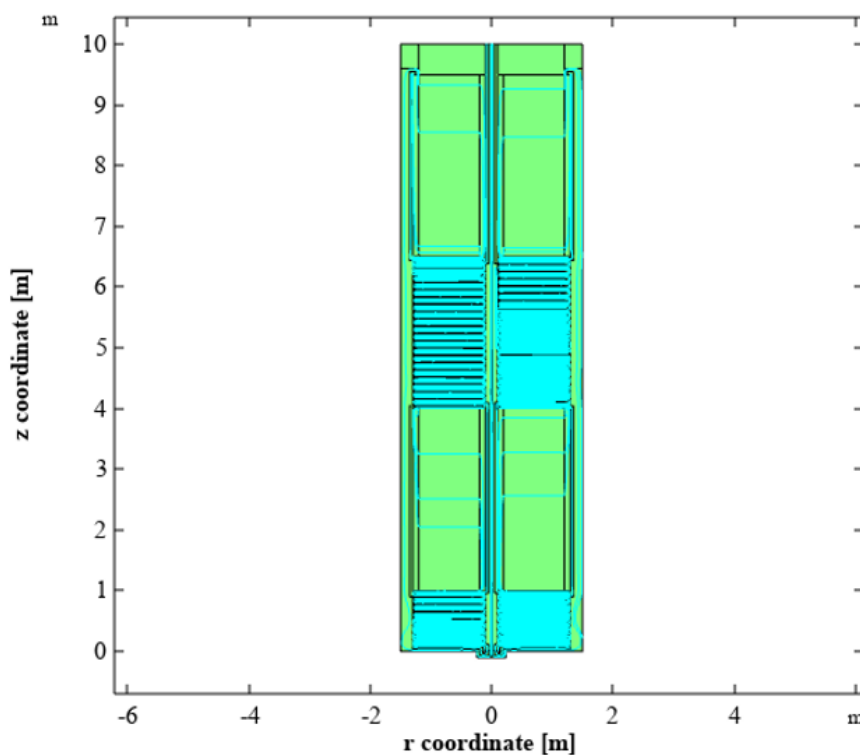


Figure 6.26: Geometry of an inter-stage cooling reactor for ammonia synthesis with 2 sets of dual beds and feed recycling. The heat exchanger domains are highlighted in light blue.

Figure 6.27 displays with more detail the concentration and temperature fields in the beds and heat exchangers in 3 time frames: 10, 30, and 6 min after the introduction of the feed, for a total flow rate of 50 L/min. The temperature of the cold and hot feed streams were set at 385 and 723 K. Strong concentration gradients are initially observed in the upper beds, which mitigate in intensity as the beds become too hot and the reaction is thermodynamically inhibited. The upper heat exchanger has a noticeable impact on reducing the temperature of the gas and enhancing conversion in the lower beds, even at later times.

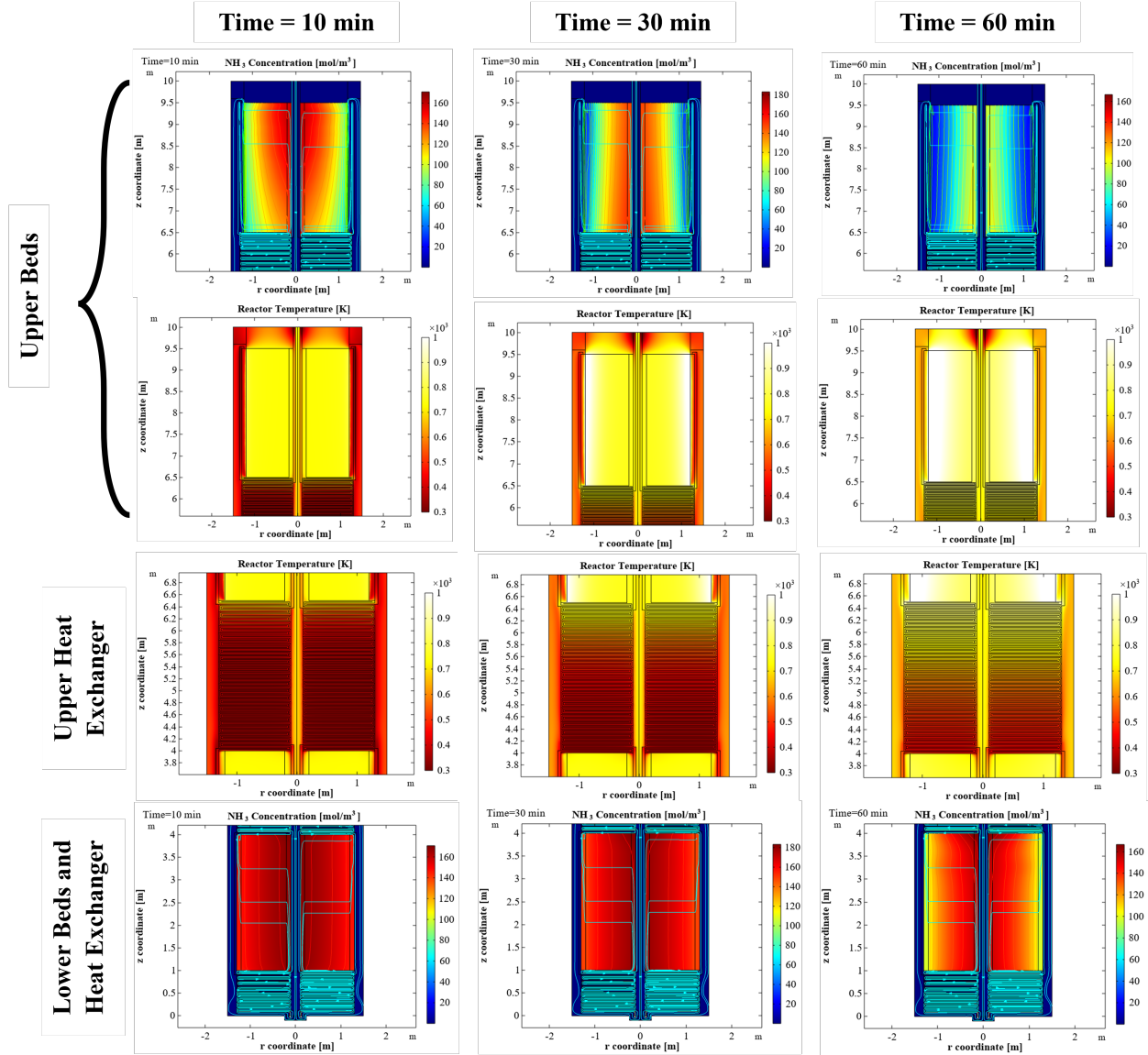


Figure 6.27: NH_3 concentration and temperature fields at 10, 30 and 60 min in an inter-stage cooling reactor for ammonia synthesis.

A multiscale CFD description is greatly enhanced if the dynamics of internal diffusion in solid catalyst pellets are captured. Even though its dynamics are generally fast due to the pellets' small dimensions and high gas diffusivities, there may be conditions or regions in a reactor that become limiting. Since the external concentration fields are not homogeneous, limiting conditions arise when the concentrations or gas velocity get too low. Figure 6.28 illustrates the concentration field in a porous section of a packed-bed ammonia synthesis

reactor. Ammonia is produced and diffused from the pores of the pellets due to internal concentration gradients, and then carried upward by the gas. External concentration gradients are consequently formed along the direction of the gas flow.

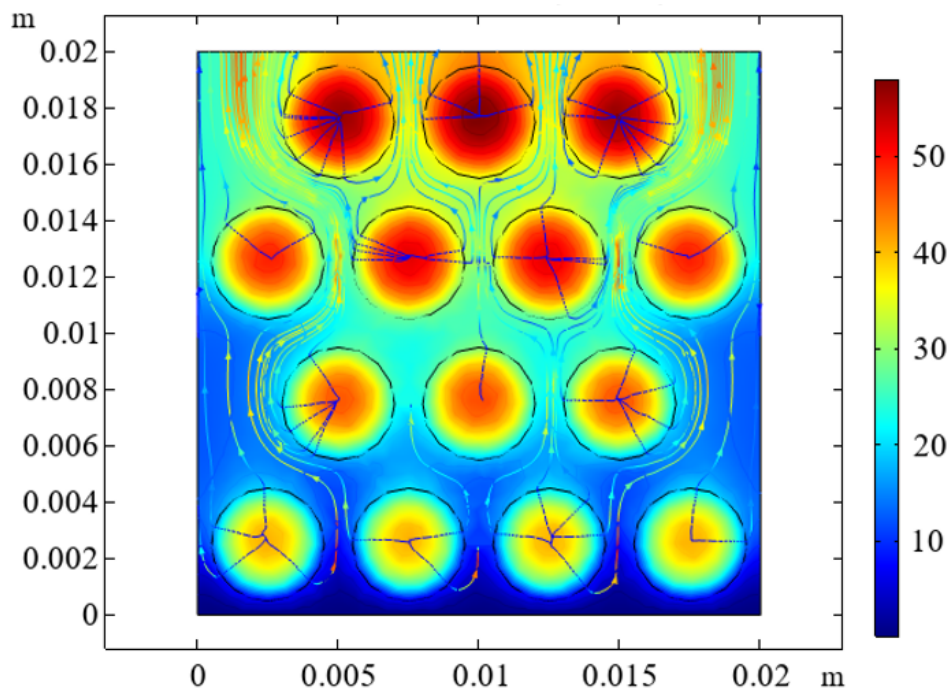


Figure 6.28: Mass transport of ammonia synthesized in a packed-bed reactor.

6.5.2 Ammonia Separation through Gas Adsorption

The separation of ammonia synthesized through the Haber-Bosch process is currently achieved by condensation, which is highly energy-demanding. Malmali et al.^[28,29] and Lin et al.^[30] have proposed an intensification of the reaction-separation system by adsorbing ammonia out from the outlet reactor stream and recycling unreacted N_2 and H_2 . Gas adsorption modeling is complex because it encompasses all the transport phenomena described previously, as well as substantial thermodynamic limitations arising from molecular interactions. The kinetics of chemical adsorptive interactions in many materials are largely unknown, so it is usual to model adsorption by assuming an instantaneous thermodynamic equilibrium between gas and adsorbent. Information provided by isotherms, such as Langmuir's (Equations 6.80 and 6.81) and for monolayer chemical adsorption or BET for multilayer adsorption, can

be incorporated into the mass transport (Equation 6.82).

$$c_{\text{ads},i} = \frac{w_{\text{max}} \cdot K_{\text{ads},T} \cdot c_{i,\text{pe}}}{(1 + K_{\text{ads},T} \cdot c_{i,\text{pe}})} \quad (6.80)$$

$$K_{\text{ads},T} = K_{\text{ads},T_{\text{ref}}} \cdot \exp \left[\frac{-\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right] \quad (6.81)$$

$$\frac{\partial(\varepsilon_b c_i)}{\partial t} + (1 - \varepsilon_b) \rho_{\text{solid}} \frac{\partial c_{i,\text{pe}}}{\partial t} \frac{\partial c_{\text{ads},i}}{\partial t} + \mathbf{v} \cdot \nabla c_i + \nabla(-D_{i,\text{eff}} \nabla c_i) = 0 \quad (6.82)$$

The most industrially utilized adsorption technologies are pressure-swing adsorption (PSA) and temperature-swing adsorption (TSA). Two or more columns operate simultaneously in alternating modes. While one goes through adsorption at high pressure, the other quickly regenerates the adsorbent by desorbing the component at low pressures or high temperatures. A proper PSA system is not readily implementable in simulation platforms; nevertheless, ASPEN has a special separate module suitable for simulating a 1D adsorption process. Figures 6.29 and 6.30 show the scheme of a dual-column PSA system, employing properties of a potential NH_3 absorbent (MgBr_2) to predict the dynamics of adsorption/desorption^[28,29]. A synchronous valve control is necessary to maintain satisfactory separation before the breakthrough, so a cycle organizer tool is used to change the opening specifications of each valve accordingly. The feed is directed to the column during the adsorption cycle, and the outlet product stream typically contains one or more separated components. A waste stream is generated by redirecting a portion of the product stream to the saturated column to remove the component during the regeneration cycle.

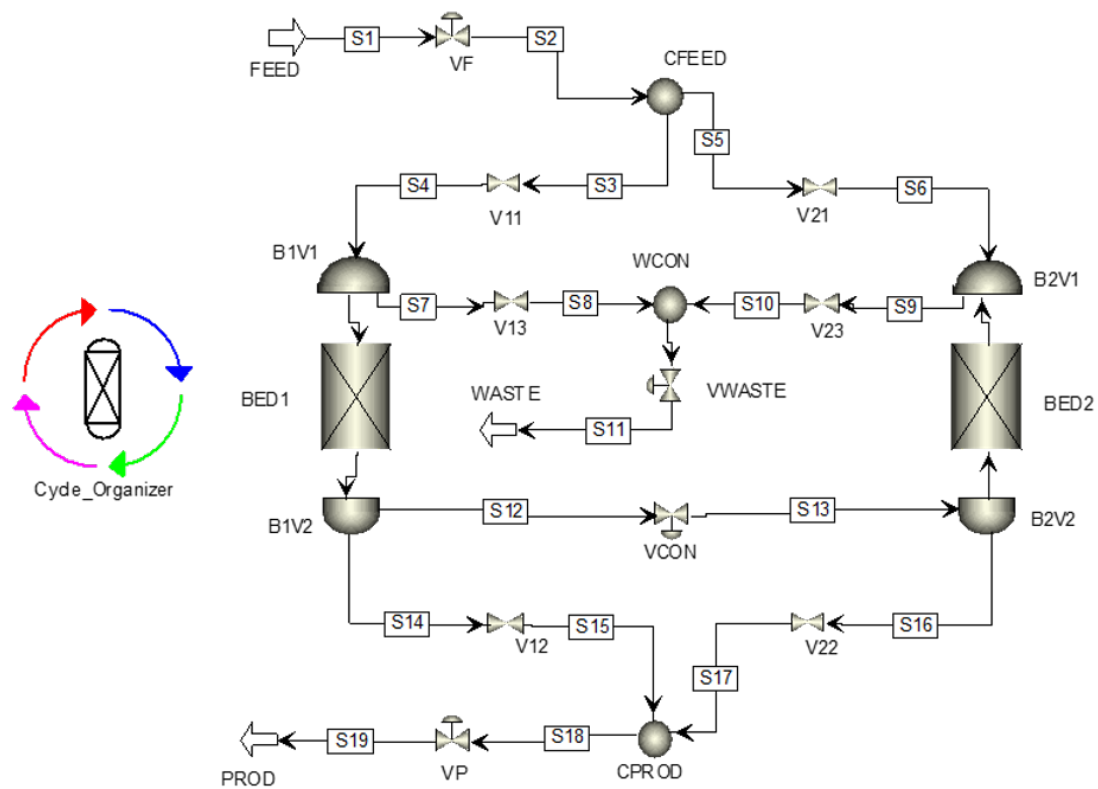


Figure 6.29: Configuration of the PSA system in Aspen Adsorption.

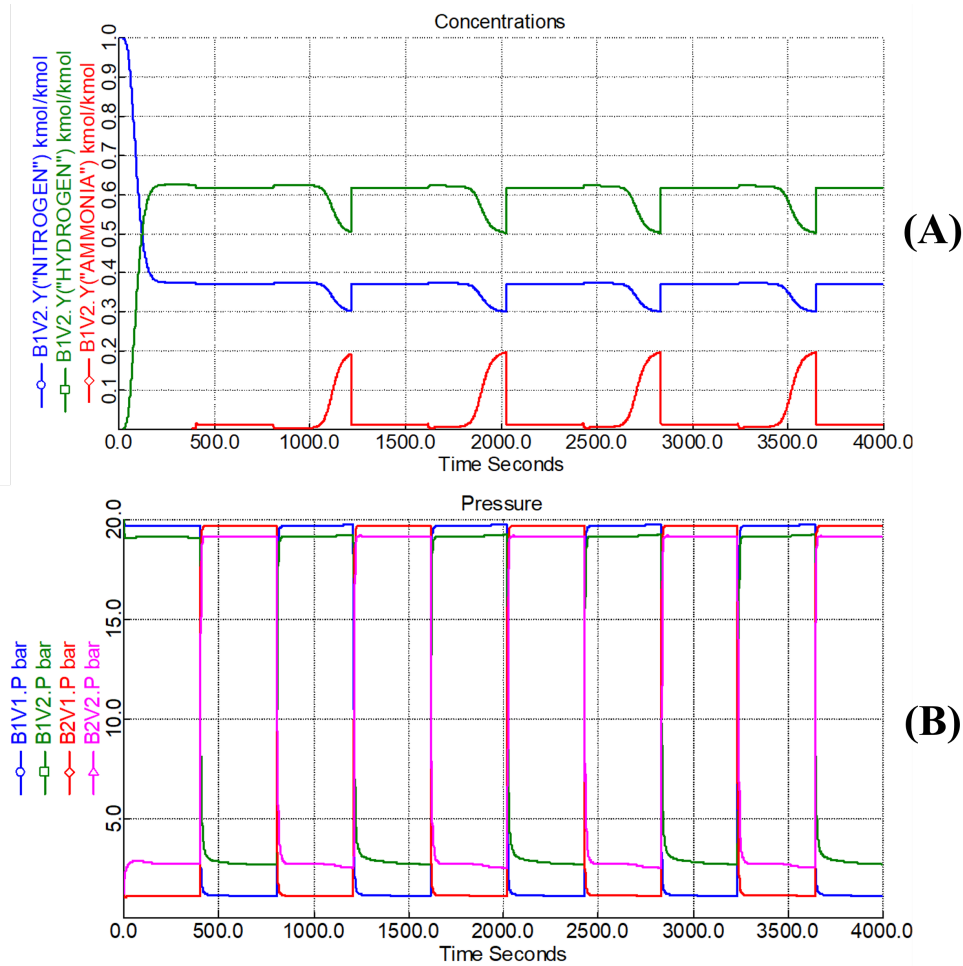


Figure 6.30: Dynamics of (A) concentration and (B) pressure in a dual-column ammonia PSA system under a regular isothermal condition ($T = 460$ K, feed flowrate = 10 mol/s). The adsorption and desorption cycles are conducted at approximately 20 and 1 bar, respectively.

A sequential integration between a 2D ammonia synthesis reactor with a 2D single-column adsorber (shown in Figure 6.31) is simulated to predict the dynamics of adsorption and desorption at TSA mode, subjected to the reactor dynamics and radial heat input. Figures 6.32 and 6.33 display how the dynamics of outlet streams are complex in both situations under regular conditions. The breakthrough time (or outlet ammonia concentration from the column) is the main output variable that should be targeted in future control studies. The mass transfer zone typically moves horizontally across the column under isothermal conditions; however, because the temperature is increasing laterally and radially, parabolic adsorption regions are formed, and ammonia escapes from the lateral parts where it is hotter. This shows that temperature-swing adsorption is a smart alternative for storing and

releasing ammonia by manipulating heat. The process is also axially affected by the inflow temperature, which is regulated by the heat removed in the reactor and the heat exchanger.

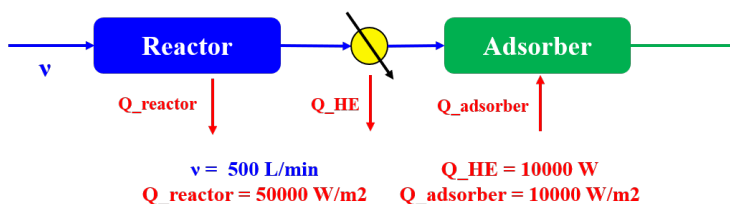


Figure 6.31: Sequential integration of ammonia synthesis reactor and adsorber.

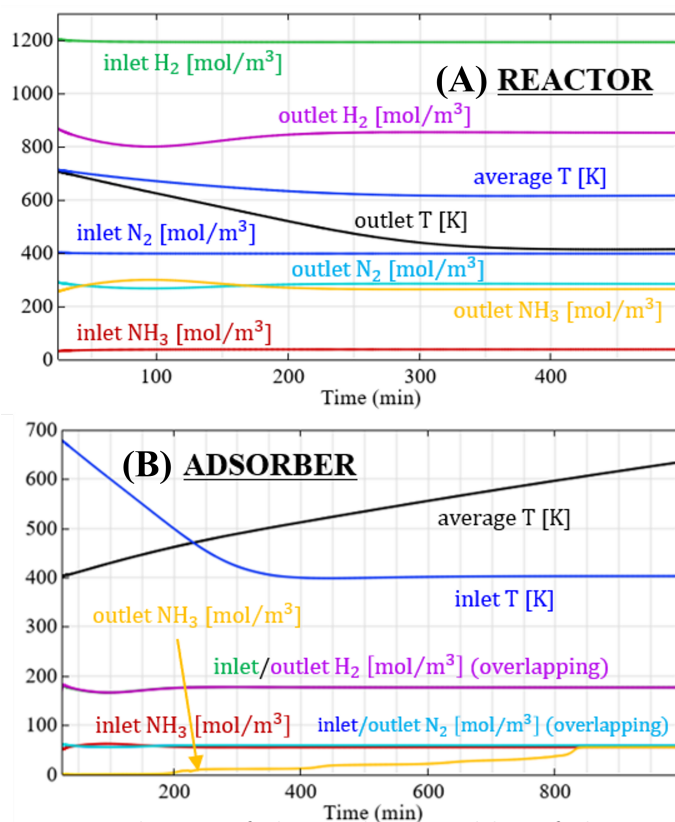


Figure 6.32: Dynamic evolution of the outlet variables of the reactor and adsorber.

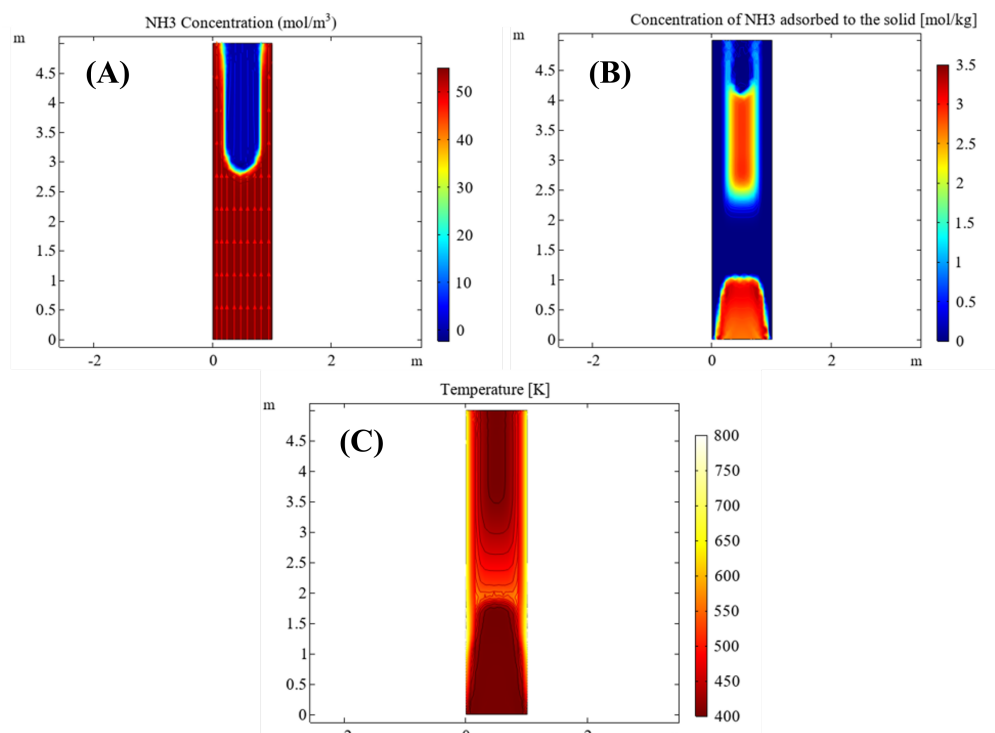


Figure 6.33: (A) Concentration fields of gaseous ammonia, (B) adsorbed ammonia and (C) temperature field in an adsorption column under conditions described in Figure 6.31.

6.6 Organ-on-a-Chip Technologies

Organ-on-a-chip (OoC) technologies comprise microfluidic cell culture devices that simulate the microarchitecture and physiological functions of living human organs. These devices can integrate multiple types of living cells within engineered microscale environments to recreate tissue-tissue interfaces, fluid flow, mechanical forces, and biochemical interactions and gradients found in vivo. OoCs are often fabricated through microfabrication and soft lithography, commonly utilizing transparent polymers such as PDMS to enable real-time imaging and monitoring. The modular nature of OoC platforms enables the study of systemic responses to drugs, toxins, or disease conditions without compromising or risking the health of real humans. Therefore, OoC technology holds promise for advancing drug discovery and toxicology testing, as well as safety, disease modeling, pharmacokinetics, and personalized medicine, by providing more physiologically relevant data than traditional 2D cell cultures or animal models. In drug delivery research, OoCs help investigate how drugs are absorbed, distributed,

metabolized, and excreted across human-relevant biological barriers. For instance, liver-on-a-chip models are commonly used to assess hepatic metabolism and potential drug-induced liver toxicity. For drug testing, OoCs allow high-resolution, real-time monitoring of cellular responses to drug candidates, including cytotoxicity, inflammation, and barrier integrity.

6.6.1 Modeling a Liver-on-a-Chip

Microfluidic Modeling

This work created a high-fidelity model for a liver-on-a-chip device. The chip consists of a solid frame with two channels for biological fluids (blood or culture mediums with specific compositions) and a central porous hydrogel domain that can embed active cellular colonies homogeneously or heterogeneously. The geometry is shown in Figure 6.34.

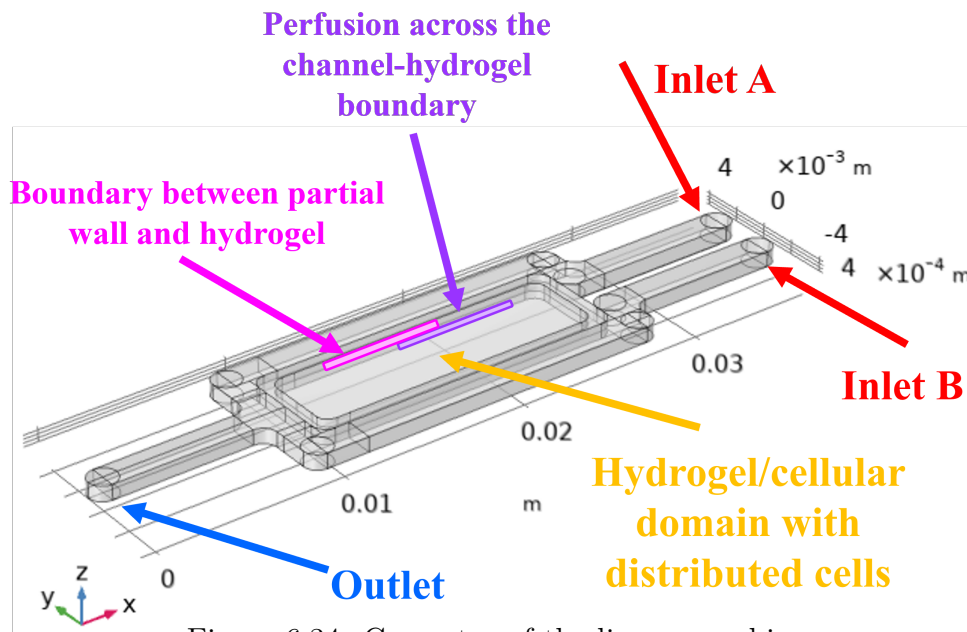


Figure 6.34: Geometry of the liver-on-a-chip.

Figure 6.35 discriminates the important domains of the device:

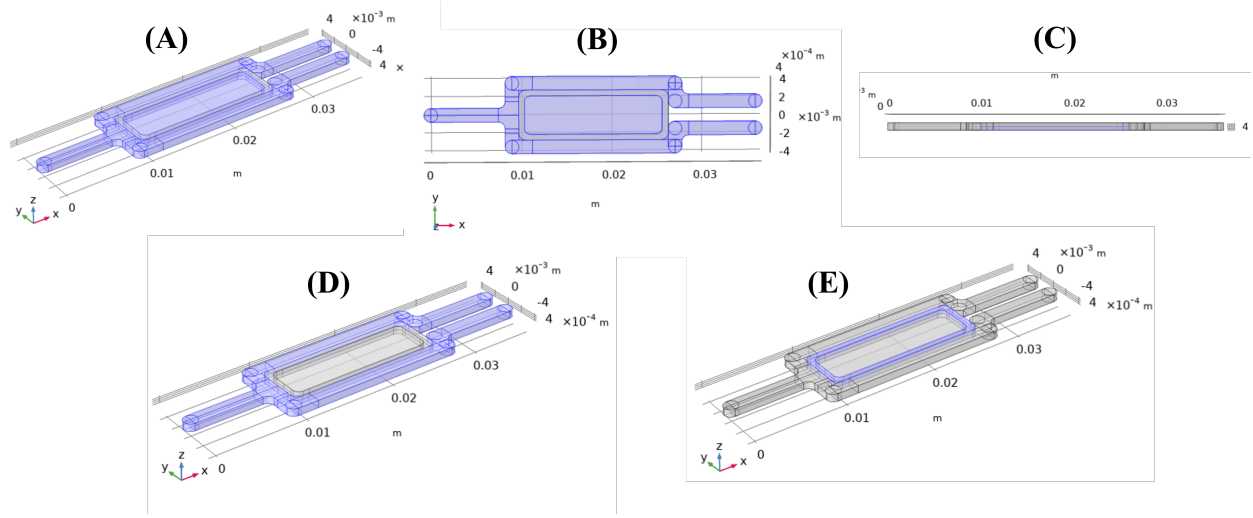


Figure 6.35: (A) Mass transfer domains, (B) superior axial view of the mass transfer domains, (C) lateral axial view of the channel-hydrogel boundary, (D) liquid medium channels, (E) partial walls (no flux).

Compounds transported in the fluid (such as amino acids, glucose, and drugs) can permeate across the permeable boundary between the channel walls and the hydrogel domain and diffuse within the latter. Metabolites produced by the cells also diffuse in the hydrogel medium and perfuse into the fluid channels, exiting the device at a common outlet. The momentum transport of the fluid in the channels is assumed to be laminar and described by the continuity and Navier-Stokes equations (Equations 6.83 and 6.84):

$$\frac{\partial \mathbf{v}}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \quad (6.83)$$

$$\rho \frac{\partial \mathbf{v}}{\partial t} + \rho (\mathbf{v} \cdot \nabla) \mathbf{v} = \mathbf{v} [-p\mathbf{I} + \mathbf{K}] \quad (6.84)$$

$$\mathbf{K} = \mu \cdot [\nabla \mathbf{v} + (\nabla \mathbf{v})^T] + \frac{2}{3} \mu (\nabla \cdot \mathbf{v}) \mathbf{I} \quad (6.85)$$

As mentioned, the species transport in the hydrogel is governed by diffusion and metabolic processes at the cellular scale, denoted by source terms in Equation 6.86. Advection is also accounted for as a primary mechanism for transporting species in the fluid.

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i) \nabla c_i + \mathbf{v} \cdot \nabla c_i = \frac{\partial c_{i,\text{cell}}}{\partial t} \quad (6.86)$$

Diffusivities can be estimated experimentally or by the Einstein-Stokes equation (6.87), which depends on the viscosity of the porous medium and the radius of the diffusing species. Other relations for diffusivity in porous media can be employed.

$$D_i = \frac{k_B T}{6\pi\mu r_i} \quad (6.87)$$

Metabolic Cellular Process I: Protein Synthesis

The model first attempts to account for the synthesis of albumin as the cellular process of interest. Albumins are the most common type of serum protein in human blood plasma and serve as a direct biomarker of a healthy liver^[31,32]. As well-documented in the literature, protein synthesis is an ultra-specific process with a rather complex chemistry. The following sequential pseudo-elementary steps summarize the process^[33,34]: (1) Gene activation and DNA transcription that forms a single-stranded mRNA template with proper genetic codification (codons); (2) Transport of the mRNA molecule from the nucleus to the cytoplasm; (3) Transport of free amino acids from blood to the interior of the cell; (4) Binding of free amino acids to tRNA molecules; (5) Transport of mRNA to ribosome; (6) Transport of amino acids-tRNA complexes to ribosome; (7) Anticodon binding of tRNA complexes to specific codon on the mRNA template; (8) Steric translocation of the mRNA template to accommodate arriving tRNA complexes; (9) Peptide bond formation between amino acids; (10); Transfer of amino acid chain to arriving tRNA complexes; (11) Detachment of empty tRNA from the mRNA template; (12) Termination with non-binding codon; (13) Transport of protein from cytoplasm to blood. Steps 3 to 11 constitute the extended translation cycle in the growth of the polypeptide chain.

No first-principles molecular model can comprehensively describe all the chemical interactions in protein synthesis. However, a functional organ-on-a-chip model must still explain the kinetics of the cellular process of interest to some degree or at least identify the lowest

or determining step. Fortunately, experimental works have given valuable kinetic insights. Many studies have shown that albumin secretion trends are typically linear in both supplemented and unsupplemented conditions^[35–38]. Generally, the higher the nutrients available, the more albumin is produced. Furthermore, even in the absence of specific amino acids in the culture medium, ribosomal RNA/enzymes can edit and conform the polypeptide chain or extract amino acids from other sources to still produce a functional protein to a lesser extent^[36]. It is noteworthy to mention that cancerous primary hepatocytes do not substantially secrete albumin^[39].

For that purpose, a lumped kinetic description is used for protein synthesis. The approach is not completely physical, but it shows practicality. It is assumed that the cellular environment is completely homogeneous, with excess amounts of amino acids and other nutrients, such that transport limitations are not limiting. The amino acids are then considered undistinguished substrates of the same chemical. The total substrate concentration is then mathematically defined as the sum of the individual amino acid concentrations, with the synthesis rate being proportional to the total substrate concentration, as shown in Equation 6.88. This reduced kinetic model has only a single unknown kinetic parameter k , which must be regressed with specific experimental data.

$$\frac{\partial c_{\text{albumin,cell}}}{\partial t} = r_{\text{albumin,cell}} = k \cdot c_s \quad (6.88)$$

$$c_s = \sum_i c_{\text{amino acid } i} \quad (6.89)$$

The rate of consumption of the amino acids must be balanced and normalized accordingly to maintain a minimal chemical consistency, as in Equation 6.90. The fraction $\frac{c_{\text{amino acid } i}}{c_s}$ attempts to establish an individual quantitative relation between each amino acid with the lumped substrate concentration, while $p_{(\text{amino acid } i/\text{ALBUMIN})}$ is the stoichiometric proportion of amino acid in the final protein structure. In total, human serum albumin consists of 585 amino acids; its complete composition is described by Peters^[40].

$$\frac{\partial c_{\text{amino acid } i, \text{cell}}}{\partial t} = - \left(\frac{c_{\text{amino acid } i}}{c_s} \right) \cdot P(\text{amino acid } i / \text{ALBUMIN}) \cdot r_{\text{albumin, cell}} \quad (6.90)$$

It would be possible to attribute specific kinetic parameters k_i to each amino acid. The flaw in those descriptions is the implication that the synthesis rate is non-zero if only one amino acid is present; however, the kinetic parameters can be adjusted to minimize this error.

$$\frac{\partial c_{\text{albumin, cell}}}{\partial t} = r_{\text{albumin, cell}} = \sum_i k_i \cdot c_{\text{amino acid } i} \quad (6.91)$$

The classical Michaelis-Menten kinetics normally describe an enzyme-substrate binding process. For a single substrate, the mechanism consists of only two elementary steps: the reversible binding of the substrate and the formation of the enzyme complex, followed by the dissociation of the latter to form a product, thereby regenerating the enzyme. The final rate equation has the form of Equation 6.92, which has 2 regressible parameters, $V_{\max}$ and K_M . Michaelis-Menten rates are approximately linear if the substrate concentration is much smaller than K_M and level off for higher substrate concentrations due to saturation of the enzymatic sites. If the mechanistic kinetic model is very correct, the parameter estimation may work. If not, the parameter estimation may lack proper physical meaning or may not be statistically significant.

$$r_{\text{MM}} = \frac{V_{\max} \cdot c_s}{K_M + c_s}; \quad V_{\max} = k_{\text{cat}} \cdot c_{\text{E0}}; \quad c_{\text{E0}} = \text{total concentration of enzyme} \quad (6.92)$$

For a process involving multiple substrate bindings, such as protein synthesis, a mechanistic description involving amino acid concentrations becomes too uncertain and complex, and species balances exhibit forms that are too unwieldy to be regressible. Gorban et al. ^[41] proposed an alternative kinetic model based on the concentration of ribosomes and various messenger RNA species.

Metabolic Cellular Process II: Bio-response to Therapeutic Drugs

Other common liver biomarkers of interest are a class of isozymes called glutathione S-transferases (GSTs), which respond to indirect cell damage by xenobiotics. The response of cells to xenobiotics, such as antineoplastic drugs, is typically treated as a highly specialized defense or adaptation mechanism that ultimately aims to deactivate the drug molecules, mitigate their impact on the cellular metabolism and facilitate their excretion. As described by Wang et al.^[42], Klotz et al.^[43] and Cai et al.^[44] specific sensors (PXR, CAR, and others) are chemically activated and bind onto the xenobiotic molecules, as soon they start diffusing through the cellular membrane and cytoplasmic environment. The activation of the sensors triggers a complex process denominated signal transduction: a series of biomolecular reactions involving several chemical receptors (proteins, hormones) that transmit morphological information about the xenobiotic to the nucleus of the cell.

In the nucleus, a specific gene is then expressed, leading to the transcription and translation of a gene product (typically another receptor or enzyme, such as GSTs) that most effectively binds to and transforms the xenobiotic molecules into less reactive species due to added steric or electronic effects. The whole response process is commonly regarded as a gene expression and is regulated according to the amount of xenobiotic present. GSTs, for instance, conjugate glutathione to the xenobiotic molecules. In the case of doxorubicin, a chemotherapy drug of widespread use, the attachment of glutathione renders the former unable to intercalate between the planar bases of the DNA and inhibit the progression of topoisomerase II in cancerous cells^[45]. In that context, the secretion of GSTs, of course, compromises the drug's effectiveness.

As it can be noted, the gene expression mechanics for synthesizing different biomarkers are similar to those of protein synthesis and, therefore, are too complex to be kinetically modeled with accuracy using first-principles chemical theories. Nevertheless, experimental investigations have also revealed some general trends in kinetic gene activation and expression. Gildor et al.^[46] discuss that the rates of secretion of gene products frequently follow a sigmoidal or logistical function of the concentration of the stimulating xenobiotic compound.

6.6.2 Simulation Results

The synthesis of albumin in the liver-on-a-chip was simulated to analyze the preliminary trends. The lumped version of the Michaelis-Menten model (Equation 6.92) was used to describe the cellular kinetics, and the parameters were determined through trial and error. A more systematic regression will be performed in the future with proper uncertainty quantification. Table 6.5 presents all the parameters involved in the simulation. The properties of the culture medium were assumed to be those of liquid water.

Table 6.5: Parameters used in the simulation of the liver-on-a-chip model.

Parameter	Value/Description
Feed flow rate at inlets A and B	1.5 $\mu\text{L}/\text{min}$
Feed composition	specified by culture medium DMEM 10569
Temperature	37°C
$D_{\text{albumin,hydrogel}}$	$3.5 \cdot 10^{-9} \text{ m}^2/\text{s}$
$r_{\text{amino acids}}$	$2 \cdot 10^{-10} \text{ m}$
μ_{hydrogel}	0.5 Pa $\cdot$ s
k_{cat}	$2 \cdot 10^{-10} \text{ s}^{-1}$
K_{M}	1 mol/ m^3
c_{E0}	1 mol/ m^3

Figure 6.36 shows the evolution of the albumin and alanine concentration fields over time in the cell. Note the homogenization of the albumin concentration in the active culture domain and the gradient in the alanine concentration along the main axis of the device or the direction of culture medium flow.

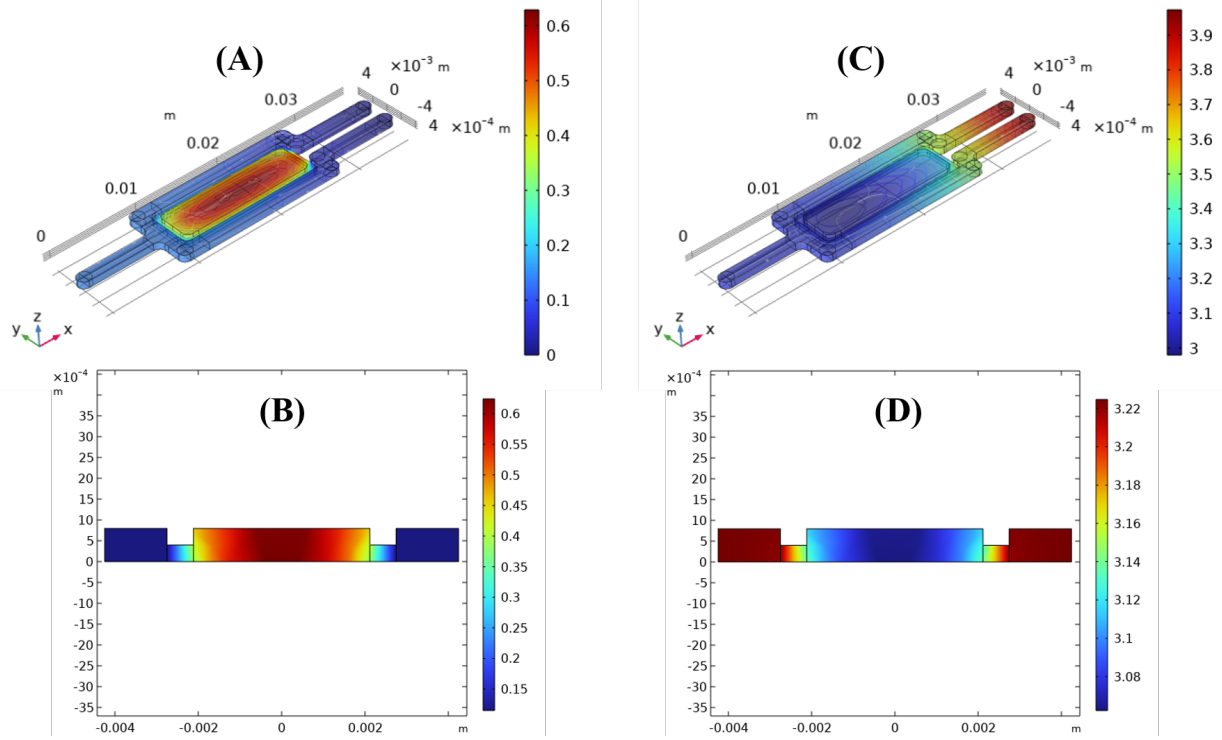


Figure 6.36: (A) Albumin concentration field [mol/m³], (B) albumin concentration field [mol/m³] on the yz cross sectional plane, at $x = 0.02$ m, (C) alanine concentration field [mol/m³], (D) alanine concentration field [mol/m³] on the yz cross sectional plane, at $x = 0.02$ m.

The computation of the average albumin production rate is performed by integrating the flux over the area of the chip outlet. Figure 6.37 presents the albumin production trend. It displays an s-shape that is expected from processes involving sequential transport and reaction. Similar trends were obtained by Yang et al.^[35] in advanced monitoring studies with a real replica of the liver-on-a-chip created in this work. In comparison to their work, the model currently underestimates albumin production, which likely reflects inappropriate kinetic parameters of the Michaelis-Menten model itself. Further investigations and collaborations are underway to proceed with data analysis and regression for a more accurate description of the metabolic kinetics.

$$\dot{m}_{\text{albumin}} = \text{MM}_{\text{albumin}} \cdot \int \int_{\text{Area} \mid \text{outlet boundary of chip}} \mathbf{n} \cdot (-D_{\text{albumin,hydrogel}} \nabla c_{\text{albumin}}) dS \quad (6.93)$$

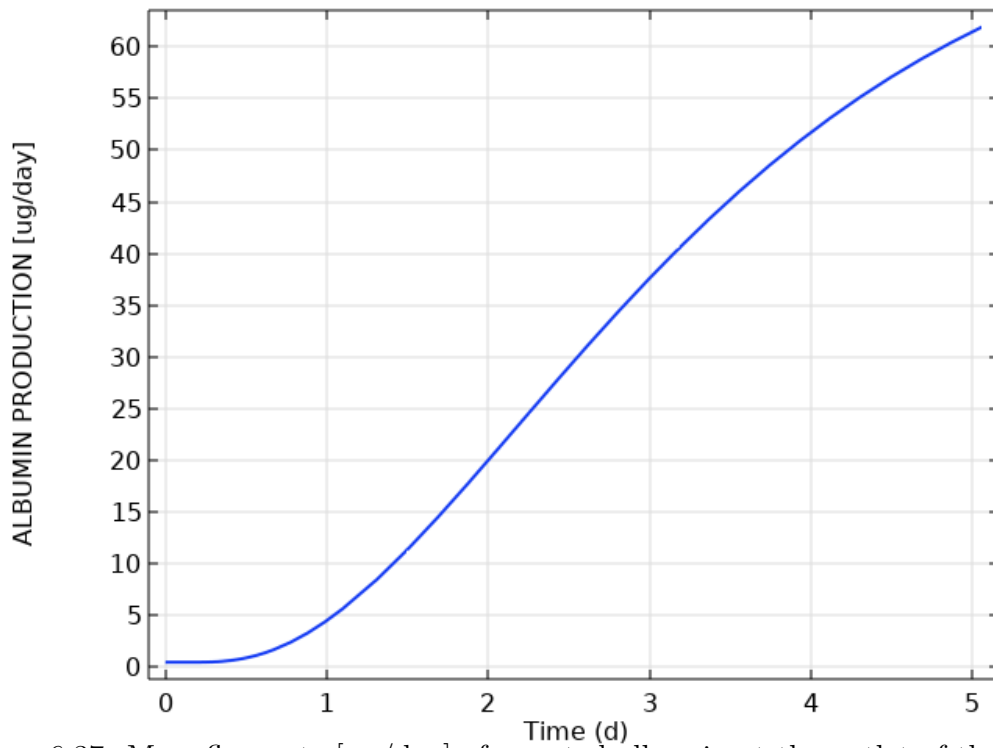


Figure 6.37: Mass flow rate [$\mu\text{g}/\text{day}$] of secreted albumin at the outlet of the chip.

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Chapter 7

Conclusion and Future Directions

The application of classical physical theories in developing high-fidelity multiscale models has proven effective across various aspects. Using platforms such as COMSOL and employing the finite element method, the coupling of complex partial differential equations enabled a more realistic and efficient evaluation of interactions between transport and reaction phenomena, as well as the geometric design effects of processes critical to the development of integrated energy systems. The renewable synthesis of hydrogen and ammonia in heterogeneous reactors has remained a relevant research topic for decades, and it is expected to continue advancing through the application of predictive models such as those developed in this dissertation.

The transfer of phenomenological information from atomic and molecular scale processes—particularly adsorption, surface reactions, and desorption—to fluid transport scales was successfully demonstrated in a carbon nanotube synthesis system. This multiscale transfer was achieved by combining methods for determining transition states and energy barriers with the subsequent resolution of a mean-field differential microkinetic model. This molecular modeling approach is believed to be the most feasible, accurate, and insightful, despite its reliance on geometric and entropic approximations, high computational demand, and a substantial degree of chemical intuition. Nonetheless, data-driven regression models (whether semi-empirical, kinetic, or otherwise) should not be overlooked, as they often capture the most realistic characteristics of the process under study. These models can be more efficiently

integrated with computational fluid dynamics (CFD) frameworks and control strategies.

This work comprehensively evaluated the dynamics of an integrated green system for hydrogen and ammonia production, as well as a modular-scale solar and wind energy generation system. The latter incorporated stochastic elements via variable wind speed. The most functionally accurate dynamic models of the chemical and energy modules were composed of nonlinear systems of parabolic partial and ordinary differential equations, respectively, coupled with nonlinear algebraic equations. These formulations imposed significant computational demands, making real-time solutions via the finite difference method or method of lines impractical. The modules exhibited significant temporal disparity: the chemical production module demonstrated faster dynamics than the green energy generation module, whose behavior was predominantly governed by the diurnal variation of solar irradiation.

Direct integration of the two modules in an open-loop simulation proved feasible, validating the operational viability of more sustainable chemical-energy systems. Optimal regulatory control of the chemical module was achieved using Model Predictive Control (MPC), employing an interior-point algorithm for optimization. However, due to the models' temporal mismatch and pronounced nonlinearity, closed-loop integration of the energy module was only realized through a supervisory-level implementation that responded to a subtractive post-regulation scheme following the optimal control of the chemical module. (Future investigations: distributed control architectures.) Although independent regulation of the renewable energy module was not addressed in this study, similar systems in the literature have demonstrated controllability.

Finally, large-scale dynamic interactions between several chemical and energy processing modules in a fixed-design community were analyzed in the context of supply chain optimization. These inherently involve fluctuating consumer demands and natural daily variations in energy. In addition, severe disruptions in power generation (outages and overgeneration) were implemented to assess the resilience and ability of the community to continuously supply consumers with the required quantities of ammonia. Ammonia storage was allowed at some sites in the community. The nonlinear dynamic optimization of the community relied only on a central optimizer, but benefited from predictions within a moving horizon before

final real-time decisions, similarly to methods in model predictive control. The optimization was marginally satisfactory using the interior point algorithm in MATLAB, but did not yield highly accurate supplies to consumers. The decision variables controlling ammonia distribution implied an oversupply and did not make very intelligent use of the ammonia storage possibilities. It was found that the optimization and performance of the community were significantly impaired by considering stochasticity in consumer demands.

Future investigations in integrative multiscale modeling should include:

- Experimental validation of the main modeled outputs to the largest extent possible.
- Deeper connection between experimental kinetic insights of atomic/molecular processes and transport phenomena models.
- Deeper exploration of the connectivity between variables belonging to different components on COMSOL, which allows for direct integration of high-fidelity models.
- Evaluation of innovative meshing techniques within the finite element method for multiphysics systems, particularly those with complex flow patterns.
- High-fidelity design of loop/recycle flow model to comprehend and leverage transport-reaction interactions.
- Implementation of reactive force fields for molecular dynamics simulations of catalytic systems and crystallization processes.
- Implementation of efficient, easy, and ready-to-use packages on MATLAB and Python for solving nonlinear sets of coupled PDEs/ODEs, particularly transient and one-dimensional. Galerkin projection methods have been used in the literature; however, they could not be coded for this work.
- Utilization of intelligent machine learning reductions or coarse-graining of multiscale dynamic models to generate tractable predictive models suitable for process optimization and control.

Bibliography

Appendix A

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Author: Thiago Oliveira Cabral, Amirsalar Bagheri, Davood B. Pourkargar

Publication: Industrial & Engineering Chemistry Research

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**Multiscale-multiphysics predictive modeling of chemical vapor deposition processes for carbon nanotube synthesis**

Author: Thiago Oliveira Cabral, Placidus B. Amama, Davood B. Pourkargar

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