



Reactor stability for the hydrogenation of liquid organic hydrogen carriers[☆]

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ABSTRACT

Liquid Organic Hydrogen Carriers (LOHCs) are promising alternatives for the safe storage and transportation of hydrogen. Among the available LOHCs, the toluene/methylcyclohexane pair has attracted significant attention owing to its favourable hydrogen-storage capacity, chemical stability, and compatibility with existing fuel infrastructures. However, the development of efficient catalytic systems and the understanding of reactor-scale operability remain critical challenges for their industrial deployment. In this work, an integrated experimental and numerical framework is proposed for the assessment of toluene hydrogenation processes. A Ru/CNF catalyst was synthesized and deeply characterized. The catalyst was subsequently tested in a laboratory-scale trickle-bed reactor under different operating conditions of temperature and hydrogen pressure. A Langmuir–Hinshelwood–Hougen–Watson (LHHW) kinetic model accounting for competitive adsorption phenomena and gas-liquid mass transfer effects was developed and calibrated using the experimental data. Kinetic parameters were estimated through a robust multi-start optimization strategy based on weighted residuals and a Soft-L1 objective function. The validated kinetic model was subsequently integrated into a dynamic reactor framework representative of an industrial-scale hydrogenation unit. Dynamic simulations, eigenvalue analysis, Strozzi–Zaldívar divergence assessment, and pseudo-arc-length continuation studies were performed to evaluate reactor operability and safety. The results demonstrated stable reactor operation throughout the investigated conditions, with no evidence of multiplicity, hysteresis phenomena, or thermal runaway behaviour. Furthermore, a batch-to-continuous start-up strategy was shown to significantly reduce the time required to reach the desired operating regime compared with conventional continuous start-up procedures.

Nomenclature

0	Initial value	OES	Optical emission spectrometry
a	Specific gas-liquid mass transfer area in the CSTR and batch	out	Outlet
a_{TBR}	Specific gas-liquid mass transfer area in the TBR	P	Pressure
A	Heat transfer surface area	$PB_{95\%}$	95% prediction band
AR	Aspect ratio	$pred$	Prediction
c	Cooling side value	$\mathcal{R}$	Reaction rate
C	Concentration	r_{tol}	Toluene conversion rate per grams of active phase

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$C_{H_2}^*$	Equilibrium hydrogen Concentration in the liquid phase	res	Residual value
$\hat{C}_{p,L}$	Liquid phase heat capacity	$\underline{res}$	Global residual vector
D_{imp}	Impeller diameter	$\underline{res}_j$	Residual vector associated with the j-th experiment
D_R	Reactor diameter	sf	Scaling factor
div	divergence	sim	Simulated value
E_a	Activation energy	t	Time
e_{av}	Average error value	$\underline{t}^T$	Transposed tangent vector
e_j	Residual distribution of the j-th experiment	T	Temperature
err_{log}	Logarithmic conversion error	TOL	Toluene

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err_x	Absolute conversion error	$\underline{u}$	System input parameters vector
$err_{x,norm}$	Normalized conversion error	U	Overall heat transfer coefficient
exp	Experimental value	$\dot{V}$	Volumetric flow rate
$\underline{f}$	Vectorial system function	V_L	Liquid phase volume (in the CSTR and batch)
H_{liq}	Total liquid phase height	$\underline{w}$	Weighting coefficients vector
H_R	Reactor height	w_{cat}	Catalyst weight
in	Inlet	$\underline{x}$	Vector of state variables
ICP	Inductively coupled plasma	$\dot{\underline{x}}$	Temporal derivative of vector of state variables
$\underline{J}$	Jacobian matrix	$\underline{y}$	Expanded state vector
K	Adsorption constant	$\Delta\tilde{H}_i$	Adsorption enthalpy of the i-th component
k_{koo}	Kinetic constant pre-exponential factor	$\Delta\tilde{H}_r$	Reaction enthalpy per unit mole
k_L	Gas-liquid mass transfer coefficient of the CSTR and batch	Δs	Continuation step size
$k_{L,TBR}$	Gas-liquid mass transfer coefficient of the TBR	ϵ	Numerical singularity factor
liq	Liquid phase	ϵ_L	Liquid hold-up
m	Temperature exponent	η	Effectiveness factor
m_{cat}	Total catalyst mass	ν_i	Stoichiometric number of the i-th component
MET	Methylcyclohexane	ρ_{bulk}	Catalyst bulk density
n	Pressure exponent	ρ_L	Liquid phase density
$\dot{n}$	Molar flow rate	ϕ	Kinetic parameters vector
n_i	Number of moles of the i-th component	χ	Conversion
N_{res}	Total number of residuals in the residual vector		

1. Introduction

The progressive decarbonization of the energy and industrial sectors is driving increasing interest in hydrogen as a carbon-free energy vector capable of supporting renewable-based energy systems [1]. Hydrogen can contribute to the reduction of greenhouse gas emissions in sectors that are difficult to electrify directly, including heavy industry, long-distance transport, and seasonal energy storage [2]. Nevertheless, despite its high gravimetric energy density, hydrogen deployment at large scale remains strongly limited by storage and transportation challenges associated with its low volumetric density, high diffusivity, and demanding operating conditions for compression or liquefaction [3,4]. These limitations have stimulated significant research efforts toward alternative hydrogen storage strategies capable of improving safety, transportability, and process integration [5]. Among the different technologies proposed for hydrogen storage, Liquid Organic Hydrogen Carriers (LOHCs) have emerged as one of the most promising solutions for long-term and large-scale applications [6,7]. LOHC systems rely on hydrogenation and dehydrogenation reaction cycles, in which hydrogen is chemically stored within an organic molecule in hydrogen-rich form and released when required through catalytic conversion [8]. Compared to conventional compressed or liquefied hydrogen storage, LOHCs offer several advantages, including safer handling conditions, compatibility with existing liquid-fuel infrastructure, and potentially high volumetric hydrogen storage capacities [9]. In addition, the liquid state of the carrier under ambient conditions simplifies transportation and distribution, facilitating the integration of hydrogen into current industrial logistics chains [10].

Several LOHC systems have been investigated in the literature, including dibenzyl toluene [11], naphthalene [12], N-ethylcarbazole [13], and BTX-based systems [14]. Among these, the toluene/methylcyclohexane pair has attracted particular attention due to its relatively high technological readiness level, favourable hydrogen storage capacity, wide availability, and comparatively low cost [15–17]. Furthermore, the hydrogenation of aromatic compounds such as toluene

represents an effective model reaction for the broader class of BTX compounds and aromatic LOHC systems, since these species exhibit similar kinetic behaviour and can often be described through a unified kinetic framework based on a representative aromatic component [18]. However, despite the extensive investigation of aromatic hydrogenation reactions, important challenges remain regarding catalyst formulation, kinetic characterization, reactor stability, and process scale-up [19]. In particular, the highly exothermic nature of hydrogenation reactions requires careful reactor design, integrating an accurate description of the catalytic behaviour in a wide range of conditions, to avoid thermal instabilities, hot spots, and potential runaway conditions, especially when transitioning from laboratory-scale experiments to industrial applications [20].

Under these premises, the formulation and characterization of catalysts represent a critical aspect in the implementation of LOHC technologies [21,22]. Noble metal catalysts based on Ru, Pt, Pd, and Rh generally exhibit high hydrogenation activity and selectivity under relatively mild operating conditions, although their economic sustainability and long-term stability remain key concerns [23–25]. In parallel, Ni-based catalysts have been traditionally extensively investigated for aromatic hydrogenation reactions due to their lower cost and industrial availability, typically employing metal loadings around 15 wt% to compensate for their lower intrinsic activity compared to noble metals [26,27]. In recent years, increasing attention has been devoted to the use of carbon-based supports [28], including carbon nanotubes [29] and carbon nanofibers (CNFs) [30], due to their high surface area, favourable transport properties, corrosion resistance, and tunable surface chemistry [31,32]. In particular, CNFs can improve transfer phenomena [33,34] while promoting effective dispersion of the active metallic phase [35]. Nevertheless, the combination of Ru active sites with CNF supports remains relatively unexplored for aromatic hydrogenation reactions, and additional investigations are needed to assess catalytic performance, structural stability, and process applicability under realistic operating conditions.

Beyond catalyst development, the deployment of LOHC technologies requires the integration of experimental investigations with advanced numerical engineering methodologies [36,37]. While most studies available in the literature mainly focus on catalyst activity, reaction mechanisms, and kinetic parameter estimation, comparatively fewer contributions address the dynamic behaviour, intrinsic stability, and safety of hydrogenation reactors under industrially relevant operating conditions [38]. This aspect is particularly critical for aromatic hydrogenation systems, which involve strongly exothermic reactions occurring in the presence of flammable and reactive species under pressurized hydrogen atmospheres. Under such conditions, the interaction between reaction kinetics, heat generation, mass transfer, and transport limitations may lead to nonlinear reactor dynamics, unstable operating regimes, and potential thermal runaway scenarios [39]. Consequently, the identification of stable operating windows and the assessment of transient reactor behaviour become essential steps for the reliable scale-up and industrial implementation of emerging technologies [40,41]. More broadly, stability- and operability-oriented reactor maps have recently been demonstrated to provide an a priori basis for identifying operating regimes, transition boundaries, and operability margins under variable design and operating conditions [41]. Local stability can be assessed through eigenvalue analysis of the reactor model, allowing the identification of stable and unstable steady states as well as the characterization of transient dynamics in response to perturbations [42]. Complementarily, global thermal stability and runaway susceptibility can be investigated through criteria based on heat generation and heat removal competition, including divergence-based approaches such as the Strozzi–Zaldívar criterion (S&Z), which provides a dynamic measure of runaway propensity in nonlinear reacting systems [43,44]. In addition, continuation methods provide a robust mathematical framework for systematically exploring reactor operability beyond nominal design conditions [45]. Unlike conventional parametric simulations, pseudo-

arc-length continuation techniques allow the solution branches of nonlinear algebraic systems to be followed continuously, even in the vicinity of folds, turning points, and multiplicity regions [46,47]. When coupled with a predictor-corrector strategy [48,49], it will be possible to construct bifurcation diagrams and identify critical operating boundaries. This methodology is particularly advantageous for highly nonlinear systems, where conventional iterative simulations may fail to capture unstable branches or hidden multiplicity phenomena [50], enabling the evaluation of the effect of operating parameters, such as coolant-side inlet temperature, on reactor conversion, thermal stability, and multiplicity behaviour, while simultaneously providing local stability information through eigenvalue tracking along the continuation path.

To address these challenges, the present work combines experimental catalyst development with advanced numerical reactor analysis within an integrated framework for LOHC hydrogenation processes. A Ru-based catalyst supported on carbon nanofibers was synthesized, characterized, and experimentally tested for the hydrogenation of toluene-based systems, allowing the derivation of an experimentally validated kinetic model suitable for reactor-scale simulations. The numerical investigation was performed considering a reference single-jacketed continuous stirred tank reactor supplied with hydrogen produced by electrolysis. The developed model accounts for reaction kinetics, adsorption phenomena, and heat and mass transfer effects, enabling the investigation of both steady-state and transient reactor behaviour under realistic operating conditions. The proposed methodology therefore provides a comprehensive framework for evaluating operational robustness, startup behaviour, and safety margins, supporting early-stage reactor design, scale-up decisions, and the development of intrinsically safer LOHC hydrogenation processes for future low-carbon energy systems.

2. Materials and methods

The present work combines experimental investigations and numerical reactor analysis to develop a systematic framework for the assessment of aromatic hydrogenation processes applied to LOHC systems. The methodology was designed to bridge catalyst development, reaction kinetics, and reactor-scale process engineering, enabling the

evaluation of both process performance and operational safety. The study was structured into five interconnected stages, as summarized in Fig. 1.

Step 1: A ruthenium-based catalyst supported on carbon nanofibers (Ru/CNF) was synthesized and characterized to evaluate its structural integrity, active phase distribution, and physicochemical properties. The catalyst preparation procedure and the characterization techniques employed are described in Section 2.1.

Step 2: The catalyst was tested under hydrogenation conditions using toluene as a compound representative of the BTX since benzene, toluene, and xylene exhibit closely related hydrogenation mechanisms and similar kinetic behaviour [18]. Hydrogenation experiments were conducted in a continuous Trickle-Bed Reactor (TBR) over a range of temperatures, pressures, and feed flow rates to generate the experimental dataset required for kinetic model development. Details of the experimental apparatus, operating conditions, and analytical procedures are provided in Section 2.2.

Step 3: The experimental conversion data were then used to develop a kinetic model based on a Langmuir–Hinshelwood–Hougen–Watson (LHHW) formulation, in agreement with the current literature [19]. Besides, previous investigations demonstrated that a global reaction approach is generally sufficient to describe the overall conversion behaviour of aromatic hydrogenation systems under practical operating conditions [19]. Model parameters were estimated through nonlinear regression procedures, yielding a quantitative kinetic description suitable for process simulation and reactor analysis. Further details regarding the kinetic formulation, parameter estimation procedure, and constitutive model used to represent the experimental reactor are presented in Section 2.3.

Step 4: The experimentally validated kinetic model was subsequently incorporated into a dynamic reactor model accounting for reaction kinetics, adsorption phenomena, heat transfer, and gas–liquid mass transfer effects. Numerical simulations were performed for a reference industrial-scale continuous stirred tank reactor (CSTR) representative of hydrogenation units supplied with electrolyser-derived hydrogen. The choice of a CSTR configuration was motivated by its ability to dampen fluctuations in reactant availability, making it particularly suitable for integration with renewable-powered electrolysis systems, whose hydrogen production may be inherently variable. Moreover, the CSTR

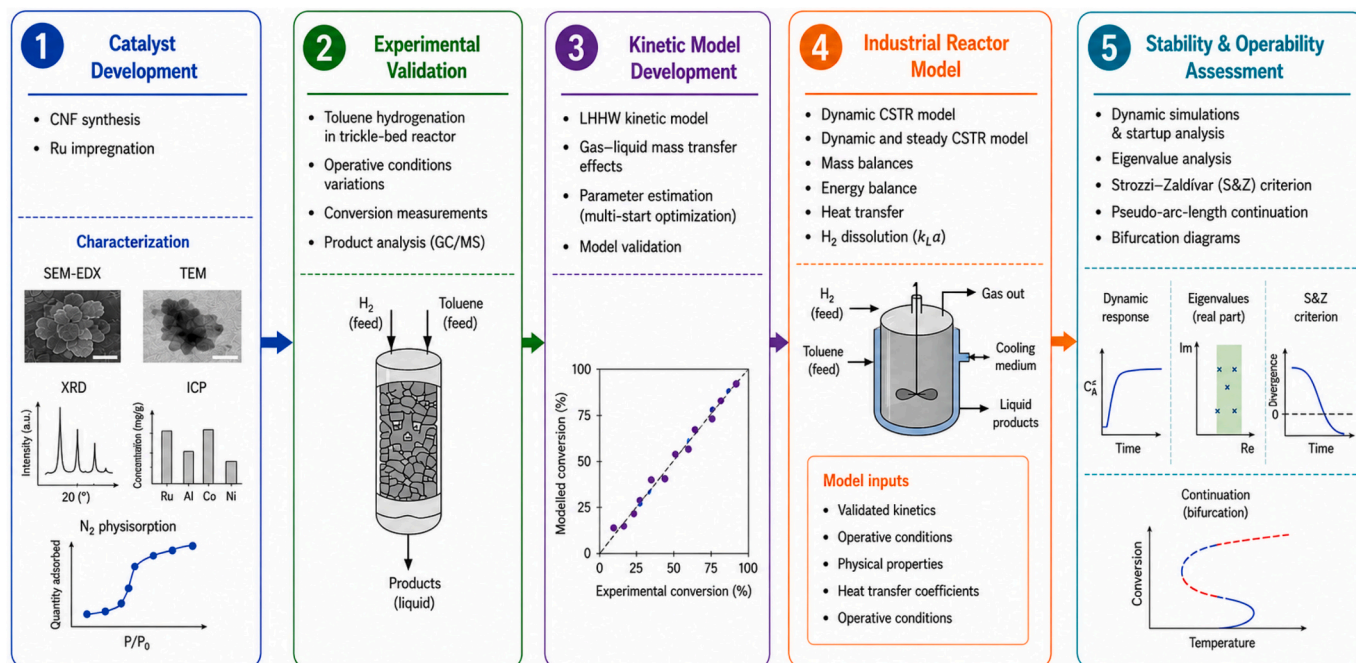


Fig. 1. Schematic representation of the workflow adopted in the present work, divided into 5 main Steps.

constitutes the fundamental building block of more complex reactor configurations, since a tubular reactor can be approximated as a series of infinitesimal stirred reactors. Consequently, the conclusions derived from the present analysis retain broader relevance beyond the specific reactor configuration considered.

Step 5: The reactor model was employed to investigate both transient and steady-state operating conditions and to assess process stability and safety. The analysis combined dynamic simulations, eigenvalue-based local stability assessment, runaway detection criteria, and bifurcation analysis. In particular, pseudo-arc-length continuation techniques were adopted to systematically explore the reactor response to parameter variations, enabling the identification of critical operating boundaries, stability transitions, and possible multiplicity regions. By integrating experimental observations with advanced numerical tools, the proposed methodology provides a comprehensive framework for catalyst evaluation, reactor design, and safety-oriented scale-up of LOHC hydrogenation technologies. Additional details concerning the industrial reactor model, simulation framework, and stability and continuation procedures are provided in Section 2.4.

2.1. Catalyst preparation and characterization

Carbon nanofibers (CNFs) were synthesized via catalytic decomposition of an equimolar CO_2/CH_4 mixture at 650°C in a rotary bed reactor. A catalyst consisting of 33.5 wt% Ni and 33.5 wt% Co supported on alumina was employed. Further details regarding the synthesis procedure have been reported elsewhere [51]. The resulting CNFs were subjected to a two-step acid purification process. In the first stage, the material was treated with 37% HCl (PA-ACS-ISO, FLUKA) at 60°C for 4 h under ultrasonic agitation to eliminate residual metallic species originating from fibre growth. Subsequently, the sample was refluxed in 65% HNO_3 (PA-ISO, PANREAC) for 1 h. This second treatment promoted the formation of oxygen-containing functional groups on the carbon surface, which enhanced the dispersion of the active phase during the subsequent impregnation step. The catalyst was prepared by depositing ruthenium directly onto the CNF support via an incipient wetness impregnation method. An aqueous solution of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (Sigma Aldrich) was added dropwise to the support to achieve nominal metal loadings of 0.25 wt%. After impregnation, the samples were dried at 105°C overnight. Subsequently, calcination and reduction were carried out in a single step under a flowing 25/75 vol% H_2/N_2 mixture at 300 Nml min^{-1} . The thermal treatment consisted of heating to 350°C at a rate of 5°C min^{-1} , followed by an isothermal period of 2 h. Eventually, the catalysts were cooled to room temperature under nitrogen flow and passivated for 3 h using a gas mixture containing 1 vol% O_2 in N_2 . Finally, the solid was sieved to obtain a particle size distribution in the range of 50–150 μm . The resulting catalyst was referred to as Ru/CNF.

X-ray diffraction (XRD) pattern was acquired using a Bruker D8 Advance Series 2 diffractometer equipped with $\text{CuK}\alpha$ radiation (Ni filter) and a graphite secondary monochromator [51]. Data were recorded over the 5° – 80° range with a step size of 0.05° and a counting time of 3 s per step. Phase identification, structural refinement, and crystallite size estimation were carried out using the DIFRAC PLUS EVA 8.0 software in combination with TOPAS, applying whole-pattern fitting based on the Pawley method. The metal content was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) [52]. Prior to analysis, the sample was dissolved using a sodium peroxide fusion procedure and subsequently analysed with a Spectroblue (AMETEK) spectrometer. Textural properties were obtained from nitrogen adsorption–desorption isotherms measured at -196°C using a Micromeritics ASAP 2020 system. The specific surface area was calculated from the adsorption branch using the BET method, while the total pore volume was derived at P/P0 greater than 0.994 and micropores contribution was evaluated using the t-plot model. Morphology and elemental composition were examined by scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX) using a Hitachi S-

3400 N instrument (Type II) [53]. Catalyst morphology was characterized by STEM on an FEI Titan Low-Base 60–300 instrument (INA-LMA Advanced Microscopy Laboratory) equipped with a CESCOR aberration-corrected probe (0.09 nm resolution) and a HAADF detector. Samples were deposited onto lacey carbon-coated copper grids prior to imaging. Particle size distribution was calculated using ImageJ software from measurements of at least 300 particles. Elemental composition was qualitatively assessed by EDX analysis of the observed nanostructures.

2.2. Experimental hydrogenation tests

The activity of the catalyst in continuous toluene hydrogenation was assessed under different pressures (30–50 bar) and temperatures (130 – 180°C). The experimental runs were carried out in a stainless-steel TBR with an internal diameter of 1/4" and a length of 30 cm. Additional information regarding the experimental setup has been reported elsewhere [52].

In each experiment, approximately 1.5 g of catalyst were loaded into the reactor. Prior to reaction, the system was heated to 150°C at a rate of $10^\circ\text{C min}^{-1}$ under a reductive atmosphere consisting of 200 Nml min^{-1} of a 50 vol% H_2/N_2 mixture. These conditions were maintained for 1 h to remove the oxide layer formed during passivation. The reactor was then pressurized with hydrogen to the desired operating pressure. Once the target temperature was reached, toluene was introduced at a flow rate corresponding to a weight hourly space velocity of 8.9 h^{-1} . The reaction products were continuously collected in a pressurized vessel, and both liquid and gas effluents were sampled at hourly intervals. The operating conditions were maintained for a minimum of 2 h, a duration previously determined to be sufficient to obtain stable and reproducible results, as the conversion remained essentially constant beyond this period according to experimental observations. Subsequently, the operating parameters were modified, and the procedure was repeated under the new conditions.

Liquid products were diluted in n-decane prior to analysis and characterized using a gas chromatograph equipped with a flame ionization detector (Clarus 580) fitted with an Elite-5 capillary column (30 m length, 250 μm internal diameter, crossbond 5% diphenyl / 95% dimethylpolysiloxane). The gaseous effluent was collected in a sampling bag and analysed using a Refinery Gas Analyzer 1157 (PerkinElmer) equipped with both flame ionization and thermal conductivity detectors. The outlet gas composition remained constant during all experiments and was composed exclusively of hydrogen which indicated the absence of hydrocarbons in the effluent stream.

Since the effluent liquid stream was only composed of methylcyclohexane and unreacted toluene, the activity of the catalyst could be evaluated with the toluene conversion (Eq. 1) and by the toluene conversion rate per gram of active phase (Eq. 2).

$$\chi = \frac{\dot{n}_{\text{TOL},\text{in}} - \dot{n}_{\text{TOL},\text{out}}}{\dot{n}_{\text{TOL},\text{in}}} \quad (1)$$

$$r_{\text{tol}} = \frac{\dot{n}_{\text{TOL},\text{in}} - \dot{n}_{\text{TOL},\text{out}}}{g_{\text{Ru}}} \quad (2)$$

2.3. Kinetic modelling

As discussed in Section 1, toluene was selected as the reference reactant for both the experimental campaign and the subsequent kinetic model development [18]. The resulting model is therefore intended to describe the behaviour of the broader BTX family while maintaining a reduced number of kinetic parameters. The overall hydrogenation process was represented through a single irreversible reaction reported in Eq. 3. Although aromatic hydrogenation may proceed through multiple elementary reaction steps and partially hydrogenated intermediates, experimental observations and previous studies indicate that the formation of these intermediate species can be neglected under the

operating conditions considered in this work [19]. As a further confirmation of that, experimental analysis of the outlet mixture does not show the appearance of any partially hydrogenated compound.



The reaction rate was formulated according to the LHHW theory, which assumes that the overall reaction rate is governed by the interplay between adsorption phenomena and surface reaction mechanisms occurring on the catalyst active sites [53]. To accurately capture the effect of a wide range of operating pressures, a pressure-dependent correction term was incorporated into the kinetic constant. This modification accounts for the influence of pressure on the reaction kinetics by introducing an empirical pressure-dependent correction factor into the modified Arrhenius expression, while retaining the temperature dependence through both the exponential and power-law terms. The resulting kinetic expression is reported in Eq. 4, together with the formulations adopted for the reaction and adsorption constants. The adsorption constants follow Van't Hoff-type relationships, whereas the kinetic constant is described by a modified Arrhenius expression including temperature and pressure correction factors. Unless otherwise specified, pressure is expressed in bar, temperature in K, concentrations in mol m^{-3} , adsorption constants in $\text{m}^3 \text{mol}^{-1}$, adsorption enthalpies in J mol^{-1} , activation energy in J mol^{-1} , and reaction rates in $\text{mol s}^{-1} \text{kgcat}^{-1}$.

$$\left\{ \begin{array}{l} \mathcal{R} = \frac{k_k C_{tol,liq} C_{H_2,liq}}{(1 + K_{tol} C_{tol,liq} + K_{H_2} C_{H_2,liq})^2} \\ k_k = k_{k\infty} T^m \left(1 + \frac{P}{10 \text{ bar}}\right)^n \exp\left(-\frac{E_a}{R_g T}\right) \\ K_{tol} = K_{tol\infty} \exp\left(-\frac{\Delta \tilde{H}_{tol}}{R_g T}\right) \\ K_{H_2} = K_{H_2\infty} \exp\left(-\frac{\Delta \tilde{H}_{H_2}}{R_g T}\right) \end{array} \right. \quad (4)$$

To maintain consistency with the experimental system and to facilitate reactor-scale calculations, the following hypotheses were posed: (i) negligible catalyst deactivation, (ii) uniform activity throughout the reactor volume and through each catalytic material itself.

Since hydrogenation occurs in a gas-liquid-solid environment, the availability of dissolved hydrogen plays a fundamental role in determining the overall reaction rate. Accordingly, the trickle reactor model explicitly accounts for gas-liquid mass transfer through a volumetric transfer coefficient, allowing hydrogen dissolution to influence the concentration available for reaction [54]. Gas-liquid equilibrium was described through Henry's law [55,56], while mass transfer between the gas and liquid phases was assumed to occur faster than the characteristic reactor dynamics. Under these assumptions, the model can capture the transition between kinetic and mass-transfer-controlled regimes that may arise under different operating conditions.

The adopted modelling framework therefore combines a simplified representation of the reaction network with a mechanistically based LHHW kinetic formulation and explicit consideration of gas-liquid mass transfer effects. This level of detail was deemed sufficient to accurately reproduce the experimental observations while preserving the computational efficiency required for parameter estimation, dynamic simulations, stability assessment, and continuation analyses performed in the subsequent sections.

For brevity, in the Supplementary Materials are reported the adopted trickle bed reactor model (Section S1) and the kinetic parameters estimation procedure (Section S2) adopted in present work to retrieve the main parameters of interest from the experimental runs.

2.4. Numerical reactor analysis

2.4.1. Reference industrial reactor configuration

The numerical analyses presented in this work were performed considering a reference industrial continuously stirred tank reactor (CSTR) representative of a liquid-phase hydrogenation unit. The process was assumed to operate in a three-phase gas-liquid-solid configuration, where liquid toluene/methylcyclohexane mixture constitutes the continuous phase, hydrogen is supplied as a gaseous reactant, and the catalyst is suspended within the reactor volume. A schematic representation of the adopted reactor configuration is reported in Fig. 2. The reactor was equipped with an external cooling jacket to remove the heat released by the highly exothermic hydrogenation reaction and maintain safe operating conditions.

The reference reactor was designed with an effective liquid working volume of 1 m^3 and a catalyst inventory of 70 kg. The selected catalyst loading represents a compromise between achieving sufficiently high reaction rates and maintaining adequate hydrodynamic conditions to ensure complete catalyst suspension throughout the reactor volume. A gas holdup of 10% was assumed, corresponding to typical values reported for mechanically agitated gas-liquid-solid hydrogenation reactors operating under moderate-to-high gas dispersion conditions. Under these conditions, the reactor contains simultaneously a continuous liquid phase, dispersed hydrogen bubbles, and suspended catalyst particles, resulting in a representative three-phase gas-liquid-solid reaction environment for industrial hydrogenation applications.

The vessel geometry was defined through an aspect ratio equal to $AR = H_R/D_R = 5$ where H_R and D_R denote the reactor height and diameter, respectively. Such a relatively large aspect ratio was selected to maximize the gas-liquid contact time and improve hydrogen utilization by increasing the gas residence time within the reactor. The reactor dimensions were calculated consistently from the specified working volume and aspect ratio. A headspace fraction of 20% was additionally considered to accommodate gas expansion, facilitate gas-liquid separation and reduce liquid entrainment with the outflowing gas.

Mixing was provided through a series of equally spaced Rushton turbines operating at 300 rpm. The impellers were positioned with a clearance equal to $D_R/2$ from both the reactor bottom and the liquid free surface, while an inter-impeller spacing equal to D_R was adopted. This arrangement was selected to ensure adequate mixing throughout the entire reactor height while minimizing the occurrence of poorly mixed regions. The impeller diameter D_{imp} was selected according to a diameter ratio $D_{imp} = 0.33D_R$ which falls within the range typically adopted for industrial gas-liquid and gas-liquid-solid stirred reactors. Rushton turbines were selected because of their excellent gas-dispersion capability and their widespread industrial application in hydrogenation processes.

The gas-liquid mass-transfer coefficient was estimated using the Garcia-Deckwer correlation, which accounts for agitation intensity, gas superficial velocity, liquid properties, and catalyst loading [57]. The

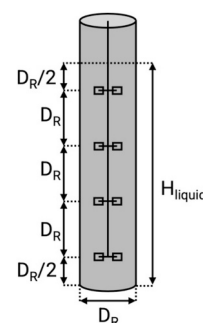


Fig. 2. Sketch of the adopted reference CSTR configuration. Here, H_{liquid} represents for the height of the liquid/sol/gas mixture under nominal working conditions.

reference hydrogen feed rate was initially determined to provide a nominal volumetric mass-transfer coefficient of approximately $k_L a = 0.03 \text{ s}^{-1}$ under the inlet temperature and pressure operating conditions, nominal liquid inventory, and 300 rpm agitation speed. During the simulations, however, the gas-liquid mass-transfer coefficient was not assumed constant but was recalculated iteratively at each integration step using the local process conditions and updated fluid properties. Consequently, the value of $k_L a$ evolved dynamically as a function of temperature, composition, gas flow rate, and hydrodynamic conditions, while the hydrogen feed rate remained fixed at the reference value determined during the reactor design stage.

The reactor was operated at a pressure of 30 bar and an inlet feed temperature of 393 K. The selected operating pressure is representative of the outlet pressure of commercial electrolyzers, thereby enabling the direct utilization of compressed renewable hydrogen while minimizing additional compression requirements. This pressure level also promotes hydrogen dissolution in the liquid phase, increasing hydrogen availability at the catalyst surface and reducing potential mass-transfer limitations. Pure liquid toluene was supplied continuously to the reactor at a mass flow rate of 0.07 kg s^{-1} , corresponding to a methylcyclohexane production capacity representative of a small-to-medium industrial hydrogen storage unit. The cooling system consisted of an external water jacket supplied at a reference inlet temperature of 393 K and a coolant mass flow rate of 0.12 kg s^{-1} . The selected liquid-feed and coolant-flow rates were chosen to obtain industrially relevant production capacities while simultaneously ensuring sufficient heat-removal capability for the highly exothermic hydrogenation reaction. In particular, the coolant flow rate was selected to provide an adequately controllable thermal environment, allowing the reactor to operate over a wide range of conditions while maintaining sensitivity to potential thermal instabilities, multiplicity phenomena, and runaway scenarios that may arise during operation.

The overall heat-transfer coefficient was evaluated dynamically from reactor-side and coolant-side heat-transfer correlations accounting for fluid properties, agitation conditions, gas holdup, catalyst loading, vessel geometry, wall thermal resistance, and fouling effects. The reactor configuration described above was adopted as the reference case for all dynamic simulations, stability analyses, and continuation studies presented in the following sections.

2.4.2. Dynamic and steady simulations

Transient simulations were carried out using the dynamic CSTR model to reproduce reactor start-up operations and evaluate the temporal evolution of the process variables. The governing differential equations were integrated until the system approached a stationary condition. During the simulations, all thermophysical properties, reaction rates, gas-liquid mass-transfer coefficients, and heat-transfer coefficients were continuously updated according to the local reactor conditions. This approach allowed the coupled evolution of species concentrations, hydrogen availability, reactor temperature, coolant temperature, and reaction rates to be accurately captured.

The transient simulations were also employed to generate physically consistent initial conditions for the steady-state calculations. Steady-state operating conditions were subsequently determined by solving the algebraic system obtained by setting all accumulation terms equal to zero in the dynamic model equations. The resulting nonlinear system was solved iteratively until convergence of all state variables was achieved. These steady-state solutions were then employed as reference operating points for the stability and continuation analyses discussed in the following sections.

In addition, the reactor was initially operated in batch mode, with catalyst, toluene, and hydrogen loaded into the vessel until a conversion level equal to 99% of the steady one was reached to assess a possible start-up procedure. Subsequently, the continuous inlet and outlet streams were activated, and the reactor was progressively transitioned toward continuous operation.

The performance of the batch-to-continuous strategy was quantitatively assessed by comparing start-up times, temperature trajectories, hydrogen consumption, and conversion profiles with those obtained from a direct continuous start-up. Particular attention was devoted to identifying potential thermal overshoots, concentration excursions, or unstable operating regions that could compromise process safety or operational flexibility. The resulting dynamic trajectories also provided valuable insight into the accessibility of the different steady-state operating points identified through the continuation analysis.

For all simulations, numerical integration was performed using variable-step ordinary differential equation solvers with adaptive time stepping to ensure accurate resolution of the coupled mass and energy balances over the wide range of operating conditions investigated. Convergence toward steady-state conditions was assumed when the temporal derivatives of all state variables became sufficiently small and no further significant variations were observed in the reactor behaviour.

The continuously stirred tank reactor (CSTR) was modelled assuming perfect mixing of the liquid, gas, and catalyst phases. Under these conditions, concentration and temperature gradients within the reactor volume are neglected, and all state variables are represented by their bulk values. Both transient and steady-state formulations were implemented. The transient model allows the dynamic behaviour of the system during start-up and operational disturbances to be accurately captured, while simultaneously providing reliable initial estimates for the steady-state solver. This strategy significantly improves the robustness and convergence of the steady-state calculations, particularly under highly nonlinear operating conditions. The resulting steady-state solutions were subsequently employed as initial points for the continuation analysis, enabling the systematic investigation of multiple operating regimes, stability boundaries, and potential process multiplicities. The constitutive model, comprising species mass balances together with reactor-side and coolant-side energy balances, is reported in Eq. 5 [58]. Steady-state operating points were obtained by setting all accumulation terms equal to zero, yielding a system of nonlinear algebraic equations describing the reactor behaviour under stationary operating conditions.

$$\left\{ \begin{array}{l} \frac{dC_{TOL}}{dt} = \frac{\dot{V}_{in}C_{TOL,in} - \dot{V}_{out}C_{TOL} + \nu_{TOL}m_{cat}\eta\mathcal{R}}{V_L} \\ \frac{dC_{MET}}{dt} = \frac{\dot{V}_{in}C_{MET,in} - \dot{V}_{out}C_{MET} + \nu_{MET}m_{cat}\eta\mathcal{R}}{V_L} \\ \frac{dC_{H_2}}{dt} = k_L a \left(C_{H_2}^* - C_{H_2} \right) + \frac{\nu_{H_2}m_{cat}\eta\mathcal{R}}{V_L} \\ \frac{dT}{dt} = \frac{\left(-\Delta\tilde{H}_r \right) m_{cat}\eta\mathcal{R} - UA(T - T_c)}{V_L \rho_L \hat{C}_{p,L}} \\ \frac{dT_c}{dt} = \frac{\dot{V}_{in,c}\rho_{c,in}\hat{C}_{p,c,in}T_{c,in} - \dot{V}_{out,c}\rho_{c,out}\hat{C}_{p,c,out}T_{c,out} + UA(T - T_c)}{V_{L,c}\rho_{L,c}\hat{C}_{p,L,c}} \end{array} \right. \quad (5)$$

Steady-state operating points were obtained by imposing zero accumulation terms in Eq. 5, resulting in a system of nonlinear algebraic equations describing the reactor behaviour under stationary operating conditions. For all reactor configurations, thermophysical properties, including density, viscosity, thermal conductivity, heat capacity, surface tension, and hydrogen solubility, were continuously updated as functions of temperature and composition [57,59]. Similarly, gas-liquid mass-transfer coefficients and heat-transfer coefficients were recalculated at each integration step using the local process conditions, allowing the models to capture the coupled effects of reaction, transport phenomena, and thermal behaviour over a wide range of operating conditions.

To investigate continuously stirred tank reactor (CSTR) start-up procedures and assess the dynamic behaviour of the scaled system, a batch reactor model was also developed. The reactor was represented as a pseudo-homogeneous gas-liquid-solid system operating without inlet or outlet streams. Perfect mixing of the liquid, gas, and catalyst phases

was assumed, resulting in spatially uniform concentrations and temperature. The batch model was primarily employed to evaluate the feasibility of starting up the industrial reactor under batch conditions and to quantify the associated process performance and safety characteristics. The governing species and energy balances are reported in Eq. 6 [60].

$$\left\{ \begin{array}{l} \frac{dC_{TOL}}{dt} = \frac{\nu_{TOL} m_{cat} \eta \mathcal{R}}{V_L} \\ \frac{dC_{MET}}{dt} = \frac{\nu_{MET} m_{cat} \eta \mathcal{R}}{V_{L,batch}} \\ \frac{dC_{H_2}}{dt} = k_L a (C_{H_2}^* - C_{H_2}) + \frac{\nu_{H_2} m_{cat} \eta \mathcal{R}}{V_{L,batch}} \\ \frac{dT}{dt} = \frac{(-\Delta \tilde{H}_r) m_{cat} \eta \mathcal{R} - UA(T - T_c)}{V_{L,batch} \rho_L \hat{C}_{p,L}} \\ \frac{dT_c}{dt} = \frac{\dot{V}_{in,c} \rho_{c,in} \hat{C}_{p,c,in} T_{c,in} - \dot{V}_{out,c} \rho_{c,out} \hat{C}_{p,c,out} T_{c,out} + UA(T - T_c)}{V_{L,c} \rho_{L,c} \hat{C}_{p,L,c}} \end{array} \right. \quad (6)$$

2.4.3. Stability analysis

The stability analysis was performed by linearizing the nonlinear reactor model around each equilibrium solution and evaluating the corresponding eigenvalue spectrum, as well as computing the divergence of the system itself. The transient reactor model can be expressed in compact form as $\dot{\underline{x}} = \underline{f}(\underline{x}, \underline{u})$ where $\underline{x}$ is the vector of state variables, $\dot{\underline{x}}$ its first temporal derivative, and $\underline{u}$ denotes the vector of operating parameters. For the present reactor model, the state vector is defined as $\underline{x} = [C_{TOL}, C_{MET}, C_{H_2}, T, T_c]$. Local stability was evaluated through the Jacobian matrix $\underline{J}$ of the nonlinear dynamic system, obtained analytically from the governing mass and energy balances, accounting for the dependence of reaction kinetics, gas-liquid mass transfer, thermophysical properties, and heat-transfer coefficients on the reactor state variables.

The local dynamic behaviour of the reactor was determined from the canonical eigenvalue problem, where the eigenvalues were calculated numerically using standard matrix decomposition routines. The stability of each operating point was classified according to the sign of the real part of the eigenvalues. A steady-state solution was considered asymptotically stable when the real part of each eigenvalue is negative, indicating that sufficiently small perturbations decay with time and the system returns to the equilibrium state. Conversely, the presence of at least one eigenvalue with positive real part, indicates an unstable operating point, where small perturbations are amplified and the reactor evolves away from the considered equilibrium condition. The same criterion was adopted during the continuation analysis to discriminate between stable and unstable solution branches.

In addition to the eigenvalue analysis, the reactor thermal behaviour was further characterized through the Strozzi–Zaldívar divergence criterion. This approach evaluates the local volumetric expansion or contraction of the dynamic trajectories in the state space and provides a complementary measure of process stability and runaway tendency. The divergence (*div*) was calculated as the trace of the Jacobian matrix, being equal to the summation over the main diagonal of the Jacobian matrix itself. In the implemented numerical framework, the divergence was evaluated both at the steady-state operating points and along the transient reactor trajectories, to ensure that both the transient and steady regimes were not prone to runaway conditions. According to the Strozzi and Zaldívar criterion, negative values of *div* indicate local contraction of the state-space volume, corresponding to dissipative dynamics and stable process behaviour. Conversely, positive values indicate local expansion of neighbouring trajectories and therefore a tendency toward instability, loss of controllability, or thermal runaway. Consequently, the divergence criterion provides an additional indicator of reactor operability that complements the classical eigenvalue-based

stability analysis.

The combined use of eigenvalue analysis and the Strozzi–Zaldívar divergence criterion enabled a comprehensive characterization of the reactor dynamics, allowing stable and unstable operating regions to be identified together with the corresponding safety margins. These results constitute the basis for the continuation and bifurcation analyses conducted in this work using a pseudo-arc-length continuation method. The pseudo-arc-length formulation allows continuation through turning points by introducing an additional arc-length constraint. Consequently, both stable and unstable solution branches can be followed continuously, enabling complete reconstruction of the reactor bifurcation structure.

For the present study, the coolant inlet temperature $T_{c,in}$, was selected as the continuation parameter because fluctuations in cooling conditions represent one of the most relevant operational disturbances affecting reactor thermal behaviour and process safety. Considering that the steady-state governing equations can be written in compact form as $\underline{f}(\underline{x}, \underline{u}) = 0$, the pseudo-arc-length method consists of a predictor–corrector procedure. Starting from a converged steady-state solution, a tangent vector to the solution branch is first computed from the augmented system reported into Eq. 7. Here s denotes the arc-length coordinate and $\underline{t}^T$ is the tangent vector from the previous continuation step. The tangent vector is subsequently used to predict a new solution point according to Eq. 8, where $\underline{y} = [\underline{x}, T_{c,in}]^T$ and Δs is the continuation step size. The predicted point is then corrected through the solution of an augmented nonlinear system composed of the steady-state equations and the arc-length constraint defined as reported into Eq. 9, which enforces orthogonality between the correction step and the continuation tangent. The resulting nonlinear system was solved using a constrained least-squares algorithm with adaptive step-size adjustment to improve robustness near strongly nonlinear regions and bifurcation points.

$$\begin{bmatrix} \underline{J} & \frac{\partial \underline{f}}{\partial T_{c,in}} \\ \underline{t}^T & 0 \end{bmatrix} \begin{bmatrix} \frac{d\underline{x}}{ds} \\ \frac{dT_{c,in}}{ds} \end{bmatrix} = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \quad (7)$$

$$\underline{y}_{pred} = \underline{y}_l + \Delta s \underline{t}_l \quad (8)$$

$$(\underline{y} - \underline{y}_{pred})^T \bullet \underline{t}_l = 0 \quad (9)$$

To evaluate the sensitivity of reactor performance to cooling disturbances, continuation calculations were performed in both forward and backward directions with respect to the coolant inlet temperature. Forward continuation corresponds to progressively increasing $T_{c,in}$, while backward continuation corresponds to decreasing $T_{c,in}$. The comparison of the two continuation paths enables identification of hysteresis phenomena and multiplicity regions, which are characteristic features of nonlinear reactor systems.

The continuation analysis was used to detect the presence of multiple steady states, fold bifurcations, and turning points. Fold points were identified through changes in the direction of the continuation branch and by monitoring the singularity conditions of the augmented Jacobian matrix. These points correspond to limits of operability where stable and unstable solution branches merge and disappear. The dynamic stability of each continuation point was evaluated using the eigenvalue-based procedure. For every converged solution along the continuation branch, the Jacobian matrix was computed and its eigenvalue spectrum determined. Operating points for which all eigenvalues possessed negative real parts were classified as stable, whereas points exhibiting at least one eigenvalue with positive real part were classified as unstable. This procedure enabled continuous stability tracking along the entire bifurcation diagram and allowed stable and unstable branches to be distinguished directly.

3. Results and discussions

3.1. Catalyst characterization

Inductively coupled plasma (ICP) analysis was performed to quantify the loading of the active phase. A ruthenium content of 0.25 wt% was measured, in agreement with the nominal composition.

The textural properties of the reduced and passivated catalyst were quantified via nitrogen adsorption isotherms at 77 K. The surface area evaluated through BET model amounted to $102 \text{ m}^2 \text{ g}^{-1}$ with a total pore volume of $0.355 \text{ cm}^3 \text{ g}^{-1}$ with a very low fraction of micropores ($0.004 \text{ cm}^3 \text{ g}^{-1}$).

The crystalline structure and phase composition of the material were investigated by X-ray diffraction (XRD), and the corresponding diffractogram is reported in Fig. 3. The detected reflections were attributed to metallic Co or Ni with a main contribution given by graphitic carbon. The presence of cobalt or nickel can be associated with previous synthesis steps and treatments applied during the preparation of the carbon nanofibers. A relatively high carbon content compared with the other elements was confirmed. Interestingly, no Ru crystallites were detected, indicating the presence of amorphous nanoparticles with a dimension lower than 2 nm.

Scanning electron microscopy (SEM) was employed to examine the surface morphology and microstructure at different magnifications (Fig. S1 – Supplementary Material). Multiple zones of the sample were analysed to ensure representative characterization. The carbon nanofiber morphology was preserved, and no significant structural alterations were observed. The fibrous structure remained intact across the analysed sections. Elemental mapping was also conducted to assess the spatial distribution of the elements within the material. The resulting maps (Fig. S2 – Supplementary Material) confirmed the presence of carbon as the predominant component of the material. Aluminium, cobalt, oxygen, and nickel were also detected, which can be related to precursor species and prior processing stages. Ruthenium, introduced during catalyst preparation, was successfully identified and appeared to be homogeneously distributed throughout the sample (Fig. S2f). A heterogeneous region with a noticeably brighter contrast was observed in Fig. S2a. Elemental mapping (Figs. S2b, S2c, and S2e) revealed that these microdomains corresponded to Ni and Co oxides, suggesting the incomplete removal of the catalyst precursor employed during CNF growth. This finding is in agreement with the XRD results, which likewise indicated the persistence of residual metal species.

STEM-HAADF analysis of the Ru/CNF catalyst (Fig. 4) demonstrated a high dispersion of Ru nanoparticles throughout the CNF support. The elemental maps (Fig. 4e) corroborated the successful nitric acid

functionalization, evidenced by the widespread distribution of oxygen across the nanofibers. Additionally, EDX analysis confirmed ruthenium as the main metallic component. The particle size distribution (Fig. 4f) was predominantly concentrated around 1.2 nm, highlighting the presence of uniformly distributed ultrasmall Ru nanoparticles.

3.2. Laboratory scale runs

Hydrogenation experiments were conducted over the Ru/CNF catalyst at different temperatures and hydrogen pressures. The corresponding results are summarized in Fig. 5.

A blank test using CNF at 40 bar and 150°C showed negligible catalytic activity toward toluene hydrogenation, with a conversion of only 6.5%. This result indicates that no significant catalytic contribution arises from residual Co and Ni species detected by XRD and SEM-EDX.

The effect of reaction temperature (Fig. 5a) showed a monotonic increase in conversion with increasing temperature. The highest conversion, equal to 75%, was obtained at 180°C , corresponding to a molar toluene consumption rate of $483 \text{ mmol}_{\text{tol}} \text{ min}^{-1} \text{ g}_{\text{Ru}}^{-1}$. This behaviour is consistent with the intrinsic temperature dependence of the reaction rate.

Similarly, an increase in hydrogen pressure resulted in enhanced catalytic performance (Fig. 5b), with higher pressures leading to higher conversion levels under otherwise identical conditions. Since hydrogen is the only reactant present in the gas phase, the total pressure is equal to the hydrogen partial pressure. Therefore, any variation in the total pressure directly reflects a proportional change in hydrogen partial pressure within the reactor. The observed pressure effect can be rationalized considering hydrogen solubility in the liquid phase. Hydrogen solubility in both cyclic and aromatic compounds increases with pressure and, in general, also with temperature, resulting in a higher presence of the reactant in the mixture [61].

Considering that the same catalyst was used throughout the entire experimental campaign, a final 240 min test was performed under the conditions employed at the beginning of the study (30 bar and 150°C) to evaluate the effect of prolonged operation on catalyst performance. As shown in Fig. S3, no evidence of catalyst deactivation was observed. Furthermore, post-reaction characterization revealed no significant changes in catalyst morphology (Fig. S4), while the elemental composition determined by SEM-EDX remained essentially unchanged (Table S1). Similarly, the XRD pattern of the spent catalyst (Fig. S5) showed no detectable Ru reflections, indicating the absence of Ru particle growth and suggesting that catalyst sintering did not occur under the investigated reaction conditions.

The results presented in this section demonstrate that CNFs constitute a promising alternative to the commonly used supports such as Al_2O_3 . Despite the low Ru content (0.25 wt%), the catalyst exhibited significant activity in toluene hydrogenation. Its performance compares favourably with values reported in the literature, although direct comparisons should be made with caution because of differences in operating conditions, catalyst formulations, and reactor configurations [12].

3.3. Kinetic analysis

The resulting kinetic parameters are reported in Table 1. All estimated coefficients exhibited physically meaningful values and signs. In particular, the activation energy was found to be consistent with the expected behaviour of aromatic hydrogenation reactions over noble-metal catalysts, while the adsorption parameters confirmed the competitive adsorption mechanism between toluene and hydrogen assumed by the adopted LHHW formulation. The pressure-correction term introduced in the kinetic constant further improved the ability of the model to reproduce the experimental observations over the wide pressure range investigated experimentally.

The quality of the regression was evaluated by comparing experimental and simulated conversion values. The results are reported in

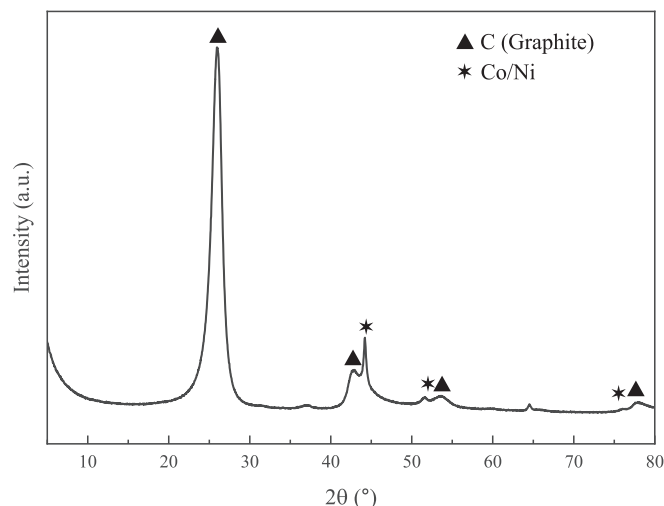


Fig. 3. XRD analysis of the reduced and passivated Ru/CNF catalyst.

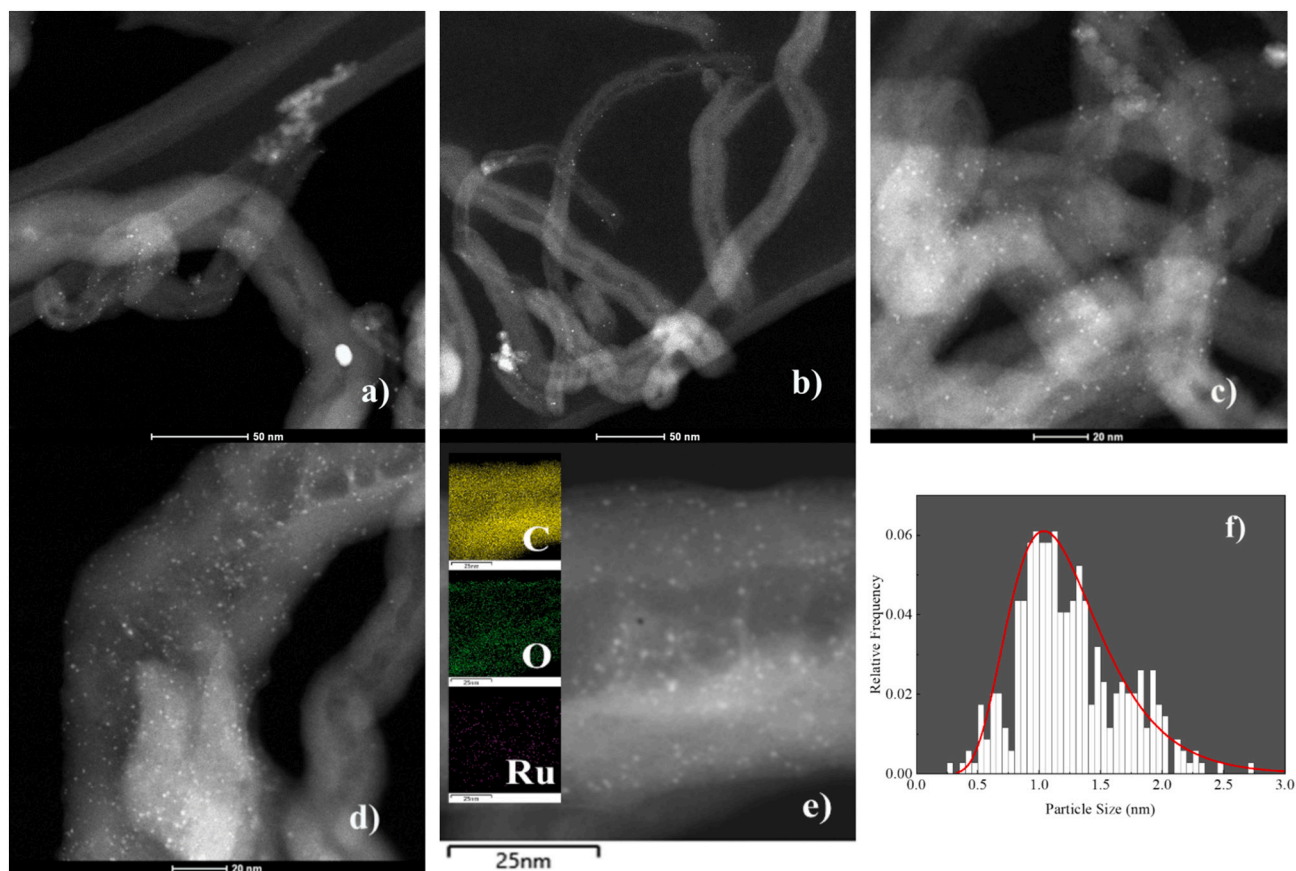


Fig. 4. HAADF images of the Ru/CNF catalyst (a, b, c, d) and EDX elemental analysis (f).

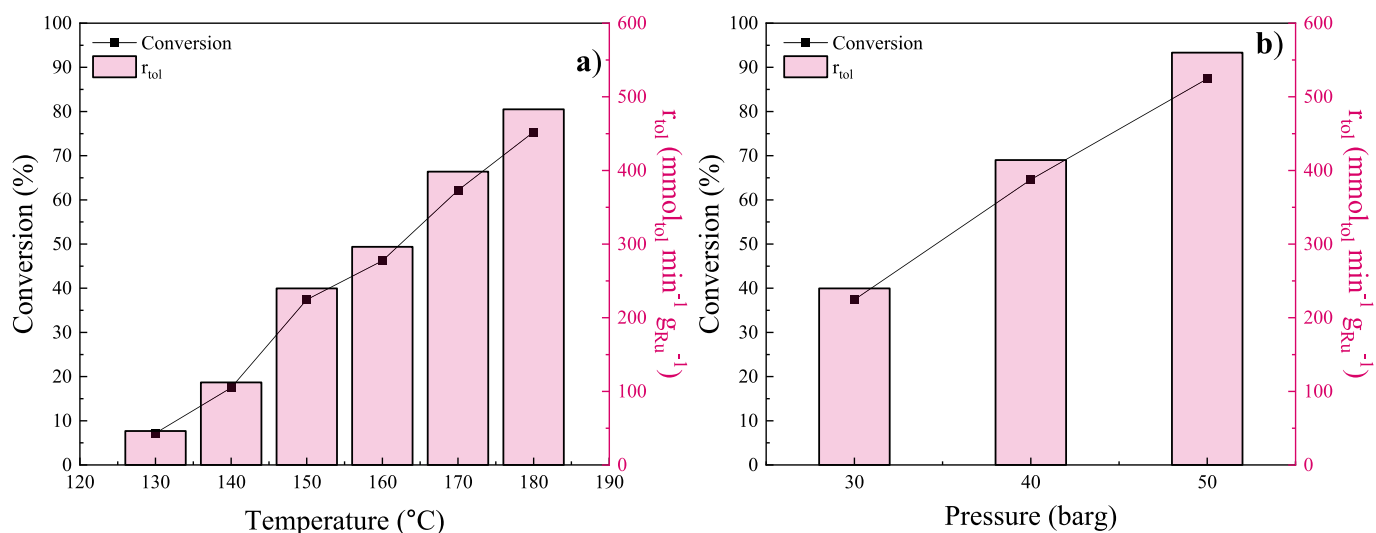


Fig. 5. Catalytic performance in toluene hydrogenation over Ru/CNF (WHSV = 8.9 h^{-1}): (a) effect of temperature at 30 bar H_2 ; (b) effect of H_2 pressure at 150 °C.

Fig. 6 through a parity plot, where the simulated conversions are plotted as a function of the corresponding experimental measurements. The diagonal line represents the ideal agreement between model predictions and experimental observations, whereas the shaded region corresponds to the 95% prediction band estimated from the residual distribution.

Overall, the reactor model reproduced the experimental data with satisfactory accuracy over the entire conversion range. All the experimental points were located within the 95% prediction band and closely distributed around the parity line, indicating the absence of significant

systematic deviations. Furthermore, no evident bias was observed at either low or high conversion levels, confirming the effectiveness of the combined residual formulation adopted during the parameter estimation procedure. This result demonstrates that the weighting strategy successfully balances the contributions of low-conversion and high-conversion experiments, preventing the optimization from being dominated by a limited subset of operating conditions.

The residual analysis further confirmed the adequacy of the selected kinetic formulation. The absence of pronounced trends in the parity plot

Table 1

Estimated kinetic and adsorption parameters of the Langmuir–Hinshelwood–Hougen–Watson (LHHW) model obtained through the multi-start parameter estimation procedure.

Kinetic coefficient set		
$k_{k_{\infty}}$	$1.99 \cdot 10^9$	$m^6 mol^{-1} s^{-1} kg_{cat}^{-1} K^{-m} bar^{-n}$
E_a	$1.65 \cdot 10^5$	$J mol^{-1}$
m	0.757	—
n	2.00	—
$K_{tol_{\infty}}$	$2.79 \cdot 10^8$	$m^3 mol^{-1}$
$\Delta \bar{H}_{tol}$	$1.00 \cdot 10^5$	$J mol^{-1}$
$K_{H_2_{\infty}}$	$2.47 \cdot 10^{-9}$	$m^3 mol^{-1}$
$\Delta \bar{H}_{H_2}$	$5.39 \cdot 10^4$	$J mol^{-1}$

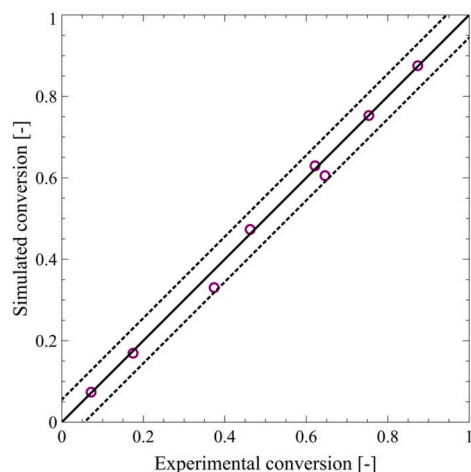


Fig. 6. Comparison between experimental and simulated toluene conversions for the optimized kinetic model. The parity line indicates perfect agreement, whereas the shaded area represents the 95% prediction band.

suggests that the adopted LHHW mechanism captures the dominant physicochemical phenomena governing the hydrogenation process, namely competitive adsorption of reactants on the catalyst surface coupled with a surface-reaction-controlled mechanism. Moreover, the explicit inclusion of gas-liquid mass transfer within the reactor model enabled a more accurate description of hydrogen availability in the liquid phase, improving the predictive capability of the kinetic model under varying pressure conditions. The resulting parameter set was subsequently employed for all reactor-scale simulations, dynamic analyses, stability assessments, and continuation studies discussed in the

following sections. The satisfactory agreement between experimental and simulated data provides confidence that the kinetic model can be reliably extrapolated to the industrial reactor conditions considered in this work.

3.4. Stability assessment and continuation study

Fig. 7 reports the dynamic response of the reactor during start-up. Specifically, on the left are reported the species concentrations temporal evolution, whereas on the right the reactor and cooling temperature, as well as the system divergence. The transient simulations indicate that the system evolves smoothly toward a unique steady-state operating condition characterized by a toluene conversion of approximately 53.2%. No oscillatory behaviour or abrupt thermal excursions were observed during the simulated operating period, suggesting that the selected reactor configuration provides adequate thermal management under the investigated conditions. Furthermore, the batch-to-continuous start-up strategy was found to significantly reduce the time required to approach the final operating condition. During the initial batch phase, the absence of inlet and outlet streams allows the reactor composition and temperature to evolve more rapidly toward the equilibrium state corresponding to the imposed operating conditions, since the system is not continuously perturbed by feed dilution or product withdrawal. Once the reactor approaches the desired operating state, the transition to continuous operation simply requires the activation of the inlet and outlet streams while maintaining the established thermal and compositional conditions. As a result, the transient duration was reduced by approximately 70% compared with a direct continuous start-up procedure, highlighting the potential advantages of this operational strategy for industrial implementation. It should be emphasized that the batch-to-continuous strategy proposed in this work refers to the industrial stirred-tank reactor considered in the numerical analysis, rather than to the laboratory-scale trickle-bed reactor employed for kinetic parameter estimation. During the batch phase, the absence of liquid inlet and outlet streams does not imply the interruption of agitation, hydrogen supply, or coolant circulation. These functions must remain active to ensure catalyst suspension, adequate gas-liquid mass transfer, and effective heat removal. Although the present simulations did not predict significant thermal excursions, the practical implementation of this strategy at industrial scale may introduce concentration and temperature gradients that are not captured by the perfect-mixing assumption. Potential risks include local hot-spot formation, insufficient catalyst suspension, temporary hydrogen-transfer limitations, and pressure or temperature excursions during the transition to continuous operation. Therefore, practical implementation would require controlled hydrogen dosing, continuous agitation and cooling, gradual

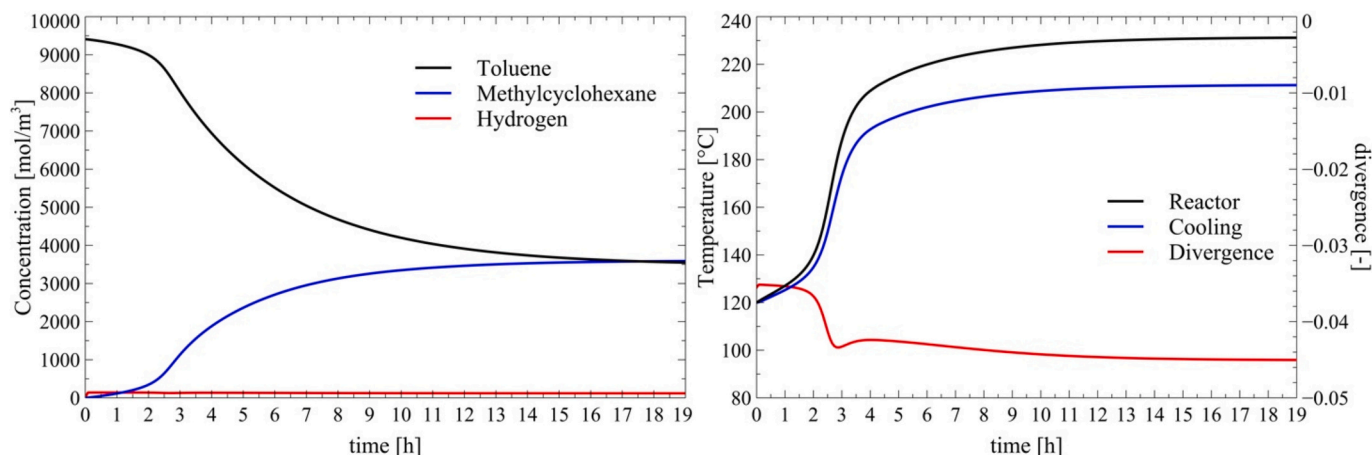


Fig. 7. Temporal evolution of the species concentration (left) and reactor temperature, cooling temperature and divergence (right).

activation of the inlet and outlet streams, and appropriate temperature and pressure monitoring and interlocks. Pilot-scale validation and a dedicated safety assessment would also be necessary before industrial application.

The dynamic stability of the system was subsequently evaluated through eigenvalue analysis and the Strozzi–Zaldívar divergence criterion. Throughout the transient simulations, the divergence remained negative, indicating a dissipative dynamic behaviour and the absence of runaway tendencies or parametric sensitive regions in which small perturbation in inputs can result in dramatic output variations [62,63]. Similar results were obtained for the batch start-up scenario, where negative divergence values were maintained over the entire simulation horizon. These observations suggest that the heat-removal capability provided by the cooling system is sufficient to compensate for the heat released by the hydrogenation reaction under the investigated operating conditions.

The eigenvalue analysis confirmed that the reactor operates within a dynamically stable region, with all perturbations decaying toward the equilibrium condition. Consequently, both the transient and steady-state analyses indicate that the selected reactor configuration can be operated safely without approaching unstable operating regimes. The simultaneous verification of negative divergence and stable eigenvalue spectra provides a consistent indication that thermal runaway conditions are not expected for the reference operating point. To investigate the existence of multiplicity regions and evaluate the sensitivity of the reactor to cooling disturbances, a pseudo-arc-length continuation analysis was subsequently performed using the coolant inlet temperature as a continuation parameter. This variable was selected because fluctuations in cooling conditions represent one of the most realistic operational disturbances capable of affecting reactor thermal stability. The resulting continuation diagram is reported in Fig. 8.

The continuation results reveal a smooth dependence of reactor performance on the coolant inlet temperature, with no evidence of fold bifurcations, ignition–extinction behaviour, or steady-state multiplicity within the investigated operating range. The forward and backward continuation branches overlap closely, indicating the absence of hysteresis phenomena and confirming the existence of a unique steady-state solution for each coolant temperature. These findings are particularly relevant from a process-safety perspective, as they suggest that moderate fluctuations in cooling conditions do not induce abrupt transitions between alternative operating states.

The continuation analysis further indicates that the reactor operates predominantly within a mass-transfer-controlled regime. As the coolant inlet temperature decreases, the reactor temperature also decreases, promoting hydrogen dissolution into the liquid phase and increasing hydrogen availability at the catalyst surface. Under these conditions, the

process remains controlled by hydrogen transport phenomena rather than by thermal feedback effects, which contributes to the observed stability of the reactor. The absence of turning points and unstable branches appears to be a consequence of both the moderate reactor conversion level and the effective gas-liquid mass-transfer characteristics provided by the selected reactor design. Further elements supporting these conclusions can be found in the Supplementary Materials (Section S5).

It is worth noting that a different behaviour would be expected if the reactor operated predominantly in a kinetic-controlled regime. In such a case, the conversion would be strongly governed by the reaction rate, which is directly proportional to the kinetic constant. Since the kinetic constant follows an Arrhenius-type dependence on temperature, even relatively small variations in reactor temperature would produce exponential variations in reaction rate and, consequently, in conversion. Therefore, decreasing the coolant inlet temperature would lower the reactor temperature, resulting in an exponential reduction of the reaction rate and a correspondingly nonlinear conversion profile. The approximately linear behaviour observed in the continuation diagrams suggests that hydrogen availability, rather than intrinsic reaction kinetics, represents the dominant limiting factor under the investigated operating conditions. This result is also consistent with the increased hydrogen solubility observed at lower temperatures, which compensates for the reduction in intrinsic reaction kinetics and contributes to the overall stability of the reactor.

The resulting stability assessment confirmed that all operating points belonging to the continuation branch remained dynamically stable. In parallel, the divergence criterion remained negative throughout the investigated parameter range, further supporting the absence of runaway conditions under the analysed operative conditions. The combined analysis therefore demonstrates that the proposed reactor configuration possesses a relatively large safety margin with respect to coolant-temperature fluctuations and can be operated safely over the investigated range of operating conditions.

Overall, the results highlight the effectiveness of combining continuation methods, eigenvalue analysis, and divergence-based runaway assessment to characterize both the performance and safety of hydrogenation reactors for liquid organic hydrogen carrier applications. The proposed methodology enables not only the identification of stable operating regions but also the systematic evaluation of process resilience against operational disturbances, thereby providing a valuable tool for reactor design and scale-up.

4. Conclusions

This work combined experimental catalyst evaluation, kinetic modelling, and reactor-scale analysis to assess toluene hydrogenation as a representative LOHC process. The synthesized Ru/CNF catalyst, containing only 0.25 wt% Ru, exhibited significant catalytic activity. Toluene conversion increased with both temperature and hydrogen pressure, reaching 75% at 180 °C and 30 bar. The experimental results were satisfactorily described by an LHHW kinetic model accounting for competitive adsorption and gas-liquid mass transfer. When incorporated into a dynamic industrial-scale reactor model, the validated kinetics predicted smooth convergence toward a unique steady state, without oscillations or significant thermal excursions. The proposed batch-to-continuous start-up strategy reduced the time required to approach the target operating condition by approximately 70% compared with direct continuous start-up. Nevertheless, its industrial implementation would require continuous agitation and cooling, controlled hydrogen supply, gradual switching to continuous operation, and appropriate monitoring and safety systems. Pilot-scale validation would also be required to assess possible temperature and concentration gradients not represented by the perfect-mixing model. Eigenvalue analysis, the Strozzi–Zaldívar divergence criterion, and pseudo-arc-length continuation consistently indicated stable reactor operation

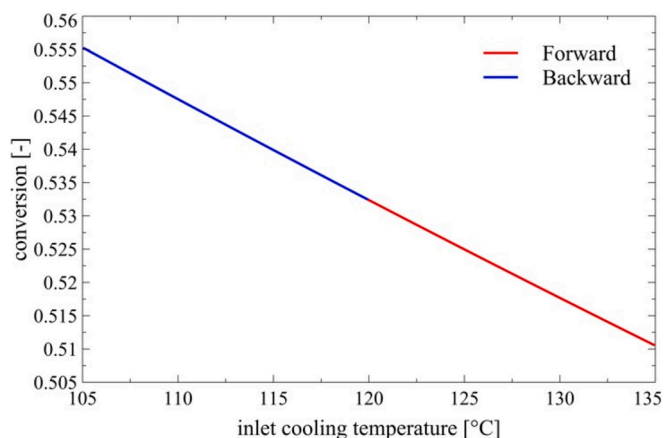


Fig. 8. Bifurcation diagram of conversion as a function of inlet cooling temperature, considering backward and forward continuation schemes.

throughout the investigated range. No fold bifurcations, hysteresis, steady-state multiplicity, or thermal-runaway tendencies were identified. The results also suggested that reactor performance was predominantly governed by hydrogen mass transfer, which limited the influence of thermal feedback and contributed to the observed operational stability. Overall, the study demonstrates the potential of Ru/CNF catalysts for LOHC hydrogenation and provides an experimentally grounded framework for evaluating reactor start-up, operability, and safety during process scale-up.

CRedit authorship contribution statement

Giuseppe Andriani: Writing – original draft, Software, Formal analysis, Data curation. **Paolo Mocellin:** Writing – review & editing, Supervision. **Christian Di Stasi:** Writing – review & editing, Methodology, Formal analysis, Data curation. **Chiara Vianello:** Writing – review & editing, Supervision, Project administration. **José Luis Pinilla:** Writing – review & editing, Project administration, Funding acquisition. **Isabel Suelves:** Writing – review & editing, Project administration, Funding acquisition. **Ernesto Salzano:** Writing – review & editing, Project administration, Funding acquisition. **Gianmaria Pio:** Writing – review & editing, Supervision, Software, Methodology.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2026.181680>.

Data availability

Data will be made available on request.

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