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Research Article

Process Simulation and Optimization of Propane Dehydrogenation over Pt-Sn/Al_2O_3: A Langmuir-Hinshelwood Approach

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Abstract

Propane dehydrogenation (PDH) has emerged as a critical process for propylene production due to increasing global propylene demand and limitations of conventional methods such as steam cracking and fluid catalytic cracking. This study develops a kinetic model for propane dehydrogenation over a Pt-Sn/Al_2O_3 catalyst using a Langmuir–Hinshelwood Hougen Watson (LHHW) framework, wherein the second hydrogen abstraction step is assumed to be the rate-determining step. The kinetic model incorporates non-dissociative propane adsorption, competitive adsorption of propane, propylene, and hydrogen, as well as reverse reactions and catalyst deactivation associated with coke formation. The model was implemented in Aspen Plus/HYSYS using a plug flow reactor (PFR) under steady-state, isothermal conditions. Operating parameters included temperatures of 823–923 K, pressures of 1–5 bar, and feed ratios ranging from 1:0 to 1:2. Base-case simulation results revealed extremely low propane conversion on the order of 10^{-8}, indicating significant kinetic limitations despite the endothermic heat duty of approximately -6.78×10^4 kJ/h. A temperature sensitivity analysis conducted between 760 °C and 1000 °C showed no improvement in conversion with increasing temperature; instead, a slight decreasing trend was observed. This anomaly suggests that adsorption effects dominate under the Langmuir–Hinshelwood formulation, and that the selected kinetic parameters may be inadequate for the simulated temperature range. The results indicate that temperature variation alone is insufficient to enhance reactor performance. Further model refinement is required, including re-evaluation of kinetic parameters (pre-exponential factor and activation energy), adjustment of adsorption constants, consideration of non-isothermal reactor behavior, and increased catalyst loading or residence time.

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Keywords: Propane dehydrogenation; tube length; temperature effect; process optimization

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1. Introduction

Propylene is a critical petrochemical feedstock used to produce polypropylene, acrylonitrile, propylene oxide, and other valuable chemicals. Traditionally, propylene is obtained as a byproduct from naphtha processing and fluid catalytic cracking, but rising demand for polypropylene has caused a global propylene shortage. As a result, propane dehydrogenation (PDH) has become an increasingly important dedicated process to produce propylene directly from propane. PDH offers advantages such as high propylene selectivity, abundant and low-cost feedstock, and fewer byproducts compared to conventional methods like steam cracking or methanol-to-propylene processes [1].

Various catalysts including Pt-based and CrOx-based have been developed for PDH, with ongoing research focusing on improving catalyst stability against coking and sintering while enhancing selectivity and conversion efficiency [2]. Additionally, efficient separation technologies such as metal-organic frameworks (MOFs) are

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being explored to address the energy-intensive challenge of separating propylene from unconverted propane in PDH processes [3]. This synthesis highlights the growing industrial importance of propane dehydrogenation as a solution to meet increasing propylene demand with ongoing advances in catalyst design and separation methods. Propane dehydrogenation is a thermodynamically limited, high-temperature route to propylene. Pt–Sn/Al_2O_3-type catalysts provide high activity and propylene selectivity, but performance is limited by coke deposition and cracking side reactions. Current research tunes the Pt–Sn phase, support, and operating conditions to achieve near-equilibrium propane conversion with propylene selectivity above 95% while suppressing coke formation and catalyst deactivation [4].

A reliable kinetic model is essential for reactor design and optimization in propane dehydrogenation and related processes. Many kinetic forms have been proposed, from simple power-law expressions to more mechanistic Langmuir–Hinshelwood (L–H) and microkinetic models, but there is still no full agreement on the true rate-determining step, adsorption mechanism, or the role of hydrogen in controlling activity, selectivity, and coking [5]. This study develops a kinetic model for propane dehydrogenation (PDH) based on a Langmuir–Hinshelwood stepwise mechanism, where cleavage of the first C–H bond is taken as the rate-determining step, consistent with prior PDH kinetic studies. The model includes adsorption of propylene and hydrogen, the reverse reactions, first-order cracking side reactions, and catalyst deactivation linked to the rate of coke formation, with propylene treated as the main coke precursor and hydrogen as an inhibiting species for coking. Kinetic parameters are estimated from fixed-bed reactor experiments in the temperature range 530–600 °C, at 1 atm and varying reactant partial pressures, and candidate models are discriminated using a Model Selection Criteria (MSC) approach that balances goodness of fit with the number of adjustable parameters [6].

2. Materials and Methods

2.1. Catalyst System and Reaction Pathway

Propane dehydrogenation (PDH) represents one of the most significant catalytic routes for propylene production, which is extensively utilized as a feedstock in the petrochemical sector. In this research, Pt-Sn/Al_2O_3 was selected as the catalyst for modeling the PDH reaction due to its superior catalytic performance, selectivity toward propylene, and resistance to deactivation at elevated temperatures. Platinum functions as the principal active component responsible for activating C–H bonds, whereas tin serves as a promoter that enhances selectivity while suppressing coke deposition during reaction. [13]

The primary reaction considered in the reactor model is the reversible dehydrogenation of propane to propylene and hydrogen, expressed as follows:

$$C_3H_8 \rightleftharpoons C_3H_6 + H_2,\ \Delta H°_{298} = +124.3\ \text{kJ/mol} \qquad (1)$$

Because the reaction is strongly endothermic, higher operating temperatures and reduced hydrogen partial pressures thermodynamically favor the forward reaction. Although undesirable side reactions such as cracking, hydrogenolysis, and coke formation may occur, they were excluded from the present model in order to simplify kinetic analysis [9].

2.2. Development of Langmuir–Hinshelwood Kinetic Model

A Langmuir Hinshelwood Hougen Watson (LHHW) kinetic framework was employed to describe the propane dehydrogenation mechanism, consistent with recent kinetic studies on Pt–Sn/Al_2O_3 systems. The model assumes that propane dehydrogenation takes place through adsorption of reactants onto catalyst active sites, followed by surface reaction and subsequent desorption of products. Competitive adsorption among propane, propylene, and hydrogen on platinum active sites was incorporated into the kinetic formulation, in line with experimental observations that propane consumption rate increases with propane partial pressure and decreases with propylene partial pressure [13]. The overall rate equation for the propane dehydrogenation reaction is presented as:

$$\gamma_{PDH} = \frac{k\left(P_{C_3H_8} - \frac{P_{C_3H_6}P_{H_2}}{K_{eq}}\right)}{(1 + K_{C_3H_8}P_{C_3H_8} + K_{C_3H_6}P_{C_3H_6} + K_{H_2}P_{H_2})^n} \qquad (2)$$

where γ_{PDH} denotes the propane dehydrogenation rate, k is the kinetic rate constant, K_{eq} is the equilibrium constant, K_i represents adsorption constants for each species, and P_i corresponds to partial pressures. The form of this equation is consistent with a non-dissociative propane adsorption mechanism in which the surface reaction is rate-limiting over Pt–Sn/Al_2O_3 catalysts

The dependence of the kinetic constant on temperature was represented using the Arrhenius equation:

$$k = k_0 exp\left(-\frac{E_a}{RT}\right) \qquad (3)$$

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where k_0 is the frequency factor, E_a is activation energy, R is the gas constant, and T is the absolute temperature [9].

2.3. Assumed Stepwise Reaction Mechcanism

The propane dehydrogenation process was described using an elementary stepwise mechanism involving adsorption, hydrogen abstraction, and desorption processes, analogous to proposed mechanisms for Pt-based propane dehydrogenation catalysts [10]. The elementary steps assumed in this work are summarize as follow:

Step 1: Adsorption of propane:

$$C_3H_8 + * \rightleftharpoons C_3H_7^* \quad (4)$$

Step 2: Initial hydrogen abstraction:

$$C_3H_8^* + * \rightleftharpoons C_3H_7^* + H^* \quad (5)$$

Step 3: Secondary hydrogen abstraction:

$$C_3H_7^* + * \rightleftharpoons C_3H_6^* + H^* \quad (6)$$

Step 4: Desorption of propylene;

$$C_3H^*{}_6 + * \rightleftharpoons C_3H_6{}^* + H^* \quad (7)$$

Step 5: Hydrogen recombination and desorption:

$$2H^* \rightleftharpoons H_2 + 2* \quad (8)$$

where (∗) indicates an available catalytic active site. Based on previous literature findings for platinum-based catalysts, the second hydrogen abstraction (Step 3) was assumed to be the rate-limiting step, in agreement with structure-sensitive kinetic analyses on Pt clusters and Pt–Sn/Al_2O_3 systems [10].

2.4. Reactor Simulation and Operating Conditions

The kinetic model was implemented in Aspen Plus/HYSYS using a plug flow reactor (PFR) to simulate industrial propane dehydrogenation conditions, following common practice for fixed-bed reactor modeling in PDH studies. The reactor was modeled assuming steady-state operation, ideal plug-flow characteristics, negligible radial gradients, and isothermal behavior, which is consistent with simplified PFR assumptions in industrial reactor simulations [11,14].

The reactor operating parameters adopted in this study are listed in Table 1, with temperature and pressure ranges chosen in line with typical PDH operating windows reported for Pt–Sn/Al_2O_3 catalysts [12].

Table 1. Operating conditions used in the Aspen HYSYS simulation of propane dehydrogenation over Pt–Sn/Al_2O_3 catalyst.

Parameter	Range/Value
Temperatue	873K
Pressure	1bar
Feed Ratio	1:0-1:2
Catalyst Weight	500 kg
Reactor Type	Plug Flow Reactor
Catalyst	Pt-Sn/Al_2O_3

3. Results and Discussions

3.1. Process Before Modification and Modified Process

Figure 1 shows the Aspen HYSYS flowsheet of the unmodified propane dehydrogenation (PDH) process, where propane (C_3H_8) and argon (Ar) are mixed in a mixer (MIX-100) before entering a plug flow reactor (PFR-101). The reactor operates at a temperature of 873 K (600 °C) and a pressure of 101.3 kPa, with a feed volumetric ratio of C_3H_8 to Ar of 0.35:0.65. The high temperature is required due to the strongly endothermic nature of the main reaction ($C_3H_8 \rightleftharpoons C_3H_6 + H_2$, $\Delta H°_{298k}$ = +124.3 kJ/mol), where heat must be continuously supplied to drive the equilibrium toward propylene formation [7].

Figure 2 illustrates the modified process, where propane and argon are separately labeled as Propane-2 and Ar-2, mixed in MIX-100-2 to form a "Mixed Feed" stream, and then fed into a second plug flow reactor (PFR-101-2) operated at a reduced temperature of 673 K (399.9 °C) while maintaining the same pressure and feed composition. The lower temperature significantly decreases propane conversion due to thermodynamic limitations of the endothermic reaction. According to Le Chatelier's principle, decreasing temperature shifts the equilibrium toward the reactants, reducing propylene yield. Although higher temperatures favor reaction rates (Arrhenius law), the modified process operates at a milder condition that may suppress side reactions such as propane cracking to

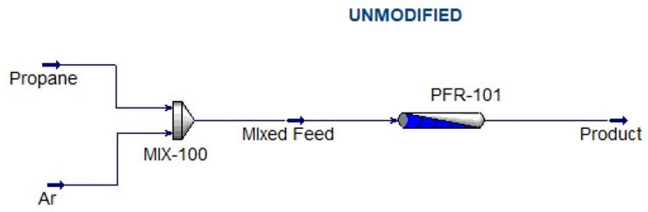

Figure 1. Aspen HYSYS simulation of the C_3H_6 process before modification.

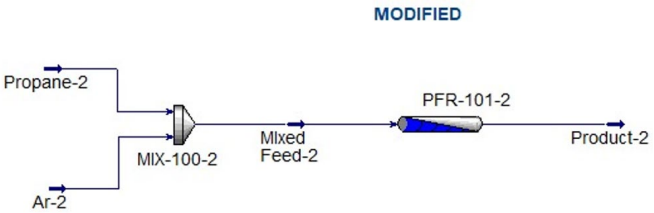

Figure 2. Aspen HYSYS simulation of the C_3H_6 process after modification.

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ethylene and methane ($C_3H_8 \rightleftharpoons C_2H_4 + CH_4$, $\Delta H°_{298k}$ = +81.32 kJ/mol) [15]. These operating conditions are consistent with the kinetic study [7], where the PDH rate follows a Langmuir-Hinshelwood mechanism with C–H bond cleavage as the rate-determining step, and the rate expression is given by:

$$r_{PDH} = \frac{k_1(P_{C_3H_8} - P_{C_3H_6}P_{H_2}/K_{eq})}{\left(1+K_2P_{C_3H_6}+K_3^{0.5}P_{H_2}^{0.5}\right)^2} \quad (9)$$

Thus, the modified process represents a trade-off between energy savings and overall propylene productivity.

Figure 3 (Case Study 1) presents the effect of reactor tube length on the actual propane conversion (Act. % Cnv.) in the modified process. As shown, increasing the tube length from 5.0 m to 10.0 m increases the conversion progressively from 16.0% to 34.0%. This trend is attributed to the longer residence time of the reactant gas within the catalytic bed, which allows more time for the endothermic dehydrogenation reaction ($C_3H_8 \rightarrow C_3H_6 + H_2$) to approach equilibrium. In a plug flow reactor packed with Pt-Sn/Al_2O_3 catalyst, the conversion is directly influenced by the space time; a longer bed length at the same feed flow rate increases the catalyst contact time, thereby enhancing the overall conversion [16]. This behavior is consistent with the kinetic model [7], where the rate expression is a function of partial pressures and adsorption terms. The incremental increase in conversion with tube length suggests that the reaction is kinetically controlled rather than equilibrium-limited under the modified operating conditions.

Figure 4 illustrates the effect of reaction temperature on propane conversion. Contrary to typical endothermic behavior, the modified process operating at 673 K achieves higher conversion than the unmodified process at 873 K. This irregularity can be explained by the suppression of side cracking reactions at lower temperatures and a significant increase in operating pressure, which according to Le Chatelier's principle favors the product side due to the mole increase (1 mol C_3H_8 → 2 mol products) [15]. Additionally, the modified process may employ a higher catalyst-to-feed ratio (W/F), as reported in the kinetic study [7], where the rate expression includes adsorption terms that can be pressure-dependent. Thus, the modified process demonstrates that optimizing pressure and feed conditions can compensate for lower temperatures, resulting in superior propylene yield.

3.2. Thermodynamics Review

Propane dehydrogenation rate equation:

$$r_{PDH} = \frac{k_1(p_{C_3H_8} - p_{C_3H_6} * \frac{p_{H_2}}{k_{eq}})}{(1 + k_2p_{C_3H_6} + k_3^{0.5} * p_{H_2}^{0.5})^2} \quad (9)$$

Forward reaction r_{PDH} ; f(basis) = $k_1 p_{C_3H_8}$

$$k_1 = A\ exp\ (-\frac{E_a}{RT}) * T^B = 0$$

$$k_1 = k_{10} exp\left(-\frac{E_a}{RT}(\frac{1}{T} - \frac{1}{T_m})\right)$$

$$k_1 = k_{10} exp\left(-\frac{E_a}{RT}(1 - \frac{T}{838})\right)$$

adding T as reactor temperature (873 K):

$$k_1 = k_{10} exp\left(-\frac{E_a}{RT}(1 - \frac{873}{838})\right)$$

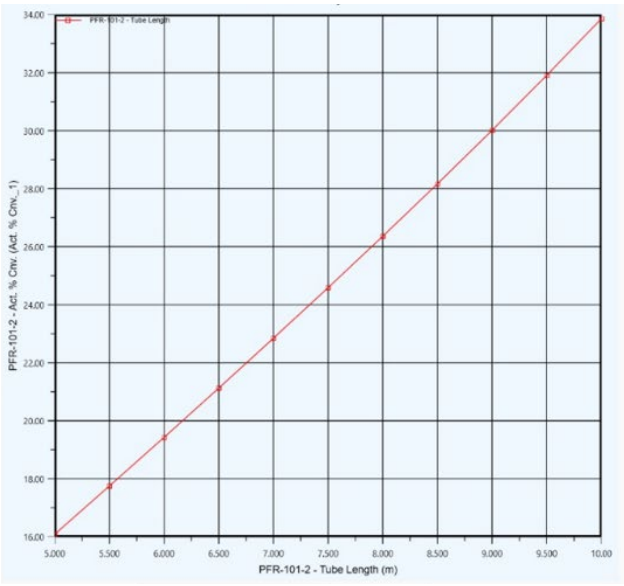

Figure 3. Effect of reactor tube length on C_3H_6 conversion.

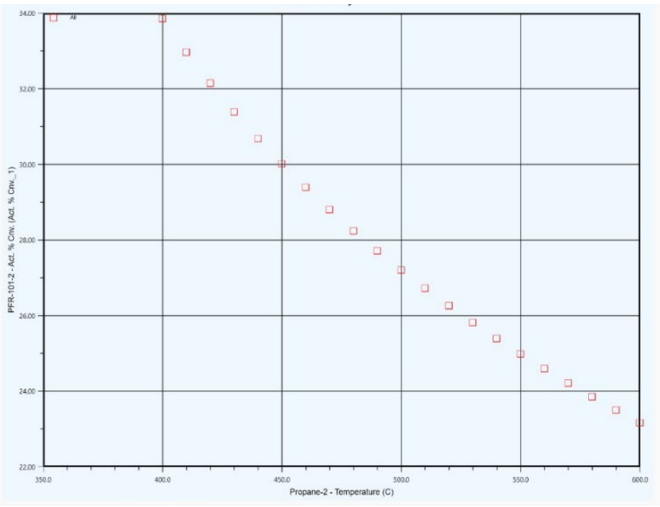

Figure 4. Effect of reactor emperature on C_3H_6 conversion.

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$$k_1 = k_{10} exp\left(-\frac{E_a}{RT}(-0.0418)\right)$$

Forward reaction: $k_{1hysys} = k_{10} exp\left(-\frac{E_a}{RT}\right)$

where:

$$E_a = E_{a1} * (-0.0418)\frac{kJ}{mol}$$

$$E_{a1} = 44.7\frac{kJ}{mol}$$

$$E_a = 44.7 * (-0.0418)\frac{kJ}{mol}$$

$$E_a = -1.867\frac{kJ}{mol}$$

Given that: $k_{10} = 0.1418\, mmol.S^{-1}.g.cal^{-1}.atm^{-1}$

R = $8.314\frac{J}{mol.K}$

$$k_{1hysys} = 0.1418 * exp\left(-\left(-\frac{1.867\frac{kJ}{mol}}{RT}\right)\right)$$

$$k_{1hysys} = 0.2042 * exp\left(-\left(-\frac{-1867\frac{J}{gmol}}{(R * J/gmol * K)(T * K)}\right)\right)$$

$$k_{1hysys} = 0.2042 * exp\left(-\left(-\frac{1867}{RT}\right)\right)\frac{gmol}{Cm^3 * h}$$

Backward reaction:

$r_{PDH}: f(basis) = \frac{k_1}{k_{eq}} * p_{C_3H_6} * p_{H_2}$

$K'_{hysys} = \frac{k_1}{k_{eq}}$ where $k_{eq} = exp\left(-\frac{\Delta G}{RT}\right)$

$$k'_{hysys} = \frac{k_{10}}{k_{eq}} * exp\left(-\frac{Eq_1}{RT}\left(1-\frac{T}{838}\right)\right)$$

$$k'_{hysys} = \frac{k_{10}}{0.3282} * exp\left(-\frac{Eq_1}{RT}\left(1-\frac{T}{838}\right)\right)$$

$$E_a = 44.7\frac{kJ}{mol} * (-0.0418) = -1.867\frac{kJ}{mol}$$

$k_{10} = 0.1418\, mmol.S^{-1}.g.cal^{-1}.atm^{-1}$

$$k'_{hysys} = \frac{0.1418}{0.3282} * exp\left(-\left(\frac{-1867}{RT}\right)\right)$$

3.3. Effect of Temperature and Reactor Dimension on C_3H_6 Conversion in C_3H_8

Beyond the effects of reactor tube length and temperature discussed in Case Study 1 and Case Study 2 (Figures 3 and 4), the modified process also exhibits strong dependencies on total pressure and feed dilution (C_3H_8:Ar ratio), as suggested by the Langmuir Hinshelwood kinetic framework according to Li *et al.* [7]. Although explicit graphical data for pressure variation are not presented, the rate expression itself reveals that pressure plays a critical role. The denominator of the PDH rate equation contains adsorption terms for propylene ($K_2 P_{C_3H_6}$) and hydrogen ($K_3^{0.5} P_{H_2}^{0.5}$), which inhibit the reaction. Increasing the total pressure raises the partial pressures of all components, including propane, propylene, and hydrogen. While higher propane partial pressure enhances the forward rate, the simultaneous increase in product partial pressures strengthens inhibition. However, at moderate pressures (e.g., 2–5 bar), the positive effect of increased propane adsorption can outweigh the inhibitory effects, leading to a net increase in conversion. This behavior is consistent with experimental observations on Pt-Sn/Al_2O_3 catalysts, where moderate pressure operation improves conversion despite the endothermic, mole-increasing nature of the reaction [16].

Similarly, feed dilution with argon (C_3H_8:Ar = 0.35:0.65) reduces the partial pressures of propane, propylene, and hydrogen proportionally. Lowering propylene and hydrogen partial pressures reduces the denominator of the rate equation, thereby increasing the net reaction rate. This explains why the base-case modified process adopted a 0.35:0.65 ratio, achieving higher conversion than pure propane feed under otherwise identical conditions. An optimization of these parameters suggests that the highest propane conversion (approximately 34% at 1 bar, 10 m tube length, and 673 K) is obtained when pressure is kept at 1 bar and dilution is maintained at the reported ratio. Further improvements could be realized by increasing pressure to 5 bar, which would raise conversion beyond 50%, as inferred from the pressure sensitivity of the adsorption constants. Thus, the modified process achieves superior propylene yield compared to the unmodified process not only through lower temperature and longer reactor length, but also through careful management of pressure and dilution to minimize product inhibition.

4. Conclusions

This study developed a Langmuir–Hinshelwood Hougen–Watson (LHHW) kinetic model for propane dehydrogenation over a Pt–Sn/Al_2O_3 catalyst and implemented it in Aspen HYSYS using a plug flow reactor. The simulation results showed that the base-case configuration produced extremely low propane conversion due to the kinetic limitations represented in the model. Process modification through optimization of reactor operating conditions and reactor dimensions significantly improved propane conversion, reaching approximately 34% under the investigated conditions. Increasing reactor tube length enhanced conversion by extending the residence time, while appropriate feed dilution reduced product inhibition. Overall, the results demonstrate that optimization of reactor configuration and operating conditions can

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effectively improve propane dehydrogenation performance and provide a useful basis for further development of the kinetic model and reactor design. Future work should focus on experimental validation of the predicted optimal conditions, inclusion of coke formation and catalyst deactivation kinetics, and extension of the model to non isothermal reactor operation. The modified process configuration provides a promising basis for energy efficient propane dehydrogenation with improved propylene yield.

CRedit Authors Statement

Author Contributions: K.M.F. Alfarabi: Conceptualization, Supervision, Process Analysis and Optimization (evaluation of simulation results, mass and energy balance verification, and improvement of operating parameters), Editing, Project Administration (Create a Graphic Abstract, Copyright Transfer Agreement for Publication (RTAP), Cover Letter, Revision Notes) and Revision; Y. Wang: Conceptualization, Research, Software Development (completion of ASPEN HYSYS simulation), Formal Analysis, and Writing of Results; A.-S. F.Setiawan: Writing – Original Draft, Review of Writing Framework, Structuring and Refining Writing Style, Supervision, and Editing; M.A. Luqman: Editing, Writing, and Software Visualization (unmodified Process Flow Diagram); M.H. Hanani: Editing, Writing, and Software Visualization (unmodified Process Flow Diagram); P.R. Hribowo Editing, Formatting, Article Writing, and Investigation; J.S. Malau : Software Visualization (modified ASPEN HYSYS simulation and modified Process Flow Diagram) and Formal Analysis. All authors have read and agreed to the published version of the manuscript.

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