# Kinetic Modeling and Reactor Optimization of n-Butane Oxidative Dehydrogenation to Butadiene with Temperature-Dependent Kinetics in a Heterogeneous Catalytic System

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## *Abstract*

Oxidative dehydrogenation (ODH) of n-butane is regarded as a promising alternative route for the efficient synthesis of 1,3-butadiene. This study proposes a temperature-dependent kinetic model formulated using a power-law approach and applies it to a plug flow reactor (PFR) simulation in Aspen HYSYS. The model incorporates consecutive dehydrogenation reactions along with competing side reactions, including cracking pathways. Simulation results indicate that the developed kinetic model adequately represents the reaction mechanism, as reflected by the formation of 1,3-butadiene as the primary product and hydrogen as a secondary product. An increase in operating temperature from 450 to 600°C significantly enhances n-butane conversion and butadiene yield, achieving values of 0.8700 and 0.8690, respectively, while maintaining selectivity nearly equal to unity. This trend confirms that the reaction rates are predominantly governed by Arrhenius-type kinetics, where higher temperatures favor the main dehydrogenation reaction over undesired side reactions. In contrast, changes in reactor volume have a comparatively minor impact on performance, indicating a kinetically controlled system with limited sensitivity to residence time. Overall, the proposed kinetic framework provides a reliable basis for evaluating reactor performance and supports process optimization and design for efficient ODH-based butadiene production.

***Keywords***: Oxidative dehydrogenation; n-butane; Butadiene; Kinetic modeling;

Aspen HYSYS

## 1. Introduction

1,3-Butadiene is one of the key compounds in the petrochemical industry. It serves as a primary raw material for the production of synthetic rubber and various elastomers that are extensively used in the automotive and manufacturing sectors [1]. Traditionally, butadiene has been recovered as a by product of the steam cracking process. However, the increasing shift toward lighter hydrocarbon feedstocks, such as ethane, has led to a significant decline in butadiene production. This situation has driven the demand for alternative technologies capable of producing butadiene directly with improved controllability and process efficiency [2].

One promising approach is the oxidative dehydrogenation (ODH) of light alkanes. Compared to conventional dehydrogenation, ODH offers thermodynamic advantages and can be operated at lower reaction temperatures [2]. In the n-butane system, the presence of oxygen not only promotes the formation of butadiene but also helps suppress coke formation, which can adversely affect catalyst performance. Nevertheless, the main challenge of this process lies in maintaining high selectivity toward butadiene, as side reactions such as cracking and deep oxidation remain difficult to eliminate.

A wide range of catalysts has been developed to enhance the performance of the ODH reaction, including vanadium-based catalysts and mixed metal oxides. Recent advances indicate that multicomponent catalysts are superior, as they provide a more optimal distribution of active sites and exhibit stable redox properties [3]. One particularly promising catalytic system is (Ni, Fe, Co)-Bi-O supported on $\gamma$-$Al_2O_3$. This system has demonstrated enhanced selectivity toward butadiene due to synergistic interactions among its constituent components [1].

In addition to catalyst development, kinetic modeling plays a pivotal role in elucidating the complex reaction network of n-butane oxidative dehydrogenation (ODH). Most existing studies employ lumped reaction mechanisms combined with power-law expressions to represent the sequential formation of butenes and butadiene alongside parallel cracking and oxidation pathways [1,4,5]. These studies demonstrate that the ODH reaction proceeds through a multi-step mechanism in which intermediate species, particularly butenes, play a critical role in determining overall selectivity toward butadiene. Furthermore, it has been reported that variations in kinetic parameters, such as activation energy and reaction order, significantly influence the competition between desired dehydrogenation reactions and undesired side reactions such as cracking [4,5]. More advanced investigations also highlight that catalyst composition and reaction environment strongly affect product distribution and reaction pathways, emphasizing the complexity of the ODH system [19,21].

Despite these advances, current research remains largely fragmented and experimentally oriented. The majority of published works focus on catalyst characterization and intrinsic kinetic parameter estimation under controlled laboratory conditions, with limited emphasis on how these kinetic models perform when translated into reactor-scale simulations. Consequently, the applicability of such models under realistic industrial conditions remains uncertain. In particular, the coupling between temperature-dependent kinetics and reactor behavior—encompassing residence time, phase distribution, and heat effects—has not been systematically explored [2].

Furthermore, although Arrhenius-based temperature dependence is widely recognized as a key factor influencing reaction rates in ODH systems, its rigorous implementation within process simulation environments is still lacking [2]. This limitation becomes increasingly critical at elevated temperatures, where competing reactions such as cracking and over-oxidation intensify, leading to non-linear effects on conversion and selectivity. In addition, integrated sensitivity analyses that simultaneously evaluate the influence of key operating variables—such as temperature, pressure, and gas hourly space velocity (GHSV)—are rarely conducted [2]. As a result, there is a lack of comprehensive understanding linking kinetic behavior to overall reactor performance.

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This study aims to develop a temperature-dependent kinetic model for the oxidative dehydrogenation of n-butane using a lumped reaction mechanism approach. Beyond kinetic formulation, the proposed model is systematically integrated into a process simulation environment using Aspen HYSYS to enable sensitivity analysis and reactor optimization. Unlike previous studies that primarily focus on experimental parameter estimation, this work emphasizes the coupling of kinetic modeling with process-level analysis to identify optimal operating conditions. The proposed framework allows simultaneous maximization of butadiene production and minimization of undesired byproduct formation, thereby providing a more comprehensive and practical basis for reactor design and optimization of ODH processes.

## 2. Methods

### 2.1 n-Butane Oxidative Dehydrogenation Process and Reaction Network

The oxidative dehydrogenation (ODH) of n-butane is an important process for the production of $C_4$ olefins, particularly 1,3-butadiene, which is widely used as a key feedstock in the petrochemical industry [1]. Compared to conventional non-oxidative dehydrogenation processes, ODH offers several advantages, including lower operating temperatures, a reduced tendency for coke formation, and the absence of thermodynamic equilibrium limitations [2].

The n-butane ODH reaction system proceeds in the gas phase and employs heterogeneous metal oxide–based catalysts. This reaction system comprises a complex reaction network involving both consecutive (series) and parallel reaction pathways [4]. The primary reaction proceeds through a stepwise (consecutive) mechanism, in which n-butane is first converted into butenes as intermediate species, followed by further dehydrogenation to form butadiene. The main reactions involved in the n-butane dehydrogenation process are presented as follows:

$$C_4H_{10\ (g,\ \text{n-butane})} \rightleftharpoons C_4H_{8\ (g,\ \text{1-butene})} + H_{2\ (g)} \quad \Delta H^\circ_{298K} = +126.1 \text{ kJ/mole} \quad (1)$$

$$C_4H_{8\ (g,\ \text{1-butene})} \rightleftharpoons C_4H_{6\ (g,\ \text{1,2-butadiene})} + H_{2\ (g)} \quad \Delta H^\circ_{298K} = +162.4 \text{ kJ/mole} \quad (2)$$

$$C_4H_{10\ (g,\ \text{n-butane})} \rightleftharpoons C_4H_{6\ (g,\ \text{1,2-butadiene})} + 2H_{2\ (g)} \quad \Delta H^\circ_{298K} = +288.5 \text{ kJ/mole} \quad (3)$$

In the first stage, n-butane undergoes a dehydrogenation reaction to form butene with the release of one hydrogen molecule, as shown in Equation (1). The product formed is butene (1-butene), which acts as an intermediate species in the formation of butadiene (1,3-butadiene) [4]. In the second stage, butene undergoes further dehydrogenation to produce butadiene with the release of an additional hydrogen molecule, as represented in Equation (2) [1]. A direct reaction pathway is also possible, in which n-butane is converted directly into butadiene without forming butene as an intermediate, as shown in Equation (3) [4].

In addition to the primary dehydrogenation reactions, the conversion of n-butane is also accompanied by various undesired side reactions. One of the major side reactions is the cracking of n-butane, which can be represented as follows:

$$C_4H_{10\ (g)} \rightleftharpoons C_2H_{4\ (g)} + C_2H_{6\ (g)} \quad \Delta H^\circ_{298K} = +93.78 \text{ kJ/mole} \quad (4)$$

$$C_4H_{10\ (g)} \rightleftharpoons C_3H_{6\ (g)} + CH_{4\ (g)} \quad \Delta H^\circ_{298K} = +71.72 \text{ kJ/mole} \quad (5)$$

$$C_4H_{8\ (g)} \rightleftharpoons 2C_2H_{4\ (g)} \quad \Delta H^\circ_{298K} = +104.8 \text{ kJ/mole} \quad (6)$$

Reactions represented by Equations (4) and (5) indicate that n-butane can decompose into ethylene and ethane, as well as into propylene and methane [4]. Equation (6) further illustrates that butene, which is expected to act as an intermediate toward butadiene formation, can instead be converted into ethylene through carbon–carbon bond scission mechanisms. This pathway reduces the availability of intermediate species for subsequent dehydrogenation reactions, thereby leading to a decrease in selectivity toward butadiene [2].

## 2.2 Kinetic Model Development

The development of the kinetic model in this study is based on a power-law kinetics approach to represent the reaction rates in the n-butane oxidative dehydrogenation (ODH) system [1]. This model is selected because it effectively describes the relationship between reaction rates and reactant concentrations in a simplified manner without explicitly considering adsorption–desorption mechanisms, and it has been widely applied in previous kinetic studies of n-butane ODH [5].

Based on the n-butane ODH reaction system simplified into three main reactions represented by Equations (1), (2), and (6), which occur simultaneously within the reactor, the corresponding kinetic model can be formulated in the form of three reaction rate expressions as follows: [1]

$$-r_{nB}=-\frac{dC_{nB}}{d\tau}=k_{12}C_{nB} \tag{7}$$

$$r_{Bu}=-\frac{dC_{Bu}}{d\tau}=k_{23}C_{Bu}^{0.75} \tag{8}$$

$$r_{Cr}=\frac{dC_{Cr}}{d\tau}=k_{24}C_{Bu}^{0.75} \tag{9}$$

Here, $C_{nB}$ and $C_{Bu}$ represent the molar concentrations of n-butane and butene (gmol $L^{-1}$), respectively, while $k_{ij}$ denotes the rate constant for each corresponding reaction pathway [1]. Equation (1) describes the initial dehydrogenation step of n-butane to butene; therefore, the rate of n-butane consumption is directly determined by its concentration. Consequently, the reaction rate at this stage is modeled using a first-order dependence with respect to n-butane, as expressed in Equation (7), assuming that the first-step reaction is governed primarily by the concentration of the main reactant without significant influence from other species [1]. For the reaction represented by Equation (2), since butene acts as an intermediate that is both formed and consumed within the reaction network, the reaction rate depends on the concentration of butene [5]. Based on experimental kinetic studies conducted by Bin Sulayman and de Lasa (2024), this reaction follows a pseudo-order of 0.75 with respect to butene, as shown in Equation (8), indicating the presence of mechanistic complexity, likely involving catalyst surface interactions in the heterogeneous system. The side reaction corresponding to butene cracking, represented by Equation (6), is also incorporated into the kinetic model. As this reaction likewise depends on the concentration of butene as an intermediate species, its rate is expressed as given in Equation (9).

The reaction rate constants are expressed as functions of the reactor temperature (T) using the Arrhenius equation, thereby enabling temperature-dependent kinetic analysis[5].

$$\mathrm{k_{ij}}=\mathrm{k^{\circ}_{ij}}\ \exp\left(\frac{-\mathrm{E_{ij}}}{\mathrm{RT}}\right) \tag{10}$$

where $k_{ij}^{o}$ is the pre-exponential factor (mol/$g_{cat}$.min), $E_{ij}$ denotes the activation energy (kJ/mol), $R$ is the universal gas constant, and $T$ represents the absolute temperature (K) (Bin Sulayman & de Lasa, 2024). In addition, the molar concentrations of the components in the system are calculated based on the volumetric flow rates and the composition of the gas mixture, and can therefore be expressed as follows:

$$\mathrm{C_i}=\frac{\mathrm{y_i F_{Tm}}}{\mathrm{MW_i\ v}} \tag{11}$$

where $y_i$ is the mass fraction of component *i*, $C_i$ is the molar concentration (gmol/L) of component *i*, *v* denotes the volumetric flow rate ($cm^3$/min), dan $MW_i$ represents the molecular weight (g/mol) of component *I* [5].

The kinetic parameters employed in this study were derived from a combination of two primary literature sources. The activation energies were adopted from Elmutasim et al. (2018), who reported activation energy values for each reaction pathway, while the pre-exponential factors were taken from Tanimu et al. (2020), who applied a power-law–based kinetic model to a similar reaction system. This combined approach was adopted to obtain a complete and consistent set of kinetic parameters for use in the simulation.

**Table 1.** Kinetic parameter

| Reaction | A (mole/$g_{cat}$.min) | E (kJ/mole) |
|---|---|---|
| $k_{12}$ (n-butane → butene) | 0.857 | 24 |
| $k_{23}$ (butene → butadiene) | 1.930 | 15 |
| $k_{24}$ (cracking) | 0.198 | 105 |

## 2.3 Temperature-Depent Kinetic Parameters

The kinetic parameters of the n-butane oxidative dehydrogenation (ODH) reaction are strongly influenced by the operating temperature; therefore, the modeling approach adopted in this study explicitly accounts for this temperature dependence. Each reaction rate constant is expressed as a function of temperature using the Arrhenius equation, which is widely applied in heterogeneous catalytic reaction systems[6].

$$k_i = A_i \exp\text{-}\frac{E_i}{RT} \tag{12}$$

In Equation (12), $k_i$ represents the rate constant of the $i$-th reaction, $Ai$ is the pre-exponential factor, $E_i$ denotes the activation energy, $R$ is the universal gas constant, and $T$ is the absolute temperature. These parameters are typically determined through experimental approaches combined with regression fitting of kinetic data obtained over a range of operating temperatures [6].

Temperature dependence becomes particularly critical in the n-butane ODH system due to the competition between butadiene formation reactions and undesired side reactions. An increase in temperature generally enhances overall conversion. However, it also accelerates cracking and deep oxidation reactions, which consequently reduce selectivity toward butadiene [2].

In multicomponent metal oxide–based catalytic systems, such as (Ni, Fe, Co)–Bi–O/$\gamma$-$Al_2O_3$, product distribution is strongly influenced by interactions among active sites and by the redox properties of the catalyst, both of which are highly sensitive to temperature. Kinetic studies have demonstrated that variations in temperature significantly affect the dominant reaction pathways as well as selectivity toward butadiene [1].

The implementation of Arrhenius parameters in Aspen HYSYS enables the simulation to dynamically capture variations in reaction rates in response to changes in operating temperature. Consequently, the temperature-dependent kinetic model provides a more realistic representation of the reaction system and serves as a robust basis for sensitivity analysis and process optimization.

### 2.4 Reactor Modeling and Simulation Using Aspen HYSYS

Reactor modeling and simulation in this study are conducted using Aspen HYSYS to evaluate the performance of the n-butane oxidative dehydrogenation (ODH) process for butadiene production. A plug flow reactor (PFR) model is employed to represent the heterogeneous catalytic reactor operating in the gas phase [7].

The system is modeled using the Peng–Robinson (PR) property package, which is well suited for gas-phase hydrocarbon systems involving components such as n-butane, oxygen, nitrogen, and reaction products including butenes, butadiene, hydrogen, and light hydrocarbons. The selection of this property package is based on its proven capability to accurately predict phase behavior and thermodynamic properties under reactor operating conditions [8].

The components included in the simulation comprise n-butane ($C_4H_{10}$), oxygen ($O_2$), nitrogen ($N_2$), 1-butene ($C_4H_8$), butadiene ($C_4H_6$), hydrogen ($H_2$), and ethylene ($C_2H_4$) as a representative cracking product. The reactor feed consists of a gas mixture with a predefined molar composition of n-butane, oxygen, and nitrogen, operated at a temperature of 450°C and a pressure of 1 atm [1].

The reactor is modeled as a plug flow reactor (PFR) under steady-state conditions, assuming ideal plug flow without axial mixing and isothermal reaction operation. The reactor parameters include a reactor volume of 0.002 $m^3$, a void fraction of 0.4, and a catalyst density of 1000 $kg/m^3$. The isothermal assumption is adopted to simplify the model and to focus the analysis on the influence of reaction kinetics on product distribution [6].

The chemical reactions are incorporated into the simulation using a power-law–based kinetic model within a heterogeneous catalytic reaction framework. Three main reactions are considered, namely the dehydrogenation of n-butane to butenes, the subsequent dehydrogenation of butenes to butadiene, and the cracking of butenes into light products [1]. The reaction rates are expressed as functions of reactant concentrations and reaction rate constants that follow the Arrhenius equation, rendering them dependent on the reactor temperature [9].

The kinetic parameters employed in the simulation, namely the pre-exponential factors and activation energies, were obtained from the literature reported by Tanimu et al. (2020) and were adjusted in terms of units to ensure compatibility with Aspen HYSYS. The reaction rate calculations were performed on a concentration basis within the gas phase [6]. The simulation was carried out by incorporating the operating conditions and kinetic parameters into the reactor model. The resulting outlet component flow rates were then used to calculate n-butane conversion, butadiene selectivity, and product yields. The developed model subsequently serves as a foundation for reactor performance evaluation and operating condition optimization in this study [7].

**Table 2.** Operating conditions

| Parameter | Values | Units |
|---|---|---|
| Temperature | 450 | °C |
| Pressure | 1 | atm |

| | | |
|---|---|---|
| Reactor Volume | 2 | $m^3$ |
| n-butane/$O_2$ ratio | 1.19 | - |
| GHSV | 0.117 | $h^{-1}$ |

**Table 3.** Feed compositions

| Components | Mole Fractions |
|---|---|
| n-butane | 1 |
| $O_2$ | 0.21 |
| $N_2$ | 0.79 |

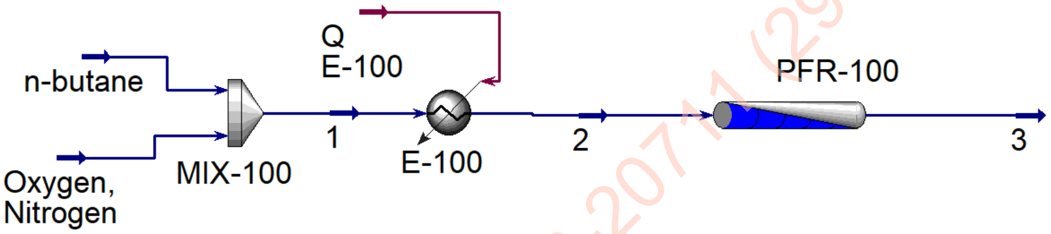

Figure 1. Simulation using Aspen HYSYS of modified process

### 2.5 Reactor Optimazation Strategy

The reactor optimization strategy in this study is aimed at identifying operating conditions that maximize butadiene production from the n-butane oxidative dehydrogenation (ODH) process. Unlike sensitivity analysis–based approaches, the optimization is carried out using a direct simulation approach in Aspen HYSYS, in which key operating parameters are systematically varied and their effects on reactor performance are evaluated [10].

The optimization is carried out using the developed heterogeneous kinetic–based plug flow reactor (PFR) model, in which the reaction rate constants are expressed as functions of temperature through the Arrhenius equation. Consequently, variations in operating conditions directly influence the reaction rates and product distribution along the reactor length [11].

The objective function employed in this optimization is to maximize the butadiene yield, which is defined as the combined result of n-butane conversion and selectivity toward butadiene. This objective can be expressed by the following equation:

$$X_{nB}=\frac{F_{nB,in}-F_{nB,out}}{F_{nB,in}}\times100\% \tag{13}$$

$$S_{BD}=\frac{F_{BD}}{F_{nB,in}-F_{nB,out}}\times 100\% \tag{14}$$

$$Y_{BD} = X_{nB} \times S_{BD} \tag{15}$$

Equation (13) defines the expression used to calculate the n-butane conversion ($X_{nB}$) which represents the fraction of n-butane that reacts within the reactor relative to the initial amount fed. Here,$F_{nB,in}$ denotes the molar flow rate of n-butane at the reactor inlet, while $F_{nB,out}$ represents the molar flow rate of n-butane at the reactor outlet [1]. The selectivity toward butadiene ($S_{BD}$) is obtained using Equation (14), which reflects the ability of the reaction system to produce butadiene relative to the amount of n-butane converted, where $F_{BD}$ is the molar flow rate of butadiene formed. The butadiene yield ($Y_{BD}$) is calculated as the product of n-butane conversion (Equation 13) and butadiene selectivity (Equation 14), thereby representing the overall efficiency of the process in converting n-butane into butadiene [4]. In addition, the optimization procedure also considers the minimization of side product formation, particularly from cracking reactions, as their presence can adversely affect process selectivity and overall efficiency [1].

The operating parameters optimized in this study include reactor temperature, the molar $O_2$/n-butane, ratio, gas hourly space velocity (GHSV), and reactor volume. Temperature variation is conducted to identify conditions that provide an optimal balance between increased conversion resulting from accelerated reaction kinetics and decreased selectivity caused by the enhancement of side reactions at elevated temperatures [12]. The $O_2$/n-butane ratio is optimized to ensure a sufficient oxygen supply to promote the dehydrogenation reaction while avoiding undesired deep oxidation reactions.

In addition, the GHSV is adjusted to control the residence time of the reactants within the reactor, where excessively high values lead to reduced conversion, while overly low values may promote undesired secondary reactions [2]. The reactor volume is also varied to evaluate the effect of contact time on conversion and product distribution [13].

The optimization process is carried out by comparing simulation results obtained under various combinations of operating conditions, after which the conditions that yield the highest butadiene production while maintaining favorable selectivity are selected. This approach enables the practical identification of optimal operating conditions without the need for complex mathematical optimization techniques [14]. Furthermore, the outcomes of this optimization strategy are used to evaluate reactor performance and to provide recommendations for the most suitable operating conditions for n-butane ODH–based butadiene production.

## 3. Results and Discussion

### 3.1 Kinetic Model Implementation and Validation in Aspen HYSYS

The implementation of the kinetic model is carried out by incorporating the Arrhenius parameters and power-law–based rate equations into Aspen HYSYS. Model validation is performed by evaluating the simulation results under baseline operating conditions to ensure that the predicted reactant conversion and product distribution are consistent with the proposed reaction mechanism. The data and results obtained from the Aspen HYSYS simulations are presented as follows.

**Table 4.** Kinetic parameters used in Aspen HYSYS simulation

| Reaction | A (gmole/cm$^3$.h) | E (kJ/gmole) |
|---|---|---|
| $k_{12}$ (n-butane → butene) | 54 | 24 |
| $k_{23}$ (butene → butadiene) | 9.648 | 15 |
| $k_{24}$ (cracking) | 16.272 | 105 |

**Table 5.** Base case operating conditions for reactor simulation

| Parameter | Value | Units |
|---|---|---|
| Temperature | 450 | °C |
| Pressure | 1 | atm |
| Reactor Volume | 2 | m$^3$ |

**Table 6.** Outlet composition at base case condition

| Components | Mole Fractions |
|---|---|
| n-butane | 0.0511 |
| 1-butene | 0.0000 |
| butadiene | 0.1063 |
| hydrogen | 0.2127 |
| ethylene | 0.0000 |

The simulation results presented in Tables 4 and 5 indicate that the dehydrogenation of n-butane leads to the formation of hydrogen and intermediate products, while a significant formation of 1,3-butadiene is observed, as shown in Table 6. This observation confirms that the reaction pathway proceeds to the advanced stages of the reaction network. The formation of butadiene from n-butane follows a sequential reaction mechanism, in which n-butane is first converted into butenes as intermediate species, followed by subsequent reactions leading to butadiene. Therefore, the presence of butadiene indicates that the reaction has progressed to the second dehydrogenation stage [1].

This behavior can be explained using the Arrhenius equation, which describes the strong dependence of reaction rates on activation energy ($E$). Although the formation of butadiene generally requires higher activation energy than the initial dehydrogenation step, the operating temperature of 450°C applied in this simulation is sufficient to overcome the energy barrier, allowing the secondary reaction to proceed [15]. In addition, side reactions such as cracking, which are associated with relatively high activation energies, remain limited under these conditions. As a result, the formation of light products such as ethylene is not significant, and selectivity toward butadiene remains high [4].

Based on the simulation results, the kinetic model implemented in Aspen HYSYS demonstrates good mechanistic consistency, as it is capable of representing the stepwise dehydrogenation pathway of n-butane. This is evidenced by the formation of intermediate species as well as final products such as 1,3-butadiene and hydrogen [1]. Under the baseline operating conditions, the formation of 1,3-butadiene occurs to a significant extent, indicating that the available energy is sufficient to drive the subsequent reaction steps toward the desired product. This observation is consistent with reaction kinetics theory, which states that reactions with higher activation energies require appropriate operating conditions, particularly sufficiently high temperatures, to overcome the activation energy barrier [16]. Therefore, further optimization of operating parameters such as temperature and residence time remains necessary to enhance conversion while maintaining high selectivity toward butadiene, ultimately achieving more optimal operating conditions [17].

### 3.2 Effect of Operating Conditions on Reactor Performance

Reactor performance is strongly influenced by operating conditions such as temperature and reactor volume. Therefore, variations in these parameters were conducted to examine their effects on n-butane conversion and product formation, particularly 1,3-butadiene. The simulation results are presented in tabulated form to facilitate comparison across different operating conditions.

**Table 7.** Effect of temperature on reactor performance

| Temperature (°C) | Conversion (Mole Fractions) | Yield Butadiene ($Y_{BD}$) | Selectivity Butadiene ($S_{BD}$) |
|---|---|---|---|
| 450 | 0.6760 | 0.6750 | 0.9980 |
| 500 | 0.7400 | 0.7400 | 1.0000 |
| 550 | 0.8060 | 0.8050 | 0.9999 |
| 600 | 0.8700 | 0.8690 | 0.9999 |

**Table 8.** Effect of reactor volume on conversion and yield at 450°C

| Volume ($m^3$) | Conversion (Mole Fractions) | Yield Butadiene ($Y_{BD}$) |
|---|---|---|
| 1 | 0.6620 | 0.6610 |
| 2 | 0.6760 | 0.6750 |

Based on the data presented in Tables 7 and 8, increasing the temperature from 450°C to 600°C has a significant effect on enhancing n-butane conversion and butadiene yield. The conversion increases from 0.6760 to 0.8700, while the yield rises from 0.6750 to 0.8690, with selectivity remaining close to unity. These results indicate that the dehydrogenation reaction is kinetically controlled and follows Arrhenius behavior, in which an increase in temperature leads to higher reaction rate constants and consequently accelerates the formation of the desired product [6]. Moreover, the consistently high selectivity across the investigated temperature range suggests that side reactions such as cracking remain relatively limited, allowing the main reaction pathway to remain dominant [18].

Variations in reactor volume at 450°C show that increasing the reactor volume from 1 $m^3$ to 2 $m^3$ results in only a moderate improvement in conversion and yield, indicating that the system is approaching a kinetic regime that is no longer highly sensitive to residence time. This phenomenon suggests that, under these conditions, the reaction rate is sufficiently high such that further increases in contact time do not lead to a significant enhancement in reactor performance [6]. Overall, temperature emerges as a more dominant parameter than reactor volume in improving reactor performance for this system.

Based on the analysis results, increasing temperature is identified as a key factor in enhancing reactor performance, particularly in terms of n-butane conversion and butadiene yield, without causing a significant decline in selectivity. This behavior indicates that the reaction proceeds effectively at elevated temperatures and remains predominantly governed by the main reaction pathway. In contrast, the influence of reactor volume is comparatively less significant than that of temperature, suggesting that process optimization should primarily focus on the regulation of thermal operating conditions. Accordingly, the selection of an optimal temperature is a critical aspect in maximizing butadiene production, while simultaneously considering energy efficiency and the potential occurrence of side reactions under more extreme operating conditions [19].

### 3.3 Product Selectivity and Yield Analysis

Selectivity and yield are key parameters for evaluating reactor performance and reaction efficiency [19]. The tendencies toward the formation of desired products and byproducts are analyzed based on the simulation results. The calculated selectivity and yield values are derived from the simulation outcomes and are presented in tabulated form as follows.

**Table 9.** Product distribution at 600°C

| Components | Mole Fractions |
|---|---|
| n-butane | 0.0193 |
| 1-butene | 0.0000 |
| butadiene | 0.1290 |
| hydrogen | 0.2581 |
| ethylene | 0.0000 |

**Table 10.** Reactor performance parameters

| Components | Value |
|---|---|
| Conversion (Mole Fractions) | 0.6760 |
| Selectivity Butadiene ($S_{BD}$) | 0.9980 |
| Yield Butadiene ($Y_{BD}$) | 0.6750 |

Based on the results presented in Tables 9 and 10, it is evident that at a temperature of 600°C, the formation of 1,3-butadiene occurs to a significant extent, exhibiting high selectivity and yield. Meanwhile, intermediate products such as 1-butene are no longer detected, indicating that the reaction has progressed to the advanced dehydrogenation stage and that the reaction pathway toward butadiene formation has become dominant. In a stepwise reaction mechanism, selectivity is strongly influenced by competition between the main reaction pathway (butadiene formation) and side reactions such as cracking, which generally become more pronounced at elevated temperatures. However, under the current operating conditions, the high selectivity observed suggests that the main reaction pathway remains dominant over undesired side reactions.

The higher activation energy required for butadiene formation implies that sufficiently high temperatures are necessary for the reaction to proceed optimally. At 600°C, the thermal energy of the system is adequate to effectively drive the secondary dehydrogenation reaction. In addition, the very low formation of side products such as ethylene indicates that cracking reactions remain limited and do not significantly reduce the yield of the target product [19]. These results further suggest that although increasing temperature generally enhances reaction rates, the applied operating conditions have not yet fully enabled effective control of reaction selectivity toward exclusive butadiene formation [20].

Based on the analysis of selectivity and yield, increasing the temperature up to 600°C significantly enhances the formation of 1,3-butadiene, as indicated by the high selectivity and yield values. This trend suggests that the reaction system is predominantly governed by the main reaction pathway leading to butadiene formation rather than by intermediate formation or undesired side reactions [19]. Overall, the operating conditions employed are sufficiently effective in directing the reaction pathway toward the target product. Nevertheless, a more comprehensive optimization approach remains necessary, including controlled temperature regulation, extended residence time, and consideration of catalyst modifications capable of lowering the activation energy for butadiene formation while maintaining high selectivity over a broader range of operating conditions [20].

### 3.4 Reactor Optimization for Butadiene Production

Reactor optimization is performed to identify operating conditions that yield the highest 1,3-butadiene production while maintaining favorable selectivity. Operating parameters such as reactor temperature and reactor volume are varied to determine the optimal conditions, taking into account the trade-off between increased conversion and the formation of undesired side products. The optimization results are presented in the following table.

**Table 11.** Comparison of Reactor Performance at Different Operating Conditions

| Parameter | Base Case | Modified Conditions |
|---|---|---|
| Temperature (°C) | 450 | 600 |
| Pressure (atm) | 1 | 1 |
| Reactor Volume ($m^3$) | 2 | 2 |
| Conversion Butadiene | 0.6760 | 0.8700 |
| Selectivity ($S_{BD}$) | 0.9980 | 0.9999 |
| Yield ($Y_{BD}$) | 0.6750 | 0.8690 |

Based on the results presented in Table 11, increasing the temperature from 450°C (base case) to 600°C (modified conditions) leads to a substantial enhancement in butadiene conversion and yield, which increase from 0.6760 and 0.6750 to 0.8700 and 0.8690, respectively, while selectivity remains high and close to unity. These findings indicate that temperature plays a crucial role in accelerating reaction rates in accordance with the Arrhenius equation, whereby the reaction rate constants increase exponentially with temperature, thereby promoting n-butane conversion and the formation of the target product [6]. In addition, elevated temperatures can enhance catalytic activity and accelerate oxidative reaction mechanisms that favor 1,3-butadiene formation [21]. The high selectivity observed under optimum conditions further suggests that the main reaction pathway remains dominant over side reactions, allowing the formation of undesired products to be effectively suppressed [18].

Based on the optimization results, increasing the temperature to 600°C is identified as the most effective condition for enhancing reactor performance in 1,3-butadiene production, yielding high conversion and yield while maintaining favorable selectivity. This behavior indicates that the reaction system operates under advantageous conditions in which the rate of the main reaction can be maximized without a significant increase in undesired side reactions. Consequently, temperature emerges as the dominant operating parameter in this process, whereas other parameters such as reactor volume play a supporting role. These findings provide a strong basis for determining optimal operating conditions and support the development of more efficient and industrially applicable ODH-based butadiene production processes.

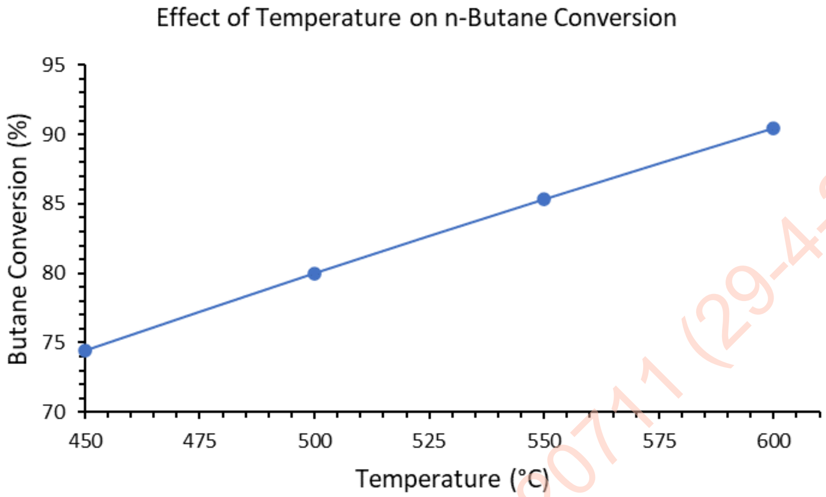

Figure 2. Effect of reactor temperature on n-butane conversion

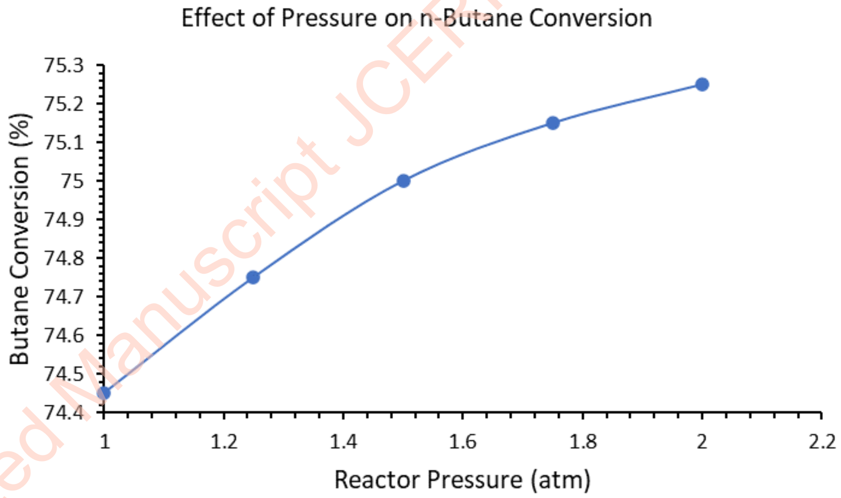

Figure 3. Effect of reactor pressure on n-butane conversion

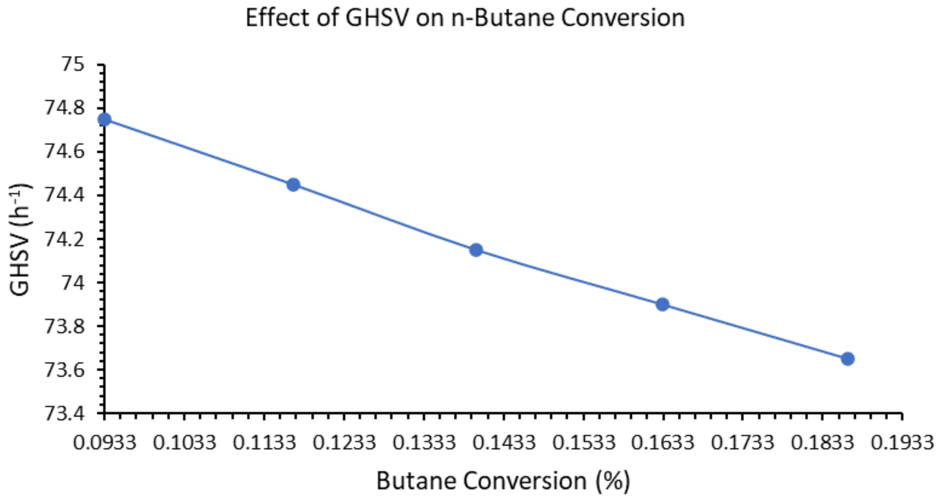

Figure 4. Effect of GHSV on n-butane conversion

The variation of operating conditions highlights that n-butane conversion in the ODH system is predominantly governed by kinetic effects. Increasing temperature from 450°C to 600°C significantly enhances conversion, reflecting strong Arrhenius dependence and the facilitation of C–H bond activation [1]. The absence of any plateau suggests that the system remains far from equilibrium within the studied range; however, this also raises the likelihood of parallel over-oxidation reactions at higher temperatures, which cannot be assessed from conversion alone [14].

In contrast, pressure exerts only a marginal influence, with a slight increase in conversion observed between 1 and 2 atm. This weak dependence is consistent with the stoichiometry of dehydrogenation reactions and indicates that pressure does not play a decisive role in controlling reactor performance [16]. Any minor enhancement is likely attributable to increased reactant concentration rather than a fundamental shift in reaction behavior [4].

GHSV exhibits a more pronounced effect, where increasing GHSV reduces conversion due to shorter residence time and limited reactant–catalyst interaction [Tanimu et al., 2020]. This confirms that the system is residence-time dependent and further supports the dominance of kinetic control [2]. Nevertheless, excessively low GHSV may promote consecutive reactions, indicating an inherent trade-off between conversion and selectivity.

The system is controlled by reaction kinetics and contact time, with temperature as the primary driver and GHSV as a critical operational parameter, while pressure remains secondary [12]. These findings emphasize that meaningful optimization requires simultaneous consideration of conversion and selectivity rather than relying on conversion trends alone [14].

## 4. Conclusion

This study successfully developed and implemented a temperature-dependent kinetic model for the n-butane oxidative dehydrogenation (ODH) reaction using a power-law approach within a plug flow reactor (PFR) simulation in Aspen HYSYS. The simulation results demonstrate that the applied kinetic model is capable of mechanistically representing the reaction pathways, as evidenced by the formation of the primary product, 1,3-butadiene, along with byproducts such as hydrogen, with product distributions that are consistent with the proposed stepwise reaction mechanism.

Variations in operating conditions indicate that temperature is the most influential parameter governing reactor performance. Increasing the temperature from 450°C to 600°C significantly enhances n-butane conversion and butadiene yield, while maintaining selectivity at very high values close to unity. This behavior suggests that, within this temperature range, the main reaction pathway remains dominant over side reactions and that the system operates under favorable kinetic conditions consistent with Arrhenius behavior. In contrast, the effect of reactor volume is relatively insignificant compared to that of temperature, indicating that the system approaches a regime in which reaction rates are no longer limited by residence time. The optimization results further demonstrate that the optimal operating condition is achieved at a temperature of 600°C, where high conversion and yield are obtained while selectivity is preserved, thereby maximizing 1,3-butadiene production.

Overall, this study confirms that the integration of temperature-dependent kinetic models into process simulations can provide representative and reliable predictions of reactor performance. Such an approach offers a strong foundation for determining optimal operating conditions and supports the development of more efficient and industrially applicable n-butane ODH processes.

## Credit Author Statement

Author Contributions: A.R. Jannah: Conceptualization, Methodology, Investigation, Resources, Formal Analysis, Writing, Review and Editing, Supervision; R.N.N.M. Prabaswari: Conceptualization, Methodology, Formal Analysis, Data Curation, Writting Draft Preparation, Resources, Visualization, Software, Project Administration; H.N. Mahsa: Validation, Writing, Review and Editing, Data Curation; M.S. Hakim: Software, Visualization, Writing, Resources, Data Curation. All authors have read and agreed to the published version of the manuscript.

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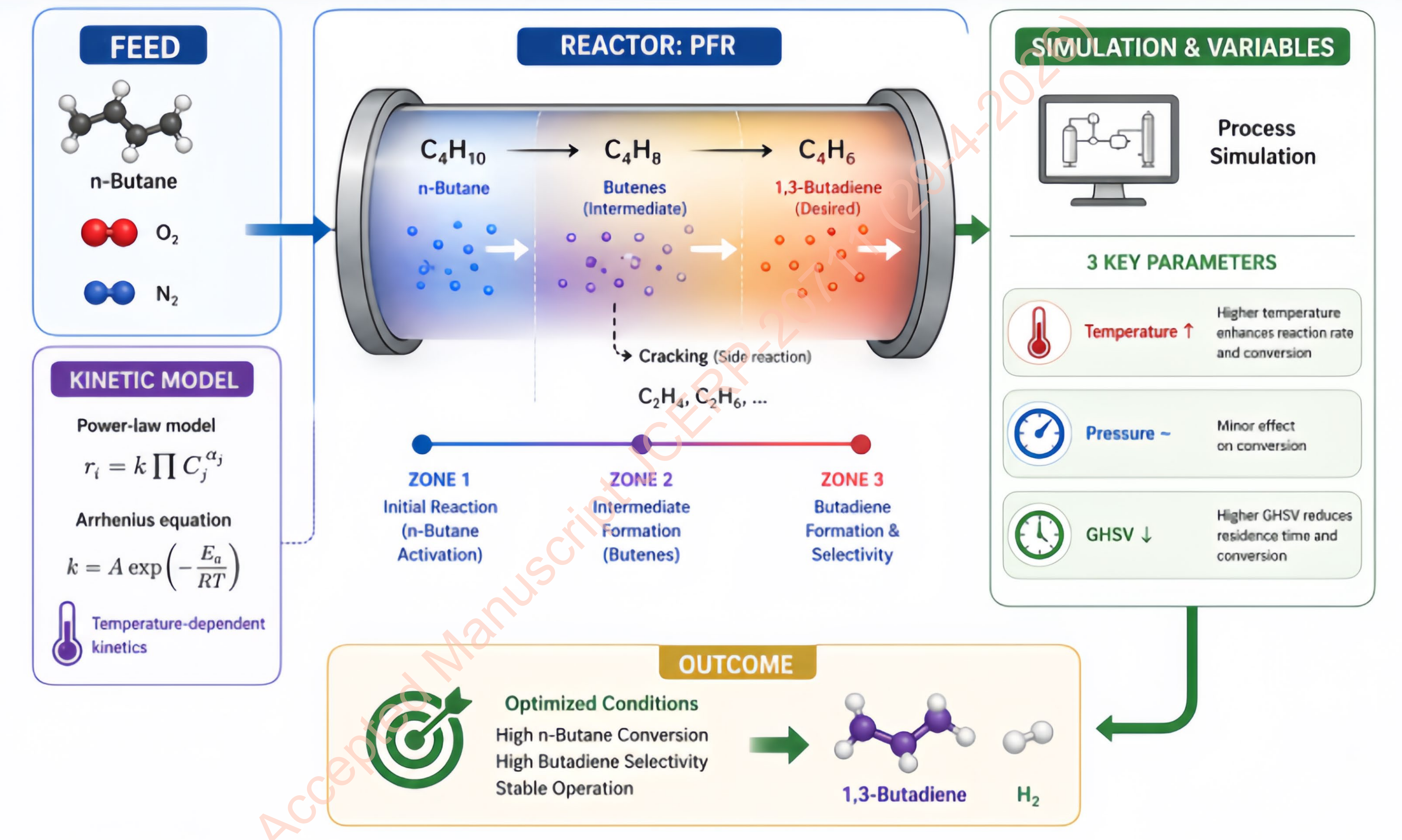
FEED
n-Butane
$O_2$
$N_2$
KINETIC MODEL
Power-law model
$r_i = k \prod C_j^{\alpha_j}$
Arrhenius equation
$k = A \exp\left(-\frac{E_a}{RT}\right)$
Temperature-dependent kinetics
REACTOR: PFR
$C_4H_{10}$
n-Butane
$C_4H_8$
Butenes (Intermediate)
$C_4H_6$
1,3-Butadiene (Desired)
Cracking (Side reaction)
$C_2H_4$, $C_2H_6$, ...
ZONE 1
Initial Reaction (n-Butane Activation)
ZONE 2
Intermediate Formation (Butenes)
ZONE 3
Butadiene Formation & Selectivity
SIMULATION & VARIABLES
Process Simulation
3 KEY PARAMETERS
Temperature ↑
Higher temperature enhances reaction rate and conversion
Pressure ~
Minor effect on conversion
GHSV ↓
Higher GHSV reduces residence time and conversion
OUTCOME
Optimized Conditions
High n-Butane Conversion
High Butadiene Selectivity
Stable Operation
1,3-Butadiene
$H_2$