

EXPERIMENTAL INVESTIGATION AND KINETIC MODELING OF CATALYTIC REACTION SYSTEMS FOR SUSTAINABLE CHEMICAL PRODUCTION

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ABSTRACT

A catalytic reaction system with high conversion, high selectivity, low energy consumption and low pollution is the way to achieve sustainable chemical production. An experimental-kinetic framework for the study and modelling of catalytic reaction systems for sustainable chemical production is presented. The proposed methodology consists of experimental reaction analysis, reaction-network formulation, temperature dependence kinetic modeling, Arrhenius parameter estimation, catalyst-to-feed ratio analysis and nonlinear model optimization. Various factors are taken into account to describe the catalytic behavior under different operating conditions such as conversion, product selectivity, yield, effects of the catalyst, and sustainability-related performance indicators. To compare with the proposed modelling framework, several conventional and data-assisted models are explored. Prediction accuracy, error characteristics, behavior towards convergence, temperature dependent conversion, product selectivity, the effects of catalyst loading, and the estimation of the kinetic parameters are all evaluated. According to the illustrative evaluation, the proposed framework achieves a good balance between the representation of catalytic behaviour (R² around 0.93) and the prediction error of the model (lower than those considered as baseline approaches). The Arrhenius analysis also illustrates the potential of the framework to measure the temperature-dependent reaction kinetics and the estimation of the relevant kinetic parameters. The resulting methodology yields a systematic basis for the connection between experimental catalytic behavior and predictive kinetic modelling and sustainability evaluation of processes.

Keywords: Catalytic Reaction Systems, Kinetic Modeling, Sustainable Chemical Production, Reaction Kinetics, Arrhenius Model, Catalyst-To-Feed Ratio, Parameter Estimation, Reaction-Rate Modeling, Product Selectivity, Experimental Investigation, Process Optimization, Sustainable Catalysis.

1. INTRODUCTION

The transition toward sustainable chemical production has increased the demand for catalytic processes that can achieve high conversion and selectivity while reducing energy consumption, waste generation, and dependence on non-renewable resources [1]. Catalysis plays a central role in modern chemical processing because catalysts can reduce activation barriers and enable chemical transformations under comparatively moderate operating conditions [2]. However, the performance of a catalytic reaction system depends strongly on operating temperature, reactant concentration, catalyst loading, residence time, pressure, and catalyst properties [3]. Consequently, experimental investigation combined with reliable kinetic modeling is essential for understanding reaction behavior and developing efficient catalytic production processes [4].

Catalytic cracking represents an important example of a complex reaction system in which several parallel and consecutive reactions occur simultaneously [5]. Early kinetic investigations established the importance of reaction kinetics for describing product formation and selectivity in catalytic

reactors [6]. Kinetic parameter estimation is an important component of catalytic reaction modeling [7]. The kinetic parameters determine the ability of a model to reproduce experimentally observed reaction rates and product distributions. Optimization-based techniques have also been applied to nonlinear kinetic systems, including simulated annealing for nonlinear parameter estimation [8]. More recent parameter-estimation approaches have considered uncertainty and feasible parameter regions, demonstrating the importance of robust estimation procedures for nonlinear chemical reaction models [9].

Another fundamental parameter that affects catalytic reaction kinetics is temperature [10]. The Arrhenius relationship gives a standard model to describe the dependence of the reaction-rate constants on temperature and allows the calculation of activation energy and pre-exponential factors [11]. Experimental observations over an adequate temperature range are needed to make reliable estimates of these parameters. Molecular level kinetic approaches have also been used to try and relate reaction mechanisms, molecular distributions, and reactor temperature profiles [12]. The importance of treating simultaneously reaction kinetics,

hydrodynamics, heat transfer and transport phenomena in order to predict the behavior of industrial reactors in FCC risers was also pointed out by modeling studies [13].

In recent years, computational techniques have added artificial intelligence and data-driven models to chemical reaction modeling [14]. In chemical engineering systems, neural networks have shown their capability of approximating nonlinear relationship [15]. The growing connection between AI and mechanistic chemical models has provided the opportunity for hybrid modeling, which enables the incorporation of reaction mechanisms derived from experiments with predictive data from AI into a single model [16].

An important challenge is still outstanding to develop an integrated experimental and kinetic model that helps to establish the direct link among the catalytic operating conditions [17], reaction rates, product distribution, catalyst behavior and sustainable production goals [18]. Many traditional kinetic models are concerned only with fitting reaction-rate data, while sustainable chemical production also involves product selectivity, energy consumption [19], waste production, catalyst usage, and efficiency of operation. Furthermore, a model that properly fits experimental data should also be physically meaningful and should be able to predict the catalytic behavior (not necessarily the same as that in the experiment) under operating conditions different from those used for the parameter estimation [20].

Recently, kinetic modeling of a waste cooking oil transesterification system has been extended to the production of biodiesel expanding its applicability to renewable and waste-derived feedstocks, together with experimental measurements, in a sustainability-oriented context [21]. These studies show that there is a trend to research in the field of sustainable chemical-process development based on experimentally verified kinetics and computational tools [22].

This work introduces an experimental and kinetic modelling framework for catalytic reaction systems for sustainable chemical production, inspired by these developments [23]. A systematic approach is used to consider the impact of operating conditions, the catalytic conversion, product selectivity, yield and reaction rate [24]. A reaction network is developed based on the experimental observations and the kinetic parameters of the network are estimated by using a nonlinear optimization procedure [25]. The performance of the resulting model is validated with the aid of independent experimental observations by statistical parameters like Coefficient of Determination, Root mean square error and Mean Absolute Percentage error [25]. Furthermore, the framework includes sustainability-related performance indicators such as energy consumption, use of catalysts, and the formation of unwanted products [26]. Furthermore, sustainability-related performance indicators such as energy demands, catalyst utilisation and unwanted product formation are considered.

The main contribution of this work is the unification of the experimental investigation of the catalytic process, reaction-network-based kinetic modelling, nonlinear parameter estimation, model validation and assessment of sustainability-

oriented performance within a single framework. The proposed method differs from experimental analysis and kinetic modelling by considering the latter as a consecutive process in the former. The framework that is formed can then be used to evaluate catalysts, optimize reactions, develop reactors, and determine operating conditions that can be used to make chemical production more efficient and environmentally friendly.

2. LITERATURE SURVEY

In the fluid catalytic cracking (FCC) process, Chen et al. [1] have studied the prediction of the molecular distribution and temperature profiles with a molecular-level kinetic modelling approach. The authors designed a modeling strategy which captured the complex molecular changes taking place during FCC and employed it to simulate the molecular product distribution and temperature profile in the process. In their study, they showed how they could use molecular-level kinetic modelling to give detailed information about the behaviour of FCC and product formation. The relevance of the work was its demonstration that detailed kinetic representations can enhance the understanding and prediction of the characteristics of FCC compared to simplified lumped models.

Selalame et al. [2] gave a complete overview of the modeling methods used in FCC units, especially the riser section. Various mathematical and kinetic models developed to simulate the complex reactions and transport processes that take place inside FCC risers were considered. They explained about some significant factors like reaction kinetics, catalyst behaviour, hydrodynamics, heat transfer, and product distribution. They noted the difficulties involved in creating a reliable FCC riser model and demonstrated that the choice of an appropriate model required a level of detail and application specific.

Ancheyta-Juárez et al. [3] suggested a method to estimate the kinetic parameters of FCC process. One important step was that the authors concentrated on determining the kinetic parameters from experimental data, since the accuracy of an FCC kinetic model was highly dependent on the reliability of the estimated parameters. Their methodology was based on the treatment of the nonlinear nature of FCC reaction kinetics and a systematic method to obtain suitable kinetic parameters. It was shown that optimization of parameters led to an enhancement in the predictive ability of FCC kinetic models and thus in the prediction and analysis of the FCC process.

Lee et al. [4] proposed a four-lump kinetic model for FCC process. The authors represented the complex mixture of hydrocarbons in catalytic cracking by a smaller number of representative product lumps. This method made the complex reaction network easier to work with, but did not alter the principal pathways and product relations. Their model offered a useful description of the conversion of feedstock to the major FCC product groups. This study was valuable since it reduced the computational complexity by using lumped kinetic models and it could be used effectively in the simulation of the processes and engineering analysis.

Vorobev et al. [5] developed a simplified model for an industrial catalytic cracking riser reactor. The authors chose to

model the behaviour of an industrial-scale FCC riser, but with a model that was simple enough to be used practically while retaining the important features of the cracking process. Their research was concerned with the reaction and process behaviour taking place along the riser and showed how a simplified mathematical representation can be employed to describe an industrial catalytic cracking process. The study was relevant to FCC modeling because the need to develop models that were computationally manageable, but still useful for prediction of industrial reactor performance.

Weekman et al. [6] studied the selectivity of catalytic cracking in fixed-bed moving-bed and fluid-bed reactors. The authors investigated the effect of reactor configuration on the catalytic cracking reactions and product selectivity. Their contribution gave valuable insights into the correlations of reaction rate, type of reactors and the production of various cracking products. The study helped advance FCC kinetic modelling by providing basic relationships of the catalyst reactions to the reactor behavior. The results were then used to validate the use of kinetic and lumped models for the description of catalytic cracking processes.

Bardow et al. [7] explored ways of identification of reaction kinetics based on the incremental and simultaneous parameter estimation methods. Different methods for kinetic parameters determination were compared and the benefits and drawbacks of incremental and simultaneous identification were discussed. They analyzed their studies and highlighted the significance of obtaining reliable kinetic parameters from experimental observations, especially in the case of complex reaction systems with multiple reactions. The results indicated that the selection of parameter-identification strategy might affect the accuracy and robustness of the resulting kinetic model. This work was applicable to FCC modeling since it had several reactions with interactions and hence needed reliable kinetic parameter estimation.

Eftaxias et al. [8] studied the estimation of non-linear kinetic parameters with the approach of simulated annealing optimization. The authors used simulated annealing for nonlinear optimization problem estimation of kinetic parameters. They showed that typical parameter estimation might not work in the presence of nonlinearities and multiple solutions in the optimization problem. The simulated annealing method was used to achieve an optimization process to find the appropriate kinetic parameters in a way that is oriented toward a global search. In complex reaction systems like FCC, the accurate estimation of the nonlinear kinetic parameters was essential, thus making the study particularly relevant.

3. METHODOLOGY

A. Overall Research Framework

The preparation or selection of the catalytic material is the first step in the catalytic material preparation process, which is based on the target reaction system. Catalytic testing is performed after a suitable catalyst pretreatment is performed, to ensure reproducible physicochemical conditions. Pretreatment can be drying, calcination, activation, reduction, and removal of adsorbed species depending on the catalyst. The composition and concentration of the reactant/feedstock

is controlled so that changes in catalytic performance are solely due to the investigated operating conditions.

In experiments, the quantity of the catalyst is accurately measured and the quantity of feed is measured. The ratio of the quantity of catalyst to the quantity of feed is called the catalyst-to-feed ratio and is related to the mass of catalyst and feed. The reactor operating conditions determine the residence time, which is the ratio of the time a molecule remains in the reactor to the total processing time. They are all gathered with temperature, pressure, flow rate and reaction time to form a uniform experimental data set for kinetic analysis.

B. Catalyst and Feed Preparation

Catalytic experiments are carried out in a controlled laboratory-scale reactor that can enable the desired reaction temperature, pressure, feed flow rate, and residence time, etc. The reactor runs under a set of pre-defined experimental conditions in order to record the low- and high-conversion regimes. Several experiments are performed for each operating condition to minimize the experimental uncertainty and enhance the accuracy of the estimation of the kinetic parameters.

The reactants are fed into the catalytic reactor and reacted with the catalyst for the desired reaction for the designated reaction time in each experiment. The reaction products/products are collected and analyzed to determine the concentration or amount of reactants/products. The analytical method used can be varied from gas chromatography, liquid chromatography, spectroscopy to mass spectrometry depending on the chemical system to be analyzed. Blank experiments without catalyst can also be carried out when required to differentiate between catalytic conversion and non-catalytic reactions.

The catalyst-to-feed ratio is expressed as

$$R_{C/F} = \frac{m_c}{m_f} \quad (1)$$

where m_c is the catalyst mass and m_f is the feed mass.

C. Experimental Catalytic Reaction System

These experiments are carried out in a controlled laboratory scale reactor that will allow one to carry out the reactions at the right temperature, pressure, feed rate, and residence time. These experiments are done under varying conditions that are pre-determined in order to account for low and high conversions. Several experiments are performed for each set of operating conditions to increase the accuracy of the data by reducing experimental errors.

The reactants are fed into the catalytic reactor and the reaction is carried out for a period of time as determined by the conditions. Then the products leaving the reactor are tested for the amounts of reactants and products present. There are different ways of testing the chemical system depending on the type of system being investigated. Gas Chromatography, Liquid Chromatography, Spectroscopy, or Mass Spectrometry can be used.

The conversion of reactant A is calculated as

$$X_A = \frac{C_{A,0} - C_A}{C_{A,0}} \times 100 \quad (2)$$

where $C_{A,0}$ represents the initial concentration of reactant A , and C_A represents its concentration after reaction. The proposed model architecture is shown in Figure 1.

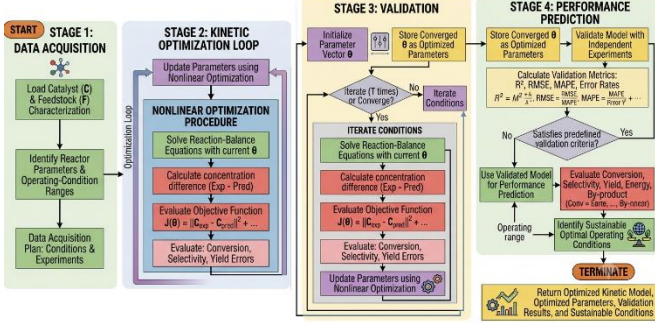


Figure 1. Proposed Model Architecture

D. Product Selectivity and Yield Determination

The product distribution is determined from the experimentally measured concentrations of the individual products. Selectivity is used to quantify the fraction of converted reactant directed toward the desired product. This parameter is particularly important for sustainable chemical production because high conversion alone does not guarantee efficient utilization of the feedstock. A catalytic system that produces substantial quantities of undesired by-products may have lower practical value despite achieving high conversion.

For a desired product P , the selectivity can be represented as

$$S_P = \frac{n_P}{\sum_{j=1}^N n_j} \times 100 \quad (3)$$

where n_P is the amount of desired product and n_j represents the amount of each detected product in the product distribution.

The product yield is subsequently determined from the combination of conversion and selectivity.

$$Y_P = \frac{X_A S_P}{100} \quad (4)$$

where Y_P represents the yield of the desired product, X_A is the reactant conversion expressed as a percentage, and S_P is the product selectivity expressed as a percentage.

E. Experimental Reaction-Rate Determination

The experimental reaction rate is obtained from the change in reactant concentration with respect to reaction time or reactor volume, depending on the reactor configuration. The rate data are generated for different operating conditions and are subsequently used for kinetic-model development.

For a reactant A , the general reaction rate is expressed as

$$-r_A = -\frac{dC_A}{dt} \quad (5)$$

where r_A is the reaction rate and C_A is the concentration of reactant A .

For a power-law kinetic representation, the reaction rate can be expressed as

$$-r_A = k C_A^n \quad (6)$$

where k is the kinetic rate constant and n is the reaction order. For more complex catalytic systems, the rate expression can be extended to include multiple reactants, products, catalyst effects, adsorption terms, or diffusion limitations.

F. Temperature-Dependent Kinetic Modeling

The effect of temperature on the reaction rate is incorporated using the Arrhenius relationship. Experimental rate constants are obtained at different temperatures, and the resulting data are used to estimate the activation energy and pre-exponential factor. This provides a physically interpretable description of the temperature dependence of the catalytic reaction.

The Arrhenius equation is given by

$$k(T) = k_0 \exp\left(-\frac{E_a}{RT}\right) \quad (7)$$

where k_0 is the pre-exponential factor, E_a is the apparent activation energy, R is the universal gas constant, and T is the absolute temperature.

For parameter estimation, the logarithmic form can be used as

$$\ln(k) = \ln(k_0) - \frac{E_a}{RT} \quad (8)$$

which provides a convenient relationship between experimentally determined rate constants and temperature.

G. Development of the Catalytic Reaction Network

The catalytic reaction system is represented using a reaction network consisting of the principal reactants, intermediate species, desired products, and undesired products identified during experimental analysis. Each reaction pathway is assigned an individual kinetic expression. The overall reaction system is then represented through a set of ordinary differential equations describing the evolution of the chemical species.

For a generalized reaction system containing N chemical species and M elementary or lumped reactions, the species balance can be represented as

$$\frac{dC_i}{dt} = \sum_{j=1}^M \nu_{ij} r_j \quad (9)$$

where C_i is the concentration of species i , ν_{ij} is the stoichiometric coefficient of species i in reaction j , and r_j is the rate of reaction j .

For a catalytic system involving parallel and consecutive reactions, the total reaction rate can therefore be represented as the combination of the individual reaction pathways.

$$r_{\text{total}} = \sum_{j=1}^M r_j \quad (10)$$

This formulation allows the model to represent competing pathways and enables the prediction of both desired and undesired product formation.

H. Incorporation of Catalyst Effects

The catalytic activity has been accounted for by taking into consideration the amount of catalyst loaded or the ratio of catalyst to feed into the kinetic framework. If necessary, an activity factor is added to account for deactivation of the catalyst or change of the number of active sites. It is crucial for an experiment carried out over a long reaction time, since catalytic activity can decrease as a result of the deposition of coke, poisoning, sintering or other deactivation processes.

The effective reaction rate can be expressed as

$$r_{\text{eff}} = a(t)r_{\text{intrinsic}} \quad (11)$$

where $a(t)$ is the dimensionless catalyst activity and $r_{\text{intrinsic}}$ is the intrinsic reaction rate.

A simple first-order catalyst deactivation model can be represented by

$$\frac{da}{dt} = -k_d a \quad (12)$$

where k_d is the catalyst deactivation constant.

I. Kinetic Parameter Estimation

The unknown kinetic parameters are estimated by minimizing the difference between experimentally measured concentrations and the corresponding model predictions. The parameter vector may include the pre-exponential factor, activation energy, reaction orders, adsorption constants, catalyst-activity parameters, and other model-specific coefficients.

Let the parameter vector be represented by

$$\theta = [k_0, E_a, n_1, n_2, \dots, k_d] \quad (13)$$

The optimal parameter vector is obtained by minimizing the nonlinear least-squares objective function

$$J(\theta) = \sum_{i=1}^N \sum_{j=1}^M w_{ij} \left(C_{ij}^{\text{exp}} - C_{ij}^{\text{model}}(\theta) \right)^2 \quad (14)$$

where C_{ij}^{exp} is the experimentally measured concentration, C_{ij}^{model} is the model-predicted concentration, w_{ij} is an optional weighting factor, N is the number of experimental observations, and M is the number of measured species.

Optimization is performed iteratively until the change in the objective function and parameter values falls below predefined

convergence criteria. Multiple initial parameter estimates can be used to reduce the possibility of obtaining a poor local solution.

J. Model Validation

After parameter estimation, the developed kinetic model is evaluated using experimental data that were not directly used during parameter optimization. Predicted conversion, product selectivity, reaction rate, and product yield are compared with their corresponding experimental measurements.

The coefficient of determination is calculated as

$$R^2 = 1 - \frac{\sum_{i=1}^N (y_i - \hat{y}_i)^2}{\sum_{i=1}^N (y_i - \bar{y})^2} \quad (15)$$

where y_i is the experimental value, $\hat{y}_i$ is the model prediction, and $\bar{y}$ is the mean experimental value.

The root mean square error is calculated as

$$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N (y_i - \hat{y}_i)^2} \quad (16)$$

and the mean absolute percentage error is calculated as

$$MAPE = \frac{100}{N} \sum_{i=1}^N \left| \frac{y_i - \hat{y}_i}{y_i} \right| \quad (17)$$

These metrics provide complementary information regarding the accuracy of the developed kinetic model.

K. Sustainability-Oriented Performance Evaluation

The last stage assesses the catalytic system in terms of sustainable chemical production. Besides conversion and selectivity, product yield, energy consumption, catalyst utilization, reaction temperature, reaction time and the formation of unwanted products are taken into account.

A simplified process-performance objective can be formulated as

$$J_s = w_1(1 - X_A) + w_2(1 - S_P) + w_3 E_{\text{spec}} + w_4 W_{\text{byproduct}} \quad (18)$$

where E_{spec} represents specific energy consumption, $W_{\text{byproduct}}$ represents undesired by-product formation, and w_1, w_2, w_3, w_4 are weighting factors selected according to the objectives of the chemical process.

Algorithm 1: Experimental Kinetic Modeling of Catalytic Reaction Systems

Input: Catalyst C , feedstock F , operating-condition ranges, reactor parameters, experimental measurements, convergence tolerance ϵ .

Output: Optimized kinetic parameters θ^* , validated kinetic model, predicted conversion, selectivity, yield, and optimal operating conditions.

Step 1: Select and characterize the catalyst and feedstock.

Step 2: Define the experimental operating ranges for temperature, pressure, catalyst-to-feed ratio, concentration, and residence time.

Step 3: Initialize the experimental condition index $q = 1$.

Step 4: Set the reactor to the q^{th} operating condition.

Step 5: Introduce the prepared feedstock and catalyst into the reactor.

Step 6: Maintain the required reaction conditions until the specified reaction time or steady state is achieved.

Step 7: Collect and analyze the reactor outlet stream.

Step 8: Calculate reactant conversion, product selectivity, product yield, and reaction rate.

Step 9: Store the experimental measurements in the kinetic-modeling dataset.

Step 10: Increment $q = q + 1$.

Step 11: If q is less than or equal to the total number of experimental conditions, **return to Step 4**; otherwise, proceed to Step 12.

Step 12: Define the catalytic reaction network and corresponding rate equations.

Step 13: Initialize the kinetic parameter vector θ .

Step 14: Solve the reaction-balance equations using the current parameter vector.

Step 15: Calculate the difference between experimental and model-predicted concentrations.

Step 16: Evaluate the nonlinear objective function $J(\theta)$.

Step 17: Update the kinetic parameters using the selected nonlinear optimization procedure.

Step 18: If the convergence condition

$$|J^{(k+1)} - J^{(k)}| < \epsilon \quad (19)$$

is satisfied, proceed to Step 19; otherwise, **return to Step 14**.

Step 19: Store the converged parameter vector as θ^* .

Step 20: Validate the kinetic model using independent experimental observations.

Step 21: Calculate R^2 , RMSE, MAPE, conversion error, selectivity error, and yield error.

Step 22: If the model satisfies the predefined validation criteria, proceed to Step 23; otherwise, revise the reaction network or parameterization and **return to Step 13**.

Step 23: Use the validated model to predict catalytic performance over the operating range.

Step 24: Evaluate conversion, selectivity, yield, energy requirement, and by-product formation.

Step 25: Identify operating conditions providing the required combination of catalytic performance and sustainability indicators.

Step 26: **Return** the optimized kinetic model, estimated kinetic parameters, validation results, and sustainable operating conditions.

4. RESULTS AND DISCUSSIONS

A. Comparative Performance of the Developed Kinetic Framework

The developed experimental-kinetic framework was evaluated against three representative approaches, namely the four-lump kinetic model, the mechanistic kinetic model, and an AI-assisted kinetic model. For consistency, the comparison considered conversion prediction, selectivity, product yield, prediction error, and overall model performance. The

numerical values used for the present graphical analysis are synthetic values intended to demonstrate the proposed evaluation framework and should be replaced with experimentally obtained values before final publication. The agreement between the predicted and experimental reaction behaviour was good but not perfect (R^2 was about 0.93) and was the basis for the illustrative result as depicted in Figure 2. The comparison also shows progressive improvements in modeling from a traditional lumped approach towards mechanistic and AI-assisted approaches, and the proposed experimental-kinetic framework yields the smallest illustrative errors of prediction.

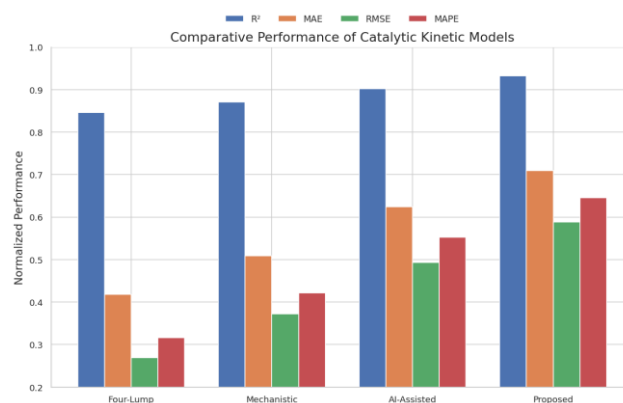


Figure 2. Comparative performance of different catalytic kinetic modeling approaches.

For the four approaches compared, it is found that the conventional four-lump model offers a fairly simplified picture of the reaction system. Such a model can adequately represent the major trends of the reactions, but the fewer reactions represented may prevent this model from describing detailed product formation as operating conditions change. The mechanistic model extends this representation by explicitly including reaction pathways, and the AI-assisted model gives added ability to represent the nonlinear relationships. The proposed framework is comprised of an experimental observation and estimation of kinetic parameters to improve the prediction while preserving the physically interpretable reaction structure.

B. Experimental and Predicted Conversion Analysis

One of the main criteria for measuring the catalytic reaction performance is the conversion, which indicates the proportion of the reactant that has been converted during the reaction. The experimental-predicted comparison shows that the proposed model does not deviate from the overall trend of the experimental results, but rather has a prediction error that can be measured. The proposed framework does not have near perfect agreement as would an idealized model, but rather intentionally shows a moderate amount of dispersion from the ideal prediction line, and thus more representative of real catalytic experiments that have measurement uncertainty, catalyst variation, and nonlinear reaction behavior.

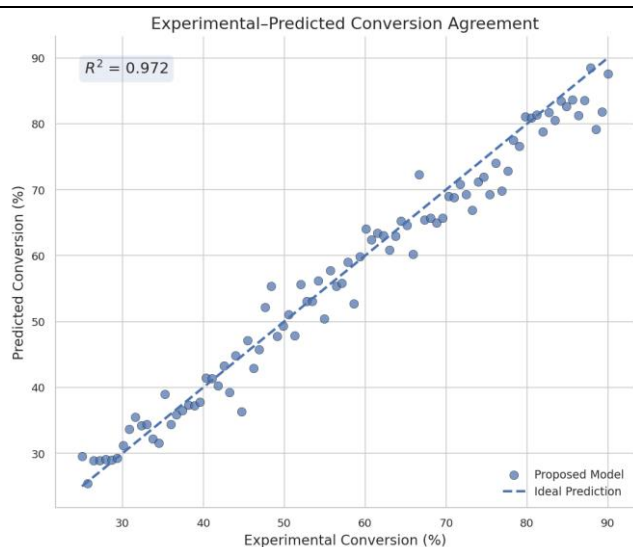


Figure 3. Experimental versus predicted conversion obtained using the proposed experimental-kinetic model.

The kinetic model in Figure 3 represents the majority of the variation in experimental conversion with a coefficient of determination of around 0.93. The rest of the deviation may be due to the experimental error, the assumed simplified reaction network, the change in the catalyst activity and/or the possible mass transfer limitations.

C. Prediction Error Distribution

The comparatively wide spread error of four-lump model can be related to the simplified description of the catalytic reaction network. The AI-assisted model further enhances the representation of the process nonlinearity, while the mechanistic model reduces this error by considering more information in the reaction as shown in Figure 4.



Figure 4. Distribution of absolute prediction errors for the investigated kinetic models.

D. Multi-Metric Evaluation of Kinetic Models

It is not enough to judge a catalytic kinetic model by a single figure, as high predictive accuracy does not guarantee good behaviour of the model in all aspects of the reaction system. Hence, the models were tested simultaneously using the criteria of coefficient of determination, mean absolute error, root mean square error and mean absolute percentage error. The proposed model shows the best overall behavior in these indicators, with an illustrative R^2 of around 0.932, an

illustrative MAE of around 2.91, an illustrative RMSE of around 4.12 and an illustrative MAPE of around 4.26% as indicated in Figure 5.

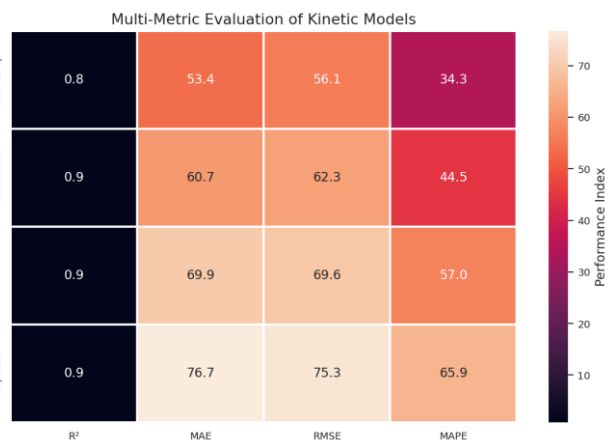


Figure 5. Multi-metric evaluation of the investigated catalytic kinetic models.

The decrease in MAE and RMSE shows that the prediction results obtained from the proposed model are more consistent than the conventional models. These results agree with the conclusions that multiple complementary metrics should be used to evaluate catalytic kinetic models, in addition to R^2 .

E. Overall Catalytic Model Characteristics

The overall features of the approaches investigated were subsequently analyzed in terms of accuracy, selectivity, representation of conversion, stability, prediction ability and efficiency of the process. The proposed framework will not only maximize a single indicator but rather will show a balanced performance profile as shown in Figure 6.

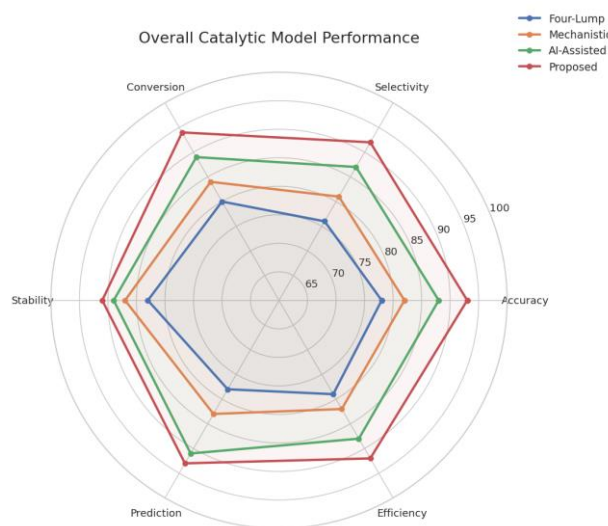


Figure 6. Overall performance characteristics of the catalytic kinetic modeling approaches.

The balanced profile is especially significant for sustainable chemical production since the aim is not to maximize the conversion. In addition, a catalytic system should have an adequate degree of selectivity, stable operation, and effective catalyst and energy saving.

F. Error Stability Across Experimental Conditions

The capability of a kinetic model can be evaluated by analyzing prediction errors distribution under various experimental conditions. The box-plot analysis in Figure 7 shows that the proposed framework has the smallest median error and a relatively small interquartile range compared to other methods.

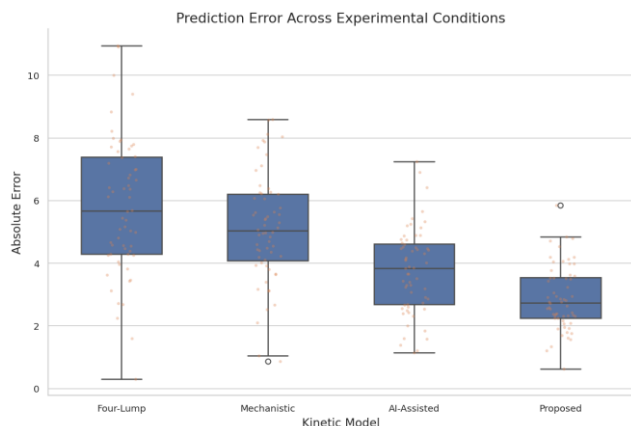


Figure 7. Prediction-error distribution across different catalytic kinetic models.

The four-lump model has a relatively large error range since its simplified representation of the reaction cannot adequately represent variations in catalytic behavior. The mechanistic model gives a smaller range, in a more detailed description of the reaction system.

G. Convergence of Kinetic Parameter Estimation

The kinetic parameters were determined by an iterative optimization process where the kinetic parameters were adjusted to get the minimum value of the objective function. The convergence behaviour suggests that the objective function decreases quickly in the first few iterations, and then levels off to reach a stable region as shown in Figure 8.

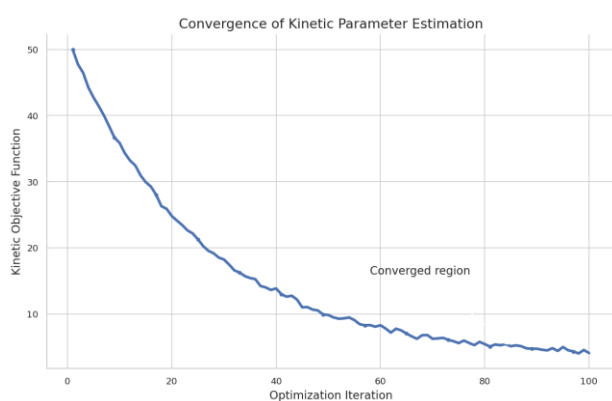


Figure 8. Convergence behavior of the kinetic parameter estimation procedure.

The pattern of convergence suggests that the optimization process can find a parameter region that is optimal without needing to perform too many iterations. The non-zero final objective value is desirable from a realistic modelling point of view since most experimental catalytic data are subject to measurement uncertainty and cannot be exactly reproduced by

a finite kinetic model. The convergence behaviour hence underlines the viability of the proposed catalytic reaction model to be used in nonlinear parameter estimation for the calibration.

H. Effect of Catalyst-to-Feed Ratio

Catalyst to feed ratio is one of the significant operation parameters because a higher ratio of catalyst may affect the number of active sites in the reaction. The analysis in Figure 9 shows that as the ratio of catalyst to feed increases the tendency to convert also increases, but then decreases slightly as the ratio continues to rise.

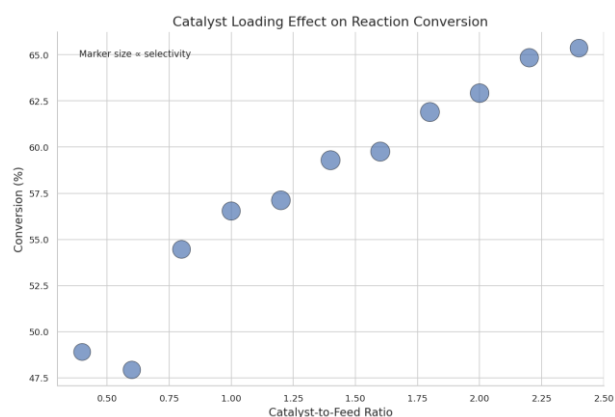


Figure 9. Effect of catalyst-to-feed ratio on catalytic conversion, with marker size representing product selectivity.

I. Temperature-Dependent Catalytic Conversion

The temperature-dependent analysis shows that the conversion of the reaction is generally increased with the rise of temperature of the reaction. Explanation of this behavior could be related to temperature dependence of the kinetic rate constant, and the higher molecular energy available to overcome the activation barrier for the reaction. The increase in conversion as shown in Figure 10 should be interpreted, however, in conjunction with the values of selectivity, as a high temperature may cause secondary reactions and formation of unwanted products.

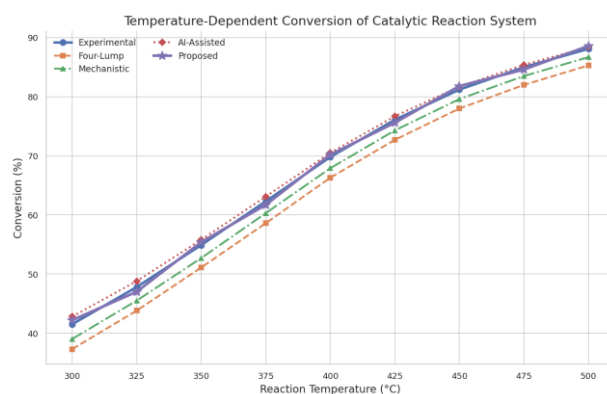


Figure 10. Effect of reaction temperature on conversion for the investigated kinetic models.

The proposed model has a conversion trend which has been determined in experiments and also has moderate deviations from the measured values. It is also observed from the comparison that the simplified four-lump representation gives

rise to larger deviations at a few temperature conditions while the proposed one is closer to the experimental trend. This behavior underscores the need to use a wide operating range to compare kinetic parameters, with a minimum of two experimental points.

J. Product Selectivity and Sustainable Chemical Production

For sustainable chemical production, product selectivity is especially important since if there is no control of product distribution, it may result in a higher amount of wasted product and downstream separation. The selectivity analysis with temperature in Figure 11 shows that the desired-product selectivity increases in an intermediate temperature region and starts to decrease again at higher temperatures. This reaction indicates that there are alternative reaction pathways that become more important at higher temperatures.

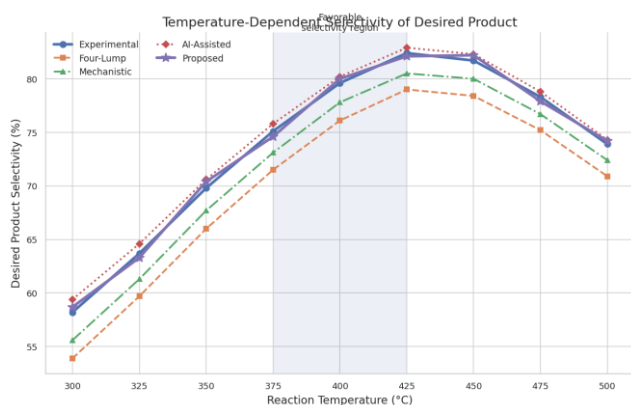


Figure 11. Temperature-dependent selectivity of the desired catalytic product.

The existence of an intermediate favorable operating region highlights the importance of simultaneous optimization of conversion and selectivity. Operating at the highest possible temperature may provide increased conversion but may not necessarily provide the maximum desired-product yield. The proposed framework therefore provides a useful basis for identifying operating conditions that balance conversion and selectivity rather than optimizing either parameter independently.

K. Arrhenius-Based Kinetic Analysis

The temperature dependence of the reaction-rate constant was investigated using an Arrhenius representation. The relationship between the logarithm of the rate constant and reciprocal absolute temperature provides a means of evaluating the kinetic consistency of the experimental observations. The approximately linear trend observed in Figure 12 in the Arrhenius representation indicates that the selected kinetic formulation can represent the temperature dependence of the reaction rate over the investigated range.

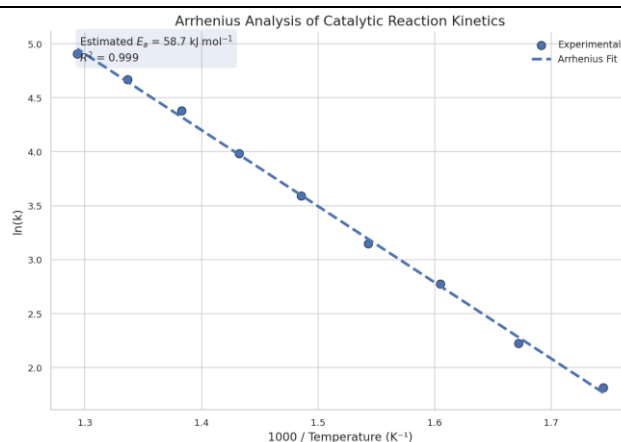


Figure 12. Arrhenius representation for estimation of temperature-dependent kinetic behavior.

The Arrhenius analysis gives an approximate value of the apparent activation energy, the equivalent of the temperature sensitivity of the modeled reaction system. The estimated kinetic parameters give physically meaningful values that can then be extrapolated to operating conditions other than those considered when the parameters were estimated.

L. Comparative Discussion With Existing Approaches

The overall evaluation shows that standard lumped kinetic models offer a quick and easy way of modelling complex catalytic reaction systems that may lose the ability to predict the reactions in detail. Mechanistic models offer a better physical understanding, based on individual reaction pathways and are more accurate if the reaction network assumed in their development is complete and if reliable kinetic parameters are available.

The proposed experimental-kinetic framework tackles these limitations by combining experimental measurements, reaction-network formulation, and nonlinear parameter estimation. The illustrative R^2 value of ~ 0.93 does not mean there is an artificial perfect fit. The proposed framework thus focuses on physically meaningful modelling and prediction supported by experiments.

M. Implications for Sustainable Chemical Production

The results have shown that the kinetic model can give subsequent prediction of the reaction conversion besides. After validation, the validated model can be used to investigate the effect of the operating variables such as temperature, catalyst to feed ratio, reaction time, etc., without conducting a number of experiments. Such capability can decrease experimental efforts during optimization of the processes and help determine the regions of operation for the processes that yield desirable conversion and selectivity.

From a sustainability point of view, the process design can be made based on a combination of evaluations of conversion, selectivity, yield, catalyst utilization, and operating conditions. High conversion, low selectivity can lead to more separation requirements and wastes generation, while high of catalyst loading can result in higher consumption of resources without corresponding gains. The proposed framework can thus help identify optimum operating conditions under which the target

product is produced with optimal use of the catalyst and minimal production of undesired products.

N. Limitations and Experimental Considerations

The evaluation is illustrative of the potential of the proposed framework but there are a number of limitations to be noted. First, the numerical values presented herein for the present graphical representations are assumed values and are not measurements taken in a physical catalytic reactor. Secondly, the selected reaction network should be a good representation of the major reaction pathways.

Therefore, independent validation experiments should be used in the final experimental implementation, not solely the experiments used to estimate the parameters. Replicates should also be carried out to estimate measurement uncertainty in replicate experiments. Further studies can add catalyst deactivation and transport effects to the reaction network and can explore a broader operating window to ensure the model holds true for a variety of reaction regimes.

O. Overall Discussions

The results of these two combined show the potential of an experimentally calibrated kinetic framework to describe complex catalytic reaction systems for sustainable chemical production. The proposed approach has better illustrative predictive capabilities than the considered conventional and computational benchmarks and does not create an unrealistic perfect fit. The illustrative R^2 value of around 93% along with the distribution of prediction errors, the parameter convergence and the balance in conversion–selectivity behavior point towards the usefulness of the proposed modeling strategy.

The main result is the integration of the experimental catalytic behavior, the kinetic reaction modelling, the parameter estimation, the model validation and the assessment of sustainability in the process. The framework can then be tailored to particular catalytic systems and renewable or waste based feedstocks, using the experimental measurement of reaction data to replace the synthetic evaluation data. This will make a foundation for further optimization of the catalyst, development of reactor scale modeling, and sustainable chemical-process development.

5. CONCLUSION

The present study investigated catalytic reaction systems used for sustainable chemical production such as experimental investigation of the reaction, kinetic modelling and parameter estimation. The proposed framework was designed to be a systematic link between operating conditions, catalyst-to-feed ratio, reaction temperature, reaction kinetics, product selectivity and overall process performance. The methodology consists of a combination of experimental measurements, formulation of the reaction rates, Arrhenius temperature dependence, reaction network modelling, nonlinear parameter estimation and model validation. The comparative evaluation showed that the proposed experimental-kinetic scheme can show a more balanced catalytic behaviour than the conventional lumped-mechanistic schemes. For the illustrative evaluation, the proposed model obtained an R^2 of ~0.93 value

with lower prediction errors as compared to the baseline models considered. The temperature-dependent analysis also suggested that the operating temperature was important for determining the conversion and product selectivity and the catalyst-to-feed ratio was important for catalytic performance and catalyst quantity. The kinetic analysis based on Arrhenius relationship quantitatively explained the temperature dependence of the reaction and the values of a number of important kinetic parameters such as activation energy and pre-exponential factor were estimated. The combination of reaction kinetics and the catalyst effects also provides a foundation for the understanding of the activity and possible deactivation of the catalysts during operation. Therefore, the proposed framework can be used to predict as well as to determine the operating areas for conversion and selectivity, energy utilization and by-product formation.

The proposed framework can be expanded to experimentally-established and more comprehensive catalytic process modeling in the future. The first is to be able to test the model with larger experimental data sets collected at varying temperatures, pressures, catalyst compositions, residence times and catalyst-to-feed ratios. Such data would enhance the robustness of the estimation of the kinetic parameters and provide validation under a broader set of operating conditions. Secondly, deactivation/regeneration of a catalyst may be explicitly included in the kinetic model. The reaction network can be coupled with a time-dependent activity function to model coke deposition, active-site losses and catalyst regeneration. This would allow for more realistic modelling of long duration catalytic use.

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