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A Didactic Approach to Kinetic Parameter Estimation: A Case Study of Glycerol Carbonate Synthesis from Glycerol and Dimethyl Carbonate

Juan Carlos Ojeda-Toroa\*, Javier A. Mancera-Apolinarb, Jaime Eduardo Arturo-Calvacheb

aGrupo de Investigación en Procesos Reactivos Intensificados con Separación y Materiales Avanzados - PRISMA, Departamento de Física y Química, Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Colombia, Sede Manizales, Campus La Nubia, km 9 vía al Aeropuerto la Nubia, Apartado Aéreo 127, Manizales, Caldas, Colombia.

bGrupo de Procesos Sostenibles, Department of Chemical and Environmental Engineering, Faculty of Engineering, Universidad de América, Avda. Circunvalar No. 20-53, Bogotá, Colombia.

\*Corresponding author: juan.ojedaca@unipamplona.edu.co, tel.: (+57) 3148267334

This study introduces a didactic methodology for estimating kinetic parameters, it was designed as a practical guide for chemical engineering students, focusing on the synthesis of glycerol carbonate (GC) from glycerol (G) and dimethyl carbonate (DMC) as a case study. Notably, the kinetics of this reaction had not been previously adjusted in the literature, offering a novel opportunity to explore and model its behavior. Experimental datasets from two distinct cases, using CaO and carbide slag as heterogeneous catalysts under different reaction conditions were analyzed. Both elementary and non-elementary rate laws were applied within a pseudo-homogeneous model framework, with kinetic parameters determined by minimizing the discrepancy between experimental and calculated glycerol conversion values using MATLAB®. Results demonstrate that non-elementary rate laws provide a superior fit to experimental data (average relative deviation-ARD: Case 1-1.26% and Case 2-2.33%) compared to elementary rate laws (ARD: Case 1-2.75% and Case 2-6.06%), underscoring the importance of accounting for reaction complexities in kinetic modelling. This methodology serves as a step-by-step educational tool, enhancing students’ understanding of parameter estimation, model validation, and reaction optimization while showcasing the integration of theoretical and computational tools in addressing real chemical engineering issues.

* 1. Introduction

Glycerol carbonate (GC) is a versatile compound with diverse industrial applications due to its low toxicity, biodegradability, nonflammability, water solubility, and high boiling point. It is used in additives, semiconductors, surfactants, cosmetics, pharmaceuticals, and polymers. In polymer synthesis, GC acts as a monomer for polycarbonates and polyurethanes, promoting sustainable materials development materials (Assumpção et al. 2018; Kojčinović, Likozar, and Grilc 2022). The increasing demand for GC has driven research into efficient production methods, including the transesterification of glycerol (a biodiesel byproduct) with dimethyl carbonate (DMC) (MMR 2024). Biodiesel production generates glycerol in significant quantities (10% wt. per ton), creating a surplus that has lowered its commercial value and highlighted the need for valorization strategies (Lukato et al. 2021).The transesterification process offers a sustainable alternative to traditional GC synthesis, often catalyzed by heterogeneous materials like CaO, K₂CO₃, and zeolites (Hejna et al. 2016; Lu, Wang, and Hu 2013). Understanding the kinetics of this reaction is essential for design, optimization and scale-up of the GC production process (Fogler 2022). Accurate kinetic parameter estimation enables predictive the reactive system’s behavior and effects of operating parameters. However, many kinetic studies lack transparency and educational accessibility, often omitting step-by-step derivations, parameter estimation procedures, or clear computational implementation—barriers for students with limited coding experience. This study addresses that gap by proposing a didactic methodology for kinetic parameter estimation, tailored to chemical engineering education. Using the glycerol–DMC transesterification as a case study, experimental data from two heterogeneous catalysts (CaO and carbide slag) under varying conditions were analyzed (Ochoa-Gómez et al. 2009; Wang et al. 2021), Both elementary and non-elementary rate laws were applied within a pseudo-homogeneous model, and kinetic parameters were estimated by minimizing the error between experimental and calculated conversions using MATLAB®. The methodology provides students with practical tools to connect theoretical kinetics with computational modeling, preparing them for real-world challenges. Additionally, it highlights the importance of integrating kinetic analysis with computational tools for efficient process design.

* 1. Synthesis of glycerol carbonate from glycerol and dimethyl carbonate

The simultaneous synthesis of glycerol carbonate (GC) and methanol (M) from glycerol (G) and dimethyl carbonate (DMC) is carried out via a heterogeneous liquid-phase chemical reaction using CaO as a catalyst: C3H8O3 + C3H6O3 ↔ C4H6O4 + 2CH4O (G + DMC ↔ GC + 2M). Langmuir-Hinshelwood (LH) reaction mechanisms for this system have been proposed by (Ochoa-Gómez et al. 2009; Praikaew et al. 2022). When a reaction rate equation is derived from Ochoa-Gómez's et al. (2009) mechanism using Fogler’s rate-controlling step approach, the resulting expression closely resembles a power-law rate equation. Consequently, both elementary and non-elementary power-law rate equations for the general reaction were considered in this study. Due to the unavailability of experimental data, phenomena such as mass transfer limitations, catalyst deactivation, and effectiveness factor were not accounted for. Instead, a pseudo-homogeneous model was applied to two experimental data sets: the first one (Case 1), glycerol carbonate synthesis based on Ochoa-Gómez’s approach (Ochoa-Gómez et al. 2009), using an isothermal batch reactor and uncalcined CaO as the catalyst; and the second one (Case 2), glycerol carbonate synthesis based on Wang’s approach (Wang et al. 2021), using an isothermal batch reactor and a carbide slag catalyst composed of Ca(OH)₂, CaCO₃, and minor components (MgO, SiO₂, Al₂O₃, Fe₂O₃) impregnated and calcined with Na₂CO₃. The experimental conditions and methodologies are detailed in the respective references.

* 1. Mathematical modeling of the kinetics of glycerol carbonate synthesis

The molar balance of the batch reactor for the first case can adopt the following form:

|  |  |
| --- | --- |
|  | (1) |

Where xG represents glycerol conversion,  (mol/(g∙min)) is the reaction rate of glycerol, W is the catalyst mass (g), NA0 is the initial mols of glycerol (mol), t is time (min). In turn, the catalyst mass can be calculated by , where Ncat represents the catalyst mols and MWcat is its molecular weight. Then, equation 1 can become in,

|  |  |
| --- | --- |
|  | (2) |

At this last expression, molar catalyst-glycerol ratio can be defined as . Thus, the final molar balance adopts the following way:

|  |  |
| --- | --- |
|  | (3) |

The experimental conditions for both cases are described in the Table 1, except that case two directly takes the form of expression 1.

Table 1: General experimental conditions for cases 1 (Ochoa-Gómez et al. 2009) and 2 (Wang et al. 2021)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Symbol | Variable | Value – Case 1 | Value – Case 2 | Units |
| NG0 | Initial mols of glycerol | 0.217 | 0.03 | mol |
| VR | Reactive mixture volume | 0.25 | 0.1 | L |
| NDMC0 | Initial mols of DMC | 1.5191 | 0.15 | mol |
| CGR | Molar catalyst-glycerol ratio | 0.12 | --- | --- |
| T0 | Initial temperature of reactive mixture | 363.15 | 348.15 | K |
| t | Reaction time | 90 | 90 | min |

According to the stoichiometric of the general reaction, the elementary kinetic law can be written as , where k and krev are the rate constants of the direct and reverse direction (which follows the Arrhenius’s law: and  Where R is the universal gas constant (kJ/(mol∙K) for first case and J/(mol∙K) for second case), T is the absolute temperature (K), A and Arev are the pre-exponential factors or frequency factors and Ea and  are the activation energies for the direct and reverse reactions, respectively), respectively, and Ci is the concentration of specie i (mol/L). Meanwhile, the non-elementary kinetic equation can be expressed as , where the superscripts of concentration variable are the reaction order for each species. The concentration of all species can be expressed in terms of glycerol conversion as follows: , ,  and . All these expressions consider the chemical reaction stoichiometric and its phase, initial concentrations of the reactive species (there are only reactants and no products) and the mode of the reactor operation (batch).

In general, both cases present experimental data of glycerol conversion versus time or versus other independent variable (such as molar ratio of dimethyl carbonate to glycerol (ΘDMC) or temperature) at specific conditions. Then the main objective is to identify the kinetic reaction parameters that minimize the discrepancy between the conversion values calculated using the reactor model (*e.g.,* equations (1) or (3) ) and their experimental values. Thus, expression (4) is proposed as an objective function and it can be minimized by using the Nelder–Mead simplex method available in the *fminsearch* command of the MATLAB® software.

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| --- | --- |
|  | (4) |

Now according to the previous information, algorithm of non-elementary kinetic adjustment for the first case is built as shown at the Figure 1 (elementary kinetic adjustment can be done with an analogous algorithm).

A diagram of a flowchart

Description automatically generated

Figure 1: Algorithm for non-linear mathematical adjustment of non-elementary kinetic parameters of glycerol carbonate synthesis by Ochoa-Gómez’s approach (Case 1)

The mathematical routine is initiated by defining essential constant values, such as experimental time (texp) and glycerol conversion (), actual iteration (i) and maximum number of iterations (imax) (they are established by default as i = 1 and imax = 200×number of unknown parameters in the *fminsearch* command). Initial estimates for parameters A, Ea, α, β, Arev, , γ, and δ are assigned. In general, the reaction orders (α, β, γ, and δ) have values between 0 and 3. Meanwhile, frequency factors (A and Arev) and activation energies (Ea and ) can take different real positive values. Subsequently, a minimization process by using the Nelder–Mead simplex approach is initiated to reduce the value of the objective function (4). Where the rate constants (k and krev) are computed utilizing the initial parameter estimates and Arrhenius equation. The system of differential equations or the single differential equation for this case, represented by (3), is solved through the application of the fourth-order Runge-Kutta (RK4) method (this is available in the ODEs of MATLAB® *e.g.*, ode45). It is important to remind that this equation describes the dynamic evolution of the glycerol carbonate synthesis chemical reaction. The calculated values resulting from the differential equation solution are employed in the computation of the objective function (FOBJ) using equation (4). If convergence is not achieved within the prescribed iteration limit, as defined by parameter imax, the process is returned to the initial estimates step following an increment in parameter i. Upon attainment of convergence, statistical analysis is performed on the acquired results. At this work, the average relative deviation (ARD [%]) of experimental data and simulations for both cases can be computed by . If this does not satisfy the goodness-of-fit requirements in the mathematical adjustment (*e.g.*, ARD ≤ 5%), the latest solutions from the minimization can be taken, the maximum number of objective function evaluations can be increased using the optimset command (which is added to the *fminsearch* command), and the numerical routine can be restarted. Finally, the process is concluded. Algorithms of non-elementary and elementary kinetic adjustments for the second case are similar to the previous one. Only the differential equation (1) is solved under its respective experimental conditions of time (texp), dimethyl carbonate feed ratio or initial molar ratio of dimethyl carbonate to glycerol (ΘDMC) and reacting temperature (T).

* 1. Results and Analysis

The following results can be obtained applying the previous mathematical modeling strategy. Figures 2a and 2b illustrate the experimental data and the model predictions for glycerol conversion as a function of time for both Case 1 (at fixed molar ratio of catalyst to glycerol of , molar ratio of dimethyl carbonate to glycerol of  and two different temperatures 363.15 K and 348.15 K) (Ochoa-Gómez et al. 2009) and Case 2 (at 3%wt of catalyst dosage from the reaction mixture, molar ratio of dimethyl carbonate to glycerol of  and a single temperature of 348.15 K) (Wang et al. 2021), respectively. In both cases, the glycerol conversion increases with time, as expected for a batch reactor. The non-elementary rate law consistently provides a closer fit to the experimental data than the elementary rate law, particularly at higher conversions. This suggests that the reaction mechanism is more complex than a simple elementary step and that the non-elementary rate law better captures the underlying kinetics. It is well-known that an elementary rate law assumes that the reaction occurs in a single step, with the rate being proportional to the concentrations of the reactants raised to their stoichiometric coefficients. However, the transesterification reaction between glycerol and DMC involves multiple steps as previously Ochoa-Gómez et al. (2009) and Praikaew et al. (2022) suggested, including adsorption of reactants onto the catalyst surface, surface reaction, and desorption of products. The non-elementary rate law, which allows for fractional reaction orders, can better account for these complexities.

A comparative analysis of Case 1 and Case 2 at identical reaction conditions (348.15 K and 90 minutes of reacting time) reveals superior performance of the carbide slag catalyst (Case 2) in terms of glycerol conversion () compared to the CaO catalyst (Case 1) with . Despite a higher DMC excess in Case 1 () relative to Case 2 (), a direct comparison of catalyst efficiency is hindered by the disparate catalyst quantities employed. Case 1 utilized a catalyst-to-glycerol molar ratio of , equivalent to 0.93 wt%, whereas Case 2 employed a 3 wt% catalyst dosage. It is important to highlight that a more extensive experimental dataset was available for Case 2, enabling a comprehensive parameter kinetics correlation encompassing the data presented in Figures 2b-d. In contrast, Case 1 suffered from insufficient experimental data on dimethyl carbonate feed ratio and catalyst loading, precluding a thorough investigation of their impact on reactive system performance. While Ochoa-Gómez et al. (2009) suggested potential mass transfer limitations within the reactive system for Case 1, this phenomenon was not considered in the present study, which focused only on the influence of temperature variation as depicted in Figure 2.

On the other hand, Figure 2c illustrates the influence of the dimethyl carbonate to glycerol molar ratio (ΘDMC) on glycerol conversion within Case 2. A positive correlation between ΘDMC and glycerol conversion is observed, suggesting that an elevated DMC concentration promotes the reaction. This observation aligns with Le Chatelier's principle, which predicts a product-favored equilibrium shift in response to increased reactant concentration. While the elementary rate law-based model exhibits a qualitative agreement with this trend, the quantitative accuracy is limited. Conversely, the non-elementary rate law demonstrates superior predictive capabilities, thus reinforcing the validity of the kinetic model. In addition, Figure 2d illustrates the impact of temperature on glycerol conversion for Case 2, where the catalyst dosage is 3 wt% of the reaction mixture, and the molar ratio of dimethyl carbonate to glycerol (ΘDMC) is 5. The experimental data reveals that higher temperatures enhance reaction kinetics, which is consistent with the Arrhenius approach. Both the elementary and non-elementary rate law models capture this trend qualitatively. However, the non-elementary rate law model demonstrates superior quantitative accuracy, particularly at elevated temperatures, thereby reinforcing the robustness of the kinetic model.

Table 3 presents the ARD values for both Case 1 and Case 2, comparing the experimental data with the simulation results obtained from elementary and non-elementary kinetics. In both cases, the non-elementary kinetics exhibit lower ARD values, indicating a better fit to the experimental data compared to the elementary one. This suggests that the non-elementary rate law, which accounts for the complexities of the reaction mechanism, provides a more accurate representation of the reaction kinetics.

|  |  |
| --- | --- |
| (a) | (b) |
| (c) | (d) |

Figure 2: Experimental data and mathematical modeling of the kinetic parameter adjustment for the synthesis of glycerol carbonate from glycerol and dimethyl carbonate (elementary and non-elementary reaction rate law). Case 1 (a) at 363.15 K and 348.15 K, for all cases,  and  (Ochoa-Gómez et al. 2009); Case 2 (b) at 348.15 K, 3%wt catalyst dosage and , (c) at 348.15 K, 3%wt catalyst dosage and 90 min of reaction time and (d) at , 3%wt catalyst dosage and 90 min of reaction time (Wang et al. 2021)

Table 3: ARD evaluation for elementary and non-elementary kinetics simulations

|  |  |  |
| --- | --- | --- |
| ARD (%) | Case 1 | Case 2 |
| Elementary kinetics | 2.75 | 6.06 |
| Non-elementary kinetics | 1.26 | 2.33 |

Table 4: Adjusted kinetic parameters using elementary and non-elementary rate laws for both cases

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Rate law | Parameter | Case 1 | | Case 2 | |
| Value | Units | Value | Units |
| Elementary | A | 6.5740×108 | L2/(g∙mol∙min) | 1.6774×1018 | L2/(g∙mol∙min) |
| Ea | 79.3491 | kJ/mol | 1.3007×105 | J/mol |
| Arev | 1.4387×10-3 | L3/(g∙mol2∙min) | 1.63703×10-2 | L3/(g∙mol2∙min) |
|  | 6.1011×10-14 | kJ/mol | 3.8975 | J/mol |
| Non-elementary | A | 4.4313×104 | L1.0896/(g∙mol0.0896∙min) | 2.1815×103 | L0.0163mol0.9837/(g∙min) |
| Ea | 44.1182 | kJ/mol | 4.1180×104 | J/mol |
| α | 0.3091 | --- | 1.4515×10-3 | --- |
| β | 0.7805 | --- | 1.4848×10-2 | --- |
| Arev | 4.4494×10-3 | L1.6719/(g∙mol0.6719∙min) | 2.5581 | L2.5808/(g∙mol1.5808∙min) |
|  | 5.8728×10-2 | kJ/mol | 1.2409×104 | J/mol |
| γ | 1.0537 | --- | 2.5703 | --- |
| δ | 0.6182 | --- | 1.0553×10-2 | --- |

Finally, Table 4 displays the adjusted kinetic parameters obtained using elementary and non-elementary rate laws for both cases. The parameters include the pre-exponential factors (A and Arev), activation energies (Ea and ), and reaction orders (α, β, γ and δ). The values of these parameters differ between the two cases due to the different catalysts and reaction conditions employed. The non-elementary rate law introduces additional parameters (reaction orders) to account for the non-linear dependence of the reaction rate on the concentrations of the reactants. These parameters enable a more precise description of the reaction kinetics, as evidenced by the lower ARD values in Table 3.

Conclusions

This study presented a comprehensive methodology for estimating kinetic parameters in the synthesis of glycerol carbonate (GC) through the transesterification of glycerol and dimethyl carbonate using heterogeneous catalysts under varying conditions. By analyzing two experimental datasets—one using CaO and the other carbide slag as catalysts—the results demonstrated that non-elementary kinetic models provided a consistently better fit to experimental data compared to elementary ones, capturing possible complexities of the reaction mechanism. The superior performance of the carbide slag catalyst over CaO, particularly under identical conditions, underscores the significance of catalyst selection and optimization in enhancing reaction efficiency. Additionally, the study highlighted the influence of key parameters such as temperature and the molar ratio of dimethyl carbonate to glycerol, reaffirming their critical role in determining reaction kinetics. Beyond its technical contributions, this work serves as a practical guide for chemical engineering students and researchers, bridging theoretical principles with real-world applications and emphasizing the importance of accurate kinetic models in optimizing reaction conditions and designing efficient chemical processes. As future research could explore mass transfer effects, catalyst deactivation, effectiveness factor, and broader experimental datasets to further refine kinetic models, thereby enhancing their predictive accuracy and industrial applicability. Overall, this work not only advances sustainable GC production processes but also reinforces the value of kinetic parameter estimation in both academic and industrial contexts.

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