

Differential Evolution for Optimizing Model Parameters in Simulation of Direct Dimethyl Carbonate Synthesis

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Dimethyl carbonate (DMC) is a versatile, non-toxic chemical used as a solvent, fuel additive, and reagent in pharmaceuticals and agrochemicals. While traditional production methods of DMC rely on toxic gases like chlorine and carbon monoxide, safer and environmentally friendly alternatives are explored to meet the rising demand. The direct synthesis of DMC from CO₂ and methanol provides a greener route but is hindered by CO₂'s stability and water-induced catalyst deactivation. Advances in catalysts and water removal techniques, like natural convection systems, are essential for improving efficiency. This study employs a data-driven model applying differential equations and literature data to simulate DMC synthesis. The Differential Evolution (DE) algorithm was applied to optimize parameters of the model. When validated with data of a real-world batch process, the model accurately predicted evolution of reaction composition ratios in time, offering a tool for predictive optimization. This approach could also support the design of other chemical processes, advancing sustainable production methods.

1. Introduction

Dimethyl carbonate (DMC) is a versatile, low-toxicity chemical widely used as a solvent, methylating reagent, fuel additive, and reactant in polycarbonate production, as well as in agrochemical and pharmaceutical industries. It is favoured for its rapid biodegradability, good blending octane, and compatibility with water streams. DMC also serves as an electrolyte in lithium-ion batteries (Kohli et al., 2022) and offers a non-carcinogenic alternative to dichloromethane and dimethyl sulphate in carbonylation and transesterification reactions (Wei et al., 2023).

Early synthesis methods, like phosgenation and oxidative carbonylation of methanol, relied on toxic gases like chlorine and carbon monoxide. Safer processes, such as ENiChem's catalytic oxidative carbonylation, produce fewer byproducts but cannot meet the rising demand of DMC (Pyo et al., 2017; Bunsaksit et al., 2024). Emerging methods, including the direct conversion of CO₂ with methanol and urea-based routes, show potential but face challenges like CO₂'s stability and water-induced catalyst deactivation (Song, 2006; Kohli, 2022).

Recent research focuses on novel catalysts and water management. Strategies like natural convection systems for water adsorption (Zheng et al., 2022) and kinetic studies using ceria nanorods (Marin et al., 2016) have improved yields. Fang and Cao (2000) presented a kinetic model for CO₂, CO, and methanol reactions, while Eta et al. (2011) studied reaction kinetics for DMC synthesis. Further research on separation processes (Pintero et al., 2007; Camy and Condiret, 2001; Li et al., 2009) and reaction mechanisms (Glaude et al., 2005; Tomishige and Kunimori, 2002) is essential to address the remaining challenges.

This simulation-based study models the direct synthesis of DMC from CO₂ and methanol using a data set from the literature (Camy et al., 2003). Focusing on input-output relationships rather than specific reaction mechanisms, the model employs differential equations to simulate the dynamic behaviour of system components.

The following sections outline the modelling approach and present simulation results, offering insights into process dynamics and validating the model's applicability.

2. Process description of direct DMC synthesis

This study focuses exclusively on the kinetics of direct methanol synthesis, with other reaction rates intentionally excluded to maintain this focus. A comprehensive review of DMC production, including various reaction rates and catalysts, is provided by Kohli et al. (2022).

This reaction involves the conversion of methanol and CO₂ into DMC with water as a byproduct, as shown by Eq(1). The challenges include CO₂'s high thermodynamic stability, low equilibrium constants, and catalyst deactivation due to water formation. Efficient water removal is essential to shift the reaction equilibrium toward DMC formation.



The incorporation of dehydrating agents, such as 2-cyanopyridine, has been widely explored. These agents enable in situ water removal, significantly improving DMC yields (Wang et al., 2021). Alternatively, operating under supercritical CO₂ conditions has been presented to enhance reaction rates and selectivity (Kohli et al., 2022). Catalyst development has played a pivotal role in optimizing this process. Despite advancements, the direct synthesis route remains limited by the need for high-pressure conditions and complex water management strategies. Future research focuses on coupling reactions to consume water in situ and developing highly active and selective catalysts for scalable, cost-effective production.

2.1 Catalysts

Catalysts play a critical role in addressing the challenges of direct DMC synthesis from methanol and CO₂. Among them, metal oxides such as zirconia (ZrO₂) and ceria (CeO₂) are widely used due to their bifunctionality based on their acidic and basic surface sites. However, these catalysts are highly sensitive to water deactivation, which can limit their long-term effectiveness. Akune et al. (2018) highlighted that the catalytic performance of ZrO₂ nanocrystals is strongly dependent on their surface properties, particularly the presence of bidentate carbonate and bicarbonate species, which act as key intermediates. Heteropolyacids, such as H₃PW₁₂O₄₀ supported on zirconia, offer effective bifunctional activity, while dehydrating agents like 2-cyanopyridine enhance yields by mitigating water's inhibitory effects (Wang et al., 2021).

Heterogeneous catalysts, like Cu-Ni bimetallic systems, excel at methanol activation but require precise metal dispersion to optimize their performance. Supported catalysts, such as Cu-Ni on thermally expanded graphite (TEG), have demonstrated high selectivity, achieving up to 89 % DMC yield under moderate reaction conditions (Bian et al., 2009). Ionic liquids have also been explored for their ability to stabilize reaction intermediates and enhance CO₂ solubility as presented by Zhao et al. (2017). Despite significant progress, challenges in scaling up and improving catalyst stability persist. Continued research concerning bifunctional and nanostructured catalysts is essential for advancing efficient and sustainable DMC production (Kohli et al., 2022).

3. Materials and methods

3.1 Data

The dataset used for the parameter optimization and model testing is summarized in Table 1. It includes five reaction mixtures, each with detailed input and outlet composition values. Notably, the conversion factor is 0.6 for mixtures 1–4 and 1.0 for mixture 5. The original data source for these values is referenced in Camy et al. (2003).

Table 1: The data used in optimization and simulation (Camy et al., 2003).

Mixture	Conversion	Feed mixture composition		Reacting mixture composition			
		X _{MeOH}	X _{CO2}	X _{MeOH}	X _{CO2}	X _{water}	X _{DMC}
1	0.6	0.667	0.333	0.333	0.167	0.250	0.250
2	0.6	0.500	0.500	0.236	0.412	0.176	0.176
3	0.6	0.167	0.833	0.070	0.824	0.053	0.053
4	0.6	0.091	0.909	0.037	0.907	0.028	0.028
5	1.0	0.091	0.909	0.000	0.904	0.048	0.048

3.2 Model structure and parameter identification

The initial model structure relies on kinetic equations, allowing decomposition and formation rates to differ during the simulation. This assumption is especially relevant for capturing scenarios like the decline in catalyst activity during synthesis. The corresponding kinetic equations for the model structure are detailed in Eq(2) – Eq(5).

$$\frac{dC_{CO_2}}{dt} = -k_1 C_{CO_2} \cdot C_{MeOH}^2 + k_2 C_{DMC} \cdot C_{H_2O} \quad (2)$$

$$\frac{dC_{MeOH}}{dt} = -k_3 C_{CO_2} \cdot C_{MeOH}^2 + k_4 C_{DMC} \cdot C_{H_2O} \quad (3)$$

$$\frac{dC_{H_2O}}{dt} = k_5 C_{CO_2} \cdot C_{MeOH}^2 - k_6 C_{DMC} \cdot C_{H_2O} \quad (4)$$

$$\frac{dC_{DMC}}{dt} = k_7 C_{CO_2} \cdot C_{MeOH}^2 - k_8 C_{DMC} \cdot C_{H_2O} \quad (5)$$

The pressure is assumed to remain constant, and the reaction rate constants (k) are modelled using the Arrhenius equation as:

$$k = k_0 e^{-\frac{E_A}{RT}}, \quad (6)$$

where k_0 is the pre-exponential factor, E_A is the activation energy, R is the universal gas constant, and T is the process temperature.

The sixteen free parameters in Eq(2) – Eq(5) were optimized using the Differential Evolution (DE) algorithm, a robust parallel direct search method (Storn and Price, 1997; Tiirio et al., 2025). It is inspired by biological evolution, employing processes such as mutation, crossover, and selection. During the mutation phase, new parameter vectors are generated by adding a weighted difference of two population vectors to a third vector. These mutated vectors are then combined with a predetermined target vector in the crossover phase to create a trial vector. DE operates with population size (NP) D -dimensional parameter vectors $x_i, G_i, \{i = 1, 2, \dots, NP\}$ as the population for each generation G . In the original algorithm, the population size remains constant throughout the optimization process. The initial population is generated randomly to ensure coverage of the entire parameter space. Unless otherwise specified, a uniform probability distribution is assumed for all random decisions (Storn and Price 1997). The model parameters were optimized using equilibrium data from the direct DMC synthesis (Camy et al., 2003), with the stoichiometric mixture composition (mixture 1, Table 1) serving as the training data. The remaining dataset (mixtures 2–5, Table 1) was reserved for model testing (Figure 1).

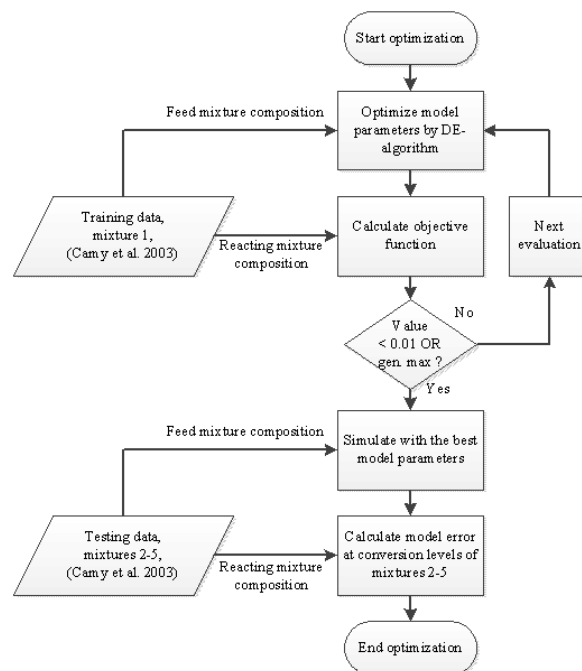


Figure 1. Parameter optimization procedure.

The objective function, Eq(7), for the DE-algorithm is here defined as the sum of the absolute relative errors for the three reacting components:

$$\min_{x \in \mathbb{R}} \left(\left| \frac{f(\mathbf{x})_{CO_2} - x_{CO_2}}{x_{CO_2}} \right| + \left| \frac{f(\mathbf{x})_{water} - x_{water}}{x_{water}} \right| + \left| \frac{f(\mathbf{x})_{DMC} - x_{DMC}}{x_{DMC}} \right| \right), \quad (7)$$

where, \mathbf{x} represents the real-valued parameter vector of the model, $f(\mathbf{x})_{(t)}$ denotes the model output for each of the three components at the methanol conversion of 0.6 based on mixture 1 after 120 minutes, and $x_{(t)}$ refers to the corresponding true values of outlet components as presented in Camy et al. (2003) at the same conversion level.

4. Results and discussion

The optimization process began with a population of 600 members, each with random values for four or sixteen model parameters. Constraints ensure that only positive values were accepted to population (Paavola, 2011). Pre-exponential factors in the Arrhenius equation were set between 0.1 and 2, and activation energies ranged from 1000 to 90,000.

A pre-simulation using the stiff solver ode23s in MATLAB® technical computing environment was conducted to identify non-converging cases, penalizing solutions with an objective function value of 10 if the summed composition exceeded 1 after 50-time steps. Converging cases were further simulated with ode45, stopping at the methanol conversion level from Camy et al. (2003). The resulting component proportions were used to calculate the objective function in Eq(7).

The DE algorithm was run with a stopping criterion of 0.01, 1000 generations, scale factor of 0.8, crossover probability of 0.8, and the strategy DE/rand-to-best/1/exp, following Paavola (2011). The best objective function value (0.0141) was reached at generation 1000, with 232,026 population members generated and mutated during the optimization.

The 16 free parameters were identified using the composition values of mixture 1 data. The reaction rate parameters (k_0) and activation energies (E_A) were consistent across the compositions. The best identified model parameters are listed in Table 2.

Table 2: The optimized parameters for the DMC-modelling with Eq(2) – Eq(5).

	Forward reaction		Reverse reaction	
	k_0	E_A	k_0	E_A
MeOH	1.6	1.1922×10^4	1.06	8.2827×10^4
CO ₂	1.54	1.4202×10^4	0.68	8.1597×10^4
Water	5.4	1.7204×10^4	2.03	1.96795×10^5
DMC	2.6	1.4643×10^4	0.62	4.5014×10^4

The model parameters ($k_1 - k_8$) were derived by applying the k_0 and E_A values from Table 2 to the Arrhenius equation as in Eq(6). The model was tested using the feed compositions of mixtures 2–5 (Table 1) to predict reacting mixture compositions. The results at the reported conversion stages are compared with equilibrium values from the literature (Camy et al., 2003) in Figure 2, where Figure 2a shows DMC values and Figure 2b depicts CO₂ values.

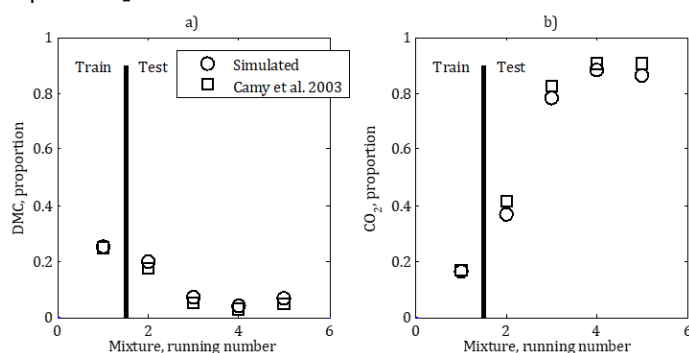


Figure 2. The simulated output data and the true values of a) DMC and b) CO₂ in the mixtures 1–5.

The dynamic behaviour of the reaction components was simulated using the stoichiometric feed composition (mixture 1). At $t=120$ minutes (conversion 0.6), the simulated reaction mixture composition matches the values in Table 1. These results are presented in Figure 3a. The developed model was further used to simulate the effect of temperature on DMC synthesis. Simulations were performed at 393.15 K, 423.15 K, and 453.15 K for a reaction time of 120 minutes, corresponding to a methanol conversion of 0.6. The results show that the

proportion of DMC in the mixture increases with temperature but plateaus at higher values. These results are shown in Figure 3b.

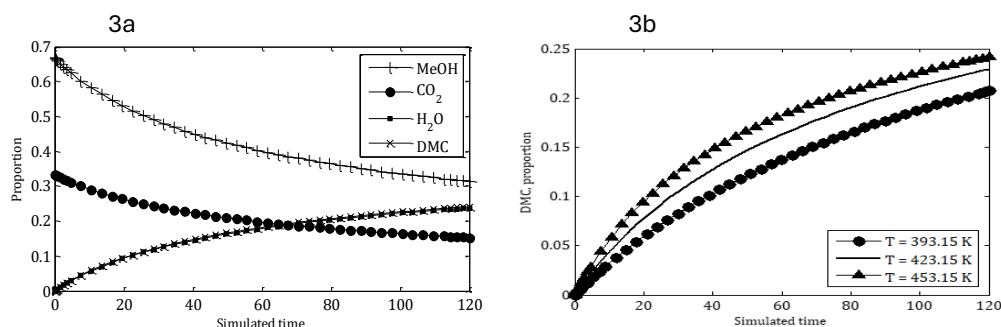


Figure 3. Simulation in time (0–120 minutes): products (3a) and the effect of process temperature (3b) on the proportion of DMC.

The DMC yield for different feed mixture compositions was simulated, with results presented in Table 3 alongside reference values from the literature and the modelling errors. For mixtures 1–4, the methanol conversion is 0.6, while for mixture 5, it is 1.0. The modelling error was calculated as the difference between the measured and simulated values of modelled variables x :

$$\chi_{\text{simulated}} - \chi_{\text{ref}} = \text{modelling error} \quad (8)$$

The modelling error is minimal for mixture 1, which was used as the training data. In mixtures 2–5, the model shows a slight positive bias for the DMC values and a negative bias for the CO₂ values.

Table 3: Proportions of DMC and CO₂ in reaction mixtures: comparison of the real measured values (ref.) to simulation results (simulated), and corresponding modelling errors.

Mixture	1	2	3	4	5
DMC, <i>ref</i>	0.250	0.176	0.053	0.028	0.048
DMC, <i>simulated</i>	0.252	0.198	0.073	0.040	0.067
Modelling error	0.002	0.022	0.020	0.012	0.019
CO ₂ , <i>ref</i>	0.167	0.412	0.824	0.907	0.904
CO ₂ , <i>simulated</i>	0.164	0.367	0.784	0.882	0.864
Modelling error	-0.003	-0.045	-0.040	-0.025	-0.040

The DMC synthesis model has been utilized in the study by Tiiri et al. (2025), where it is integrated into a model of carbon capture and utilization (CCU) process chain. In that context, the model is used to simulate DMC-subprocess performance under varying dynamic operating conditions, thus supporting system identification.

5. Conclusions

This article provides a brief overview of DMC synthesis, its background, and key research interests. A model structure for direct DMC synthesis was developed and tested with a real dataset. The model, based on differential equations representing the main reaction, was optimized using the Differential Evolution (DE) algorithm. The 16-parameter model was applied to accurately predict reacting mixture compositions, closely matching the measured values. Notably, the output of this straightforward model aligns with results from a more complex physical model structure. The dynamic model enables real-time monitoring and predictive optimization of the formation and decomposition of mixture components in direct DMC synthesis. The simulation results suggest that this data-driven modelling approach could be extended to other chemical synthesis processes, providing a versatile tool for improving process efficiency and sustainability in real-time operations.

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