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Optimal conditions for single-cycle and multi-cycle reactions based on a kinetic model

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Abstract. The study is focused on the catalytic reaction of alcohols with dimethyl carbonate. We studied optimal conditions for the reaction by multi-objective optimization based on a kinetic model. We analyzed objective functions (product yield, productivity, and profitability) for single- and multi-cycle reactions.

1. Introduction

The key goal of modeling of a chemical process is to find optimal conditions that maximize the product yield and ensure high product quality. The use of mathematical modeling markedly reduces the cost of modification of operating processes and commercialization of new processes of chemical engineering. Optimization at the theoretical level is carried out by many researchers. Most of them, however, restrict themselves to the physicochemical optimization criteria (yield, conversion, selectivity) without including the economic evaluation (cost of the reactants and products). As a consequence, the optimal reaction conditions found in this way have to be considerably corrected for actual process designs [1-3].

While choosing an optimization subject (chemical reaction), one can select various objective functions (optimization criteria) and reaction characteristics. For some reactions, conditions are to be optimized for a continuous process (optimization of a multi-cycle process). For other reactions it is necessary to perform evaluation and find extreme values of objective functions for a single cycle [4-7].

In this study, optimization was carried out for the homogeneous catalytic reaction of alcohols with dimethyl carbonate (DMC) in the presence of W(CO)₆ complex as a catalyst.

\[
\text{ROH} + (\text{MeO})_2\text{CO} \xrightarrow{\text{W(CO)₆}} \text{ROMe} + \text{ROCO}_2\text{Me} + \text{CO}_2 + \text{MeOH}
\]

ROH, ROMe, ROCO₂Me (R=C₆H₁₃) are detectable result substances. This is a new, green-chemistry reaction. Dimethyl carbonate is an efficient substitute for currently used toxic chemicals such as dimethyl sulfate and methyl halides [8, 9]. For the new catalytic reaction, the development of a
2. A kinetic model for the reaction of alcohols with dimethyl carbonate catalyzed by W(CO)$_6$ metal complex

A mathematical model for this reaction was developed as a system of ordinary differential equations (ODEs) [14-16]. The proposed reaction scheme is second order reaction was used to construct a kinetic model of the reaction. The kinetic parameters found for various reaction conditions are summarized in Table 1: $k_j$ - rate constants of steps, $E_j$ - activation energy of reactions.

| Stages                                      | $T$, °C | $E_j$   |
|---------------------------------------------|--------|--------|
| W(CO)$_6$ $\rightarrow$ W(CO)$_5^-$ + CO   | 160    | 132.80| 04    |
| W(CO)$_5^-$ + MeOCO$_2$Me $\rightarrow$ W(CO)$_2$CO$_2$Me + MeO$^-$ | 180    | 127.4±2,5 |
| W(CO)$_2$CO$_2$Me + ROH $\rightarrow$ ROMe + CO$_2$ + HW(CO)$_5^-$ | 200    | 71.6±2,1 |
| W(CO)$_2$CO$_2$Me + ROH $\rightarrow$ ROCO$_2$Me + HW(CO)$_5^-$ | 160    | 90,9±1,3 |
| HW(CO)$_5^-$ + MeO$^-$ $\rightarrow$ MeOH + W(CO)$_5^-$ | 180    | 50,7±0,04 |

Table 1. The kinetic parameters of the W(CO)$_6$-catalyzed reaction of alcohols with DMC (R=C$_6$H$_{13}$) ($[k_j]$=[L/(mol min)], $[E_j]$=[kJ/mol]).

This kinetic model can be used to solve the optimization problem for the reaction conditions. Setting up an optimization problem requires the presence of objective functions, variable parameters, and some constraints on the parameters.

3. Analysis of the objective functions for optimization of chemical reaction conditions

The variable parameters for optimization in the problems of chemical kinetics can include such parameters as temperature, type of the catalyst, concentration of the catalyst, and pressure. The experimental studies of this reaction were carried out using different initial amounts of the catalyst and temperatures [8]. Therefore we take temperature, initial amount of the catalyst, and the reaction time as variable parameters. The physico-chemical constraints on these parameters were discussed earlier [17, 18].

The general form of the objective function of optimization based on the kinetic model can be presented as:

$$ R(x, x^0, t^*, \eta, \mu, T) \rightarrow \text{max}, $$

where $x$ is the concentration vector of compounds, mol/L; $x^0$ is the vector of initial concentrations of compounds, mol/L; $\eta$ is the vector of compound weights (e.g., costs of chemicals, rubles); $\mu$ are additional expenses, rubles; $t^*$ is reaction time, min; and $T$ is temperature, °C.

The following criteria can be used to optimize the conditions for the chosen chemical reaction according Described by Equation (1).

1) Yield of the target product $x_{prod}$, which depends on the reaction time and temperature:

$$ R_1(t^*, T, x^0) = x_{prod}(t^*, T, x^0) \rightarrow \text{max}. $$

This is the primary criterion. The concentration of the target product would affect other objective functions used for the optimization (profitability, profit return).

The one-cycle scheme for the chemical reaction between DMC and alcohols (Table 1) does not take into account the subsequent decomposition of the target product. Therefore, the curve showing the product yield reaches its maximum and no longer changes (Fig. 1). For the conditions illustrated in fig. 1, the optimal reaction time in the presence of the W(CO)$_6$ catalyst is 70 min.
Figure 1. Yield of the target product ROMe for the reaction of DMC with alcohols at $T=180^\circ$C in the presence of the W(CO)$_6$ catalyst (3 mmol).

2) Productivity $B$ of the process is defined as the product yield per unit time. When the amount of the product is proportional to the reactant conversion, the productivity is defined as:

$$R_\text{i} (t^*, x^0_\text{i}, T) = B(t^*, x^0_\text{i}, T) = N(t^*) x^0_\text{i} \xi_{\text{i}X_\text{i}} (t^*, T) M_{\text{i}X_\text{i}} \rightarrow \text{max},$$

(3)

where $B$ is reaction productivity, [g/(L day)]; $N$ is the number of cycles per day [day$^{-1}$]; $\xi_{\text{iX}}$ is the reactant conversion, fraction; $M_{\text{i}X_\text{i}}$ is the reactant molar mass [g/mol], $t_\text{d}$ is the delay time between the cycles, min.

The maximum productivity does not always correspond to the maximum conversion. The maximum conversion is attained after a longer period of time, which leads to smaller $N$ (Fig. 2).

The optimal reaction time for attaining the highest productivity at $T=180^\circ$C is 90 min (for the delay time of 60 min) and 120 min (for the delay time of 300 min).

3) Profitability criterion is defined as the ratio of the sum of income to the capital investment:
Here $x_{\text{prod}}$ is the concentration of the reaction products; $x_{\text{source}}$ is the reactant concentration; $\eta$ is the vector of a specific weight of the costs of components (normalized by the sum of the component costs and expenses); $\psi$ refers to the variable expenses (normalized by the sum of the component costs and expenses); $A$ describe the constant expenses (normalized by the sum of the component costs and expenses); $P_r$ is the number of products; $S_r$ is the number of reactants.

The time variation of the profitability $P$ for this reaction is illustrated in Fig. 3.

![Figure 3. Variation of the profitability with time for the W(CO)$_6$-catalyzed reaction of DMC with alcohols](image)

The values of the profitability criterion (5) do not depend on the number of cycles. For the reaction conditions under consideration ($T=180^\circ$C), the optimal time for the maximum profitability is 90 min. This time does not depend on the number of cycles.

The times required to reach the maximum values for the chosen optimization criteria are summarized in Table 2.

| Catalyst amount of 3 mmol. $T=180^\circ$C | Per cycle | Per day (delay time 60 min.) | Per day (delay time 300 min.) |
|----------------------------------------|-----------|----------------------------|-------------------------------|
| Profitability                          | 90 min    | 90 min                     | 90 min                        |
| Productivity                           | -         | 70 min                     | 100 min                       |
| The target product yield               | 110 min   | 90 min                     | 120 min                       |

It follows from Table 2 that these criteria are mutually independent with respect to time as the control parameter. However, for catalytic reactions, the temperature and the initial amount of the catalyst are also control parameters. As shown in [19, 20] the maximum values of all criteria for the reaction of DMC with alcohols are attained at the highest temperatures, but at different reaction times and different initial catalyst amounts.

4. Multi-objective optimization of the catalytic reaction conditions

For solving the multi-objective optimization problem, methods providing the so-called bargaining solutions are used [21].
The multi-objective optimization implies that the area of solutions occur among the Pareto solutions [21]. The decision maker (DM) is interested in a compromise solution. In the case of the multi-objective optimization, the search for several Pareto-optimal solutions was made in [21-28]. In most cases, the user has the opportunity to choose the optimal solution out of this set.

The concept of Pareto-optimal solutions is presented in Fig. 4 in which crosses in the criteria space \( R \) correspond to the Pareto-optimal solutions, while the triangles correspond to non-optimal solutions.

Let \( U=(u_1, u_2, \ldots, u_{|U|}) \) be the vector of variable parameters. The set of acceptable values of \( U \) is \( D_U \). If \( R(U)=(R_1(U), R_2(U), \ldots, R_{|R|}(U)) \) is the vector of objective functions, then function \( R(U) \) maps set \( D_U \) to a certain set \( D_R \), which is the attainability domain. From set \( D_R \), it is possible to select subset \( D_R^* \) of the points that are not dominated by other points [22]. Set \( D_R^* \) is an approximation of the Pareto front. Subset \( D_U^* \subset D_U \), corresponding to set \( D_R^* \), is called the Pareto set [23].

The finite-dimensional approximation of the sets \( D_U^*, D_R^* \) in the developed information system is carried out using the genetic algorithm NSGA-II for the Pareto approximation [29, 30]. While solving the multi-objective optimization problem using the NSGA-II algorithm, each solution (point) is assigned a rank. The non-dominant points have the first rank, the points that are dominated only by first-rank points have the second rank etc. Also, the crowding of the obtained solutions is evaluated; the greater the distance between them, the higher the population diversity. In every iteration of NSGA-II, the offsprings are chosen on the basis of the solutions ranks and crowding (proximity). Then crossing and mutation of selected solutions is performed, which ensures the diversity of the next population. The parents and offsprings are combined into one population corresponding to the best solutions etc.

The NSGA-II algorithm is implemented in a variety of programming environments, including the Matlab software (MATrixLABoratory). Matlab is actively used for chemical reaction modeling and optimization. It includes extensibility packages for solving diverse problems in which mathematical calculations and modeling are required.

The «gamultiobj» function has been developed to solve multi-criteria problems in Matlab. It generates a set of Pareto-optimal solutions. The optimum is identified by using a controlled genetic algorithm (based on the NSGA-II algorithms). This is done with both solutions with a higher rank (elitism) and those improving the fitness function diversity (even if their rank is lower). Also, the distance between the solutions and the distance mapping for the Pareto boundary is used. It is possible to specify the number of populations, the number of solutions, and crossing and mutation parameters. Parallelization of calculations is possible.

The multi-objective optimization problem was solved for the reaction of dimethyl carbonate with alcohols in the presence of W(CO)\(_6\) metal complex. Two sets of pairwise independent objective
functions were used: firstly, the target product yield and profitability (Fig. 5, 6) and, secondly, the productivity and profitability (Fig. 7, 8). The results of calculations are shown in Figs 5-8.

![Figure 5](image5.png)

**Figure 5.** Pareto front approximation with the NSGA-II algorithm for the catalytic reaction of DMC with alcohols at 180°C applying the target product yield - profitability objective functions.

![Figure 6](image6.png)

**Figure 6.** Pareto set approximation with the NSGA-II algorithm for the catalytic reaction of DMC with alcohols at 180°C applying the productivity–profitability objective functions.

For the multi-cycle process, profitability–productivity and the target product yield–reaction time were considered as the objective functions (Figs 7 and 8).

![Figure 7](image7.png)

**Figure 7.** Pareto front approximation with the NSGA-II algorithm for the catalytic reaction of DMC with alcohols at 180°C applying the productivity–profitability objective functions.
Figure 8. Pareto set approximation with the NSGA-II algorithm for the catalytic reaction of DMC with alcohols at 180°C applying the target product yield - reaction time objective functions.

The Pareto front and set approximations obtained in this way for the conditions of single-cycle and multi-cycle reactions are different. The attainment of the optimal values in terms of the profitability–productivity criteria requires shorter reaction times than that in terms of the profitability–target product yield criteria. In the calculation of productivity (product yield per definite time), every reaction cycle stops before the maximum yield is attained. The rate of formation of the target product decreases with time and the shorter reaction time is matched by a larger amount of the catalyst.

The DM can choose the reaction conditions on the basis of comparison of the Pareto set and front approximations for the corresponding objective functions (Figs 6, 8). When it is necessary to obtain the maximum yield of the target product (the target product is highly valuable), the Pareto set and front approximations for the single-cycle process are applicable (Figs 5, 6). For a continuous reaction (which gives a mixture from which the target products are isolated in other reactors), it is recommended to use the Pareto set and front approximations for a multi-cycle process (Fig. 7, 8).

5. Conclusions
Optimal conditions for a complex catalytic reaction were studied by multi-objective optimization techniques on the basis of the kinetic model of the reaction. The single-cycle and multi-cycle reaction criteria were used as the objective functions. The objective functions for optimization of the reaction conditions (product yield, productivity, profitability) were analyzed. For the W(CO)_6-catalyzed reaction of DMC with alcohols, the times required to reach the maximum values of the optimization criteria were determined. The problem of multi-objective optimization of the conditions of single-cycle and multi-cycle reaction of DMC with alcohols was solved. It is shown that if is necessary to obtain the maximum yield of the target product, the Pareto set and front approximations for the single-cycle reaction can be used. In the case of a continuous reaction (the reaction product is a mixture from which the target products are isolated in other reactors), it is recommended to use the Pareto set and front approximations for a multi-cycle process.

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