

Interrelation between single-cycled catalytic reaction objective functions optimization and multi-cycled production on a basis of a kinetic model

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Abstract. The optimal conditions for carrying out a complex catalytic reaction were searched based on the kinetic model. Physic-chemical optimization criteria and economic criteria (profitability, profit) were target optimization functions. Target optimization functions were considered for both single-cycle and multi-cycle production. Their interrelation was defined.

Keywords: single-cycle, multi-cycle, kinetic model.

1. Introduction

The main goal in the chemical processes modeling is optimize conditions of reaction. At the same time, the costs for production and its debugging in real conditions of factory processes are significantly reduced. Optimization at the theoretical level is carried out by many researchers, but most of them are limited to physico-chemical optimization criteria (output, conversion, selectivity), not taking into account economic evaluations of the process (cost of reagents, reaction products). As a result, the optimum values of the reaction conditions during the real process have to be significantly corrected [1-3].

When choosing an optimization object (chemical reaction), the objective optimization functions (criteria) and the process conditions can be different. In some reactions, the conditions for conducting require an optimum for continuous production (optimization of multicyclic production). For other processes, it is necessary to evaluate and find optimum of the objective functions for one cycle reaction [4].

In the work, the object of optimization is the homogeneous catalytic reaction of alcohols with dimethyl carbonate (DMC) in the presence of a metal complex catalyst $W(CO)_6$. The reaction is new and refers to "green chemistry". Dimethyl carbonate is an effective substitute for existing toxic reagents - dimethyl sulfate and methyl halides [5]. For a new catalytic reaction, it is necessary to construct a kinetic model [6, 7], based on the found kinetic parameters. After it is necessary to optimize the process conditions.

2. The kinetic model of the reaction of alcohols with dimethyl carbonate in the presence of a metal complex catalyst $W(CO)_6$

Earlier, in [8, 9], a mathematical model of the reaction was constructed in the form of a system ordinary differential equations (ODE). Based on the proposed scheme for the reaction, a kinetic model of the reaction is constructed. The kinetic parameters found for different reaction conditions are shown in Table 1.

Table 1. Kinetic parameters of the catalytic reaction of alcohols with DMC in the presence of the catalyst $W(CO)_6$ ($[k_i] = [l/(mol \cdot min)]$, $[E_i] = [kcal/mol]$).

Stages	T, °C			E_j
	160	180	200	
$W(CO)_6 \rightarrow W(CO)_5^+ + CO$	$(4,00 \pm 0,01) \cdot 10^0$	$(6,30 \pm 0,01) \cdot 10^1$	$(8,60 \pm 0,01) \cdot 10^1$	$31,70 \pm 0,01$
$W(CO)_5^+ + MeOCO_2Me \rightarrow W(CO)_5CO_2Me + MeO^-$	$(9,00 \pm 5,20) \cdot 10^{-2}$	$(1,25 \pm 0,71) \cdot 10^0$	$(1,65 \pm 0,89) \cdot 10^0$	$30,4 \pm 0,6$
$W(CO)_5CO_2Me + ROH \rightarrow ROME + CO_2 + HW(CO)_5$	$(2,23 \pm 1,04) \cdot 10^0$	$(1,14 \pm 0,49) \cdot 10^1$	$(1,14 \pm 0,49) \cdot 10^1$	$17,1 \pm 0,5$
$W(CO)_5CO_2Me + ROH \rightarrow ROCO_2Me + HW(CO)_5$	$(1,27 \pm 0,37) \cdot 10^{-1}$	$(6,52 \pm 1,10) \cdot 10^{-1}$	$(1,03 \pm 0,28) \cdot 10^0$	$21,7 \pm 0,3$
$HW(CO)_5 + MeO^- \rightarrow MeOH + W(CO)_5^+$	$(1,20 \pm 0,01) \cdot 10^3$	$(3,48 \pm 0,01) \cdot 10^3$	$(3,85 \pm 0,01) \cdot 10^3$	$12,10 \pm 0,01$

Based on the developed kinetic model, it is possible to solve the problem of optimizing the reaction conditions. Statement of optimization problem assumes existence of objective functions, variable parameters and constraints on variable parameters.

3. Analysis of target optimization functions

Variable parameters for optimization in tasks of chemical kinetics are temperature, type of catalyst, catalyst concentration, pressure, etc. Experimental studies of the process were carried out at different initial values of amount catalyst and values of temperature. On this basis, as variable parameters, we consider temperature, initial amount of catalyst and time of reaction, physico-chemical limitations which are presented in [10].

In general, the optimization objective function based on the kinetic model has the form

$$R(x, x^0, t^*, \eta, \mu, T) \rightarrow \max, \quad (1)$$

where x - vector of substance concentrations; x^0 - vector of initial substances concentrations; η - vector of substance weights; μ - additional expenses; t^* - reaction time, min; T - temperature, °C.

To optimize conditions for carrying out chemical reaction, in accordance with (1), the following criteria can be used [11].

1) The output of target product x_{prod} , depending on time reaction and temperature:

$$R_1(t^*, T, x^0) = x_{prod}(t^*, T, x^0) \rightarrow \max. \quad (2)$$

This criterion is considered in first place, because concentration of the target product at the time of reaction end affects on other objective optimization functions (profitability, profit).

The scheme of single-cycle chemical transformations DMC with alcohols (Table 1) does not take into account subsequent decomposition of the target product. The curve of output changing reaches a maximum and does not change (Fig.1). For this conditions optimal reaction time in the presence of the $W(CO)_6$ catalyst is 70 min.

2) Productivity B - determines the product output per unit of time. The analysis of productivity in the case when amount of obtained product is directly proportional to conversion of initial reagent [3]:

$$R_2(t^*, x_i^0, T) = B(t^*, x_i^0, T) = N(t^*) x_i^0 \xi_{X_i}(t^*, T) M_{X_i} \rightarrow \max, \quad (3)$$

$$N(t^*) = \frac{1440}{t^* + t_{id}}, \quad (4)$$

where B - process productivity [g/(lit*day)]; N - amount of cycles [day^{-1}]; ξ_{X_i} - reagent conversion; M_{X_i} - reagent molar mass [g/mol], t_{id} - idle time between cycles.

In this case, the maximum productivity does not always correspond to the maximum conversion, because it takes more time to reach the maximum conversion, which leads to a decrease in the value of N (Fig. 2).

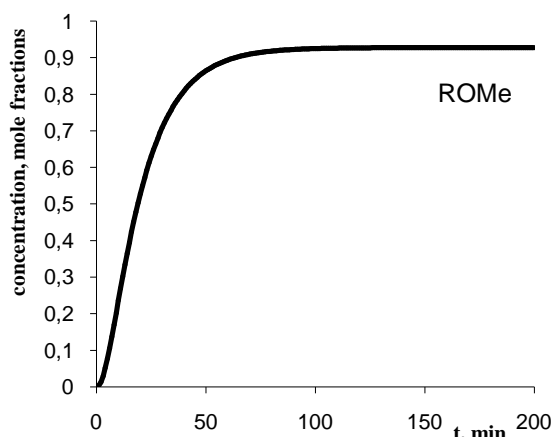


Figure 1. Product output of reaction between DMC with alcohols at $T = 180^{\circ}\text{C}$ and amount of catalyst is 0.003 moles in the presence of $\text{W}(\text{CO})_6$, for the product ROME.

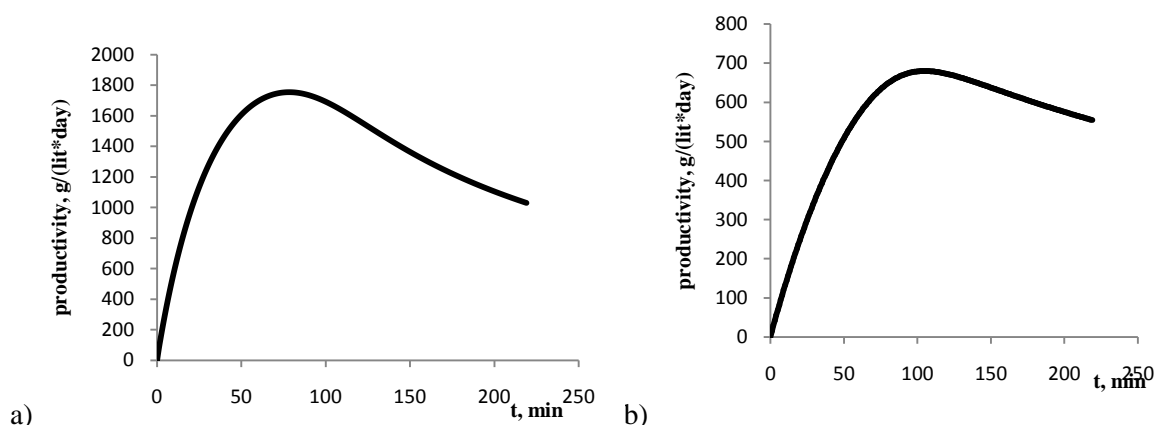


Figure 2. Productivity changing in reaction between DMC with alcohols in the presence of $\text{W}(\text{CO})_6$ at $T = 180^{\circ}\text{C}$ with idle time: a) 60 min, b) 300 min.

The values of productivity B pass through a maximum with increasing reaction time (Fig. 2). For $t^*=0$, we have the equality $B = 0$, because at initial time the conversion of reagent is zero. As $t^* \rightarrow \infty$, the value of B also tends to zero, because number of cycles N tends to zero (4).

According to calculations, at $T=180^{\circ}\text{C}$, the optimum reaction time for achieving maximum productivity is 90 minutes (idle time - 60 minutes) and 140 minutes (idle time - 240 minutes).

3) Profitability criterion P which is equal to sum of profits divided on investments:

$$R_3(t^*, \mathbf{x}^0, T) = P(t^*, \mathbf{x}^0, T) = \frac{\sum_{prod=1}^{Pr} x_{prod}(t^*, T, \mathbf{x}^0) \cdot \eta_{prod}}{\sum_{source=1}^{Sr} x_{source}(t^*, T, \mathbf{x}^0) \cdot \eta_{source} + \psi(t^*, T) + A} \rightarrow \max. \tag{5}$$

where x_{prod} – concentration of products; x_{source} – concentration of reagents; η – vector of specific price weights of components (norm. to sum of components prices and costs); ψ – variable costs (normalized); A – constant costs (normalized); Pr – amount of products; Sr – amount of reagents.

Change in profitability P in time is illustrated in Fig. 3.

Profitability (5) is a relative indicator, therefore its values do not depend on the number of cycles. For the considered reaction conditions ($T = 180^{\circ}\text{C}$), the optimum time to reach the maximum profitability is 90 minutes. independently from number of cycles.

For considered optimization criteria, times for achieving their maximum values are given in Table 3.

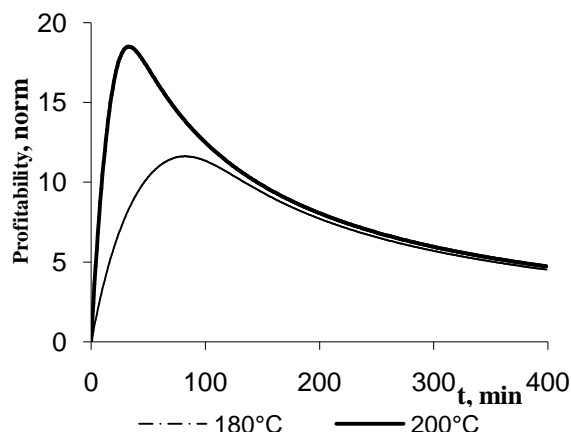


Figure 3. Profitability changing in reaction between DMC with alcohols at amount of catalyst is 0.003 moles in the presence of $W(CO)_6$.

Table 3. Times for reaching maximum values of optimizing criteria in reaction between DMC with alcohols in the presence of $W(CO)_6$.

	Catalyst amount 0.003 moles. T=180°C.		
	Per cycle	Per day (idle time 60 min.)	Per day (idle time 300 min.)
Profitability	90 min	90 min	90 min
Productivity	-	70 min	100 min
Product output	110 min	90 min	120 min

Table 3 shows the interdependence of criteria for control parameter "time". But for catalytic reactions control parameters are also temperature and initial amount of catalyst. It was shown in [12, 13] that for the DMC reaction with alcohols a maximum at all criteria is reached at the maximum temperature, but at different values of time reaction and different initial amounts of the catalyst.

4. Multi-objective optimization conditions of catalytic reaction.

To solve the problems of multi-objective optimization methods are being actively developed in recent years, allowing to receive so-called negotiation set of solutions [14].

Let $U=(u1, u2, \dots, u/U|)$ - vector of variable parameters. The set of admissible values of vector U - D_U . If $R(U)=(R_1(U), R_1(U), \dots, R_{R/}(U))$ – vector of objective functions, then function $R(U)$ displays D_U in some set D_R (attainability domain). From set D_R one can single out a subset D_R^* points, which are not dominated by other points [15]. Множество D_R^* - is an approximation of Pareto front. A subset $D_U^* \subset D_U$, corresponding to set D_R^* , is called Pareto set [15].

In developed information system for finite-dimensional approximation of sets D_U^* , D_R^* a genetic algorithm of Pareto-approximation of NSGA-II is applied [16]. When solving a task of multiobjective optimization, NSGA-II algorithm of each individual is assigned a rank. Non-dominated points have the first rank, points that are dominated only by points of the first rank have a second rank, etc. Also, the density of obtained individuals is estimated: a greater distance between individuals, a greater the diversity of a population. At each iteration of NSGA-II algorithm, a descendants are selected based on rank and crowding (proximity) of an individuals. Further, a crossing and mutation of selected individuals is performed, which ensures diversity of next population. Parents and descendants are united in one population with best solutions, etc.

Solution of a problem of multi-objective optimization of conditions for carrying out a single-cycle reaction of dimetholcarbonate with alcohols in the presence of metal complex catalysts was performed for two sets of pairwise independent objective functions: output of target product and profitability (Figures 4, 5); productivity and profitability (Figure 6, 7). The results of a computational experiments are presented in Fig. 4-7.

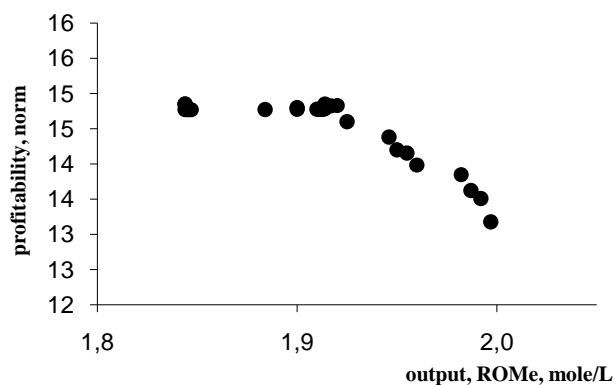


Figure 4. Approximations of Pareto front for catalytic reaction between DMC with alcohols by NSGA-II algorithm at 180°C for a target functions "product output - profitability".

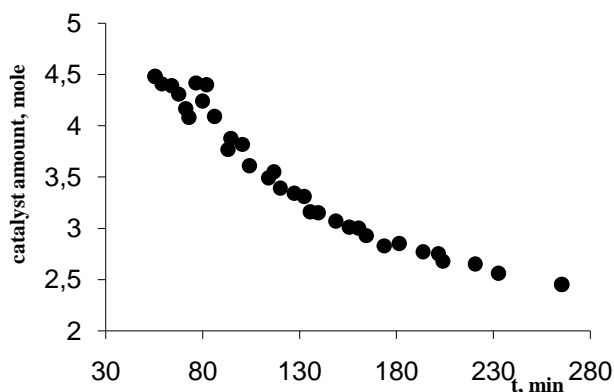


Figure 5. Approximation of Pareto set for catalytic reaction between DMC with alcohols by NSGA-II algorithm at 180°C for a target functions "productivity-profitability".

For multicyclic production, "profitability-productivity" was considered as the objective functions, as well as "product output- reaction time" (Fig. 6,7).

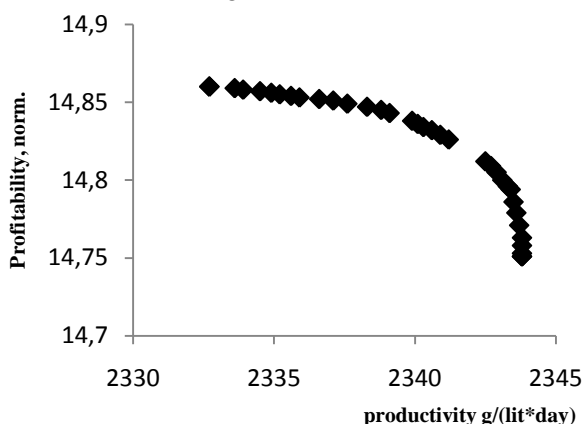


Figure 6. Approximations of Pareto front for catalytic reaction between DMC with alcohols by NSGA-II algorithm at 180°C for a target functions "productivity - profitability".

The obtained approximations of Pareto front and set for conditions of single-cycle and multicyclic production differ. In order to achieve an optimum when choosing the "profitability-productivity" criteria, a shorter reaction time is required than for the criteria "profitability - product output". This is due to the fact that when calculating the productivity (product output for a certain time), each

production cycle is stopped until the output maximum is reached, since the rate of formation target product slows down with time, and a smaller amount of a reaction corresponds to a larger amount of catalyst.

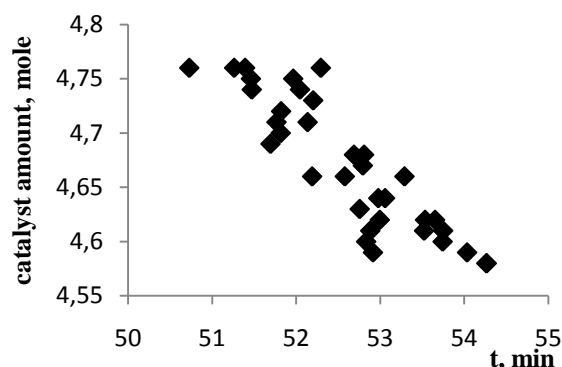


Figure 7. Approximation of Pareto set for catalytic reaction between DMC with alcohols by NSGA-II algorithm at 180°C for a target functions "product output- reaction time".

A decision maker can choose reaction conditions based on a comparison of Pareto set approximations for a corresponding objective functions (Fig. 5, 7). In the case where it is necessary to achieve the maximum output of the target product (when target product is very valuable) possible to use the Pareto front and set for single-cycle approximation (Figures 4, 5). In the case of continuous production (when reaction product is a mixture, from which the target products in the other reactors are further isolated), it is more expedient to use Pareto front and set approximations for multicyclic production (Fig. 6, 7).

Thus, an optimal conditions for carrying out a complex catalytic reaction using multiobjective optimization methods based on a kinetic model of a process are investigated. Criteria for single-cycle and multicyclic productions are considered as objective functions.

5. Acknowledgments

The reported study was funded by RFBR according to the research projects № 18-07-00341, 18-37-00015 and by the President of the Russian Federation SP-669.2018.5 stipends.

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