Optimization of chemical reactions by economic criteria based on kinetics of the process

K.F. Koledina[1,2], S.N. Koledin[1,2], I.M. Gubaydullin[1,2]

[1]Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, Prospect Oktyabrya 141, 450075, Ufa, Russia

[2]Ufa State Petroleum Technological University, Kosmonavtov St. 1, 450062, Ufa, Russia

Abstract

The paper deals with the formulation and solution of the inverse kinetic problem, methods of chemical reactions optimization by economic criteria on the basis of a process kinetic model. Yield of a target product, productivity, profit and productivity are considered as indicators.

Keywords: dimethylcarbonate; kinetic model; theoretical optimization; economic criteria; Hooke-Jeeves method

1. Introduction

"Green chemistry" is a scientific direction in chemistry, which can include any improvement in chemical processes that positively affects the environment. "Green chemistry" involves the use of low-toxic and non-toxic initial reagents.

Twelve principles of green chemistry should be noted, which were developed by scientists Anastas P. and Warner J. [1] which are used by scientists:

1. It is better to prevent waste than to treat or clean up waste product after it is formed.
2. Synthesis methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Wherever practicable, methodologies of synthesis should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Chemical products should be designed to preserve their efficiency and usage while reducing toxicity.
5. Better to not use at all auxiliary substances (e.g. solvents, separation agents, etc.) if there are any, they must be innocuous when used.
6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthesis methods should be conducted at ambient temperature and pressure.
7. A raw material or feedstock should be renewable rather than depleting wherever technically and economically practicable.
8. Reduce amount of receiving intermediate products whenever its possible (blocking group, protection / deprotection, temporary modification).
9. Catalytic reagents (as selective as possible) are better then stoichiometric reagents.
10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous products.
11. Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. Substances and the form of a substances used in a chemical process should be chosen to minimize potential for chemical accidents, including releases, explosions, and fires.

The reaction of alcohols with dimethyl carbonate (DMC) meets many of these principles. DMC is an effective substitute for toxic methyl halides (MeX, X = I, Br, Cl) and phosgene (3th, 4t[h] principles). It is produced with CO_2 as initial reagent. For reactions, involving DMC, only a catalytic amount of transition metal complexes is required, resulting in no waste (10th principle). According to the literature, the reactivity of DMC is moderate [2-6]. In order to reduce the energy costs of the reaction (6th principle), catalysts are used. As a result, alkylmethyl esters of alcohols and alkylmethyl carbonates are formed with the process selectivity of 95-98% (2th, 6th, 9th principles).

The reaction is new, it is implemented only in the laboratory. To study its mechanism, it is necessary to develop a mathematical model and, based on the results of the constructed mathematical model, to carry out optimization.

The reaction of DMC with alcohol in the presence of the catalyst W (CO) 6 leads to the formation of four products: ROMe, $ROCO_2Me$, CO_2 and MeOH.

$$ROH + (MeO)_2CO \xrightarrow{W(CO)_6} ROMe + ROCO_2Me + CO_2 + MeOH$$
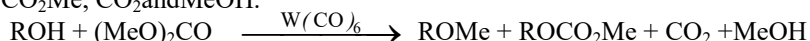
2. Mathematical model

A mathematical model of chemical kinetics is a system of nonlinear ordinary differential equations (SNODE) with the initial given data, i.e. the Cauchy problem (1) [7].

$$\frac{dx_i}{dt} = \sum_{j=1}^{J} v_{ij} w_j, i = 1, \ldots I,$$

(1)

$$w_j = k_j^0 \cdot \exp\left(-\frac{E_j^+}{RT}\right) \cdot \prod_{i=1}^{I} (x_i)^{|\alpha_{ij}|} - k_{-j}^0 \cdot \exp\left(-\frac{E_j^-}{RT}\right) \cdot \prod_{i=1}^{I} (x_i)^{|\beta_{ij}|}$$

initial conditions: at $t = 0$, $x_i(0) = x_i^o$;

where v_{ij} is stoichiometric coefficients; J is number of stages; x_i is concentration of substances participating in the reaction, mol/l; I is number of substances; w_j is j-th speed stage, 1 / min; k_j, k_{-j} is rate constants of direct and reverse reactions; E_{j+}, E_{j-} is activation energies of direct and reverse reactions, kJ/mol; R is universal gas constant, equal to 8.31 kJ / (mol * K); T is temperature, K; α_{ij} is negative elements of the matrix (v_{ij}); β_{ij} is positive elements (v_{ij}); k_j^0, k_{-j}^0 is pre-exponential factors, 1 / min.

The solution of the direct problem is the SNODE solution with initial data and given kinetic parameters up to some fixed time t*.

Such SNODE tasks of chemical kinetics are mostly stiff systems. Therefore, for their numerical solution Implicit Rosenbrock third-fourth order Runge-Kutta method is used with degree three interpolating the Maple [8] and the multi-step Gir method of variable order in Matlab.

The inverse problem is the determination of the kinetic parameters by matching the calculated kinetic curves with the experimental ones by functional (2).

$$\sum_{q=1}^{Q} \sum_{i=1}^{I} \left| x_{pi}^r - x_{pi}^e \right|$$

(2)

where x_{pi}^{exp} and x_{pi}^{calc} is experimental and calculated concentrations of components; I is number of substances; Q is number of measuring points.

The inverse problem was solved in the Matlab environment using the genetic algorithm and the Hook-Jeeves direct search method [9].

3. Results and Discussion

Fig.1. shows kinetic model for catalyst reaction of DMC with alcohols in the presence of W(CO)$_6$.

On the graphs of Fig.2 are shown corresponding kinetic curves and correspondence between the calculated values and the experimental data. Based on the developed kinetic model, a theoretical optimization of the process was carried out. A distinctive feature of the work is application of economic criteria at the level of laboratory experiments.

In general, the criterion for optimizing the chemical process has the form (3) [10-11]:

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

(3)

Where R is optimization function, η is vector of the substance weights, μ is additional cost.

For chemical reactions performed in the laboratory optimization, the following indicators of the process economic efficiency can be used as optimization criteria:

1) Productivity - the volume of output per unit time (4).

$$R : B = N \cdot C_{x_i^0} \cdot \xi_{x_i^0}(t^*, T) \cdot M_{x_i} \rightarrow max$$

(4)

where B is process productivity [g / (mol * day)]; N is number of cycles per day [day^{-1}]; C_{xi}^0 is initial value of initial reagent [mole fractions]; ξ_{xi}^0 is conversion of initial reagent; M_{xi}^0 is molar mass of the initial reagent [g / mol].
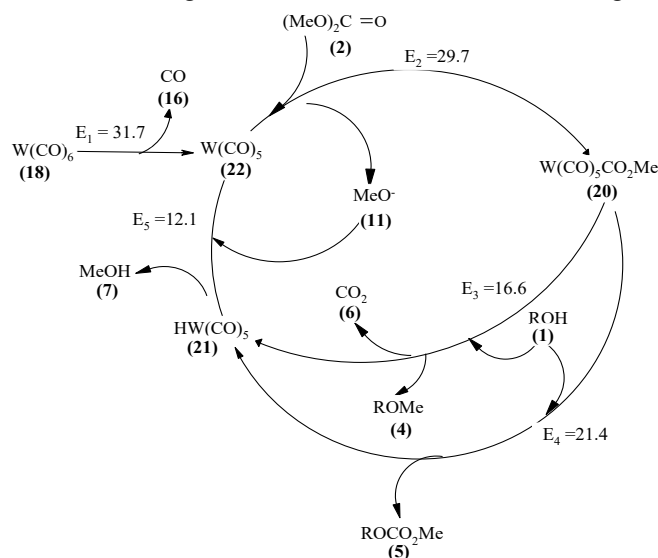

Fig. 1. Kinetic model of reaction with alcohols in the presence of tungsten hexacarbonyl.

a) for catalyst amount 0.001 mol, T = 160°C   b) for catalyst amount 0.003 mol, T = 200°C
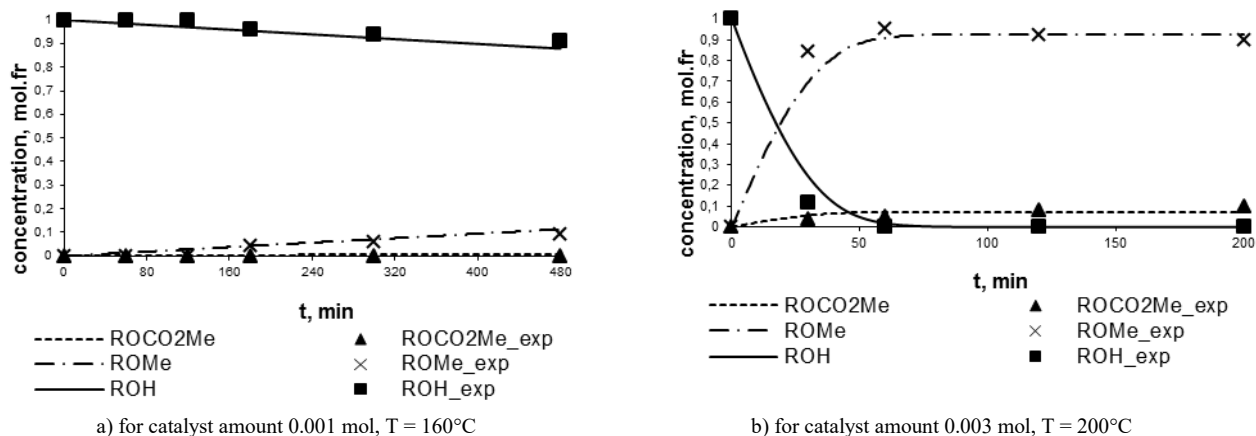
Fig.2. Graph of correspondence of experimental data (points) and calculated values (lines) of observed substrates concentration changing according to the scheme of chemical transformations in the presence of $W(CO)_6$.

2) Profit. The profit depends on difference between price of product and its cost, as well as on output (5).

$$R : E = \sum_{prod=1}^{Pr} x_{prod}(t^*,T) \cdot \eta_{prod} - \sum_{source=1}^{Sr} x_{source}(t^*,T) \cdot \eta_{source} - \psi(t^*,T) - A \to max \qquad (5)$$

where x_{prod} is concentration of reaction products; x_{source} is concentration of initial reagents; η is weight of components (normalized); $\psi(t)$ is variable costs (normalized); A is constant costs (normalized); Pr is number of products; Sr is number of initial reagents; E is normalized profit.

3) Profitability. Profitability is defined as the ratio of the amount of profit to the volume of investment (6).

$$R : E = \frac{\sum_{prod=1}^{Pr} x_{prod}(t^*,T) \cdot \eta_{prod}}{\sum_{source=1}^{Sr} x_{source}(t^*,T) \cdot \eta_{source} + \psi(t^*,T) + A} \to max \qquad (6)$$

where P is normalized profitability.

Assuming an idle time between cycles of 1 hour (60 min.), the values of maximum process productivity and productivity at maximum yield of target product X5 are given in Table 1 for reaction with tungsten hexacarbonyl catalyst by (4).

Table 1. Indicators of DMC conversion, time, productivity under the condition of maximum product yield and maximum productivity in the temperature range.

T, °C	tungsten hexacarbonyl				
	maximum productivity			maximum yield ROMe (ξ_{X2}=0,26)	
	conversion (MeO)₂CO	Reaction time, min	B, g /(mol * day)	Reaction time, min	B, g /(mol * day)
160	0,180	220	721	440	583
180	0,220	80	1763	140	1459
200	0,235	33	2836	50	2652
220	0,250	18	3597	22	3558

Thus, it can be seen that with DMC maximum possible conversion, an economically optimal solution is not achieved, because smaller conversion value corresponds to shorter reaction time, which leads to an increase in overall productivity.

The value of profit is determined by (5). The weights of substances depend on the cost of reagents on the market according to http://www.acros.com and http://www.sigmaaldrich.com. Then the graph of profit changing from time for different values of temperature has the form (Fig. 3).

Figure 3 shows the following patterns:

a) There is a temperature range with positive profits, and if the temperature is higher, maximum profit is attained earlier (170-220°C). It is worth noting that the decrease in the value of profit occurs more sharply, if the temperature is higher. This is probably because at a high temperature the reaction conversion occurs faster. When one of the reagents (alcohol) is completely consumed, value of the second reagent conversion cannot be increased and profit decreases due to variable costs (for example, to maintain a temperature).

b) At a temperature of 150°C, the profit value goes to negative area, but you can also see maximum profit (or minimum loss).

Profitability changing in the process from time is shown in Figure 4.

Figure 4 shows that the profitability reaches a maximum and decreases with time, which is explained by the costs of maintaining the set temperature. With increasing temperature, a maximum value of profitability comes earlier.
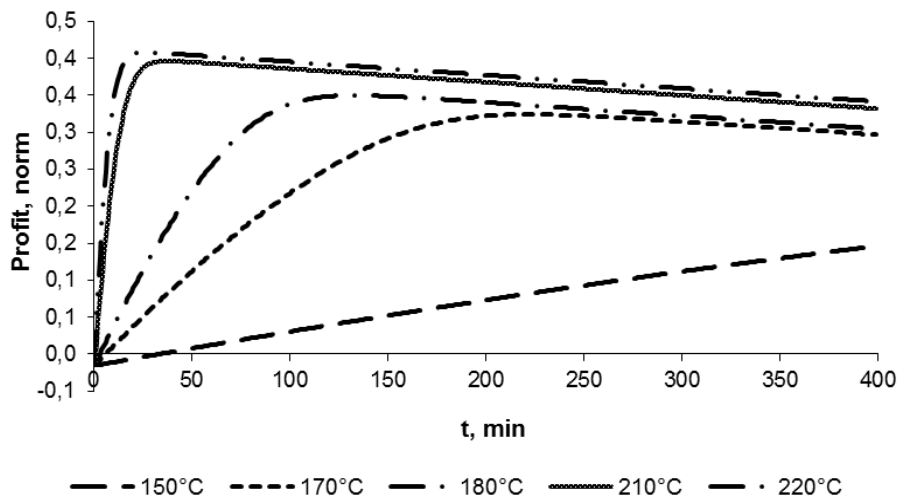
Fig.3. Profit changing from time for different temperatures (catalyst amount 0.003 mol), in the presence of $W(CO)_6$.
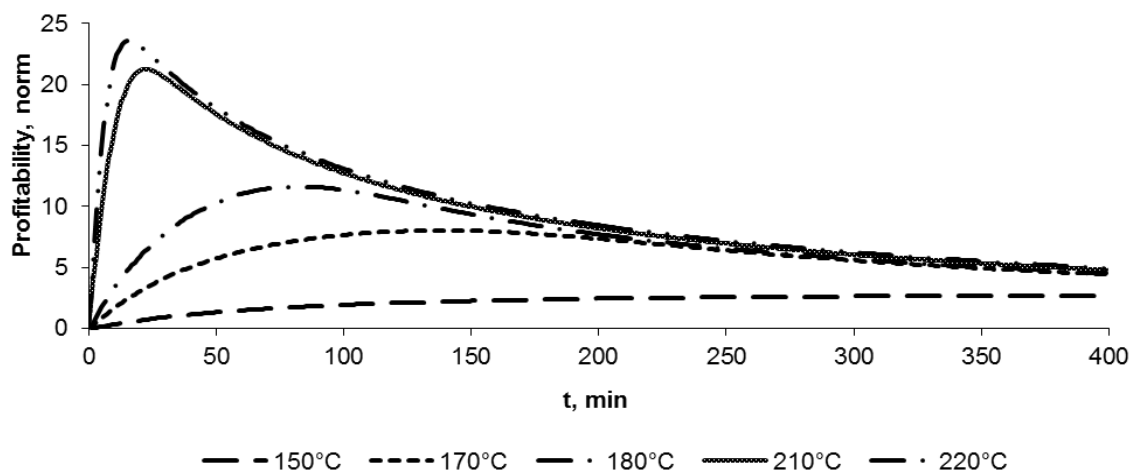

Fig. 4. Profitability changing from time for different temperatures (catalyst amount 0.003 mol), in the presence of $W(CO)_6$.

Each curve for the profit margin, as well as the productivity and yield of the target product passes through a maximum. From the points of maximums, we construct the optimum temperature profile, putting in correspondence to each instant of time the temperature at which the maximum of the target criterion is reached. Then the optimum temperature profile for all the indicators will take the form (Fig. 5).
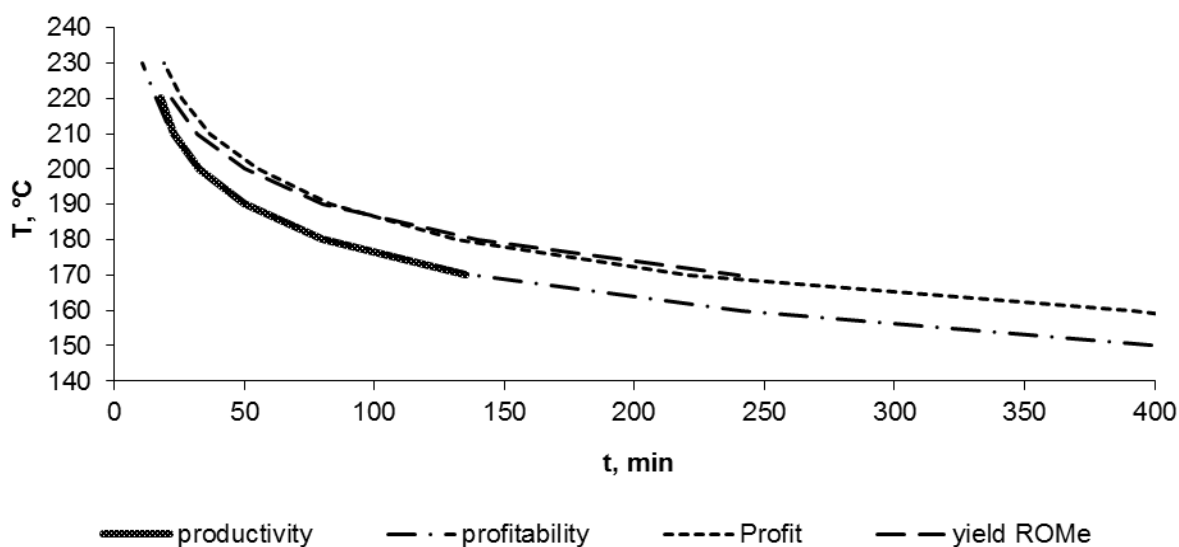

Fig. 5.Temperature reaction profiles for various economic parameters for the $W(CO)_6$ catalyst.

The above reaction temperature profiles characterize the optimal reaction conditions (temperature and reaction time). Based on the results of the work, the overall temperature profile is given for all targets.

The overall temperature profile (Figure 5) for tungsten catalysts clearly demonstrates high correlation between productivity and profitability, as well as between yield and profit.

4. Conclusion

The catalytic reaction of alcohols with DMC in the presence of tungsten hexacarbonyl is considered in this work. The formulation and solution of the inverse kinetic problem, the method of optimization of chemical reactions by economic criteria based on the kinetic model of the process are given. As indicators, the yield of the target product, productivity, profit and profitability are considered. For the reaction of alcohols with DMC in the presence of $W(CO)_6$, correlations are observed between productivity and profitability, as well as between yield and profit.

Acknowledgements

References

[1] Anastas PT, Warner J C. Green Chemistry: Theory and Practice. New York : Oxford University Press, 1998; 30 p.

[2] Tundo P. New developments in dimethylcarbonate chemistry. Pure and Applied Chemistry 2001; 73: 1117–1120.

[3] Khusnutdinov RI, Schadneva NA, Maykova YuYu. Synthesis of alkyl methyl ethers and alkyl methyl carbonates by reaction of alcohols with dimethyl carbonate in the presence of tungsten and cobalt complexes. Russian Journal of Organic Chemistry 2014; 50(6): 790–795.

[4] Koledina KF, Koledin SN, Schadneva NA, Gubaidullin IM. Kinetics and mechanism of the catalytic reaction between alcohols and dimethyl carbonate. Russian Journal of Physical Chemistry A 2017; 91(3): 442–447.

[5] Koledin SN, Koledina KF, Gubaidullin IM. Kinetic model of catalytic interaction alcohols with dimethyl carbonate in the presence of various catalysts. Materials V all-russian scientific-practical conference timed to the 110th anniversary of the birth of Academician A.N. Tikhonov, 17-19 november 2016. Sterlitamak. Part I. Sterlitamak: Sterlitamak branch of BashGU, 2016: 159–165. [in Russian]

[6] Koledin SN, Koledina KF, Gubaidullin IM. Kinetics of reaction in the study economic efficiency in chemical production. Mathematical modeling of processes and systems. Materials III all-russian scientific-practical conference with international participation Sterlitamak, 4-6 december, 2014: 30–32. [in Russian]

[7] Koledina KF, Koledin SN, Gubaidullin IM, Safin RR, Ahmetov IV. Information system for constructing a kinetic model of a catalytic reaction, planning an economically optimal chemical experiment. Control Systems and Information Technology 2015; 3(61): 79–84. [in Russian]

[8] Koledina KF, Gubaidullin IM. Kinetics and mechanism of olefin catalytic hydroalumination by organoaluminum compounds. Russian Journal of Physical Chemistry A 2016; 90(5): 914–921.

[9] Hook P, Jeeves TA. Direct solution search for numeric and static problems. M.: Mir, 1961; 219 p. [in Russian]

[10] Koledin SN, Koledina KF, Gubaidullin IM, Spivak SI. Determination of optimal conditions for catalytic processes based on economic criteria. Chemical industry today 2016; 10: 24–35. [in Russian]

[11] Koledin SN, Koledina KF. Optimal control and sensitivity of the optimum in problems of chemical kinetics. Journal of Middle Volga Math. Soc. 2016; 18(3): 137–144.