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

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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. \cite{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 (3\textsuperscript{rd}, 4\textsuperscript{th} principles). It is produced with CO\textsubscript{2} as initial reagent. For reactions, involving DMC, only a catalytic amount of transition metal complexes is required, resulting in no waste (10\textsuperscript{th} principle). According to the literature, the reactivity of DMC is moderate [2-6]. In order to reduce the energy costs of the reaction (6\textsuperscript{th} principle), catalysts are used. As a result, alkylmethyl esters of alcohols and alkylmethyl carbonates are formed with the process selectivity of 95-98% (2\textsuperscript{nd}, 6\textsuperscript{th}, 9\textsuperscript{th} 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)\textsubscript{6} leads to the formation of four products: ROMe, ROCO\textsubscript{2}Me, CO\textsubscript{2} and MeOH.

\[
\text{ROH} + (\text{MeO})\textsubscript{2}\text{CO} \xrightleftharpoons{\text{W/(CO)}_6} \text{ROMe} + \text{ROCO}_2\text{Me} + \text{CO}_2 + \text{MeOH}
\]

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) \cite{7}.
\[
\frac{dx_j}{dt} = \sum_{i=1}^{I} v_{ij} w_j, i = 1, \ldots, I,
\]

\[
w_j = k_j^0 \exp\left( -\frac{E_j^+}{RT} \right) \prod_{i=1}^{I} (x_i)^{a_{ji}} \exp\left( -\frac{E_j^-}{RT} \right) \prod_{i=1}^{I} (x_i)^{b_{ji}}
\]

\[
\text{initial conditions: } at \ t = 0, x_{j}(0) = x_{j}^0;
\]

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

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).

\[
\sum_{q=1}^{Q} \sum_{i=1}^{I} |x_{pi}^{\text{exp}} - x_{pi}^{\text{calc}}| \rightarrow \text{max}
\]

where \( x_{pi}^{\text{exp}} \) and \( x_{pi}^{\text{calc}} \) 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 \( \text{W(CO)}_6 \).

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]:

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

Where \( R \) is optimization function, \( \eta \) is vector of the substance weights, \( \mu \) 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).

\[
R : B = N \cdot C_{x^0} \cdot \xi \cdot \eta (t^*, T) \cdot M_{x_i} \rightarrow \text{max}
\]

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

Fig. 1. Kinetic model of reaction with alcohols in the presence of tungsten hexacarbonyl.
2) Profit. The profit depends on difference between price of product and its cost, as well as on output (5).

\[ R : E = \sum_{\text{prod}=1}^{Pr} x_{\text{prod}}(t^*, T) \cdot \eta_{\text{prod}} - \sum_{\text{source}=1}^{Sr} x_{\text{source}}(t^*, T) \cdot \eta_{\text{source}} - \psi(t^*, T) - A \rightarrow \max \]  

where \( x_{\text{prod}} \) is concentration of reaction products; \( x_{\text{source}} \) is concentration of initial reagents; \( \eta \) 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).

\[ R : E = \frac{\sum_{\text{prod}=1}^{Pr} x_{\text{prod}}(t^*, T) \cdot \eta_{\text{prod}}}{\sum_{\text{source}=1}^{Sr} x_{\text{source}}(t^*, T) \cdot \eta_{\text{source}} + \psi(t^*, T) + A} \rightarrow \max \]  

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>
<thead>
<tr>
<th>T, °C</th>
<th>tungsten hexacarbonyl conversion (MeO):CO</th>
<th>maximum productivity</th>
<th>maximum yield ROMe (( \xi = 0.26 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>160</td>
<td>0.180</td>
<td>220</td>
<td>721</td>
</tr>
<tr>
<td>180</td>
<td>0.220</td>
<td>80</td>
<td>1763</td>
</tr>
<tr>
<td>200</td>
<td>0.235</td>
<td>33</td>
<td>2836</td>
</tr>
<tr>
<td>220</td>
<td>0.250</td>
<td>18</td>
<td>3597</td>
</tr>
</tbody>
</table>

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.
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).

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

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References