Mathematical Modeling of the Hardware Design of the Catalytic Process of Hydrocarbon Processing at the Design Stage

SALIM ASADOV, ALI AKHUNDOV, DILGAM TAGIYEV

Nagiyev Institute of Catalysis and Inorganic Chemistry
1143 Baku, H. Javid ave. 113
AZERBAIJAN
dtagiyev@rambler.ru

Abstract: - The technology of hydrocarbon processing, in addition to methane, also implies the involvement in the processing of its higher homologues - hydrocarbons. Currently, non-oxidative methods are being developed for gas feedstock processing, including their dehydrogenation to olefins. Technological schemes for the process of oxidative dehydrogenation of hydrocarbons are diverse and depend on the method of carrying out the process - continuous or periodic. This article presents the results of the development of modeling and determining the optimal parameters of the catalytic continuous processing of hydrocarbons on the example of oxidative dehydrogenation. On the basis of the constructed mathematical model of the kinetics of the process of oxidative dehydrogenation of hydrocarbons, the problem was solved by constructing a theoretically optimal temperature profile. Our laboratory data on the oxidative dehydrogenation of n-butane to divinyl and isopentane to isoprene were used as initial data when choosing a model, constructing an algorithm and calculations. This made it possible to identify the optimal regions of the regime parameters of the studied processes.

Key-Words: - mathematical model, catalytic process, hydrocarbon processing, optimal parameters.

1 Introduction

In recent years, the contribution to the industry of kinetic and thermodynamic modeling of processes, including petrochemical reactions, has increased significantly. In addition, the improvement of methods of analytical chemistry, the development of mathematical models and the development of computing tools have led to a deeper understanding of the kinetics of petrochemical reactions, especially in mixtures with a large number of compounds. Taking into account the overall objective of improving the quality and yield of the product, it is obvious that the final commitment to the production of any chemical substances often depends on its profitability and other economic factors. In this aspect, an important role is assigned to chemical kinetics, which is based on chemical reactions; the latter in turn depend on factors such as concentration, pressure and temperature.

Understanding chemical kinetics is important for obtaining the necessary data on the mechanisms of reactions taking into account the intermediate products of these reactions. The knowledge of the mechanism can be checked only after a detailed kinetic study. Kinetic studies cover a wide range of different points of view. In particular, in petrochemical processes, chemical reactions occur in various phases, such as gas, liquid and solid phases, solutions using various solvents, gas-solid phase and others [1].

In recent years, the role of petrochemical kinetics and reaction engineering in manufacturing technologies has grown. For example, new experimental methods have been developed to track petrochemical reactions. The availability of computers has improved the modeling of complex chemical reactions and the stability analysis of the reactors used. These measures led to an improvement in the design of industrial reactors. A growing number of industrial patents are now associated with new catalysts and catalytic processes, synthetic polymers and new reactor designs [2].

Complexity of solving the problem of modeling petrochemical processes is associated, first of all, with the absence of any method for obtaining and / or separating a mixture of substances and the absence of a practical general method for justifying the hardware design of the process.

Oxidative dehydrogenation of hydrocarbons (ODH) in the fixed oxide catalyst (OC) layer belongs to the perspective direction in the petrochemical industry [3-5].

Namely, the ODH belongs to the class of processes for which mathematical modeling methods have not been developed to solve the problems of theoretical optimization of the temperature profile (TOTP), to determine the optimal values of the control parameters: temperature, pressure and composition of the reaction mixture, its feed rate in reactor.

Technological schemes for the process of oxidative dehydrogenation of hydrocarbons are diverse and depend on the method of carrying out the process - continuous or periodic.

Continuous process. This is a simultaneous feed to the catalyst of a hydrocarbon and an oxidizing agent (air or oxygen). Under conditions of saving of hydrocarbon raw materials, air as an oxidizing agent is undesirable, since as a result of the process there is a constant accumulation of ballast nitrogen. But the main problems are a large heat release during reaction, the use of a tubular reactor or a fluidized bed (isothermal reactors), expensive heat carriers for high temperatures (800-900°C). Therefore, when implementing the process on an industrial scale, it is necessary to solve the problem of heat removal and utilization of heat energy.

Periodic process. For example, methane dimerization (or oxidative dehydrogenation and cracking of C2-C3 alkanes) is carried out by oxygen of the catalyst lattice. The process consists of several cycles: the oxidized catalyst is in contact with methane; nitrogen expulsion removes dimerization products; air expulsion regenerates the catalyst; nitrogen expulsion and repeating the cycle. In the case of periodic process, several technological schemes are possible.

Considering this, the purpose of this work is the modeling and development of an algorithm for the implementation of optimal instrumentation of petrochemical continuous processes, for example, the oxidative dehydrogenation of hydrocarbons. Note that, for optimization, we used our experimental data on the oxidative dehydrogenation of two processes [3-5]; n-butane to divinyl and isopentane to isoprene.

Below are the TOTP results of highly exothermic, with complex mechanism, OD reactions of n-butane to divinyl and isopentane to isoprene, which allowed to carry out the optimal calculation of the reactor and determine its optimum parameters. At the design stage, this will enable to select a reactor in which the process approaches the theoretically optimal regime, and for operating reactors it makes it possible to determine the possibilities for its intensification [6-13].

2 Methodical and Theoretical Part

Statement of the problem, algorithm and method for the numerical solution of the TOTP problem. The main theoretical optimization of the processes of ODH is a mathematical model of the kinetics of processes at a given temperature T and initial conditions $\tau = 0$; $P_i(0) = P_i(\tau)$

$$\frac{dP_i}{d\tau} = \sum_{j=1}^{m} W_j = f_j(P_i, T) \quad (1)$$

where W_j is the total reaction rate for the considered routes, mol / l (cat)·sec: P_i is the partial pressure of the i-th component, kPa.

The solution of the problem of theoretical optimization, in particular, of the ODH allows to choose the reactor type, estimating the potential possibilities of the process and determining the TOTP. The latter allows to calculate the maximum yield of the target product with the greatest selectivity from a unit volume of the catalyst. In this case, the following criterion can be used to determine TOTP:

$$I = \max \sum_{j=1}^{m} P_j(\tau_k) \quad (2)$$

where TOTP satisfies the constraint

$$T_{\min} \le T \le T_{\max} \quad (3)$$

To solve the problem of finding the TOTP, we will use the Pontryagin maximum principle, proceeding from the fact that in a controlled system anywhere in the acceptable range of the control variable it is impossible to satisfy the necessary condition of control stationarity. In the acceptable range, the Pontryagin function is written using the Hamiltonian function H [14]. To find the TOTP, we construct auxiliary functions λ_j satisfying the following system of equations with boundary conditions:

$$\frac{d\lambda_j}{d\tau} = -\frac{\partial H}{\partial P_i} = \sum_{j=1}^{m} \lambda_j \frac{\partial f_j}{\partial P_i} \quad (4)$$

$\lambda_i(\tau_k) \equiv 0$, $\lambda_j(\tau_k) \equiv 1$ $i \neq j$ $i = \overline{1,m}$ $j = \overline{1,n}$.

Here we assume that control $T(\tau)$ (Tmin, Tmax) for fixed values of $P_i(\tau)$, in the Hamiltonian function

$$H = \Sigma \lambda_j \acute{r}_j = H(P_i, T) \qquad i = \overline{1,m} \quad j = \overline{1,n} \quad (5)$$

T(τ) reaches a maximum, i.e. in the Hamiltonian equation the condition is satisfied

$$H[T(\tau)_{opt}, \overline{P}_{opt}, \overline{\lambda}_{opt}] = \max H[T(\tau)_{opt}, \overline{P_j}_{opt}, \overline{\lambda}_{j\,opt}] \quad (6)$$

Then the theoretical optimization of the control of the ODH process reduces to solving the boundary value problem of the system of equations (1), (2), (3) with the search at the nodal points of integration of the maximum of the Hamiltonian of system (4). The search for optimal control was carried out on the basis of the maximum principle by the method of successive approximations. The calculation algorithm was based on the integration of system (1), (3) by the Runge-Kutta method [13] with constraints (1), (3).

A block diagram of the numerical solution algorithm for determining the TOTP by the ODH process is shown in Figure. The algorithm for the numerical solution of the problem: the first approximation of the temperature distribution $T^{(1)}$ along the length of the reactor is arbitrarily given and a direct system of kinetic equations (1) is solved, in which the rate constants are functions of $T^{(1)}$. The values of the partial pressure $P_i(\tau_k)$ at the end of the reactor are determined. Next, the direct (1) and conjugate (4) problems are solved together with the boundary conditions given at the point (τ_k) from right to left, and at each nodal point we consider the temperature providing the maximum of the function H in equation (5) and satisfying condition (6).

3 Results and Discussion

Theoretical optimization of the process was reduced to solving the boundary-value problem of the system of equations (1), (4) and (5) from right to left, condition (6) is determined not at each integration step, but at nodal points with interval τ. The finding of the Hamilton maximum (6) was carried out by the random search method, which greatly reduced the number of iterations and accelerated the convergence of computations.

Thus, the block diagram of the algorithm for numerical solution of the problem for determining the TOTP allowed to determine the optimal conditions for carrying out the ODH process.

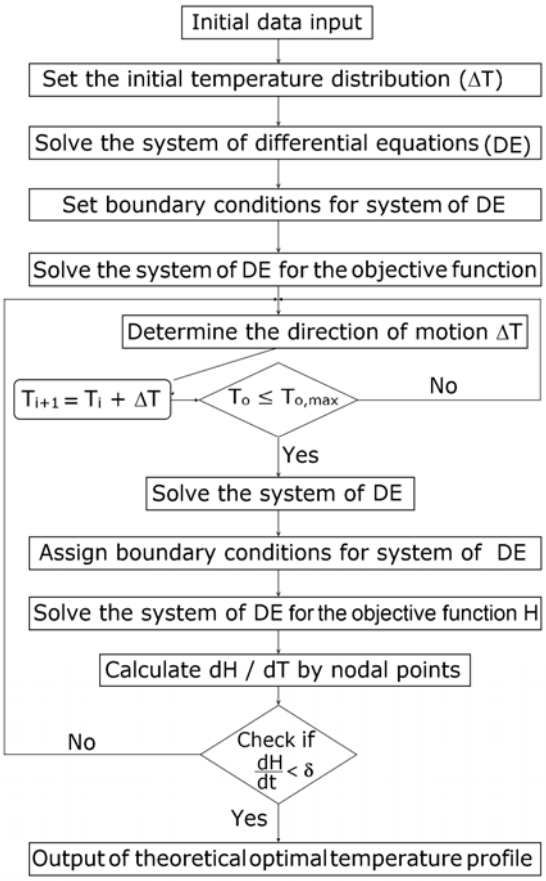

Figure. The block diagram of the algorithm for numerical solution of the problem for determining the TOTP.

4 Conclusion

In the course of theoretical optimization, optimal parameters were found - temperature, pressure, and composition of the reaction mixture in the systems under study. The theoretical calculations carried out, including the optimal apparatus design of the reactor, are in satisfactory agreement with the experimental data of the catalytic hydrocarbon systems. The proposed approach leads to qualitatively and quantitatively new possibilities for determining the hardware design of chemico-technological schemes and evaluating the characteristics of the extracted chemical products. In the theoretical optimization, optimal parameters were found - temperature, pressure, and composition of the reaction mixture in the studied systems of oxidative dehydrogenation

processes of n-butane to divinyl and isopentane to isoprene.

Acknowledgments

This work was supported by the Scientific Fund of State Oil Company of the Azerbaijan Republic - SOCAR (project No. 12LR - AMEA. 04.01.2018).

References:

[1] K.A. Coker, *Modeling of Chemical Kinetics and Reactor Design*, Gulf Publishing Company, Houston, Texas, 2001, 1126 p.

[2] R.W. Missen, C.A. Mims, B.A. Saville, *Introduction to Chemical Reaction Engineering and Kinetics,* John Wiley & Sons, 1999, 692 p.

[3] S.M. Asadov, A.A. Akhundov, Teoreticheski optimal'nyy temperaturnyy profil' protsessov okislitel'nogo degidrirovaniya uglevodoro-dov (Theoretically the optimal temperature profile of the processes of oxidative dehydrogenation of hydrocarbons), *Azerbaijan Oil Industry*, № 6, 2015, pp. 52-55. [in Russian].

[4] S.M. Asadov, A.A. Akhundov, Modelirovaniye i optimizatsiya kataliticheskogo protsessa okislitel'nogo degidrirovaniya izopentana v izopren (Modeling and optimization of catalytic process of oxidative dehydrogenation of isopentane in isoprene, *Azerbaijan Oil Industry*, № 7-8, 2015, pp. 56-59. [in Russian].

[5] S.M. Asadov, A.A. Akhundov, Matemati - cheskaya model' upravleniya kataliticheskim protsessom s uchastiyem uglevodorodov (Mathematical model of control of a catalytic process involving hydrocarbons), in book: *Fundamental and Applied Problems of Physics*. Russia. Saransk, 2015, pp. 273-278. [in Russian].

[6] E. Yu, G. Dobbie, M. Jarke, S. Purao (eds.), *Conceptual Modeling*: 33rd International Conference, ER 2014, Atlanta, GA, USA, October 27-29, 2014, Proc. Springer International Publishing, 2014, 496 p.

[7] N. Danaev, Y. Shokin, A. Darkhan (eds.). *Mathematical Modeling of Technological Processes*: 8th International Conference, CITech 2015, Almaty, Kazakhstan, September 24-27, 2015, Proc. Springer International Publishing, 2015, 223 p.

[8] C. Eck, H. Garcke, P. Knabner. *Mathematical Modeling*. Springer International Publishing, 2017, 519 p.

[9] P. Neittaanmдki, S. Repin, T. Tuovinen. *Mathematical Modeling and Optimization of Complex Structures*. Springer International Publishing, 2015, 328 p.

[10] I. Regupathi, V. Shetty K, M. Thanabalan (eds.). *Recent Advances in Chemical Engineering*: Select Proc. of ICACE 2015. Publisher: Springer Singapore, 2016, 360 p.

[11] P. Neittaanmдki, S. Repin, T. Tuovinen (eds.). *Mathematical Modeling and Optimization of Complex Structures*. Springer International Publishing. Switzerland, 2016, 328 p.

[12] M. Ochowiak, S. Woziwodzki, M. Doligalski, P.T. Mitkowski (eds.). *Practical Aspects of Chemical Engineering*: Selected Contributions from PAIC, Springer International Publishing, Switzerland, 2017, 465 p.

[13] L.M.F. Lona, *A Step by Step Approach to the Modeling of Chemical Engineering Processes*, Springer International Publishing, 2018, 173 p.

[14] V. Badescu, *Optimal Control in Thermal Engineering*, Springer International Publishing, 2017, 584 p. DOI: 10.1007/978-3-319-52968-4.