Representation of the process of oxidative regeneration of coked catalysts in a fixed layer based on graph theory

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Abstract. Representation of processes by means of graphs allows increasing their visibility in comparison with the technological scheme. This makes it possible to facilitate the design of chemical plants, especially in the case when going from the principal graph to more complex graphs of the same production. The presented representation of chemical technology processes based on graph theory is of a purely qualitative nature. The article shows the technological scheme and the resulting graph of the process of oxidative regeneration. Quantitative regularities derived from this theory can form the basis of optimization of the oxidative regeneration.

1. Introduction

Chemical industry production includes complexes of various processes. Before building a chemical plant, it is necessary to develop a production process plan, which involves developing the individual process technologies, considering their interconnections. «Any complex technology is not a mechanical sum of separate processes. The optimal modes for carrying out particular processes independently do not ensure the best work of the whole plant» [1]. Each process shall be harmonious not only from a technical point of view; it shall also fulfill the economic requirements [2]. The objective of achieving the minimum prime cost is very complicated. The issue of reducing the production costs is solved by analyzing the structure of processes, the nature of production costs, etc. [3–8]. A prerequisite for the successful solution of these tasks is the analysis of chemical and technological processes in general.

The study of complex chemical industries is called the study of processes (the study of flow structure). The word «process» here is understood in the widest sense, since it can apply to anything from a single device to an entire plant [9]. The object of study is the production facilities of modern chemical industry analyzed based on technological schemes or using graphs, which are more illustrative.

2. Analysis of chemical production facilities using the theory of graphs

Such a study started with the comparison of technological schemes, but it was found out that they cannot be used for the comparison. Within the framework of the study of processes, they can be
compared by substitution of technological schemes for the graphs and the subsequent analysis based on the theory of graphs. It emerged that any chemical production facilities, even the most complex ones, can be represented as consisting of objects and each of such objects can be classified within one of the four classes.

1. Reactors - devices in which chemical transformations take place.
2. Allactors - devices in which only physical processes occur.
3. Tanks - construction for the storage of intermediate products.
4. Lines - devices for managing the flows.

Objects 1, 2 and 3 are here in after referred to as the operational units.

Such classification allows both describing the chemical production facilities and studying them quantitatively using the theory of graphs, while technological schemes provide only qualitative information. A quantitative analysis of chemical production facilities using the theory of graphs becomes possible due to the fact that the set of processes described by graphs is modeled by matrices [9,10]. Since the method of analysis is graphical, the word «graph», first suggested by Koenig [11, 12], appeared.

The graph theory is a mathematical tool for analyzing the schemes, in which points in two-dimensional space represent the objects, and the relationship between the objects is shown by lines [10]. The points of the set in the graph theory are called the points of the graph, and the lines connecting them are called edges. In the graphs of chemical production facilities, the points are operational units, and the edges are the lines.

A characteristic feature of graphs describing the processes of industrial chemistry is that they are the directed graphs, that is, the directions can be assigned to all their edges. This is because the movement of flows along the lines in the processes of industrial chemistry usually occurs only in one direction. When the process is represented by graphs, the points of graph do not differ qualitatively, that is, they can denote any object. In the processes of industrial chemistry, the points (operational units) can be of three types, and they are not exchangeable.

Initially, all the points of graphs were designated by the same points, and the lines along which the material or energy is transferred were indicated by arrows pointing in the direction of motion [11]. Then it emerged that the graphs of industrial chemistry become more illustrative if their points contain the information on the purpose of a particular operational unit. Also, two extreme types of graphs are used to illustrate the processes: principal and technological graphs. Principal graphs provide only a scheme of the model of the chemical process of processing raw materials into the final product. They illustrate only the most important reactors, and, if necessary, some allactors. All reactors, allactors, tanks, all equipment for the transfer and all routes of materials are illustrated on technological graphs.

Legend.
Operational units corresponding to the points of the graph are designated with the symbols shown below:

- Reactor: black circle (●)
- Allactor: white circle (O)
- Reservoir: square (□)

Tanks for storing raw materials and finished products are not shown on the graphs at all, as they do not characterize the process.

Devices for transferring materials (which correspond to the edges on the graph) are shown depending on the aggregate state of the substance being transferred.

Designation of edges of the graphs of the processes of industrial chemistry:

- Solid matter: ------ →
- Liquid matter: →→
- Gaseous matter: ···································
- Suspension: ··········································

Arrows indicate the direction of movement.
The graphs of industrial chemistry can be classified into four types:

1. Direct-flow open graph, i.e. a graph in which the mass flows have the same direction.
2. Counter-flow open graph, i.e., a graph in which the major mass flows have opposite directions.
3. Direct-flow closed-loop graph represents the process in which the circulation of one of the substances takes place. The number of subgraphs can be open or closed.
4. Counter-flow closed-loop graph represents the process in which the counter-flow circulation of two substances takes place.

Based on the analysis of properties of the industrial chemistry processes, it can be mathematically demonstrated that only the above four types of graphs can exist [11].

The difference between the graphs of industrial chemistry and other graphs is that the conditions for the movement of mass flows in the processes are determined.

Each process in industrial chemistry is characterized by three factors:
1. Directional movement of incoming and outgoing mass flows, so that, as noted above, each graph of chemical technology is oriented.
2. The sum of the masses at the input \( \sum_{i=1}^{n} A_i \) is equal to the sum of the masses at the output \( \sum_{j=1}^{m} A_j \), since it is impossible to accumulate matter inside the process scheme \( \sum_{i=1}^{n} A_i = \sum_{j=1}^{m} A_j \).
3. Three types of dependences can correlate the number of incoming \( n \) and outgoing \( m \) flows: \( n < m \), \( n = m \), \( n > m \).

Graphs of processes of industrial chemistry can be of different complexity. The simplest model representing only the chemical scheme of the technological process without the auxiliary equipment is called the principal graph. The technological graph is obtained by representing a complex chemical production (chemical plant). Between these two cases, there is a range of transition graphs, the shape of which varies depending on the number of operations under consideration.

Complex technological graphs can be made more illustrative by splitting them into subgraphs. This option is expedient when representing complex technological processes, especially in case of complex processes of combined production. As a result, complex graphs and combined graphs are obtained [9]. Let us consider the application of the theory of graphs for particular industrial processes important for today’s industrial chemistry.

3. Application of the theory of graphs to simulate the process of oxidative regeneration of butane dehydrogenation catalyst

The process of deactivation takes place in any petrochemical industry, accompanied by the deposition of carbon on the surface of the catalysts thus reducing their activity. This problem can be solved by oxidative regeneration.

The oxidative regeneration of cocked catalysts is a combination of chemical reactions proceeding when oxygen interacts with coke, because of which coke is removed in the form of gaseous oxidation products: carbon oxides, water vapor, and sulfur oxides in some cases [12].

Let us consider the chemical-technological graph of the process of oxidative regeneration of catalysts.

![Figure 1. Scheme of oxidative regeneration of catalyst of one-stage butane dehydrogenation.](image-url)

1 – furnace, 2 – reactors, 3 – ejector.
The catalyst of vacuum dehydrogenation of butane is regenerated in a contact apparatus, the reactive unit is composed of eight apparatuses that ensure the continuity of the process. After completion of the dehydrogenation cycle, the apparatus is blown and air is fed into it. Coke burn off is performed at a temperature of 600–650°C. The regeneration cycle lasts for 8 minutes, the gases are removed by a 3-ejector, the catalyst is restored when the hydrocarbon gas is fed from the reactor. Dehydrogenation of butenes to butadiene takes place in a system of two reactors with a fixed-bed catalyst. One apparatus operates in catalyst regeneration mode, and the other - in dehydrogenation mode. A steam-air mixture at a temperature of 620-650 °C performs the regeneration, oxygen concentration is within 1-2%, and the duration of two cycles is 30 minutes. Dehydrogenation takes place first, followed by regeneration. The switching of the operation from the dehydrogenation phase to the regeneration phase consists in replacing the butene in the vapor mixture with a certain amount of air [13].

Figure 2. Technological scheme of regenerations of catalyst for dehydrogenation of butenes: 1-heat exchanger; 2-furnace; 3-reactor; 4-wasteheat exchanger.

Figure 3. Graph of regenerations of catalyst for dehydrogenation of butenes: allactor a¹ - heat exchanger; a² - furnace; a³ - reactor; a⁴ – waste heat exchanger.

The comparison of figures 2 and 3 shows that the graphs are perceived much more easily than the traditional technical schemes. This is because the range of operational units is shown using one point of the graph (in this case – a).

4. Application of the theory of graphs to simulate the process of oxidative regeneration of cracking catalyst
Let us consider more complicated refining processes, for example, include catalytic cracking to produce high-octane gasoline components. The quality of the process products is influenced by the composition of the raw materials, the technological parameters of the process, such as temperature and pressure, as well as the properties of the catalyst. During the process of cracking, coke deposits are formed on the catalyst, such deposits can be removed by catalyst regeneration. An example of a reactor unit is shown in figure 4 [14].

Therefore, the process of catalyst regeneration occurs in one apparatus. However, several processes take place in the regenerator. The air is heated up to the regeneration temperature in the preheater, then the air is mixed with the coked catalyst. A chemical reaction of oxidation (combustion) of coke from the catalyst surface occurs, after which the combustion gases are removed from the regenerator and the catalyst returns to the reactor after cooling. Thus, an operational technological scheme of the process
of regeneration of catalytic cracking catalyst can be developed based on the above. The scheme is shown in figure 5.

Figure 4. Technological scheme of a reactor unit of a modern catalytic cracking unit: 1 — catalyst uplift zone; 2 — raw material sprayer; 3 — overflow device with ideal upward plug-flow; 4 — riser; 5 — regenerator [14].

Figure 5. Operational scheme of catalytic cracking catalyst regeneration process: I – coked catalyst, II – air, III – hot air, IV – mix of coked catalyst and air, V – mix of regenerated catalyst and flue gas, VI – hot regenerated catalyst, VII – regenerated catalyst, VIII – flue gas; 1 – heat exchanger, 2 – mixer, 3 – reactor, 4 – separator, 5 – cooler.

Let us demonstrate the process of oxidative regeneration of catalytic cracking catalyst using the theory of graphs. To optimize the chemical and technological process, the following classification of graphs is used [15]:
1) Flow graphs;
2) Informational flow graphs;
3) Signal flow graphs;
4) Reliability graphs.

The main properties of the graphs in relation to the description of chemical and technological processes are as follows:
1) Orientation, since the movement of matter and energy in the system has a certain direction;
2) Asymmetry, since not all neighboring elements of the system are interconnected by reverse process flows;
3) A single chain of flows of matters or energy interconnects connectedness, all the elements of the system.

Flow graphs include [15]:
1) Parametric graphs;
2) Material graphs compiled according to the flowrates of physical flows;
3) Thermal graphs.

Let us compile a flow graph for the process of oxidative regeneration of catalytic cracking catalyst based on the operational scheme (figure 5).
Figure 6. Flow graph for the process of oxidative regeneration of catalytic cracking catalyst: the physical flow of the system is characterized by the following parameters: \( m_i \) – total flowrate of a physical flow.

Only the system elements with the changing flowrate are used to compile a material graph of the flowrates of physical flows. The operators in which the flowrate changed are the points of the graph; the flows themselves are the edges of the graph. Flowrates do not change in operators 1, 3, 5. In operator 1, the airflow is heated, i.e. the temperature rises, but the air flowrate does not change. In operator 3, chemical transformation (burning) takes place, but the flowrate remains the same. In operator 5 cooling takes place, i.e. temperature drops, but the catalyst flowrate does not change. Flowrate changes only in operators 2, 4, consequently, these operators are the points of the graph. In addition to the operators, raw material and product flows shall be included in the material graph of flowrates. Therefore, the graph includes \( F_1 \) and \( F_2 \) - the flows of catalyst and air, respectively. \( S_1 \) and \( S_2 \) are the output of products, regenerated catalyst and combustion gases, respectively.

Figure 7 shows the thermal flow graph.

Figure 7. Thermal graph for the process of oxidative regeneration of a catalytic cracking catalyst: 1-5 are the numbers of the points corresponding to operators; \( F_1 \) is the flow of coked catalyst; \( F_2 \) is the flow of fresh air; \( S_1 \) is the flow of regenerated catalyst; \( S_2 \) is the flow of combustion gases; \( Q_1 \) is the flow of heat supplied to the system for air heating; \( Q_2 \) is the flow of heat carried away when cooling the regenerated catalyst; \( i_1 \) is the heat of coke combustion; \( H_1 \) - \( H_{11} \) are the heat flows inside the system.

Chemical graphs can be used to describe the chemical mechanism of processes, including the catalytic ones. Chemical graphs are classified as follows [15]:

1) Molecular;  
2) Bipartite;  
3) Signal.

Molecular graphs characterize the structure of a chemical bond. Molecular graphs allow to solve problems with coding, structural peculiarity, branching, etc. Atoms are the points of the graphs, and chemical bonds are the edges. The structure of catalysts can also be illustrated by molecular graphs.

Bipartite graphs are used to optimize paths; they require the smallest number of intermediate reactions, the minimum number of reagents. Molecules are the points of such graphs, and interactions between molecules, i.e. chemical bonds are the edges.

Signal graphs characterize the kinetics of chemical processes. Information variables are the points of the graphs, signal interconnections are the edges.
An adjacency matrix, an incidence matrix, is compiled based on the theory of graphs. Mathematical models can be developed based on these matrices.

For the catalytic cracking process, let us consider one of the known variants of the mechanisms of the kinetics of this process [16].

\[
\begin{align*}
K + O_2 &\leftrightarrow [K-O_2] \rightarrow [K-O] \\
[K-O_2] &\rightarrow CO_{ad} \rightarrow CO_2^+ \\
[K-O] &\rightarrow CO_{ad} \rightarrow CO^+ \\
[K-O] &\rightarrow H_2O_{ad} \rightarrow H_2O \\
CO + 1/2O_2 &\rightarrow CO_2
\end{align*}
\]

Bipartite graph for this reaction is shown below in figure 8.

**Figure 8.** Bipartite graph for the process of oxidative regeneration of hydrocarbon cracking catalyst.

Using this graph, adjacency and incidence matrices can be compiled and the order of analysis of the target system of chemical reactions can be defined.

The advantages of graph models include their flexibility, wide possibilities and variety of applications. Theoretical graph algorithms and the search for control procedures based on them are much more efficient than others in many cases are. The advantage of this method is that the method allows determining the fastest way to solve a problem in case of a significant number of possible solutions. The graphs can also be used to determine the method of analyzing a complex system, the solution of which is not obvious at first glance.

5. Conclusion

Thus, the presentation of a process with the graphs is more illustrative as compared with the technical scheme. The presentation of process of industrial chemistry based on the theory of graphs described above has a purely qualitative nature at the initial stage. However, such a presentation allows determining the procedure for analyzing the equipment for the compilation of a mathematical model, which will allow optimizing the oxidative regeneration processes of the butane dehydrogenation catalyst and the oxidative regeneration of the cracking catalyst to reduce the prime cost of products.

6. References

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