Getting of Benzine from Residues of Methyl-Tret-Butyl ether Production Using Microwave Radiation

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Abstract. Benzine getting from used butane-butylene fraction from unit of methyl-tret-butyl ether production through oligomerization is one of ways to increase efficiency and ecological compatibility of process. Usually, the technology of producing oligobenzine is based on the generation of thermal energy required for the oligomerization reaction when burning solid or gaseous fuels in furnaces. Safety and ecological compatibility of this process may be significantly improved with microwave radiation used during reactions. The use of microwave energy will heat only the catalyst, which will be in contact with the butane-butylene fraction.

It is possible to estimate the process parameters in the static and dynamic modes by numerically solving a system of equations that mathematically describe oligomerization under the influence of microwave radiation. It is established that the oligomerization process is intensified, and the energy costs are reduced.

1. Introduction

Methyl-tret-butyl ether as a quality modifier is increasingly used in the production of commercial motor gasoline, and its world production volumes are continuously increasing.

It is also possible to obtain gasoline through oligomerization from the used butane-butylene fraction (BBF) from the unit of the production of methyl-tret-butyl ether (MTBE).

2. The traditional technology of residual butene-butylene fraction production of methyl-tret-butyl ether

Consider the existing industrial technology of BBF oligomerization (Figure 1) [1].

This is a combined process for producing dienes from BBF and their dimerizing. As a result of these reactions, aromatization of saturated and unsaturated hydrocarbons and the alkylation of aromatic hydrocarbons also occur. The set of reactions can be represented as follows:

\[ \text{C}_8\text{H}_{16} \xrightarrow{k^3} \text{C}_6\text{H}_4(\text{CH}_3)_2 \]

\[ \text{C}_6\text{H}_6 \xrightarrow{k^5} \text{C}_5\text{H}_{10} \]

\[ \text{C}_4\text{H}_8 \xrightarrow{k^2} \text{C}_3\text{H}_8 \]

\[ \text{C}_2\text{H}_10 \xrightarrow{k^4} \text{C}_2\text{H}_6 \]

\[ \text{C}_4\text{H}_6 \xrightarrow{k^1} \text{C}_3\text{H}_8 \]

\[ \text{CH}_4 + \text{C}_3\text{H}_6 \]

\[ \text{C}_6\text{H}_6 + \text{C}_3\text{H}_{10} \]
k1, k2, k3 - rates constants of the reactions of dehydrogenation, dimerization and aromatization, respectively;
k-1, k-2 are the rates constants of the corresponding back reactions;
k4, k5 are the rates constants of cracking reactions.

According to this scheme, the dehydrogenation rate should be higher than the dimerization rate (k1 > k3). In addition, the condition k3 > k2 should be observed and, most importantly, the aromatization should proceed much faster than cracking (k5 < k3 > k2).

The raw material is waste butane-butylene fraction. It is a colorless gas, which is heavier than air and insoluble in water. The vapors form explosive mixtures with air, which can spread far from the leak place.

Typical hydrocarbon composition of raw materials (% mass.) is isobutane - 65-75; n-butane – 1.5-5; n-butylene - 17-20; isobutylene - 4-5; trans-butene - 3-7; cis-butene – 0.5-2.5; ΣC5 - traces. The sulfur content in the raw material does not exceed 0.002 (% mass.).

The oligomerization reaction is exothermic, so it is necessary not to allow the reactor overheat by additional heat release as a result of a chemical reaction.

The synthesis of oligobenzine is carried out mainly on the catalyst BAK-70m, which is zeolite modified with zinc and gallium [1].

The temperature in the lower layers of the catalyst rises to 470 °C with an increase in the volumetric feed rate of raw materials up to 3 h-1. Such a high temperature, without changing the overall yield of the catalyst, leads to an increase in the proportion of aromatic hydrocarbons in it. The temperature of the catalyst can be reduced to 420 °C by lowering the temperature at the entrance to the catalyst bed, which allows adjusting the content of aromatic hydrocarbons in oligobenzine.

The reactor unit (Figure 1) consists of four reactors working in pairs. Two cycles are carried out simultaneously - oligomerization reaction and catalyst regeneration. The separation of the reaction products is carried out by rectification.

![Figure 1. Traditional oligomerization scheme.](image)

Thus, the traditional technology of oligobenzine production is based on the fact that the thermal energy required for the oligomerization reaction is transferred through heat exchangers at burning solid or gaseous fuels in furnaces [1].

3. Features of obtaining benzine in microwave reactors
In contrast to the traditional technology of heating the reaction mass, the use of microwave energy involves warming up only the catalyst that will be in contact with the BBF. This is due to the different abilities of the gaseous fraction and the solid catalyst to absorb the electromagnetic energy of the microwave range. In this case, the catalyst will transfer accumulated heat to the reaction mass (after the field energy is converted) [2].
Figure 2 shows a diagram of the electrodynamic microwave reactor for the process of producing benzene.

![Diagram of the electrodynamic microwave reactor](image)

**Figure 2.** Diagram of the electrodynamic microwave reactor for the process of producing benzene.

The proposed method of influence to the technological medium using an electromagnetic field creates a number of advantages.

The substances are heated only in the reactor, which makes it possible to exclude from technology some complex heat exchange equipment and a fuel burning furnace. This will lead to economical and ecological effect.

The heating rate of the catalyst is determined only by the speed of propagation of an electromagnetic wave in the medium, the dielectric properties of the medium, and the radiation power.

The contactless method of energy transfer in all catalyst volume, having a high speed, causes small inertia in regulation the heating temperature of the substance [1].

The mathematical description of the process allows evaluating the operating modes of the reactor, to optimize the processes parameters, to develop units for automatic control. It is possible to make a system of partial differential equations characterizing heat exchange processes for the oligomerization process occurring in an electrodynamic microwave reactor. The resulting system of equations has appearance:

\[
c_i \rho_k \frac{\partial T_i}{\partial t} = \lambda_k \frac{\partial^2 T_i}{\partial z^2} - \alpha_e \alpha (T_i - T_f) - (1 - \varepsilon) q_v
\]

(1)
\[ c_f \rho_f e \frac{\partial T_f}{\partial t} = \lambda_f \frac{\partial^2 T_f}{\partial z^2} - c_f G \frac{\partial T_f}{\partial z} + \alpha_s a(T_f - T_i) + \Delta H \]  \hfill (2)

\[ \frac{\partial}{\partial t} \left( \frac{1 - X}{G/\rho_f} \right) = -\frac{De}{G/\rho_f} \frac{\partial^2 X}{\partial z^2} + \frac{\partial X}{\partial z} - r_0 \left( \frac{\rho_f}{GC} \right)_o \]  \hfill (3)

\( T_p, T_i \) are the temperatures of the BBF and the catalyst, respectively;
\( c_f \) is the isobaric heat capacity of the gas;
\( c_k \) is the heat capacity of the solid phase;
\( \varepsilon \) is porosity;
\( \lambda_f \) is the effective thermal conductivity of BBF;
\( \lambda_d \) is effective thermal conductivity of the catalyst;
\( G \) is the mass velocity;
\( q_v \) is the volumetric power of heat sources.

We can estimate the oligomerization process parameters in the static and dynamic modes solving the system of equations (1-3) by numerical methods [1].

As a result of approximate calculations it was found that the oligomerization process is intensified, and energy costs are reduced.

The safety of operation of this reactor is additionally ensured by adaptive control, operatively monitoring the substances heating, which is especially important for the exothermic reaction.

4. Summary
The use of microwave radiation improves the ecological efficiency of production, its safety and reduces energy consumption significantly. The use of contactless heating technology using microwave energy in combination with modern control systems eliminates many of the negative aspects of existing facility, improving production performance and product quality.

5. References
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