SECONDARY PROCESSES OF PROPANE AND BUTANE MIXTURE AND THEIR THERMODYNAMIC PROBABILITY

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During the thermal decomposition of a fraction consisting of a mixture of propane and butane at high temperatures in the absence of air, not only primary dehydrogenation and cracking reactions occur, but also various secondary reactions [1-3]. These secondary reactions are mainly associated with the formed unsaturated low-molecular hydrocarbons (ethylene, propylene, etc.), which, due to their high reactivity, undergo various rearrangements and complex transformations in various directions. Dimerisation and trimerisation of olefins. Unsaturated hydrocarbons such as ethylene and propylene can react with each other at high temperatures without the participation of a catalyst, forming large molecular hydrocarbons [4-7].

Alkylation of low molecular weight saturated hydrocarbonsSubstances such as propane and butane react with olefins to form isomers or larger products. Dehydroaromatization of hydrocarbons such as ethylene Dehydroaromatization of hydrocarbons such as ethylene Ethylene, propylene, butylene, and other olefins are subjected to multi-stage dehydrogenation at high temperatures to form aromatic compounds such as benzene, toluene, and xylene. Carbon-carbon bond cleavage (C-C cleavage). These reactions are a common form of cracking of C_3-C_4 hydrocarbons and are carried out in practice by a radical mechanism. Secondary dehydrogenation reactions (hydrogen evolution). These reactions can occur at high temperatures, but are much less likely to occur in practice. The standard Gibbs free energy change ($\Delta G°$) is the main criterion for assessing the thermodynamic probability of secondary processes [8-10].

This indicator determines the possibility of a spontaneous reaction:

If $\Delta G° < 0$, the reaction is thermodynamically feasible and can occur spontaneously. If $\Delta G° > 0$, the reaction is thermodynamically unfavourable and cannot occur spontaneously without the influence of external energy. The reaction of ethylene formation from ethane (dehydrogenation) is thermodynamically possible only at temperatures above 1100 °C, i.e. under these conditions the standard Gibbs free energy change ($\Delta G°$) has a negative value ($\Delta G° < 0$). Hydrogenation of propylene. It is thermodynamically possible above 1150°C; secondary decomposition of propylene, which involves the cleavage of the C-C bond, is considered a process that can occur above 800°C.

Figures 1-3 show graphically the change in the ΔG^0 values corresponding to the secondary transformation processes of ethylene-unsaturated hydrocarbons with increasing temperature. Based on these relationships, the following conclusions can be drawn. The ΔG^0 value for the dimerisation process is usually greater than 0 and increases with increasing temperature, i.e. this process is temperature-independent. For the aromatisation (dehydroaromatization) reaction, ΔG⁰ begins to become negative at 900-1000°C, which means that this reaction is possible at higher temperatures. For the processes of C-C bond cleavage, ΔG⁰ decreases starting from 500°C and reaches its lowest values around 800°C.

During the decomposition of the propane-butane fraction, the resulting olefins actively participate in secondary reactions. Processes such as dehydroaromatization, dimerisation, and alkylation based on ethylene and propylene can occur at high temperatures, but the ΔG⁰ value and reaction time affect their efficiency. Secondary hydrogenation processes are thermodynamically possible only at very high temperatures (1100-1150°C) and are rarely encountered in practice.

The G⁰–T relationship is the most reliable basis for determining the equilibrium direction and probability of reactions.

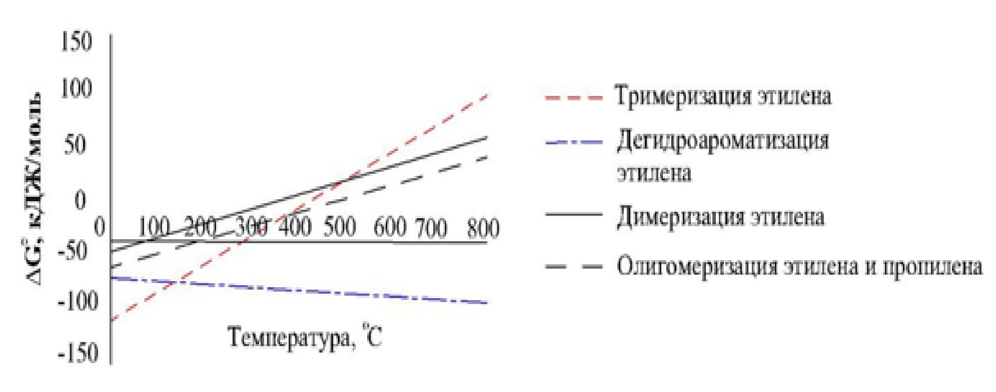

Figure 1. Effect of temperature on ethylene conversion processes.$\Delta \boldsymbol{G}^{\mathbf{0}}$

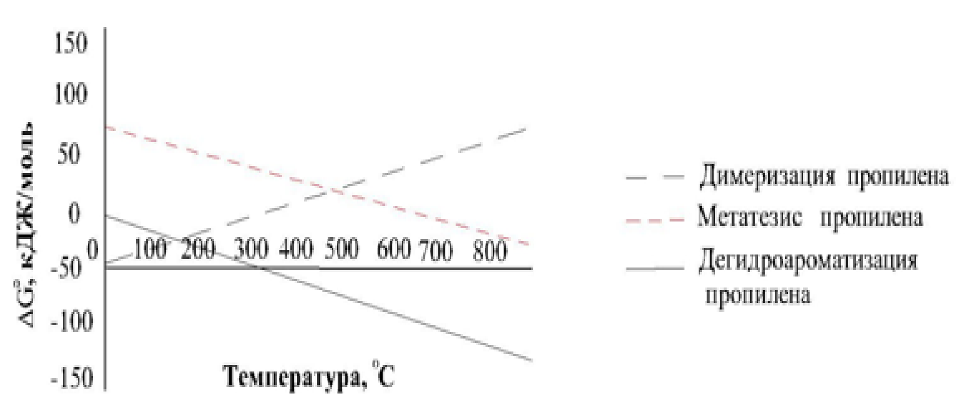

Figure 2. Effect of temperature on propylene conversion processes.$\Delta \boldsymbol{G}^{\mathbf{0}}$

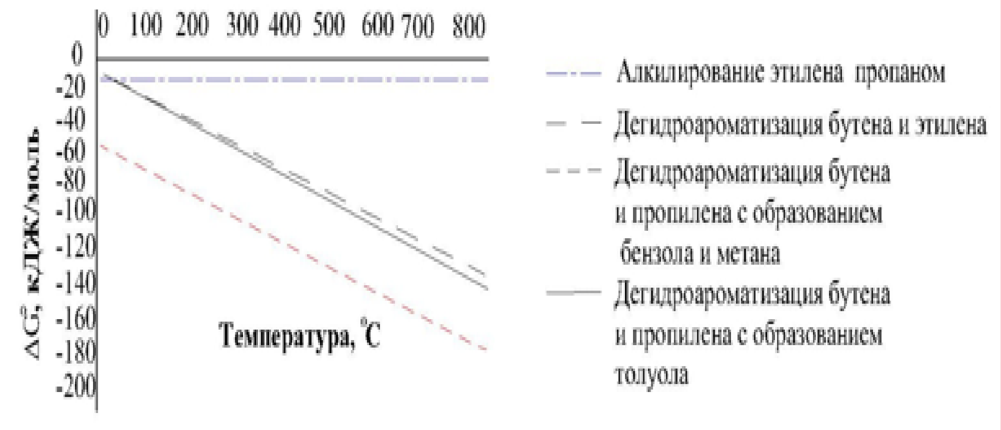

Figure 3. Effect of temperature on conversion processes of unsaturated ethylene series hydrocarbons.ΔG^0

Secondary reactions occurring during the decomposition of a propane-butane mixture at high temperatures in the absence of air - processes such as dehydrogenation, isomerisation, cracking, polymerisation and aromatisation - have a significant impact on the overall efficiency of the reaction. In this work, the thermodynamic potential of these reactions was analysed using the standard Gibbs free energy (ΔG°).

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