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Relationship between macrokinetic parameters thermolysis process and topological characteristics for hydrocarbons molecules

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Abstract

Knowledge of the kinetic parameters in molecular thermal transformation processes with the formation of gaseous products is of great importance for petrochemical and the oil refining industry. This is especially relevant for the technology of thermolysis processes can be divided into thermal cracking and hydrocarbons pyrolysis. The study of the thermolysis kinetic parameters allows to choose the optimal modes of these thermal processes. Phenomenological approach based on the study of the effective kinetic parameters of the thermolysis process is applied in this paper. We study the effective rate constants of the transformation of raw material molecules into the final product without a detailed description of the elementary mechanism and intermediate stages in a process. Various homologous series of hydrocarbons containing PI-electrons were studied as objects of research. Methodology "structure-property" is used in this research paper. For the first time, the relationship between effective kinetic parameters thermolysis of hydrocarbons in a wide temperature range from 370 to 600 °C with topological indices of the molecular graph is considered. The Wiener index and a sum of squares eigenvalue spectrum of the molecular graph, are used as topological indices. The latter index reflects the Hückel spectrum of the energy states of molecules. Five-factor dependence of kinetic parameter of the thermolysis effective activation energy on the topological indices is established by the least squares method according to the algorithms of multiple regression analysis. Significance of the model coefficients were estimated. Adequacy of the calculation was evaluated by comparing the values of the experiment and statistical data obtained. It is possible to characterize the quality of the QSPR regression model by a multiple correlation coefficient R = 0.96, which was confirms a strong connection between topological characteristics of hydrocarbon molecules and their kinetic parameters. Pre-exponential factor of the thermolysis can be estimated through activation energy on the basis of compensation effect. A relationship is established between effective kinetic constants thermolysis process of hydrocarbons and structural and chemical characteristics of hydrocarbon molecules. The obtained results make it possible to predict the thermolysis process in a temperature range from 370 to 600 °C provided that information about the structure of hydrocarbon molecules is known.

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