

1. The rate of thermal cracking of individual hydrocarbons (% reacted hydrocarbons) decreases with a rise in pressure. The yield of low-boiling, cracking products drops and the relative content of higher-boiling hydrocarbons in the cracking products rises (in comparison with the original hydrocarbons). In addition, the refractive indices of the high-boiling products drop with a rise in pressure.
2. A low hydrogen pressure retards and a high hydrogen pressure accelerates thermal cracking (cf. exp. Nos. 48 and 40, 39, 38 in table 1, and also exp. Nos. 51-53 and 55-58 in table 2). The refractive index of the residue obtained in cracking under high hydrogen pressure approaches the value for the original hydrocarbon, which indicates very insignificant formation of hydrocarbons with a large number of carbon atoms.
3. Catalytic cracking of n-heptane on an aluminosilicate catalyst is accelerated by high pressure (cf. exp. Nos. 52 and 49, Nos. 54, 57 and 55, 56 in table 1).
4. High hydrogen pressure accelerates catalytic cracking on an aluminosilicate catalyst.
5. During catalytic cracking under pressure a larger number of isomers of the original hydrocarbons is formed and fewer high-boiling products than during thermal cracking under the same conditions.

It should be stressed that the retardation of thermal cracking under high pressure cannot be attributed to a shift in the chemical equilibrium. In our experiments the equilibrium was not reached. This follows particularly from a comparison of the results of thermal and catalytic cracking at the same temperature and pressure. Thus, in thermal cracking at 420°C and a pressure of 1000-1300 atm. 39.8% of n-heptane remains unchanged (exp. No. 13), and in catalytic cracking 20.9% (exp. No. 49); in these experiments the yield of gaseous and low-boiling liquid decomposition products was 20.5 and 64.5% respectively calculated on n-heptane. Due consideration should be given to the fact that at high pressures the polymerization, hydrogenation and alkylation reactions are intensified, which reactions substantially decrease the free energy value of the total thermal cracking process under pressure.

This investigation thus shows that the acceleration in cracking of paraffins with a rise in pressure, as observed by some investigators, is restricted to the low pressure range and that at high pressure the rate of thermal decomposition decreases.

The acceleration of catalytic cracking of n-heptane by high pressure reflects a real difference between the thermal and catalytic processes. It may be assumed that in the catalytic process the slowest stage of the total process, which determines its rate, is the adsorption of hydrocarbon or another reaction with the catalyst.

The rules of thermal cracking observed at high pressure can be accounted for on the basis of an analysis of the chain mechanism. However, this problem lies beyond the scope of this investigation.