

Lecture 4 INFLUENCE OF OPERATING CONDITIONS

The influence of temperature on a complex process such as thermal cracking must be examined from the point of view of both the modification of the thermodynamic equilibriums and of the relative rates of the decomposition and other reactions that take place within the process. Practical results show that in pyrolysis, the ratios ethene/ethane and propene/propane are close to those for equilibrium. The increase in temperature has a favorable effect on the conversion to alkenes. Increased temperature has a favorable effect also on the formation of butene from butane and of butadiene from butene, which however, enter in competition with the cracking of butane to ethene and ethane. Despite the fact that the increase of temperature favors the production of ethene, propene, and butadiene, it is not possible to reach a maximum production of all these three hydrocarbons in the same time. The reason is in the difference among the rates of the reactions that produce them and in the fact that the desired products suffer further decomposition. Accordingly, the production of each of the three hydrocarbons passes through a maximum, which for propene and butadiene, occurs earlier than for ethene. For this reason, a pyrolysis furnace may be operated either for maximizing the production of ethene, or that of propene. The two objectives can not be reached in the same time. Higher operating temperatures also favor the equilibrium for the formation of aromatic hydrocarbons from alkylcyclohexanes, which leads to an increased production of aromatic hydrocarbons with increased temperature in the pyrolysis of naphta. Concerning the influence of temperature on the kinetics of the chain decomposition involving free radicals, it is interesting to note that with increasing temperature the average molecular mass of the formed products decreases. Since in pyrolysis, the length of the kinetic chain is of a few hundred interactions, the composition of the products will be determined by the propagation reactions, which are repeated over and over again. The initiation and termination reactions can be neglected.

The effect of temperature on the rate constants of thermal processes is generally expressed by the Arrhenius equation:

$$k = Ae^{-E/RT}$$

The influence of pressure

The important increase of the equilibrium conversion that accompanies the decrease of the operating pressure for the conversion of ethane to ethene, of propane to propene and, especially of 1-butane to butadiene. The conversion at equilibrium increases even stronger with the decrease of pressure in the dehydrogenations of the 6-carbon atoms ring cyclo-alkanes to aromatic hydrocarbons. Concerning the equilibrium for the formation of acetylene from ethene, the reduction of pressure favors the increase in conversion. This effect however, seems to be somewhat less important than for the conversion of the ethane to ethene. The polymerization of the alkenes, produced during the processes of cracking under high pressure, is favored by the increase in pressure. The effect of pressure upon the kinetics of the radical chain decomposition may be analyzed also by examining its influence on the mechanisms of the following reactions:

1. β -cleavage of free radicals
2. substitution reactions, i.e. the reactions of radicals with feed molecules

As in the analysis of the effect of temperature, here also the effect of the initiation and termination reactions on the products of the decomposition may be neglected.

The influence of feed composition

The molecular mass and the chemical composition of the feedstock determine the conversion as well as the distribution of the products obtained from thermal processes. This connection between the characteristics of the feedstock and the result of the process is expressed quantitatively by the kinetic equations and the rate constants.

For feedstocks consisting of residue, the content of resins and asphaltenes is high and an intense formation of carboids begins much before the maximum for the first intermediary product - gas oil is reached. The formation of insoluble material is generally dependent on the content of asphaltenes, resins, and polycyclic hydrocarbons in the feedstock. For this reason, in the visbreaking process and generally during the cracking of the residues in tubular furnaces, where the intense formation of carboids leads to the coking of the tubes, the weight fraction of the obtained gas oil depends on the position of the curve of carboids.

In industrial practice, the highest conversion that may be obtained in the furnace during the cracking of a residue is expressed usually as a percentage of gasoline produced. Typical conversions are of: 6-10% from straight run residue and 2-3% from heavy residues.

The influence of steam introduced in the reactor

Water vapor (steam) introduced into the reactor has a complex effect on thermal processes. Steam acts firstly as an inert diluent, decreasing the partial pressures of all components of the reaction. Second, steam is usually being introduced into the last sector of the furnace tubes, where it causes a significant increase of turbulence. This prevents the deposit of asphaltenes on tubes walls that possibly begin to be separated from the colloidal solutions. In this manner phenomena leading to coking of the tubes are prevented.

This effect is especially important in the processes of residue cracking -visbreaking and delayed coking. In this process, steam increases the conversion to the first intermediary product and increases the length of the cycle between two decoking operations.

In the pyrolysis process the action of the steam is more complex. The main effect is the fact that for the same final pressure at the exit from the coil, by decreasing the partial pressures of the hydrocarbons the steam displaces the equilibrium towards the formation of supplementary amounts of ethene, propene, butadiene, isoprene, and aromatic monocyclic hydrocarbons, by means of the very products that constitute the objective of the process.

Note that the exit pressure in the pyrolysis furnaces cannot be decreased below some limits. These limits are determined by the aspiration pressure of the compressors and by the pressure drop in the succession of cooling and separation equipment situated between the exit from the furnaces and the compressor group. The introduction of steam leads to the decrease of partial pressures, therefore having an effect similar to that which could be obtained if it were possible to reduce the pressure below the limits imposed by the system.