

Lecture №13 «Pyrolysis. General Issues of Commercial Pyrolysis»

Thermal cracking at low pressures - **pyrolysis** or steam cracking - was used worldwide earlier than cracking at higher pressures.

- The pyrolysis process (steam cracking), is today the most important cracking process and the most important purveyor of raw materials for the petrochemical industry. Its impact may be characterized by world consumption of the main products supplied by this process, presented in Table 1.

- The production of chemicals brings the highest added value to petroleum. Therein resides the present importance of pyrolysis as the main supplier of raw materials for the organic synthesis industry.

World Production of
Main Products for Chemical Industry
Provided by the Pyrolysis (thousands
metric tons/year)

Year	Ethene	Propene	Butadiene
1970	19,380	8,670	–
1975	23,650	12,060	3,445
1980	34,900	17,790	5,060
1985	41,840	21,900	5,979
1990	52,400	25,200	–
1995	70,200	–	6,200

General Issues of Commercial Pyrolysis

Feedstock selection. The selection of feedstocks for pyrolysis is based on technical and economical conditions, namely:

1. The feed availabilities, taking into account the most reasonable use of various petroleum fractions.
2. The products that pyrolysis should deliver for various downstream petrochemical processes.
3. The limitations imposed by pyrolysis technology.

The last aspect refers to the fact that the pyrolysis in tubular heaters cannot process residual fractions due to excessive coke formation. The pyrolysis of **fuel oil and of other residues** is possible only in systems with a solid heat carrier where the coke is deposited on the carrier and it is burned during the reheating step.

The use of **ethane** constitutes the most reasonable solution if ethene is the only product desired. Indeed, besides pyrolysis, the only other use for ethane is as fuel. However, the use of ethane in pyrolysis presupposes the existence of crude oil or of rich fields of natural gas.

Propane and butane are also used as feed for pyrolysis. There is strong competition for using these hydrocarbons as liquefied gases. In some regions of the world, this use completely eliminates especially butane as feed for pyrolysis. Concerning n-butane, it must be mentioned that besides its use as liquefied gas, important amounts are used as an additive to gasoline for increasing vapor tension, especially as a replacement for isopentane. Smaller amounts of n-butane are used in dehydrogenation.

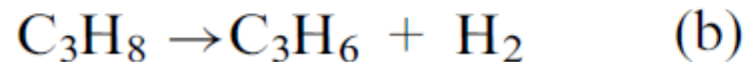
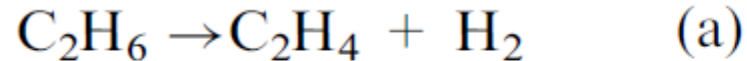
The use of **naphtha** as pyrolysis feedstock was developed initially in countries lacking natural sources of natural gases. Besides ethene and propene, important quantities of butadiene, isoprene and aromatic C₆ – C₈ – hydrocarbons are produced.

The use of gas oil and especially of vacuum gas oil as pyrolysis feedstock occurred more recently. The pyrolysis of gas oils in tubular heaters requires the solution of specific problems related to the higher propensity for coking and the higher reaction rate of these feedstocks.

Concerning the chemical composition of liquid feedstocks, note the need to limit their content in aromatic hydrocarbons and to practically eliminate alkenes, both conditions leading to the formation of coke. The concentrations of other classes of hydrocarbons determine especially the ethene/propene ratio in the effluent. In present conditions, when pyrolysis aims at maximizing the production of ethene, feedstocks with a prevalent concentration of n-alkanes are preferred.

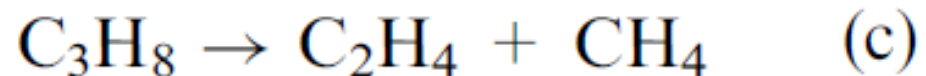
The use in pyrolysis of liquid feedstocks as opposed to gases may be determined also by the necessity to obtain, besides ethene, other important hydrocarbons in petrochemistry, especially butadiene, C₆–C₈ aromatics, and isoprene.

Process conditions and reactor types. Ethene currently represents the main product of the pyrolysis process. Accordingly, the reaction system and technological conditions are selected so as to maximize the yield of this product. Thus, thermodynamic considerations on the approach to equilibrium in a process condition for the reactions:



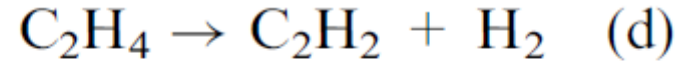
show that the maximum yield of ethene is favored by high temperatures and reduced partial pressures.

It is to be mentioned that reaction (b) is in competition with the parallel transformation:

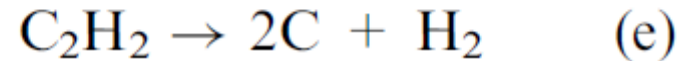


the equilibrium of which, at the temperatures of the pyrolysis, is completely displaced to the right.

The ethene formed by way of reactions (a) and (c) also suffers decompositions, especially following the reaction:



followed by



At the usual temperatures practiced in various pyrolysis systems, the amount of acetylene present in the effluent is limited by the equilibrium of reaction (d) to a few percentage points. The excess of acetylene is decomposed according to reaction (e). It follows that the yield of ethene passes through a maximum, that imposes the limitation of the residence time in the reactor. Analogously, the yield of propene also passes through a maximum. The difference is that, while the maximum of ethene yield shows a strong increase with temperature due to the displacement to the right of the equilibrium of the reaction (a), the maximum of propene increases much slower due to the competition of reactions (b) and (c). The latter orients the transformation towards producing ethene and not propene.

In general terms, the operating conditions that maximize the yield of ethane are:

1. High coil outlet temperatures (COT), limited by the increase of acetylene formation that occurs at temperatures that exceed 1000 °C.

2. Low partial pressures of the reactants and of the products at the outlet from the system, corresponding to low pressure and to a possible dilution with inert gases or steam.

3. Short reaction residence time, of the order of seconds, or fractions of a second. The higher the temperature, and molecular mass of the feedstock, the lower should be the reaction time.

Products separation. The problems of the separation of the products from pyrolysis do not depend on the reaction system but is in great measure dependent on the processed feedstock.

The separation is divided conventionally in the hot section and the cold section. The hot section contains the rapid cooling of the effluent as soon as it leaves the reactor (quenching), its cooling, and the separation of the heavy products, used as fuel, of the gases and of the gasoline.

The cold section contains the processing of the gases, which in the case of pyrolysis of liquid fractions consists of the following main operations: compression, separation of H₂S and CO₂ with diethanolamine followed by washing with a solution of NaOH, cooling, removal of the water vapors by condensation and of the water traces by drying.

Then, the demethanation and the separation of the C₂, C₃, and C₄ fractions are carried out, and also of the heavier hydrocarbons. From each of these three fractions, the acetylene and its homologues are removed by selective hydrogenation, after which the separation by fractional distillation of the ethene from ethane and of the propene from propane is carried out.

The ethane, the propane, and other fractions are pyrolyzed separately in special heaters. After quenching, the effluents are introduced in the effluents deriving from the other heaters.

Butadiene is recovered from the C₄ fraction by selective extraction. Other individual components may be extracted (for instance 1-butene by adsorption on zeolites) if required by the downstream petrochemical industry. Also, the separation of isoprene from the C₅ fraction is performed. The purification of isoprene to the specification purity for the fabrication of the stereospecific rubber is quite difficult.

Pyrolysis naphtha can be used as a component for automotive fuel after it is selectively hydrogenated for removing unstable hydrocarbons, which are gum generators. From the fraction 60–135°C, the aromatic C₆–C₈ hydrocarbons could be extracted with selective solvents after the complete hydrogenation of the alkenes.