

OVERVIEW WORLD TECHNOLOGIES OF PYROLYSIS AND PERSPECTIVE OF DEVELOPMENT

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In this article was made research of the process of pyrolysis and modification of this process. It's was viewed existing technology which are represented by different company. It's determined directions of development and perspectives of using this process in different fields of industry.

Keywords: pyrolysis, steam cracking, petrochemical, olefins, process of waste, hydrolysis, catalytic pyrolysis, initiated pyrolysis, oxidative pyrolysis, monomers

Pyrolysis is hardest type of cracking to produce lighter products compare with feed.

The main aim of pyrolysis of hydrocarbon in the modern period it is production of light unsaturated hydrocarbon's gases (olefinic hydrocarbons) such as ethylene, propylene, benzene, butadiene, isoprene, isobutylene, butanes, acetylene, because this gases are used mainly to produce great quantity of important substances and polymaterials. In addition pyrolysis it is best economical solution to produce this gases, because another methods more expensive. So pyrolysis is process of destruction of feed with high temperature usually more than 650–700 °C.

Oil feed stock can be divide on two main type: liquid and gaseous. Depending on the type of feed it's can be produced mixtures with different specifications (table 1).

Table 1

Approximate mat balance of pyrolysis with different feed stock [1]

Products, % mass	Gaseous feed			Liquid feed	
	ethane	propane	butanes	naphtha	gas-oil
H ₂ and methane	13,0	28,0	24,0	26,0	23,0
Ethylene	80,0	45,0	37,0	30,0	25,0
Propylene	1,1	14,0	16,4	14,1	14,4
Butadiene	1,4	2,0	2,0	4,5	5,0
Butene mixture	1,6	1,0	6,4	8,0	6,0
C ₅₊	1,6	9,0	12,6	18,5	32,0
Ratio propylene/ethylene	0,03	0,3	0,5	0,4	0,6
Propylene content into C ₃ fraction	86,7	58,3	99,0	98,3	96,7

Various companies propose different variant of process of pyrolysis but all of them quite flexible in terms of feed stock. The company which have most popular licences is Technip, ABB Lummus Global, Linde, Kellog Brown & Root, Stone & Webster.

According to Technip's technology process run with high temperature in the presence of steam which add into the coils in the radial chamber of furnace. Outlet temperature about 880 °C in depend on quality of feed and demanding severity of process. This process provide high selectivity according to ethylene and propylene and at the same time decrease coke formation.

According to licence of ABB Lummus Global it's produce ethylene for polymerization with purity 99.95 % vol. Feed is heated and cracked in the presence of steam by tubular furnace, outlet temperature 815–870 °C. Special construction of the coils of this furnace guarantee short residence time that why this furnaces called SRT. This technology is characterized high outlet of olefinic hydrocarbons, long run time and mechanical durability of equipment.

Kellog Brown & Root propose wide choice of feed which can use in it's furnaces from ethane to vacuum gas-oil. This furnace called SCORE, have straight coils, short residence time about 0.1 s and low working pressure. Special construction furnace guarantee high outlet of olefinic hydrocarbons.

Main directions of progress in the field of pyrolysis there are optimization of process, improving furnace construction and improving automatic control by computerization.

For example designed in the last time ceramic furnaces (Stone & Webster) increase conversion and efficiency of process thanks to very high temperature and absence of coke formation.

ABB Lummus Global propose new furnace too which called SRT-X. In recent time observe tend to increasing capacity of unit of pyrolysis which vary close to 1.4 million ton per year.

In addition ABB Lummus Global propose include special technology CD Hydro which combine catalytic distillation and hydrogenation of nonoperating products into technological scheme of olefenic hydrocarbons separation. According this technology

hydrogenation of acetylenes and dienes will carry out during one stage instead of four stages. This technology allow decrease capex in the unit on 5–7 % [2].

An R&D laboratory in N-Novgorod has developed an original method for catalytic thermolysing a propan-butan hydrocarbon material into ethylene, three times more productive than existing industrial methods, and without gumming-up. An original catalyst-modifier is developed for coating pyrolysis reactors, which increases ethylene yield and suppresses soot generation. Application of this approach in a laboratory allowed thermolysing propan-butan material with ethylene yield up to 93-98 %, and without gumming-up [3].

Most actual problem now it's necessary widening source of feed stock and decreasing specific consumption of feed. Necessity of decreasing of capex and opex demand to look for new modification of pyrolysis, basically it is a using heavier feed stock as a fuel oil, vacuum gas-oil, oil and so on. It's proposed new method of pyrolysis some of them there are catalytic pyrolysis, initiated pyrolysis, oxidative pyrolysis and hydrolypyrolysis.

During development of catalytic pyrolysis was be researched many catalyst heterogeneous and homogeneous. Study demonstrated that heterogeneous catalytic pyrolysis increase selectivity and conversion of process so it's means that increase outlet of ethylene. It's selected best heterogeneous catalyst such a metavanadate of potassium, oxides of indium, oxides of potassium, oxides of magnesium, some zeolite [4].

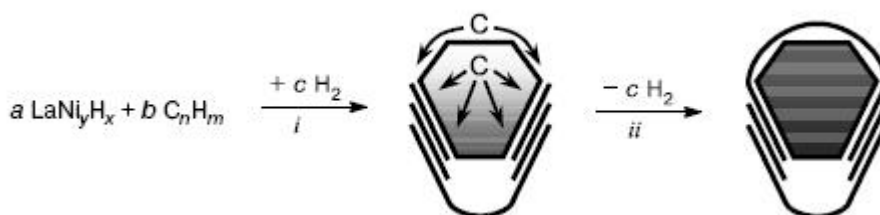
Firm Asahi recently developed of two catalytic systems for pyrolysis of light hydrocarbons: Al-Si zeolite with pore size 0,5-0,65 nanometers with the additive of organic peroxide, and with the additive of iron. Expertises were spent at temperature 600-800 °C and pressure 0,1-3 MPa. This process is characterized by low temperature of reaction. The best results has a test with zeolite of containing 0,8 % peroxide, at such concentration total yield of ethylene and propylene is about 48,3 %.

Chinese firm Sinopec International and scientific research institute of oil refining of the Chinese People's Republic developed new process and zeolite catalyst to processing heavy cuts to olefins with high yields. Process is licensed by firm Stone and Webster and called DCC - Deep catalytic cracking [5].

Group of researchers from SK corporation (Seoul, South Korea) and State Korea Researching Institute of Chemical Technology has developed new way to produce ethy-

lene and propylene from oil. Advanced catalytic olefin process allows increase volume of production and decrease consumption of energy. Temperature of new process about 700 °C. So relatively low temperature allows reduce energy consumption on 20 % and at the same time increase production of ethylene and propylene on 30 % [6].

One more direction of using cat pyrolysis is production special individual substances. For example carbon nanofibers were synthesized by the pyrolysis of ethylene and methane on hydrides of intermetallides LaNi_nH_x ($n = 2, 3, 5$; $x = 0.1-4$). The influence of parameters of the synthesis (temperature and the ratio of gases in an $\text{Air} : \text{H}_2 : \text{C}_2\text{H}_4$ (CH_4) mixture) on the structure of nanofibers thus formed was studied. Hydrides of nickel intermetallides are more efficient catalytic systems than metallic nickel-carbon [7].



There are many various additives and initiators. Interesting results were demonstrated with the additive representing a mixture of four-six inorganic salts in aqueous solution. In quantity in 0,01 % of mass. it promotes oxidation of coke with formation of carbon dioxide and carbon monoxide. The additive contains compounds which boil at high temperature, in that case does not contaminate products and does not degrade technological indexes of process.

Company Nalco Exxon Energy Chemicals has developed new inhibitors of coke formation Coke-Less which basis of organophosphorous compounds for pyrolysis plants. At concentration of inhibitor several million⁻¹, the life time of pyrolysis plant increase by 2 times [8]. Also following initiators are widely known: halogens, organic peroxides and hydrogen peroxide, hydrogen, propadiene and methyl acetylene.

There is a process in presence of hydrogen and is called hydrolysis. Characteristic property of the given process is presence in a reaction zone increased pressure of hydrogen and short residence time, high yield of ethylene and propylene, low coke formation. Process is exothermic, that decrease need for heat. Process is

supposed to be spent at very high temperatures (up to 900 °C), residence time has less 0,1 second, the high partial pressure of hydrogen. As result of use hydrogen the volume of products which tend to troubles with separation of products. To remove this troubles it was proposed lead this process with high pressure up to 2–2.5 MPa. In this conditions if we have gasoline as a feed stock we will have outlet of ethylene in the products about 40 % [9]. At all advantages hydrolysis has not received technical application.

Australian firm CSIRO together with firm BHP has carried out the program of studies for an estimation of a technical and economical opportunity of an alternative way of olefin production from natural gas on the basis of reaction of oxidizing transformation of methane.

In new process OXCO in a fluidized bed reactor go reaction of oxidizing transformation of methane and pyrolysis of ethane and the higher alkanes present in natural gas. This process is very selectivity [10].

Process of Japanese firm Ube is spent in fluidized bed of heat carrier at presence of steam and the oxygen used for partial incineration of raw. Temperature of pyrolysis 880 °C, contact time is 0,2-0,3 seconds. Yield of ethylene at pyrolysis of oil is about 28 % [11].

Also pyrolysis use to process wastes of different materials: solid domestic wastes, wastes of polymaterial. This direction of pyrolysis is very prospective, and now it's exist some implementations in this field.

Plasma furnace to process Solid Domestic Wastes (SDW). Unassorted wastes (but it's demand to exclude wastes which content mercury) a sent to locking loading chamber by conveyor. Further from loading chamber in doses wastes are sent to furnace where are cracked and burnt by streams of plasma from two plasmatrons. Gas which go out from plasma chamber goes to afterburning chamber where gas finally burn out and wastes decompose.

Consumption of energy to produce synthesis gas and vitrified slag from SDW equal 1200 kW·hour per ton of wastes. Regeneration of electrical energy from producing synthesis gas by turbine generator with efficiency 30 % equal 2400-3000 kW·hour per ton of wastes. So additional energy which can be sell equal 1200-1800 kW·hour [12].

The complex offered has following advantages:

- It is absolutely wasteless and ecologically safe; it will really help to solve critical social and ecological problem - industrial districts and cities cleaning from solid domestic and building waste.

- It is highly remunerative and is compensated during 1-2 years from the beginning of construction.

- It can be installed and introduced into operation during 1-2 months at capital outlays in any region of Russia and abroad.

- It is efficient and at the same time it has small dimensions.

- The process is carried out continuously, rather than cyclically as in the case of many analogous devices, what makes the operation more comfortable.

- Full process automation.

- It allows processing of those industrial waste, the processing of which is either unprofitable or not developed yet.

- This complex completely provides itself with energy resources (electric energy and heat). The surplus of these resources is sold to population and industry.

One more method of high-temperature pyrolysis to process polymaterial wastes. Polypropylene (PP), polyethylene (PE), polyethylene terephthalate (PETP), polyvinylchloride (PVC), polystyrene (PS), polyamide (PA) and other are used as a feed stock in this method. Conditions of pyrolysis (temperature, fractionation of component and so on) are determined in each concrete case in depend on mixture of wastes. All complex organic compounds transform to more simple nontoxic paraffinic, olefinic, cyclical, aromatic and heterocyclic compounds. This mixture is further processed by condensation, catching, distillation, rectification, etc. to get trade products [13].

Most important products:

- styrene, isoprene, acetone, naphthalene, acetonitrile, coumarone, cresols, fluorene, phenanthrene, anthracene, imidol, etc.;

- nitrogen compound: dibenzo-pyrrole, indole, pyridine and picolinic connections;

- sulfur-containing: thiophene, carbon bisulphide;

- aromatic hydrocarbons: benzol, toluene, o-m-p-xylenes, mesitylene, styrene, indene, coumarone, etc.;

- Resins and their fractions (oil): naphthalene, absorption, anthracene, etc.

CONCLUSIONS

Pyrolysis it's one of the most important processes of petrochemistry but main advantage this process to compare with another that it's quite flexible process in terms of feed stock. In addition in recent time this process quite active use to process different industrial waste and it's very good advantage too for future development. And finally we can see that in the last time oil lose your position as a fuel but at the same time needs in polymaterial increase more and more it give good perspective such process as pyrolysis.

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