ANALYSIS OF DEVELOPMENT OF TECHNOLOGY OF PRODUCTION OF SECONDARY PRODUCTS FROM PYROLYSIS DISTILLATE

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ABSTRACT
In chemical reactions, two or more chemical elements are formed during pyrolysis. The work of several scientists on the production of additional products from these elements is analyzed. As a result of this analysis, innovative technologies have been fully developed.
KEYWORDS: *Furnace pyrolysis, thermal, catalytic, convection, radiation, zeolite, Cosmos.*

1. INTRODUCTION
Currently, the demand for polymer products is growing under ordinary conditions. With this in mind, the use of alkynes and alkenes obtained in the pyrolysis process is very demanding. Pyrolysis occurs mainly at 800-1000 ° C. Alkanes are converted directly into alkynes and alkynes. This is not to say that ethylene and propylene are the most important substances in everyday life.

2. THERMAL TRANSFORMATIONS OF ALKANES
The thermal transformations of alkanes proceed by a radical chain mechanism. Molecular reactions play an insignificant role, and ionic reactions under conditions of thermal gas-phase non-catalytic processes are practically absent, since the heterolytic decomposition of the C – C bond requires an energy of ~ 1200 kJ / mol, while a homolytic one is ~ 360 kJ / mol. The thermal reactions of alkanes lead to lower alkenes. The experimental data on the composition of the products of thermal decomposition of alkanes are well explained by the radical-chain reaction mechanism. Methane is thermally stable. Its thermal destruction proceeds above 560 ° C. However, at a noticeable rate, the reaction proceeds at temperatures above 1000 ° C. The main reaction products are acetylene, ethylene, ethane, carbon and hydrogen. The transformation proceeds according to the following scheme:
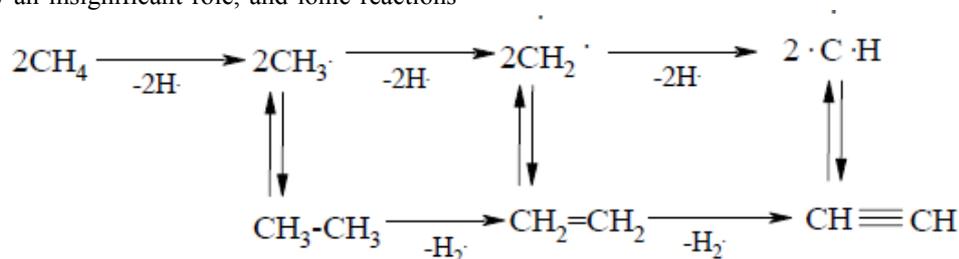
In the process of methane cracking, along with acetylene, ethane, ethylene, benzene, methylacetylene, etc. are also formed in small quantities. The process is also complicated by the decomposition of methane into carbon and hydrogen:
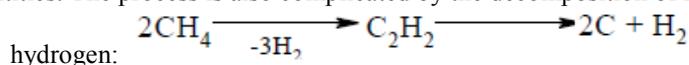
Ethane is less stable than methane: its destruction begins at a temperature of ~ 500 ° C. At 800 ° C, the reaction

$$CH_3 \text{—|—} CH_3 \longrightarrow 2CH_3\cdot$$
$$2CH_3\cdot + CH_3\text{-}CH_3 \longrightarrow CH_4 + C_2H_5\cdot$$
$$C_2H_5\cdot \longrightarrow CH_2{=}CH_2 + H\cdot$$
$$H\cdot + H\cdot \longrightarrow H_2$$
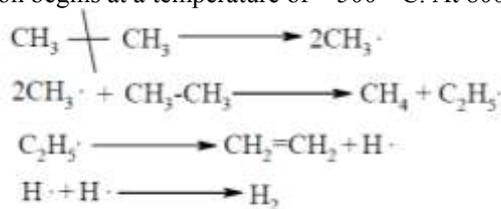
proceeds at a significant rate:

Propane is already split at a temperature of 450 ° C in two directions:

$$CH_3CH_2CH_3 \longrightarrow \begin{cases} CH_3CH{=}CH_2 + H_2 \\ CH_2{=}CH_2 + CH_4 \end{cases}$$
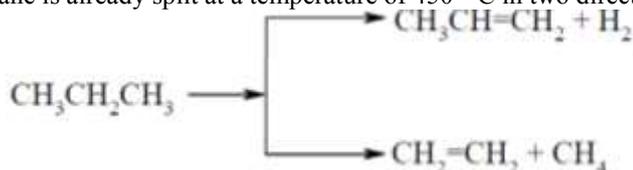
Starting from butane, the decomposition of alkanes via the –C — C– bond becomes predominant. The relative rate of alkane cracking increases with increasing molecular weight, which is explained by a decrease in the dissociation energy of C-C bonds in the middle of the molecule and an increase in the number of C-C bonds with a low dissociation energy:

- The number of carbon atoms in the molecule 5 6 7 8 10 12 20
- Relative cracking rate 1 4 9 10 32 46 120

The cracking of n-butane can be represented by the following scheme. In the beginning, due to a bond break -C-C- in the weakest place, primary free radicals are formed (chain initiation):

$$CH_3CH_2CH_2CH_3 \longrightarrow \begin{cases} 2\ CH_3\dot{C}H_2 \\ CH_3\text{-}CH_2\dot{C}H_2 + \dot{C}H_3 \end{cases}$$
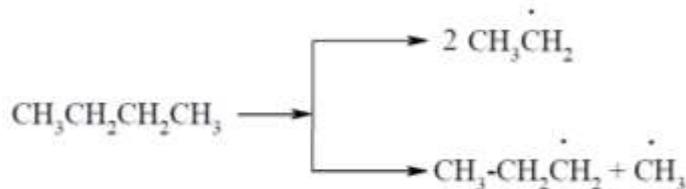
Then the process develops in two possible directions. In the first direction, large, relatively unstable radicals (C3 and higher) spontaneously decay with the formation of more stable methyl and ethyl radicals or hydrogen atoms and the corresponding alkene molecules:

$$CH_3CH_2\dot{C}H_2 \longrightarrow \begin{cases} CH_3CH{=}CH_2 + \dot{H} \\ CH_2{=}CH + \dot{C}H_3 \end{cases}$$
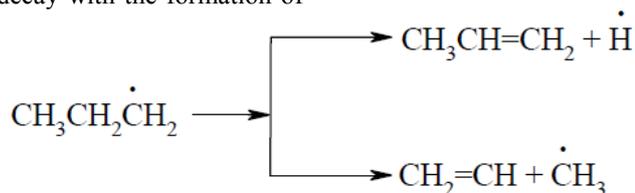
In the second, decay-stable, but extremely reactive methyl and ethyl radicals and hydrogen atoms react with the starting molecules, tearing the hydrogen atom away from them:

$$\dot{H}(\dot{C}H_3;\ \dot{C}_2H_5) + C_4H_{10} \longrightarrow H_2(CH_4; C_2H_6) + \dot{C}_4H_9$$

As a result, hydrogen, methane, ethane and butyl radicals are formed. Butyl radicals further decompose:

$$CH_3\text{-}CH_2\cdot\text{|}\cdot CH_2\dot{C}H_2 \longrightarrow CH_3\dot{C}H_2 + CH_2{=}CH_2$$
$$CH_3\cdot\text{|}\cdot CH_2\dot{C}HCH_3 \longrightarrow \dot{C}H_3 + CH_2{=}CHCH_3$$

The resulting small radicals react again with the starting molecules. A chain process is developing. Chain termination occurs through the recombination and disproportionation of radicals. The main part of the chain reaction products is formed at the stage of chain development, therefore, the total cracking process of n-butane can be described by a system of two parallel reactions:

3. PYROLYSIS OF ALKANES

The patterns of thermal decomposition of hydrocarbons to a certain extent change upon the

transition from thermal cracking conditions (470-540 ° C) to pyrolysis conditions (700-1000 ° C). Temperature affects the mechanism of the process and the composition of the products. The total reactions occurring during pyrolysis and cracking can be divided into three main groups:

1) primary cracking and dehydrogenation reactions leading to the formation of alkenes;
2) secondary alkenes conversion reactions - polymerization and condensation;
3) reactions of direct molecular decomposition, in which pyrocarbon, hydrogen and partially acetylene are formed.

Under conditions of high pyrolysis temperatures with a very significant energy saturation of molecules, the concentration of radicals increases. This leads to a decrease in chain length and an increase in the role of radical chain decomposition, in which individual hydrocarbons decompose independently of each other. An increase in temperature accelerates reactions with higher activation energies, as a result of which the ratio between different radical reactions changes. The importance of more energy-intensive reactions of the decay of radicals increases in comparison with less energy-intensive reactions of addition. Temperature also affects secondary alkenes conversion reactions. Alkenes decay, proceeding with high activation energies, is significantly accelerated with increasing temperature in comparison with alkene condensation reactions characterized by lower activation energies. And finally, temperature determines the ratio between the main groups of pyrolysis reactions (primary, secondary and pyrocarbon formation). The activation energies of these types of reactions can be arranged in a row:

$$E_3 > E_1 > E_2,$$

where E1 is the activation energy of the primary reactions; E2-activation energy of secondary reactions; E3 is the activation energy of elemental decay. If the purpose of the thermal process is to obtain alkenes, the reaction must be carried out at a high temperature so that the rate of the primary reactions is higher than the rate of the secondary processes. However, raising the temperature above 900 ° C is impractical, since in this case decomposition reactions begin to occur at a noticeable rate. To obtain low molecular weight alkenes, the process must be carried out under reduced pressure. However, the technological features of the process, requiring high feed flow rates to ensure a short reaction time, are associated with overcoming significant hydraulic resistances, which creates increased pressure at the inlet to the reaction coil. Hydrocarbon pressure decreases are achieved by diluting the raw materials with inert substances (usually water vapor). The rate of pyrolysis of hydrocarbons increases in the presence of molecular hydrogen. The methyl radical, which conducts a chain pyrolysis process along with atomic hydrogen, in the presence of molecular hydrogen reacts in two parallel reactions -

with a hydrogen molecule and an initial hydrocarbon, for example, hexane:

$$CH_3 + H_2 \; CH_4 + H$$
$$CH_3 + C_6H_{14} \; CH_4 + C_6H_{13}$$
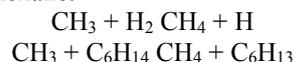
At a temperature of 827 ° C, the rate constant of the first reaction is an order of magnitude higher than the second (at equal concentrations of H2 and C6H14). The reaction rate of the methyl radical with alkenes is also lower than the rate of interaction with hydrogen (for 1-butene, the rate constant differs by 4 times).

The resulting atomic hydrogen reacts with hydrocarbon molecules of the feed. The rate constant of this reaction is 2-3 orders of magnitude greater than the rate constant for the interaction of hydrocarbons with a methyl radical. As a result, molecular hydrogen plays the role of a homogeneous catalyst for the overall pyrolysis process. In addition, it suppresses to a large extent the diene formation reactions by reacting with vinyl radicals (CH2 = CH.) And preventing their addition to ethylene. The consequence of this is a decrease in the yield of heavy condensation products.

4. THE PERFORMANCE OF THE FURNACE BLOCK

The operating parameters of pyrolysis furnaces in a particular ethylene production are determined by the need for ethylene and propylene. After putting ethylene plants into operation, as a rule, they evaluate the compliance of design parameters of furnace blocks with actual ones. At the same time, during the pyrolysis of raw materials typical for a particular production, the optimal process parameters are determined that make it possible to obtain target products in predetermined ratios and reveal the balances of raw material decomposition. For this purpose, technological and thermotechnical tests of furnace blocks are carried out.

Methodology for determining indicators. Using sampling systems in which fractional condensation of hydrocarbons C5 and higher is carried out, the material balance of decomposition of the processed raw materials is determined.

The composition of the products of the pyrolysis of hydrocarbon raw materials is determined by the analysis of samples of the vapor-gas mixture, while analyzing its gaseous and liquid hydrocarbon parts.

Samples are taken using an outlet welded to the vertical section of the pyrogas pipeline after a ZIA with a slope of 10 ° to prevent condensate from flowing back into the pipeline. A sampling tube is connected to the branch, which reaches the middle of the pipeline; the inlet of the tube is beveled 15 ° and this part is turned to the side in the opposite direction of flow. The tube is equipped with a valve system that allows it to be inserted during operation. An in-line or temporary sampling system is connected to the sampling tube.

A typical sampling system is shown in the figure.
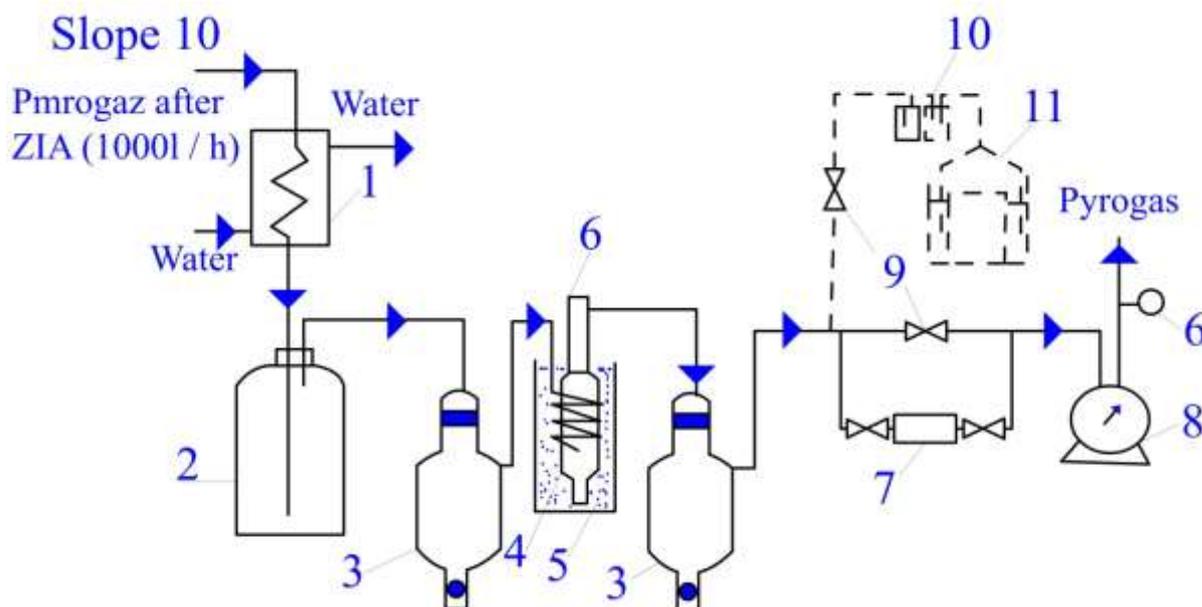
Fig. 1 Scheme of the sampling system of pyrogas

1-fridge; 2-condensate separator; 3-dehumidifiers; 4-condensate trap; 5-cooling mixture; 6-thermometers; 7-gas trap; 8-gas watch; 9-clamps; 10-flow indicator; 11-gas meter

The selection rate of 18-25l / min, the duration of the selection of 1.0-1.5 hours. During this time, 1000-1500 l of pyrogas is passed through a dry gas meter and 300-450 g of liquid pyrolysis products are obtained, which is sufficient to calculate the yields of pyrolysis products with satisfactory accuracy.

The analysis of gaseous (with the determination of hydrocarbons up to C5) and liquid parts of the sample, along with the analysis of the feedstock, is carried out in laboratory conditions by a chromatographic method. The density and fractional composition (Angler distillation) of raw materials and liquid products are also determined.

The analysis of the group composition of raw materials is carried out by a chromatographic method, as a rule, on three instruments: on a column with a stationary phase [tris (2-cyanoethoxy) propane], the content of aromatic hydrocarbons is determined, with 13X zeolites, the content of C5-C11 cyclanes, on a capillary column with OV siloxane The -1-content of n-alkanes and, in difference, calculate the content of alkanes of isomeric structure.

5. PYROLYSIS OF HYDROCARBONS IN MOLTEN MEDIA

Among promising methods for the thermal processing of hydrocarbons, pyrolysis of hydrocarbon fractions in molten media should be mentioned. Its advantage is the ability to process almost any type of raw material from light hydrocarbon gases to heavy liquid fractions (vacuum gas oil, crude oil); highly efficient heat transfer due to direct contact of the raw material with the melt and a highly developed heat transfer surface; the simplicity of continuous evacuation of solid decomposition products (soot, coke) from the reaction zone, which eliminates the need for periodic shutdowns of the reactor for coke burning.

Some metals (lead, bismuth, cadmium, tin, etc.) and their alloys, salts — chlorides, carbonates, etc. — or multicomponent salt melts, as well as slag (oxide) melts, are used as a melt. Metal melts have high thermal conductivity, low viscosity, but they are intensively oxidized and relatively expensive. Salt melts do not have the main drawback of metal - intense oxidizability, but they have lower thermal conductivity compared to metals, and some have high volatility and thermal instability, which complicates the separation and regeneration of melts. Relatively cheap slag melts are characterized by high melting points, not too high viscosity, increased aggressive effect on structural materials, so they are rarely used.

The methods of contacting the processed hydrocarbons with the melt are different - bubbling through the melt layer, processing in the dispersion of the molten medium or during the film flow of the melt, etc. According to the method of supplying to the raw materials from the outside, it can be transferred from the outside to the reaction zone similarly to the pyrolysis process in tube furnaces. A bubbling and subsequently dispersive pyrolysis process in the gas lift system was developed using salt melts.

A significant set of studies on the pyrolysis of hydrocarbons and oil fractions in melts with the study of various methods of instrumentation of the process was carried out by the Moscow Institute of Chemical Technology Lomonosov under the leadership of Professor N.S. Pechuro.

We studied the method of processing hydrocarbons in a dispersed molten medium (lead)

circulating according to the principle of gas lift, with the feedstock serving as the transporting agent and the coolant circulating in a closed cycle. The pyrolysis results of propane n-heptane, light straight-run gasoline (50-142 ° C) and Baku crude oil with the addition of 40% water vapor are presented in table 1.

Table 1. Product yields (%) during pyrolysis of various types of raw materials in a molten circulating lead environment

Product	propane	n-heptane	Petrol	Raw oil	Product	propane	n-heptane	Petrol	Raw oil
H_2	1,41	0,27	1,11	0,77	$\Sigma\, C_4H_{10}$	-	0,16	0,08	0,13
CH_4	31,63	13,25	20,49	14,52	$\Sigma\, C_4H_{10}$	-	6,11	2,26	2,13
C_2H_6	4,65	9,13	3,89	3,76	C_4H_6	-	3,62	4,76	4,20
C_2H_4	45,20	42,28	34,71	29,8	Liquid products	-	1,03	5,60	5,81
C_3H_8	5,33	0,77	0,23	0,27					
C_3H_6	10,01	19,8	10,02	11,35	Coke	4,47	3,48	16,85	27,26

During pyrolysis in a dispersion of molten heat carrier, high yields of ethylene can be obtained, but yields of propylene are lower than during thermal pyrolysis. A significant amount of coke is also formed, which, however, with appropriate design, can be removed from the reaction zone, while maintaining the continuity of the process. Pyrolysis in the presence of molten coolants was tested under the conditions of an enlarged pilot plant, and the results obtained are in good agreement with laboratory ones.

A higher degree of mixing of hydrocarbons with the medium and acceleration of heat transfer are achieved by conducting the process in a stream of heated coolant vapor. The unit for the pyrolysis of hydrocarbons in a medium of heated condensing coolant vapor is made in the form of a closed circulation system. The coolant vapors from the evaporator enter the reaction zone, where, when condensed, they report the necessary heat of the raw materials to the raw materials. The coolant is separated from the pyrolysis products in a separator and returned to the evaporator. Pyrolysis in a stream of condensing coolant vapor is characterized by significantly less coke formation compared to a process in a medium of a diverted coolant.

The method of pyrolysis and the method of quenching of pyrolysis products in devices with a liquid coolant were developed at the G.M. Energy Institute Krzhizhanovsky. They are based on the principle of the so-called "sharp jet", which is formed by blowing a gas jet - hydrocarbon feedstock onto the surface of the melt, whereby a hydrodynamic cavity (hole) is obtained in which heat and mass transfer intensively proceed. In the apparatus with a liquid coolant (lead) in the reaction temperature range of 640-950 ° C, it was found that ethylene yields of up to 38% can be obtained by pyrolysis of straight-run gasoline, by pyrolysis of crude oil up to 22%, 20-30% of solid oil is also formed products (soot and coke).

The disadvantages of the pyrolysis of hydrocarbons in the presence of a molten coolant are the need for heating and circulation of the coolant, as well as the difficulty of separating it from the reaction products. These disadvantages are deprived of the methods of pyrolysis of hydrocarbons in the presence of melts, but with an external supply of heat, for example, pyrolysis in tube furnaces with a dispersion or dispersion-ring melt flow. The melt in these processes improves the heat transfer between the heated wall of the reactor and the flow and slows down (or prevents in the case of a dispersion-ring flow in the presence of a melt film on the wall of the reactor) coke deposition in the reaction zone.

A process has been developed (under the brand name "Cosmos" by Mitsui Petrochemical, Japan) for the pyrolysis of hydrocarbons in molten salts in tubular furnaces with external heating. A salt mixture using a eutectic mixture consisting of Na2CO3, K2CO3 and Li2CO3 with a low melting point and relatively high heat resistance. In the process scheme, a conventional tube furnace is used, equipped with a salt melt circulation system (Fig. 2)
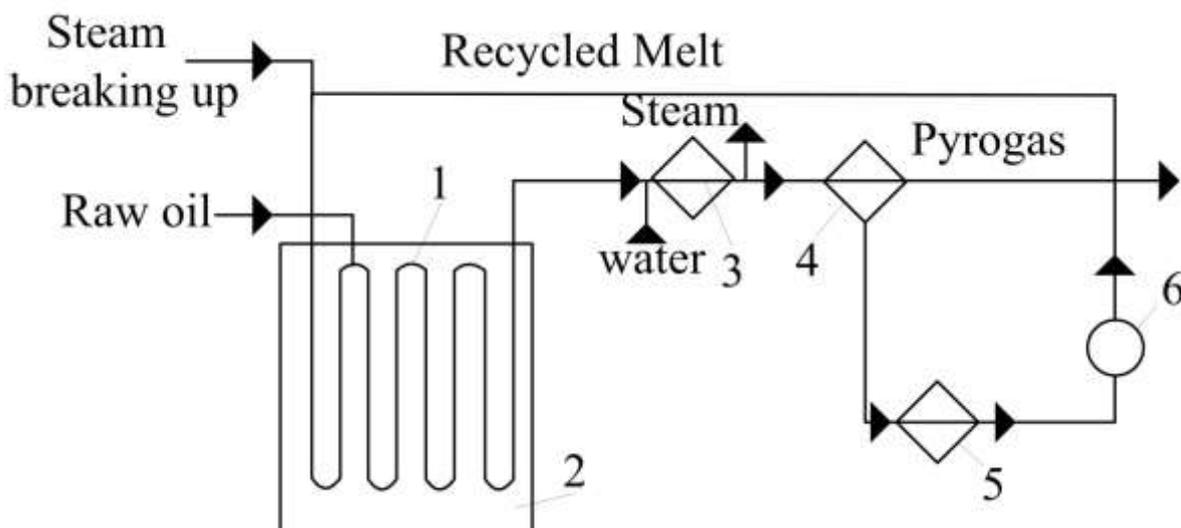
Fig.2 Scheme of the process of pyrolysis "Cosmos"

1-reaction coil; 2-tube furnace; 3 quenching and evaporation apparatus; 4-separator; 5-capacity for melt; 6-pump

The inner walls of the reactor are covered with a film of melt moving in the dispersion-ring mode in the same direction as the feed stream, therefore, coke is not deposited on them. In reaction coils from tested materials, only low-sulfur oils with a sulfur content of not more than 0.2% can be processed to avoid corrosion of the equipment. Table 2 shows the yields of the main pyrolysis products of direct distillation gasoline and crude oil from the Taching deposit (China) in the Cosmos process. Pyrolysis conditions: feed consumption 3 kg / h, coil wall temperature at the outlet, 800 ° С, steam ratio: 1.33, melt: feedstock 2.0, residence time 0.55-0.6 s.

The Cosmos process has a number of disadvantages: a high content of CO and CO2 in the pyrolysis products, relatively low thermal conductivity of the salt film of the melt, a significant multiplicity of the circulation of the melt, and increased steam consumption. These disadvantages can be eliminated on their basis (for example, lead and mixtures based on it). The movement of the melt is carried out in a dispersion-ring mode.

On the surface of the reactor 10-2 ÷ 10-4cm, which protects the surface of the coil from coke deposits and improves heat transfer. At the same time, the heat stress on the surface of the coil can be increased by 5-7 times compared with processes without melt, which will reduce the length of the coil and the residence time of the raw material in it (up to 0.05 s), as a result of which the yield of the target products will also increase. For example, ethylene yield during straight-run gasoline pyrolysis as a result of reduced residence time increases from 26-28 to 41%. The negative moments of pyrolysis with this melt are due to the disadvantages of using metals as a melt, the difficulty in separating molten metals from the pyrolysis product.

Table 2. The output of the main products in the process of pyrolysis "Cosmos"

Gasoline pyrolysis				Crude oil pyrolysis			
component	exit, %	Component	exit, %	component	exit, %	component	exit, %
H_2	1,12	C_3H_6	16,63	H_2	2,09	C_3H_6	11,19
CH_4	11,55	C_3H_8	0,31	CH_4	12,48	C_3H_8	0,16
C_2H_2	0,54	C_4	11,37	C_2H_2	0,30	C_4	6,65
C_2H_4	27,79	CO	0,20	C_2H_4	25,19	CO	1,3
C_2H_6	2,29	CO_2	1,68	C_2H_6	2,21	CO_2	15,3

6. CONCLUSION (Вывод)

The results of this analysis show that the transformation of the pyrolysis process into a composite structure, at the same time, the production of finished products from distribution products and innovative technologies that produce them in accordance with the requirements of the exporter. If we apply this to our country, we will achieve economic efficiency. Because, if you look at the example of the Shurtan gas condensate field in our country, during the pyrolysis at 800-1000 ° С additional raw materials are produced, except for ethylene and propylene. However, two products are made of polyethylene and polypropylene and are exported as semi-finished products. Say, in the process acetylene, pentane, monomers, etc. to. also

produce. However, the product is not made from these additives.

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