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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

DEVELOPMENT OF THE TECHNOLOGY OF THE PYROLYSIS PROCESS OF C_1-C_4 HYDROGENS OF CATALYTIC CRACKING WITH NAPHTHA

Speciality: 3321.01 – Petroleum-gas-hard coal processing and technology

Field of science: Technical

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The work was performed at the Institute of Petrochemical Processes named after Y.H. Mammadaliyev of Azerbaijan National Academy of Sciences at the laboratories of "Catalytic cracking and pyrolysis" and SOCAR "Azerikimya" PU Ethylene-Polyethylene plant

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GENERAL CHARACTERISTICS OF THE WORK

Relevance of the topic and the degree of elaboration. Recently, the dynamics of development of the petrochemical industry in the world is growing at a very high speed. The construction of huge, multi-tonnage complexes that produce monomers such as ethylene and propylene, which are the basis of the petrochemical industry, as well as the modernization of outdated productions has gained a lot of momentum. At the same time, the gasoline fraction used as a raw material for the production of ethylene and propylene monomers is being replaced by other alternative raw materials and extensive work is being done in order to achieve a high yield. As a continuation of such works, reconstruction works are being carried out in the oil and petrochemical industry in our Republic. Depending on the properties of new types of alternative raw materials, the application of modern-type pyrolysis furnaces to production is of great significance[1]. Until today, the decomposition of hydrocarbon raw materials in tubular pyrolysis furnaces used in the industry is the only widely used process in the petrochemical field of the world.[2]

Since the 50s of the 20th century, the main industrial process for obtaining small molecular olefins C_2-C_4 has been widely used pyrolysis of various types of hydrocarbon raw materials - primary processing gasoline, ethane, propane, n-butane and their mixtures, oil and gasoil fractions.

It was planned to use 1 million tons/year of directly fired gasoline as raw material in the "EP-300" facility of "Azerikimya" PU in Azerbaijan. However, due to the recent high level of demand for gasoline, it has become necessary to replace it with other alternative raw materials purchased at the facilities of the "Oil Refinery" factory. As an alternative raw material, the oil refinery named after H. Aliyev has great potential. By widely using by-products such as gasoline, C_1-

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[1] A.I. Babayev, S.R. Hajiyeva, Z.A. Mammadov. Technology of production of ethylene-propylene and ways to solve the environmental problem. Sumgayit: "Bilik" - Publishing House. – 2014. – 315 p.

[2] M.I. Rustamov, V.M. Abbasov, A.M. Maharramov, N.A. Salimova, Z.C. Seyidov, M.M. Abbasov. Basic organic and petrochemical synthesis. 2003. c. 256.

C_2 (dry gas) and C_3-C_4 fractions from "Catalytic Cracking" and "Gradual Coking" units as raw materials, obtaining quality monomers such as ethylene and propylene with maximum productivity is an urgent issue.

The relevance of the research is confirmed by the inclusion of the scientific direction of the stages of this work separately in the thematic plan of scientific-research works of the Institute of Petrochemical Processes named after Academician Y.H. Mammadaliyev of the Ministry of Science and Education of Azerbaijan.

Object and subject of research. The research object of the dissertation is C_1-C_2 (dry gas), propane-propylene, butane-butylene and low octane gasoline fractions obtained from the "Catalytic cracking" and "Gradual coking" units of the oil refinery. The subject of the dissertation is the use of C_1-C_2 (dry gas), propane-propylene, butane-butylene and low-octane gasoline fractions as raw materials for the production of ethylene and propylene monomers.

Goals and objectives of the study. The main goal of the work is to intensify the reactions in the direction of obtaining ethylene and propylene during the pyrolysis of coke gasoline, that is, to minimize the second, third and polycondensation reactions in the pyrolysis process and to increase the yield of quality ethylene and propylene in the pyrolysis process of C_1-C_4 hydrocarbons obtained in the oil refinery facilities with naphtha.

In order to achieve this goal, the following tasks were performed in the dissertation work:

- determination of optimal mode parameters for obtaining the maximum yield of ethylene and propylene along the length of serpentine pipes in the radiation part of industrial pyrolysis furnaces;
- construction of a mathematical model of the process and its implementation on a computer;
- identification of the developed mathematical model with the simulated process in order to ensure its adequacy, i.e. qualitative correspondence of the model to the real process;
- optimization of the process using a mathematical model of the process, i.e. determination of the optimal mode and structural parameters of the process ensures the highest or lowest value of the

criterion of optimality (objective function) characterizing the efficiency of the real process.

- Treatment of C_1-C_2 (dry gas) fractions from "Catalytic cracking" and "Gradual coking" units from sour gases H_2S and CO_2 and application to the "EP-300" complex as raw materials;
- Removal of ethylene and propylene from C_1-C_2 (dry gas) fractions from "Catalytic cracking" and "Gradual coking" units;
- Mixing ethane and propane from the C_1-C_2 (dry gas) fractions obtained from "Catalytic cracking" and "Gradual coking" units with ethane and propane obtained from gasoline pyrolysis and returning them to the joint SRT I type ethane furnace as recirculation to obtain ethylene and propylene with maximum productivity;
- Purification of propane-propylene fraction from "Catalytic cracking" and "Gradual coking" units from mercaptans and other mixtures; development of the technology of mixing the PPF fraction of the catalytic cracking with the PPF obtained from the pyrolysis process and feeding "EP-300" to the propylene separation boiler and returning the propane separated from the cubic part of the boiler to the ethane pyrolysis furnace as recirculation.
- Mixing the butane-butylene fraction obtained from the "Catalytic cracking" and "Gradual coking" units with the butylene-divinyl fraction obtained from the pyrolysis process in an optimal ratio and choosing the optimal mode parameters of the pyrolysis process to obtain ethylene-propylene with maximum yield as a raw material by hydrogenating the mixture in the presence of a Pd catalyst;
- Selective hydrogenation of acetylene, methyl acetylene, propadiene and allenes in ethane-ethylene and propane-propylene in order to increase the yield of ethylene and propylene by 2-2.5% mass with the presence of Pd catalyst, building a kinetic and mathematical model for choosing the optimal mode;
- After separating the divinyl fraction from the content of the butylene-divinyl fraction obtained from pyrolysis, choosing the optimal technological parameters (raw material: water vapor ratio, reaction time and temperature) to obtain maximum ethylene and propylene in the ethane pyrolysis furnace with the participation of the ethane fraction of the remaining butylene-isobutylene fraction;

Research methods. Scientific research works were carried out in the laboratory and in semi-industrial and industrial facilities created on the basis of the presented technological schemes

The accuracy of the scientific results obtained in the dissertation was proven by modern physical research methods (chromatographic, spectrophotometric, scanning electron microscope (SEM), X-ray diffractograms).

The main provisions of the defense:

- The purification of C_1-C_2 (dry gas) fractions from sour gases H_2S and CO_2 obtained from "Catalytic cracking" and "Gradual coking" units of the oil refinery was studied as absorption method with monoethanol amine. The complete composition of purified dry gas and pyrogas obtained from the pyrolysis process was studied, mixing them with each other to obtain ethylene and propylene and giving EP-300 was studied.

- The technology of selecting adsorbents for cleaning the propane-propylene fraction obtained from "Catalytic cracking" and "Gradual coking" units from mercaptans and other mixtures has been studied.

- By mixing the butane-butylene fraction obtained from the "Catalytic cracking" and "Gradual coking" units with the butylene-divinyl fraction obtained from the pyrolysis process in different proportions, the optimal mode was found with the presence of a Pd catalyst.

- The results of the conversion along the length of the four-inch serpentine tube located in the radiation part of the industrial pyrolysis furnaces, the results of the calculated values of the process of the yield of ethylene + propylene and pyrolysis products as a whole were calculated.

- The thermodynamic parameters of the complete mathematical model were determined by determining the pressure drop expressions taking into account the turns of the serpentine pipe of the pyrolysis furnace.

- An optimal control scheme of the pyrolysis process of C_2–C_4 hydrocarbon gases has been developed.

- Co-pyrolysis of propane-propylene and butane-butylene (C_3 + C_4) fractions obtained from catalytic cracking with the addition of hydrogen was studied.

- Results were calculated according to mathematical models of gasoline pyrolysis, as well as ethane and propane fed to pyrolysis recycling.

Scientific novelty of the study: For the first time:

- The technology of supplying the C_1-C_2 (dry gas) fraction from the "catalytic cracking" unit to the EP-300 complex has been developed. The components contained in the C_1-C_2 (dry gas) fraction were fractionated together with ethylene and propylene obtained from the pyrolysis process.
- The components contained in the C_1-C_2 (dry gas) fraction are fed to the ethane pyrolysis furnace as ethane and propane recirculate obtained by fractionation together with ethane and propane obtained from the ethane and propane pyrolysis process, monomers such as ethylene and propylene were produced.
- In order to increase the productivity of ethylene and propylene, the pyrolysis process of the C_3+C_4 (compressed gas mixture) fraction obtained from the "Catalytic Cracking" unit with the presence of hydrogen in the amount of 0.005÷0.04% of the raw material was studied and the technology was developed.
- Optimizing the process using the mathematical model of the process, determining the optimal mode and structural parameters of the process, that is, the highest or lowest value of the criterion of optimality (objective function) characterizing the efficiency of the real process was studied.
- In order to increase the productivity of propylene, AxSorb 984, AxSorb 902 and AxTrap 194 brand adsorbents were used to clean the propane-propylene fraction from the "Catalytic Cracking" unit and given to propylene calon in the EP-300 complex. Pure propylene was removed from the top of the calon and ethylene and propylene were obtained from the propane pyrolysis furnace.

Theoretical and practical significance of the research. High-quality ethylene and propylene monomers are obtained by optimizing the parameters such as the residence time of the raw materials in the reactor, ratio with water vapor, maintaining temperature and partial pressure, in order to intensify the C_1-C_4 hydrocarbon gases received at the oil refinery and the low-octane gasoline fraction in the pyrolysis furnaces of the "EP-300" production has been determined.

In addition to obtaining ethylene and propylene from the C_1-C_2 dry gas fraction, using other fractions, i.e., conducting the hydrogenation process from H_2, using it as fuel gas in pyrolysis furnaces after separating CH_4- with high purity, obtaining sulfuric acid from H_2S and CO and CO_2 it was recommended to use it as a raw material in the production of methanol and urea.

Since different types of raw materials are used in the research work, the technology of pyrolysis process with the presence of hydrogen was developed from the C_3+C_4 (LPG) fraction of "Catalytic cracking" in the pyrolysis furnace of the "EP-300" unit.

The optimal design methodology of the chemical-technological complex (CTC) has been developed.

In order to constantly reduce the amount of unreacted ethane in the pyrolysis process, the optimal technology of joint pyrolysis of gasoline, ethane and propane was developed.

Approbation and application. The main results of the dissertation were discussed at the following conferences: "FARGAN-2006" conference, Voronezh (October 8-14, 2006); "Study of the kinetics of gas-phase hydrogenation of the C_2 fraction of hydrolysis furnaces on the promoted catalyst G-58C"; Chem-reactor-17, (May15-17, 2006) Athens-Crete, Greece; "Develoment of the mathematical model of process of pyrolysis of dearomatized distilled gasoline in the presence of fuel gas"; Baku International Congress, (Baku, June 7-9, 2007) on the subject "Regeneration and utilization filled zeolites in drying process"; Voronezh (2006, May 30-June 2) MMTT-19 International Scientific Conference on the subject "Development of a mathematical model of the process of pyrolysis of straight-run gasoline in the presence of fuel gas", Mathematics application issues and new information technology, Republican Scientific Conference, Sumgayit (November 26-27, 2007) on the subjects "Mathematical modeling of the process of ethane pyrolysis with recycling" and "Optimization of the process of selective hydrogenation of the ethane-ethylene fraction of pyrolysis gas based on a mathematical model"; Materials of the scientific conference dedicated to the centenary anniversary of corr.

member of Academy of Sciences of Azerbaijan G.H. Afandiyeva, (Baku, 2-3 2007) on the subject "Mathematical model of the process of hydrogenation of C_2, C_3 fractions of pyrolysis gas"; Republican scientific-practical conference dedicated to the 100th anniversary of Academician S.C. Mehdiyev, (December 2-3, Baku-2014) on the subject" Economic optimization and control of a multi-flow pyrolysis furnace"; The Ministry of Education of the Republic of Azerbaijan Sumgayit State University VIII traditional international scientific conference dedicated to the Year of Industry "Ecology and Protection of Life" (December 2-3, Baku-2014) C_1-C_2 hydrocarbons of the catalytic cracking unit as a raw material source, on the subjects "Cleaning of hydrogen-sulfide contained in the C_1-C_2 fraction received at the Oil Refinery named after H. Aliyev and elimination of the related environmental problem, obtaining pure benzene from light pyrolysis resin by hydropyrolysis method"; Scientific conference dedicated to the 92nd anniversary of the birth of Baku State University H. Aliyev, Baku, May 7-8, 2015 on the subject "Methods of solving environmental problems of sulfur compounds and acetaldehyde in the pyrogas obtained during the pyrolysis process by applying modern technologies"; Republican scientific conference on "Lubricants, fuels, special liquids, additives and reagents" dedicated to the 50th anniversary of the establishment of the Additives Chemistry Institute named after Academician A. Guliyev. October 13-14, Baku-2015 on the subject "Application of hydrogenated propylene oligomer obtained from propane-propylene fraction as compressor oil for polyethylene production". Materials of the Republic Scientific conference dedicated to the 80 year old of the institute of Catalysis and Inorganic Chemistry named after M. Naghiyev, November 15-16, 2016. "VNIIOS-science" 2016, Conference on the operation of ethylene benzene production, October 11-13, 2016, Zvenigorod city; "VNIIOS-science" 2016 Conference on the operation of benzene ethylene production on the subject "Technology for purifying the C_1-C_2 fraction from acid gas and sulfur compounds and preparing raw materials for the production of ethylene and propylene"; "VNIIOS-science" October 19-23, 2017, Zvenigorod on the subject "Cleaning of PPF and modernization of the PPF separation column at the Ethylene-Polyethylene plant" Azerikimya

SOCAR; Proceedings of the international scientific conference "Functional monomers and polymer materials with special properties: Problems, perspectives and practical views" held jointly by ARTNSDU and ANAS PMI November 15-16, 2017 on the subjects "Kinetic model of decene-1 alkylation of aromatic hydrocarbons in gasoline and kerosene fractions and study of gas dynamic properties of turbo compressor using C_1-C_4 fractions obtained from catalytic cracking with pyrolysis gas"; International scientific conference dedicated to the 85th anniversary of Academician Rafiga Alirza Aliyeva November 16-17, 2017 on the subject "Methods of purification and separation of ethylene-propylene from dry gases of catalytic cracking"; Baku State University, Scientific conference dedicated to the 95th anniversary of the birth of H. Aliyev, Baku-2018, on the subject of "Capture of moisture in process gases in industry with synthetic zeolites and recovery of used zeolites and return to the process"; Materials of the scientific conference "Naghiyev Readings" dedicated to the 110th anniversary of Academician M.Naghiyev, 2018, on the subject of "Development of a chemical-technological scheme for the extraction of ethylene from dry gas". Ministry of Education of the Republic of Azerbaijan, Ganja State University, International Scientific Conference 04-05 2018, Actual problems of modern natural and economic sciences. Technology of integration of C_1-C_4 gases obtained from the "Coke" unit of the Heydar Aliyev Oil Refinery into the production of "EP-300". The International Scientific Conference on Actual Problems of Modern Chemistry dedicated to the 90th anniversary of the Institute of Petrochemical Processes named after Academician Y.H. Mammadaliyev, October 2-4, 2019. International conference “Modern problems of theoretical and experimental chemistry” devoted to the 90th anniversary of Academician Rafiga Aliyeva, September 29-30, 2022 Baku, Azerbaijan. "Use of heavy pyrolysis resin as raw material in delayed coker unit" topic. Materials of the III International Conference of Azerbaijan State Oil and Industry University, March 02-03, 2023. Reports were made on complex processing technology of by-products obtained in Petrochemical Processes. A conference dedicated to the 90th anniversary of Academician Sahib Museyib oghlu Aliyev "Synthesis of petrochemicals, polyfunctional monomers, oligomers and polymers, June 23, 2023" reports on the research of the pyrolysis process of propane in industrial furnaces have been reported.

Published scientific works. The materials of the dissertation work have been published in 57 scientific works, of which 24 are articles, 29 are abstracts of reports of international and republican scientific conferences, and 3-methodical materials, 1- monograph, Intellectual Property Agency of the Republic of Azerbaijan, Patent - 2. Scientific works were published in Journal of "Azerbaijan Chemistry", Journal of "Chemical Problems", Journal of "Chemical Industry, Moscow", Journal of "Chemistry and Technology of Fuels and Oils, Moscow", "Petrochemical and oil refining processes", Journal of "Petrochemistry and Oil Refining", Journal of "Chemical Engineering", Journal of "Theoretical Basis of Chemical Technology, Moscow", Journal of "Chemical Technology and Biotechnology, Perm", Journal of "Chemical Technology Moscow" and other journals.

Author's personal participation. Setting the issue, collecting and summarizing literature data, preparing experiments, preparing samples for research, systematizing results, preparing articles and theses, as well as disclosing and summarizing data from physical and chemical analyzes were prepared by the author.

The organization where the dissertation work was performed. The dissertation work was carried out at the "Oil Refining" plant named after Heydar Aliyev, "EP-300" production of the "Ethylene-Polyethylene" plant of Azerikimya production union, ARETN, Institute of Petrochemical Processes named after Academician Y.H. Mammadaliyev.

The scope and structure of the work. The dissertation consists of an introduction (17760 marks), seven chapters, a literature review (94680 marks), an empirical part (57900 marks), chapter 3 (52650 marks), chapter 4 (26600 marks), chapter 5 (35900 marks), chapter 6 (39200 marks), chapter 7 (32500 marks), conclusion (3216 marks), list of 311 scientific literature cited and appendices. Printed on 360 (without attachments) computer pages. The thesis includes 58 tables, 74 pictures and 2 schemes. The total volume of the dissertation consists of 360406 characters (excluding tables, pictures, schemes, bibliography and appendices).

The introduction provides information on the relevance, goals, tasks, scientific innovation, and practical importance of the dissertation work.

Chapter one (literature review). The resources of raw materials for pyrolysis processes, the analysis of processes for the production of olefins in the world, the structure of the tubular pyrolysis furnace, the modern technologies of catalytic cracking and coking processes, the efficient use of by-products obtained in the facilities, the modern state of research and optimization of the pyrolysis process are shown.

The second chapter. Raw materials, catalysts, rules of conducting experiments and analysis of products, experimental study of the kinetics of selective hydrogenation of acetylene and its homologues contained in EEF and PPF was carried out. Chromatographic analysis methods of raw materials, products and other hydrocarbons, including determination of hydrogen in pyrolysis gases, methodology for determination of carbon 2 oxides and carbon 4 oxides in hydrocarbon gases, etc. were presented. In order to increase the yields of ethylene and propylene, the kinetics of selective hydrogenation of acetylene and its homologues contained in EEF AND PPF on G58 C catalyst was experimentally studied. An analysis of the proposed reaction products in the selective hydrogenation of EEF and PPF and a thermodynamic account of the reaction mechanism are presented.

The third chapter. "Catalytic cracking" and "Gradual coking" units clean sour gases and other mixtures in the dry gases and analyze the synthesis technology of ethylene and propylene in the "EP-300" unit. The results of studies on the compatibility of technological equipment and communications in the "EP-300" facility for the processing of dry and liquefied gases are presented and the technological parameters for their safe operation are defined..

The fourth chapter. After separating ethylene and propylene from the gases of the oil refinery, the optimal regime and structural parameters were determined using the mathematical model of the process of returning ethane and propane from pyrolysis to the pyrolysis furnace together with ethane and propane.

The fifth chapter. In order to study the kinetic regularities of the pyrolysis process, the optimal design methodology was applied, and a mathematical description of the process reflecting the characteristics of recirculates was compiled. On the basis of the kinetic model, CO and CO_2 production reactions, water vapor and temperature effects on the output of the target products at different loadings of the raw materials were studied**.** A comparison of the results of the pyrolysis process was made in recirculation and without recirculation, separate fuel gas supply and other modes and the possibilities of operational management of the process have been determined.

The sixth chapter. Optimization and mathematical modeling of industrial pyrolysis process of butane-butylene fraction was studied. In order to get a complete mathematical model of the process, heat balance and hydrodynamic equations in the recirculation flows according to the kinematic model were added. The values of the kinetic and thermodynamic constants calculated according to the industrial indicators of the "EP-300" device have been determined. The block diagram of the optimal control algorithm of the pyrolysis process of C_2-C_4 hydrocarbon gases is given. Joint pyrolysis of propane-propylene and butane-butylene fractions of catalytic cracking with the participation of hydrogen was studied. Based on the analysis of the experimental indicators of the distribution of pyrolysis products, an idea of the mechanism of pyrolysis with the presence of hydrogen was given.

The seventh chapter. A methodology is presented for the optimal design of CTC of the chemical-technological complex for joint processing of cracking and pyrolysis gases. On the basis of the mathematical model of CTC, which includes complete kinetic models of all selected processes, its optimization was carried out, and the optimal regimes of processes that ensure the maximum productivity of CTC for all intended products were determined, and the scheme of the chemical-technological complex was developed. The results of modeling and optimization of the pyrolysis process were presented. Values of exponential factors of mass stoichiometric coefficients, activation energies and rate constants are given.

Results, list of used literature and appendices are presented at the end of the dissertation.

THE MAIN CONTENT OF THE WORK

Treatment of C_1-C_4 gases obtained from oil refinery facilities from sour gases and use as raw material in EP-300 unit

Samples of C_1-C_2 (dry gas), propane-propylene, butane-butylene and hydrogenated gasoline fractions obtained from the "Gradual coking" unit were taken as raw materials for conducting scientific research and the analysis results were as follows.

Composition of dry gas obtained from "catalytic cracking", %, mass: H_2 -2,19; CO_2-2,4; CO-2,74; CH_4-20,68; N_2 -11,5; C_2H_4 -17,5; C_2H_6-19,54; C_3H_8-3,82; C_3H_6-8,52; n-C_4H_{10}-2,4; i-C_4H_{10}-1,27; t-butene-2-1,05; i-C_5H_{12}-4,01; cis- butene-2- 0,8; H_2S-1,5.

Composition of dry gas obtained from "gradual coking", %, mass: H_2-1,2; CO_2-0,48; CO-1,12; CH_4-45,96; N_2 -0,18; C_2H_4 -3,7; C_2H_6-23,8; C_3H_8-3,82; C_3H_6-12,7; n-C_4H_{10}-1,1; i-C_4H_{10}-0,66; t- butene-2-0,7; i-C_5H_{12}-0,01; cis- butene-2- 0,7; H_2S-1,5.

Propane-propylene fraction obtained from "catalytic cracking", %, mass: C_2H_6-1,0; C_3H_8-21,0; C_3H_6-72,15; butene-1-1,4; i-butane-2,7; isobutylene -1,4; H_2S-100 ppb; Mercaptans RSH-500 ppb; COS-100ppb;AsH_3-3ppm; PH_3-3ppm.

Composition of the butane-butylene fraction obtained from "catalytic cracking", %, mass: ΣC_2-0,1; C_4H_6-0.15; C_3H_8-0.25; C_3H_6—0.07; i-C_4H_{10}-30.78;

n-C_4H_{10}-12,41; C_4H_8 -α+i 11.8%; trans C_4H_8-16,09%; cis-C_4H_8-12.11; butene-1-11.18%; ΣC_5-0,1%; ΣS-167,4 ppm; propodiene-0.02 ppm; methylacetylene-0,06%.

The composition of the hydrogenated gasoline fraction obtained from the "gradual coking" unit: color - transparent; ρ= 0,6826 g/cm^3; first boiling t^{0}C-28; 50^{0}C at 10%; 83^{0}C at 50%; final boiling t^{0}C-150. Chemical composition%, mass: aromatic k.h-5.64; naphthene k.h.-26.1; paraffin k.h.-35.68; isoparaffin -30.46; unsaturated k.h.-0.83; x-peak-1.29.

Hydrocarbon contents of raw materials and obtained pyrolysis products were determined using a "Chromotex-5000" brand gas chromatograph with a flame ionization detector. In order to study the kinetic regularities of the pyrolysis process, the main scheme of the pyrolysis unit installed in the Central scientific research laboratory of the "Ethylene-Polyethylene" plant is given in Fig. 1. As raw materials, samples of primary processing gasoline, ethane, propane-propylene and butane-butylene fractions were pyrolyzed separately and in a mixed case according to the scheme given in Fig. 1. Collected gaseous hydrocarbon samples are supplied to the mixer from flask No. 1. In addition, water vapor enters here from capacity No. 2. Hydrocarbons and water vapor are mixed and enter the conversion chamber of the furnace. The length of the convection chamber is L= 60 cm, the inner diameter is d=10 cm. After the convection stage, the raw materials enter the radiant stage of the furnace at a temperature of 500^0C together with steam and water vapor. These stages are conventionally divided into two zones: solid heating (length ≈30 cm) and reaction zone (length ≈ 120 cm) with inner diameter of the pipe dd =10 mm. The temperature regime given by pyrolysis conditions ($775÷850^0$C) is equal to the maximum temperature in the reaction zone. At this temperature, reactions of thermal decomposition of hydrocarbons take place with the production of olefins. A cooling agent (for example, water, dry ice) is used to cool the pyrogas at the outlet of the furnace in coolers No. 11 and 12 in an instant. The cooled pyrogas is supplied to separator No. 13. The liquid products of pyrolysis from the separator are collected in capacity No. 17. Then the amount is determined and sent to the chromatograph for analysis. After separator No. 13, gaseous products are cooled with cooling agent in additional refrigerator No. 14 and sent to separator No. 15. Separation of pyrogas products in gaseous and liquid form continues here. Liquid products are collected in measuring container No. 17 and gas products are measured by gas meter No. 16 and sent to the chromatograph for analysis.

Raw materials and materials

Co-pyrolysis of C_1-C_4 hydrocarbons obtained from "catalytic cracking", "gradual coking" and gasoline units with naphtha, as well as the pyrolysis process with the presence of hydrogen, was carried out in a laboratory experimental pyrolysis unit.

Gaseous technical nitrogen is used for blowing the pyrolysis reactor. The samples of the products coming out of the pyrolysis furnace are taken according to the scheme given in Fig 2.

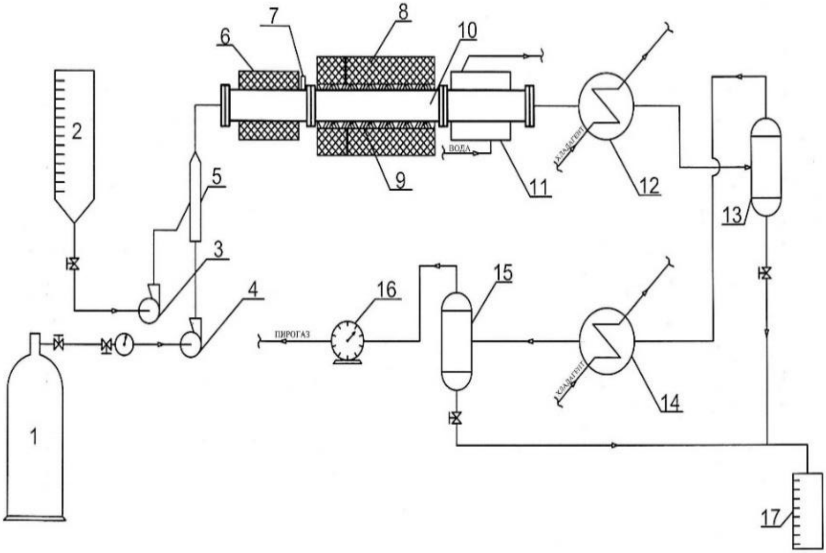

Figure 1. The main technological scheme of the laboratory pyrolysis unit.

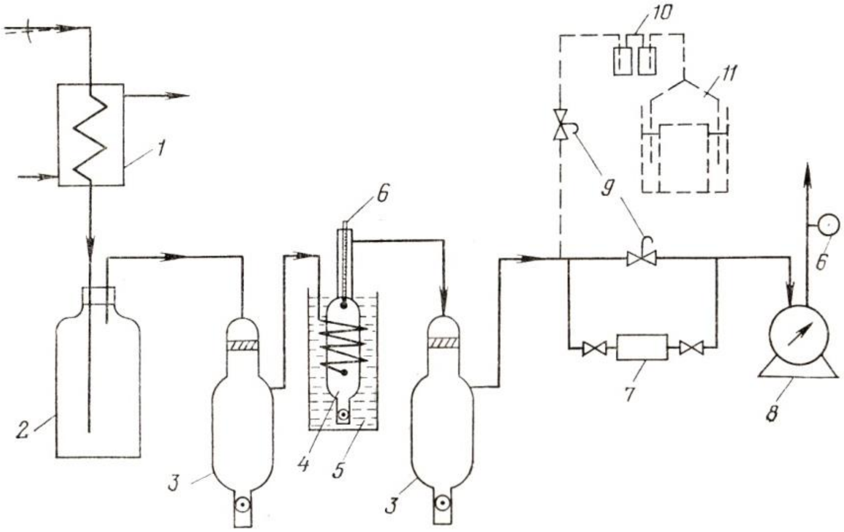

Figure 2. Scheme of the device for taking pyrogas analysis from pyrolysis furnaces.
1 - cooler, 2 - container for separating condensate, 3 - water trap, 4 - container for condensate, 5 - cooling agent, 6 - thermometer, 7 - gas holder, 8 - gas meter, 9 - handle, 10 - flow indicator, 11 - gasometer.

The sampler is placed on the upstream side and equipped with a drawer system. The scheme of the sampling system is given in figure 2. The sample is taken at a speed of 18-25 l/min and for a period of 1-1.5 hours and a total of 1000-1500 liters of pyrogas passes through the gas meter. The amount of collected liquid hydrocarbons should not be less than 300-450 grams. The primary raw material sample, gas and liquid parts of pyrogas are analyzed separately in laboratory conditions by chromatographic method. The analysis of the group composition of gasoline was carried out by the chromatographic method on the "Chromotek-5000.1" device. Sorbent dura-bond DB-1; capillary tube 100 m x 0.25 mm x 0.50 µm; detector-ion flame; gas carrier - Consumption 10 ml/min, pressure - 97 kPa; A mixture of H_2, consumption - 40 ml/min + air - consumption 400 ml/min is given for the combustion of the flame. Chromatographic analysis of the pyrogas obtained from the pyrolysis process was performed on the

"Chromotek-5000.1" device. The device is equipped with 3 nozzles. 1st column consists of - 20% sebasonitrile impregnated with chromosorb 9 m x 2.1 mm; 2nd column consists of - Hayesep No. 80/100 2 m x 2 mm+NaX 60/80 3 m x 2 mm; 3rd column consists of NaX 60/80 3 m x 2 mm. The detector is heat transfer, the temperature of the column is 50°C, the temperature of the detector is 150°C. Gas carrier 1st column Ar- consumption is 16.6 ml/min; 2nd column H_2 consumption is 25 ml/min; 3rd column H_2 consumption is 23 ml/min; pressure of gas carriers in all three columns is 90 kPa. Analytical results of pyrogas obtained from the decomposition of coke gasoline at a temperature of 860^0C, %, mass: H_2-1,694; CO_2 – 0, 1785; C_{6+}, C_5 olefins - 0,2788; C_2H_4 – 33,97; C_2H_6-4,593; C_3H_8 - 1,895; C_3H_6 - 16,96; C_2H_2 -0,9380; i-C_4H_{10} -2,588; n-C_4H_{10} - 0,3571; Propadiene – 0,2652; Butene-1- 0,4353; i-butene -2,022; Trans butene-2 – 0,1719; Cis-butene-2 – 0,1622; CH_4 – 31,46; CO- 0,1279; Methylacetylene – 0,4049; Butadien -1,3-1,504 is given.

The analyzes of ethylene and propylene were carried out in accordance with the requirements of GOST 25070-2013 on the "Chromotek-5000.1" chromatograph device. Al_2O_3 50 m x 0,53mm x 15,0 mkm as a sorbent for the 1st column, for the determination of gaseous hydrocarbons; № 80/100 2m x 3 mm and porapak № 80/100 4 m x 3 mm for the 2nd column, Determination of CO and CO_2 in hydrocarbon gas. In the determination of hydrocarbons, N_2 as carrier gas-10 ml/min., detector ion flame-H_2+air for combustion, H_2 consumption-30 ml/min., air-400 ml/min., column temperature 60÷180°C, detector temperature 250°C, the evaporation temperature is 120°C. In the determination of CO and CO_2, as a gas carrier, N_2-30 ml/min., H_2 consumption-30 ml/min., air-400 ml/min., column temperature 60÷ 180°C, detector temperature 250°C, evaporation temperature is 120°C. Analysis of finished product ethylene: Volume fraction of ethylene, % -99,9; Volume fraction of propylene, %-0.005; Volume share of methane and ethane, %, - 0.1; Volume share of acetylene, %, butadiene, volume share of propodiene, % 0.0005; Volume share of carbon-2 oxide, % 0.001; Volume fraction of carbon dioxide, %-0.0005; Volume fraction of methanol, %-0.001; Mass fraction of oxygen, in the pipeline, %-0.0002; Mass density of sulfur,

mg/m^3-1; Mass fraction of water, %-0.001; The volume fraction of ammonia is set to 0.0001%.

The analysis of propylene was carried out on the "Chromotek-5000.1" chromatograph device. Analytical results of the propylene product: volume share of propylene, %-99.9; Ethylene volume fraction, %-0.005; Volume fraction of acetylene, % - 0.001; Volume fraction of C_4 hydrocarbons, %- 0.002; Diene, (propodiene, butadiene) volume fraction, %-0.001; Volume fraction of hydrogen, % - 0.001; Volume fraction of CO_2, %-0.001; Volume share of CO, %-0.0005; Volume fraction of ethane, %-0.2; Volume fraction of O_2, %-0.0003; Volume share of sulfur, mg/m^3- 3; Volume fraction of water is set mg/m^3-0.0005.

Determination of small amount of acetylenic compounds in the composition of monomers obtained from the selective hydrogenation of acetylene, methyl acetylene, propodiene and allenes in the ethane-ethylene and propane-propylene fractions obtained in the "EP-300" unit with the presence of a Pd catalyst was determined in the "Chromotek-5000.1" chromatograph. Corbxen TM 1006 PLOT sorbent was filled into a capillary column (30m x 0.32mm).

Detector - ion flame, gas carrier H_2-consumption-4.5 ml/min, hydrogen+air mixture for flame- H_2-consumption-4.5 ml/min, air consumption-500 ml/min. the temperature of the column is 150-185°C.

The effect of hydrogen as an inhibitor of coke formation in the pyrolysis of hydrocarbons in the presence of hydrogen is observed regardless of the molecular weight of the raw material.

It should be noted that at high pressure (1^{-10} MPa) the pyrolysis of hydrocarbons with the initiator remains unchanged, referring to the increased role of ethylene in the hydrogenation reaction of ethane.

$$\frac{Gs.b}{Ms.b} : \frac{Gp.x}{Mp.x} = Nsb : Np.x \quad (1)$$

Here: Ms.b and Mp.x. - molecular mass of water vapor and raw materials, g/mol; The results of the mass composition of water vapor and hydrogen gas mixtures of hydrocarbon raw materials supplied to the pyrolysis reactor inlet are given in table 1.

Table 1

Determination of mass composition of steam-gas mixture

Composition of pyrolysis gases	Molecular mass of components	Mass of components, g	Mass composition of pyrolysis gases, %
Hydrogen	N_h	$M_h \cdot N_h = m_h$	$(m_h/\sum m_i) \cdot 100\% = g_h$
Water vapor	N_{sb}	$M_{sb} \cdot N_{sb} = m_{sb}$	$(m_{sb}/\sum m_i) \cdot 100\% = g_{sb}$
Raw material	N_x	$M_x \cdot N_x = m_x$	$(m_x/\sum m_i) \cdot 100\% = g_x$
Total	$\sum N_i$	$\sum m_i$	100

The total consumption of water vapor and hydrogen at the entrance of the pyrolysis reactor of the raw mixture of hydrocarbons in the unit of time G_{total}, g/min.) is calculated according to the formula (2):

$$G_{ümumi} = \frac{V_{ümumi} \cdot 273 \cdot M_{orta}(P_{bar} + P_{izobar}) \cdot \eta}{22,4 \cdot P_{bar} \cdot (t + 273)} \qquad (2)$$

$V_{ümumi} = \frac{V_{r.z.} \cdot 60}{\tau \cdot 1000}$ - volume velocity of steam gas mixture at the pyrolysis reactor inlet, dm^3/min.

$V_{r.z.}$ = 62,8cm^3 – the volume of the reaction zone in the pyrolysis reactor;

$M_{orta} = \frac{M_{baş.} + M_{son.}}{2}$ average molecular weight of the vapor gas mixture at the inlet and outlet of the pyrolysis reactor.

$M_{baş.} = \sum m_i / \sum N_i$ - molecular weight of the steam-gas mixture at the pyrolysis reactor inlet;

$\sum m_i$ – total mass of pyrogas components, grams (table 1).

$\sum N_i$ - sum of moles of vapor-gas mixture components, mol. (table 1)

M_{son} = 24,19g/mol - The molecular mass of pyrogas mixture at the outlet of the pyrolysis reactor was taken as the molecular mass of pyrogas from the outlet of the serpentine pipes of the SRT-II and SRT-

VI type pyrolysis furnaces of the Ethylene plant according to the report of Lummus Global USA.

$P_{bar} = 1 kq / sm^2$ - atmospheric pressure inside the reactor;

$P_{izobar} = 0 kq / sm^2$ - overpressure inside the reactor;

ɳ = 1 min – the time appropriate to give the mixture.

The supply (consumption) rate of each component of the steam-gas mixture at the entrance of the pyrolysis reactor per unit time is calculated in the order presented in table 2. The average volume of raw materials was 150-160 cm^3.

Table 2

Determination of the delivery rate of each component of the steam-gas mixture

Composition of pyrolysis gases	Mass fraction of pyrolysis gases, %	Specific gravity of pyrolysis gases, t=20^{0}C	Rate of release of pyrolysis gases	
			Mass, g/min	Volume
Hydrogen	g_h	$\mathcal{P}_h$, g/ dm^3	$(g_h/100\%) \cdot G_{total}=G_h$	$G_h/\mathcal{P}_h$, dm^3/min
Water vapor	g_{sb}	$\mathcal{P}_{sb}$, g/ cm^3	$(g_{sb}/100\%) \cdot G_{total}=G_h$	$G_{sb}/\mathcal{P}_{sb}$,cm^3/min
Raw material	g_x	$\mathcal{P}_x$, g/ cm^3	$(g_x/100\%) \cdot G_{total}=G_x$	$G_x/\mathcal{P}_x$, cm^3/min

After the end of the pyrolysis process, the liquid pyrolysis products and water condensate are discharged from the cooling separator into the separator and stored for two hours for stratification. After stratification, the liquid products are separated from the water condensate and the water is placed in the freezing chamber for 20 hours for crystallization of the condensate residues (freezing temperature -100^{0}C). Then the liquid products are separated from the ice layer and the mass is weighed on an analytical balance. Then, according to GOST2177-99 (ISO 3405-88), the fraction of hydrocarbons of pyrolysis liquid products corresponds to pyrolysis resin at a temperature above 200^{0}C.

After the end of the pyrolysis process, i.e. after the furnace has completed its operating hours, it is blown with a mixture of steam and air. Analytical samples are periodically taken from the composition of blown gas, mainly by determining the amount of CO and CO_2, the amount of coke in the furnace is determined.

Chromatographic determination methods of hydrocarbons

Pyrolysis of the main products of the hydrocarbon gas mixture was carried out by the gas chromatographic method in "Chromotek-5000.1" brand chromatographs and equipped with the following columns. The 1st column is 9 meters long and has an inner diameter of 2 mm. The prepared sorbent consists of 20% sebaso-nitrile impregnated with chromosorb and the size of the grains is 1-2 mm. The 2nd column is 3 meters long, 2 mm inner diameter and filled with Hayesep No. 80/100 2m x 2mm+NaX 60/80 sorbent. The 3rd column is 3 meters long, has an inner diameter of 2 mm and is filled with NaX 60/80 sorbent. A temperature of 50°C is maintained in the column; In the detector, the temperature of the heat transmitter is kept at 150°C. The cylinders are supplied with gas carriers as follows. The pressure of the gas-carrying cylinders is maintained at 90 kPa and the consumption consists of the following: Argon is supplied to the 1st column as a carrier gas at a rate of 16.6 ml/minute; hydrogen is supplied to the 2nd column at a rate of 25 ml/minute; hydrogen is supplied to the 3rd column at a rate of 23 ml/min.

The analysis of the pyrogas taken from the SRT-II pyrolysis gasoline furnace was carried out using the "Chromotek-5000" brand chromatograph device. Analysis of the gas obtained from the decomposition of coke gasoline in pyrolysis furnaces %, mass: H_2-1,694; CO_2- 0,1785; C6+, olefins C5+ 0,2788; C_2H_4- 33,97; C_2H_6-4,593; C_3H_8- 1,895; C_3H_6- 16,96; C_2H_2- 0,938; i-C_4H_{10}- 2,588; n-C_4H_{10}- 0,3571; Propodiene -0,2652; butene-1-0,4353; i-butene- 2,022; trans-butene -2-0,1719; CH_4-31,46; CO-0,1279; methylacetylene – 0,4049; butadiene -1,3-1,504 is set.

The analysis of the pyrogas taken from the SRT-I pyrolysis ethane furnace was carried out using the "Chromotek-5000" brand chromatograph device. Analysis of pyrolysis gas %, mass:

H_2-3,798; CO_2- 0,0268; C6+, olefins C5 -1,658; C_2H_4- 51,53; C_2H_6- 18,57; C_3H_8- 0,6317; C_3H_6- 2,229; C_2H_2- 1,239; i-C_4H_{10}- 1,743; n-C_4H_{10}- 0,567; Propodiene-0,535; butene-1-0,098; i-butene- 0,019; trans-butene -2-0,049; CH_4-15,64; CO-0,324; methyl-acetylene – 0,1225; butadiene-1,3- 2,166 is set.

Description of the experimental setup for the study of kinetic regularity

All studies were carried out in the laboratory pyrolysis unit shown in Figure 3. The device consists of three main parts: reaction preparation, reaction, analytical parts.

The study of the kinetic regularity of the process in Figure 3 serves to determine the consumption of the gases used in the preparation part of the scheme of the laboratory experimental unit and their purification from mixtures.

Gas purification was carried out in glass columns filled with calcium chloride, activated carbon and silica gel (5). Gases were supplied from cylinders (1) equipped with two-chamber reducers (2). With the help of rotameters (6), the consumption of gases was determined with precise adjustment drawers (3). Before cleaning, nitrogen passes through the monostat (4) and serves to release gases from the reaction zone into the atmosphere.

The supply of gases to the reaction zone was performed by a tap (7) with two inlets and one outlet from the reactor. The propane passes through the valve (8) and the bubble flow meter (10) and at the same time the valve in the exhaust line (9) is used. The reaction part consists of a non-gradient reactor (11), a furnace (13), and a sampler (14). Reactor 11 is equipped with a thermocouple located in the reaction zone. After the reactor, the reaction products pass through the samplers (14) and the two-channel drawer (15), and then they are either discharged into the atmosphere by means of the drawer (15) or fed into the analysis system by means of the drawer (16).

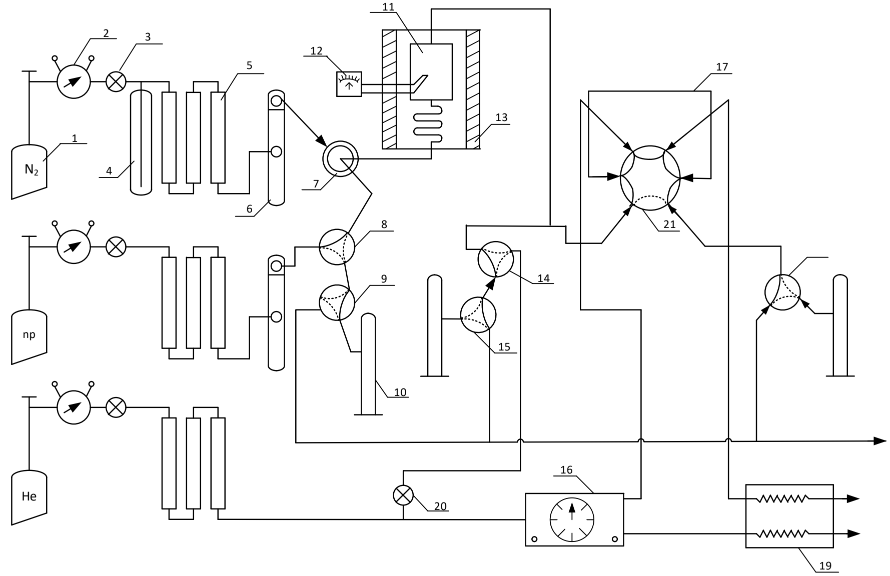

Figure 3. Description of the experimental setup for the study of kinetic regularity:
1 – gas cylinder, 2 – two-chamber reducer, 3 – drawer for precise adjustment, 4 – monostat, 5 – gas purification column, 6 – rotameter, 7, 8, 9, 15, 18 – drawers with three outlets, 10 – foam consumption meter, 11 – reactor, 12 – potentiometer, 13 – oven, 14 – two-channel drawer, 16 – block for injecting gas sample into chromatograph, 17 – petle, 19 – chromatograph, 20 – drawer, 21 – six-channel drawer. Values of gas velocities and Reynolds number in the pipe calculated for different diameters: Re=$10\cdot10^5$; linear velocity -173.7 in a 2" inch pipe; Re=$5\cdot10^5$; linear speed-43.4 in a 4" inch tube, Re=$3\cdot10^5$; linear speed was -19.3 in a 6" inch tube.

Besides these, paraffin greatly complicates the solution of the issue of optimal design of the pyrolysis process of hydrocarbons and leads to the development of a special methodology. In the first stage, only the main decomposition reaction of hydrocarbons is recorded and it includes the fulfillment of the following clauses:

1. Determination of the hydrodynamic regime of the tubular reactor at the given productivity and different diameters of the tubes.

2. Experimental study of the kinetic regularities of the pyrolysis process of paraffin hydrocarbons in a laboratory pyrolysis unit with the aim of drawing up the stoichiometric and gross-kinetic general formulas of the process.
3. Development of a mathematical model of the process based on general stoichiometric and gross-kinematic formulas, heat balance formula and pressure difference.
4. To study the pyrolysis process of paraffin hydrocarbons based on a mathematical model in a reactor of different diameters at a given productivity.

İkinci mərhələ üçün aşağıdakı ardıcıl işlər aparılır. For the second stage, the following sequential works are carried out.

1. Compile the stoichiometric formulas of the propane pyrolysis process by recording the second and third reactions.
2. To work out a complete kinetic model of the process corresponding to them
3. Finding the kinematic parameters of the model based on the results of experimental studies.
4. Development of a complete mathematical model taking into account the recirculation features of the process.
5. Process optimization and process research based on the developed model.

In order to fulfill the clauses in the first stage, the following values of the main parameters of the process according to the verified methodology were adopted in the example of the propane pyrolysis process.

1. The temperature of propane at the inlet of the reactor is T=866 K, and at the outlet is T=1200 K, due to the condition that the materials of the pipes are kept at the highest temperature.
2. Consumption of raw materials (G=3200 kg/h of propane).
3. In order to ensure the passage of the given flow through the separator coil located after the reactor the pressure at the inlet of the reactor should not be less than P=4.2 atm and at the outlet should not be less than 1.95 atm.
4. The conversion of propane is taken at the limit of 85%.
5. 15×5M brand steel was chosen for the process, its specific gravity

is 7850 kg/m^3.

Determination of the hydrodynamic regime

Practically, the pyrolysis process carried out in a furnace consisting of serpentine tubes can ideally be viewed as a process carried out in a compression-extraction reactor.

The hydrodynamic regime of the flow of raw materials through the pipes is characterized by the value of the Reynolds formula.

$$Re = \frac{u d_d \gamma}{\mu g}$$

Here:u – linear velocity of flow, m/sec; d_d– inner diameter of the pipe, m; γ – specific gravity of gas, kg/m^3; μ – dynamic coefficient of viscosity kg·s/m^2; g – gravitational force, m/sec^2. From the point of view of the effect of temperature, the reaction products occupy the smallest volume at the beginning of the reaction tube. If the eddy flow according to Reynolds exceeds 10,000, the number of moles of reactants in different sections of the reactor increases, and they heat up to a higher temperature than at the beginning. Therefore, it is sufficient to determine the Re number at the entrance of the reactor. It is known that both in terms of the effect of temperature and in terms of chemical reaction, the smallest volume of reactants occupies at the beginning of the reaction tube. If the Reynolds number is greater than 10000 (developed eddy current), it will be deliberately higher in the remaining parts. Because, firstly, the number of moles passing through any arbitrary section increases as the reaction proceeds, and secondly, those entering the reaction will decompose there to a higher temperature than before. Therefore, it is sufficient to determine the Reynolds number at the reactor inlet.

Experimental study of the kinetics of hydrogenation of the ethane-ethylene fraction over the G-58C catalyst

The process of selective hydrogenation of the ethane-ethylene fraction of pyrolysis gas is traditionally carried out with the presence of palladium catalysts. High selectivity catalysts currently successfully used to hydrogenate acetylene in EEF are palladium catalysts belonging to the G-58 group. The kinetic laws of acetylene hydrogenation were studied in an ideal compression reactor in a fixed bed of industrial catalyst G-58C. Figure 4 shows the rate dependence of acetylene conversion. As can be seen from the figure, the decrease of the volume velocity from 10000 to 7000 s^{-1} causes a slow conversion of acetylene, and the subsequent decrease causes a rapid increase in the conversion. This dependence also manifests itself with an increase in temperature. Figure 5 shows the dependence of the partial pressure of hydrogen on the volume velocity of the raw material at different temperatures (^{0}C). As can be seen from the figure, the partial pressure of hydrogen increases as the volume velocity increases at any temperature.

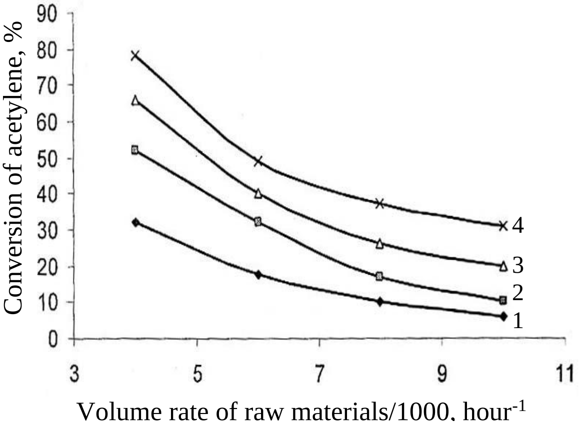

Figure 4. Dependence of acetylene conversion at different temperatures (^{0}C) on the volume rate of raw materials: 1 – 30, 2 – 45, 3 – 60, 4 – 75. P=0.6 MPa.

As can be seen from Figure 4-6, the degree of hydrogen conversion decreases with the increase of the raw material volume rate at temperatures of 30 and 45^{0}C, and the hydrogen conversion rate exceeds the maximum at temperatures of 60 and 75^{0}C. Based on our kinetic studies, the most probable scheme of these reactions was recommended.

Figure 5. Dependence of partial pressure of hydrogen on volume rate of raw material at different temperatures (^{0}C): 1 – 30, 2 – 45, 3 – 60, 4 – 75. P=0.6 MPa.

Figure 6 shows the dependence of the hydrogen conversion rate on the raw material volume rate.

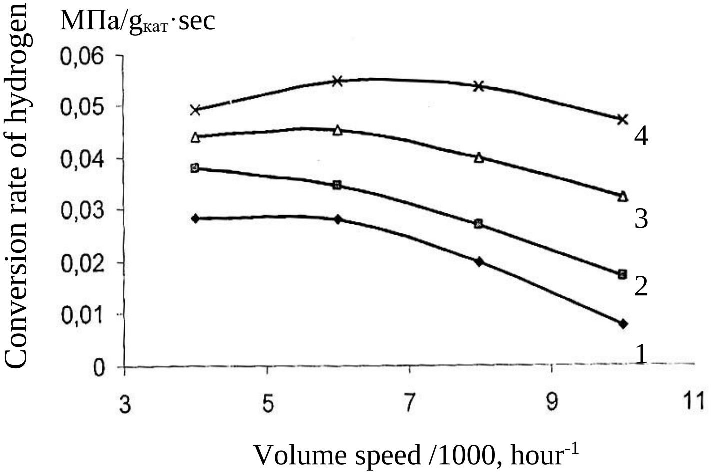

Figure 6. Dependence of the rate of hydrogen conversion on the volume rate of raw materials at different temperatures (^{0}C): 1 – 30, 2 – 45, 3 – 60, 4 – 75. P=0.6 MPa.

Construction of a kinetic model of acetylene hydrogenation

in the ethane-ethylene fraction

To integrate the kinetic equation of the reaction at constant pressure, it is necessary to take into account the change in the volume of the reaction mixture, the kinetic equation must include the change in the volumes of the components in the reaction. However, considering that the amounts of acetylene and hydrogen in the ethane-ethylene fraction are small, (0.5-2.0% by mass and 0.3% by volume, respectively), while the amount of ethylene and ethane are on the contrary high, (75-80% mass and 20-25% mass) , then a slight decrease in volume during the reaction is obtained and can be ignored. In this case, the integration of the kinetic equation can be carried out analogously to the integration of the kinetic equation of the reaction in constant volume.

The more likely mechanism III and its kinetic model are given.

Mechanism III: Equilibrium is established in the adsorption process, hydrocarbons and hydrogen are adsorbed in different types of active centers, hydrogen is dissociated into atoms during adsorption. The following assumptions were made when building the kinetic model according to the mechanism:

1. The adsorption coefficient of ethane is small compared to the adsorption coefficients of acetylene and ethylene and can be neglected;
2. The equilibrium concentrations of partially hydrogenated compounds are established practically instantaneously;
3. The rate of hydrogenation of acetylene is greater than the rate of hydrogenation of ethylene: $k_{-1} \leq k_2$ and $k_{-3} \geq k_4$.

Assuming the above assumptions, the rate equations for the hydrogenation of acetylene and ethylene are obtained as follows:

$$r_{acetylene} = \frac{-k_1 \cdot b_2 P_2 \cdot \sqrt{b_1 P_1}}{(1+b_2P_2+b_3P_3+b_4P_4)(1+\sqrt{b_1P_1})}$$

$$r_{ethylene.} = \frac{-k_2 \cdot b_3 P_3 \cdot \sqrt{b_1 P_1}}{(1+b_2P_2+b_3P_3+b_4P_4)(1+\sqrt{b_1P_1})}$$

where b_1, b_2, b_3, b_4 are adsorption coefficients of hydrogen, acetylene, ethylene and carbon dioxide; P_1, P_2, P_3, P_4 are partial pressures of hydrogen, acetylene, ethylene and carbon dioxide; k_1, k_2 are rate constants of acetylene and ethylene hydrogenation reactions.

Scheme of CO_2 and H_2S purification of dry gas with monoethanolamine.

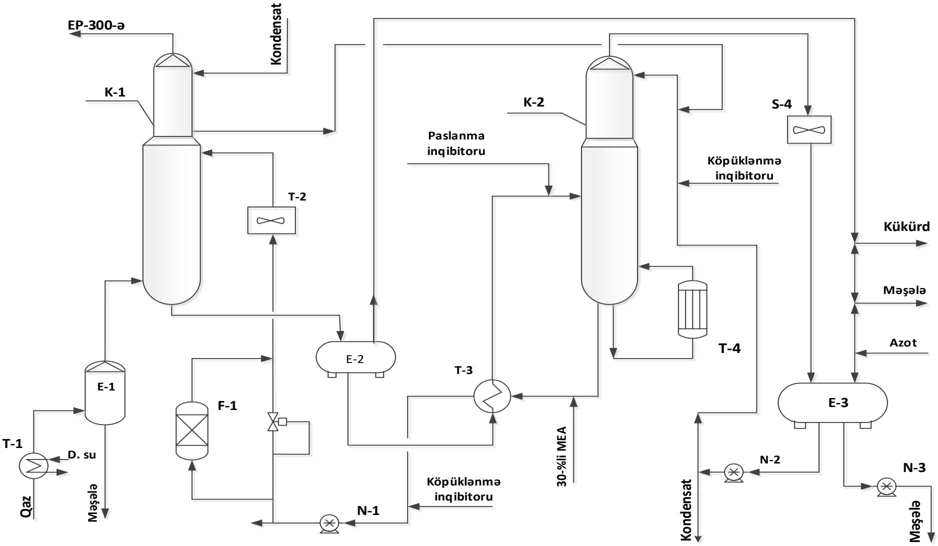

Fig. 7. CO_2 and H_2S purification scheme of dry gas with monoethanolamine. K-1-absorber, K-2-desorber, N-1,2,3- pumps, T-1,2,3-heat exchangers, T-4-boiler, E-1, 2, 3- tanks, S- 4-seperator.

According to the scheme shown in Figure 7, the absorption process is carried out by feeding the K-1 column with a 15% monoethanolamine solution to remove H_2S and CO_2 compounds from the dry gas. With pump N-1, 15% monoethanolamine solution is supplied to the upper part of K-1 column, passing through T-2 heat exchanger. The dry gas fraction enters from the lower part of the boiler. The process of chemisorption proceeds with the release of heat. A temperature of 40-50^{0}C and a pressure of 1 MPa are kept in the tank. The purified dry gas fraction from the upper part of the K1 column is sent to the "EP-300" unit for processing. The saturated monoethanolamine solution coming out of the lower part of the K-1 column enters the E-2 tank, and from there it passes through the T-3 heat exchanger and is fed to the K-2 desorber. In order to maintain a temperature of 120-125^{0}C in the cube of the desorber, it is equipped with boiler number T-4 working with water vapor in the cubic part of the K-2 boiler. A temperature of 100^{0}C is maintained above the desorber. As a result of the desorption process at a temperature of 120^{0}C, the H_2S and CO_2 compounds absorbed by the monoethanolamine solution pass through the S-4 separator and enter the E-3 capacity. The liquid part is returned to the upper part of the desorber by means of the N-2 pump, and the sour gases coming out from the upper part are directed to be used for sulfur extraction or burned in a flare. A part of the monoethanol solution coming out of the desorber cube passes through the T-3 heat exchanger and is supplied to the absorber No. 1 by means of the N-2 pump.

It consists in carrying out a reaction with amine compounds by transferring the acidic components (H_2S, COS, CS_2 and CO_2) contained in the dry gas to the aqueous phase. In the absorber No. 1, at a pressure of 1.0 MPa, at a temperature of 40-45^{0}C, the dry gas fraction is extracted by means of 15% monoethanolamine. In the extraction stage, the reaction proceeds according to equations (1), (2), (3) and (4).

$$2RNH_2 + H_2S \leftrightarrow (RNH_3)_2S \qquad (1)$$

$$(RNH_3)_2S + H_2S \leftrightarrow 2RNH_3HS \qquad (2)$$

$$2RNH_2 + CO_2 + H_2O \leftrightarrow (RNH_3)_2CO_3 \ (3)$$

$$(RNH_3)_2CO_3 + CO_2 + H_2O \leftrightarrow 2RNH_3H_2\,CO_3 \quad (4)$$

Here, R– CH_2CH_2OH. The amount of sour gases in dry gas; H_2S - decreased from 2% to 0.0001%, and CO_2 decreased from 3.25% to 0.015%. The presence of oxygen in the extraction process can result in an additional reaction.

$$2RNH_2 + 2H_2S + O_2 \rightarrow R(NH_2)_2H_2S_2O_3 + H_2O \qquad (5)$$

Some of the salt compounds involved in the reaction form complex compounds with iron and accelerate the corrosion of equipment. With the presence of COS, reaction equation (6) follows.

$$2\,RNH_2 + COS \rightarrow RNHCOSH{\cdot}NH_2R \qquad (6)$$

The reaction in the presence of CC_2 is shown in equation (7).

$$2\,RNH_2 + CS_2 \rightarrow RNHCSSH{\cdot}NH_2\,R \qquad (7)$$

Here, R is an amine group.

Cleaned dry gas is sent from the oil refinery to the "EP-300" unit for processing through a 62 km long pipeline using a compressor. The chemical composition of dry gas (Fig. 8) was determined in the Chromotek-5000 chromatograp.

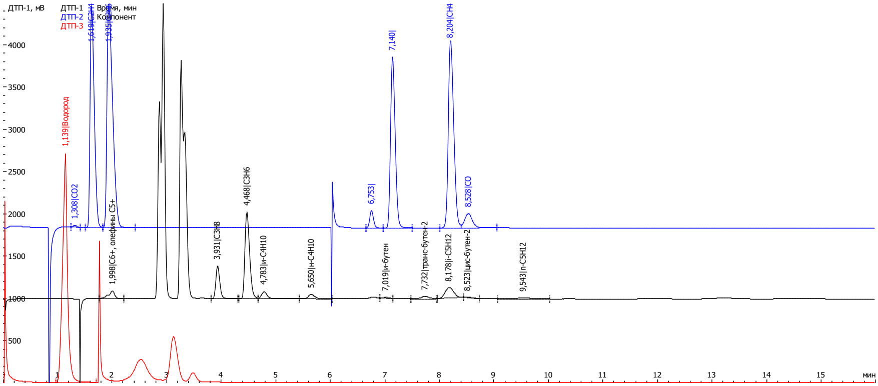

Figure 8. Diagram of dry gas produced on the Chromotek-5000 device.

The peaks indicated by the red line indicate concentrations of CO and CO_2. The peaks indicated by the black line indicate the concentration of H_2.

Part of the water contained in the propane-propylene fraction from "catalytic cracking" is initially separated during cooling in the T-1 position cooler in the unit (Figure 9). Hydrocarbon water separated from the propane-propylene fraction is collected in the precipitator of the phase E-2 position capacity and sent to the underground drainage capacity according to the level. E-2 position capacity mode parameters: pressure P= 1.8 MPa; temperature t= 15^0C, level L= 80% is maintained. The process of drying the propane-propylene fraction and complete purification from harmful compounds is carried out in adsorbers at positions C-41 and C-42. When one of the adsorbers is in working condition, the other one is being regenerated or kept in reserve. AxSorb 902 brand adsorbent, consisting of two systems with high adsorption capacity and long-term operation, i.e. low input part propane-propylene fraction, is used for absorption of moisture in $C\text{-}4_{1\text{-}2}$ position adsorbers. Adsorbents mainly consist of Al_2O_3, which have high absorption capacity. In the upper part of the $C\text{-}4_{1\text{-}2}$ adsorber, AxSorb 984 brand adsorbent is used to absorb small amounts of sulfur compounds. The propane-propylene fraction leaving the C-4$_{1-2}$ adsorber enters the C-5 position adsorber. In the C-5 adsorber, arsenic and phosphine are cleaned using the AxTrap194 brand adsorbent of the "Axens" company.

Propane-propylene fraction C-4$_{1-2}$ adsorber from bottom to top, passing through AxSorb 902 and AxSorb 984 adsorbents is dried from moisture in the first layer and in the second layer it is cleaned of sulfur compounds. The consumption of the propane-propylene fraction supplied to the C-4$_{1-2}$ adsorber is automatically adjusted by returning it to the E-2 capacity from the output of the N-3 pump. AxSorb 984, AxSorb 902 and AxTrap 194 brand sorbents mainly consist of Al_2O_3+ promoter.

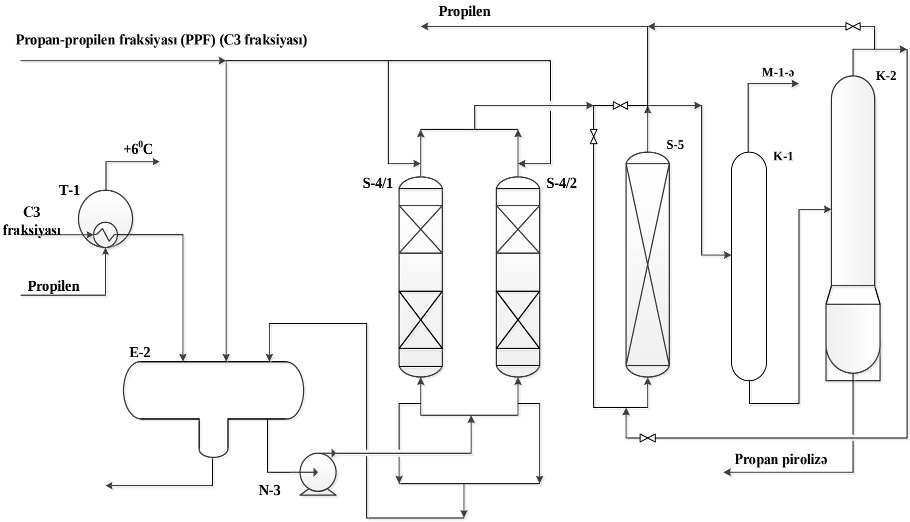

Figure 9. The main scheme of the method of purification of propane - propylene fraction from micromixtures using the adsorption method. T-1 – heat exchanger, E-2 – tank, N-3 – pump, C-4$_{1-2}$ – adsorbers for cleaning PPF from moisture and sulfur compounds, C-5 – adsorber for cleaning PPF from impurities such as arsenic and phosphine , K-1 – deethanization column, K-2 – propane separation column from propylene.

Application of the butane-butylene fraction obtained from catalytic cracking together with the butylene-butadiene fraction obtained from the pyrolysis process as a raw material for pyrolysis furnaces

It was important to carry out the process of joint hydrogenation of the butane-butylene fraction from the "Catalytic cracking" unit of the oil refinery and the butylene-butadiene fraction (BBF) obtained from the pyrolysis process of the "EP-300" complex. So, the butylene-butadiene fraction obtained from the pyrolysis process is sold abroad at a very cheap price, since it has no application area in our Republic. For this reason, it is possible to obtain very good raw materials for the pyrolysis process by complex hydrogenation of butane-butylene and butylene-butadiene fractions with the presence of a catalyst. The C_4 fraction obtained from the pyrolysis of the "EP-300" unit contains up to 45% divinyl and only 10% butanes, the rest being butylenes.

During the hydrogenation of the C_4 fraction, divinyl (C_4H_6) is converted to isobutylene ($1\text{-}C_4H_8$), butylene to n-butane, butylenes containing cis-butene and trans-butene-2 fraction simultaneously to n-butane, isobutylene ($iso\text{-}C_4H_8$) to isobutane ($i\text{-}C_4H_{10}$), propylene (C_3H_6) in the C_4 fraction turns into propane (C_3H_8)

First, acetylenic compounds are hydrogenated in the pursuit of the C_4 fraction, and then divinyl hydrogenation takes place (Fig. 10):

$$C_4H_6 + H_2 \rightarrow 1\text{-}C_4H_8 + 28\ \text{kcal/g.mol}$$

First, butylene is formed, and in the next stage it is converted to n-butane:

$$i\text{-}C_4H_8 + H_2 \rightarrow n\text{-}C_4H_{10} + 30\ \text{kcal/g.mol}$$

At the same time, butylenes containing cis-butene-2 and trans-butene-2 fractions are converted into n-butane:

$$2\text{-}C_4H_8 + H_2 \rightarrow n\text{-}C_4H_{10} + 28\ \text{kcal/g.mol}$$

Isobutylene is converted to isobutane:

$$izo\text{-}C_4H_8 + H_2 \rightarrow i\text{-}C_4H_{10} + 28\ \text{kcal/g.mol}$$

The pressure created in the process should ensure compression of the liquid phase and the pressure is maintained at 2.0-2.5 MPa. The hydrogen used in the C4 fraction hydrogenation unit is obtained from dry gas and the pyrolysis process. The hydrogenation process is carried out in an adiabatic reactor (Fig. 10).

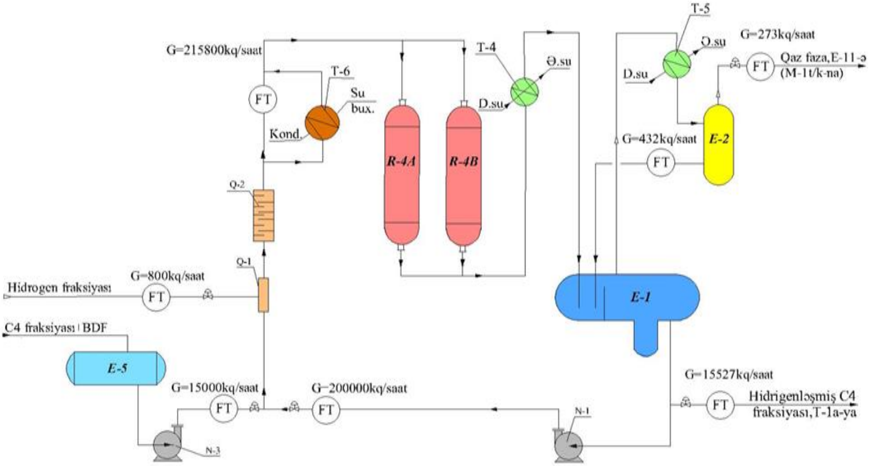

Figure 10. The main scheme of the C4 fraction hydrogenation unit. E-1-E-5 tanks, N-1, N-3-pumps, E-2 separator, T-4,5,6-heat exchangers.

Analysis of butane-butylene from catalytic cracking and butylene-butadiene fractions obtained from pyrolysis after mixing in a ratio of 2:1 is as follows: Ethane 0.01; Propane-11.04; Methyl-acetylene – 0.01; Propylene-14.95; Iso-butane -22.35; n-butane-9.62; Isobutylene – 8.12; Trans-butene-2-7,47; Cis-butene-2-4,27; Butadiene 1,3- 14,42; Butene-1-7,20; Sulfur compounds-0.002; C5-0.22; Water-0.33.

Composition of the butane-butylene fraction obtained from catalytic cracking, %, mass: Ethane-0.01; Propane-16.55; Propylene - 22.42; Isobutane -25.96; n-butane - 10.75; Isobutylene – 7.12; Trans-butene-2 - 6.70; Cis-butene-2 - 4.52; Butene-1 - 5.73; Sulfur compounds-0.002; C_5-0.24

Catalytic cracking gas supplied to EP-300 production and pyrolysis gases are mixed together in the E-10 position separator and fed to the M-1 position five-stage turbocompressor inlet. Then, from the fourth stage, the three-zone neutralization with a pressure of 16 kg/cm^2 enters the cylinder No. 9. The main technological scheme is given in figure 11. The neutralization tank consists of three zones and plates. It is neutralized with 15% NaOH alkali and cleaned of carbon dioxide and hydrogen sulfide. The neutralization reactions are as follows.

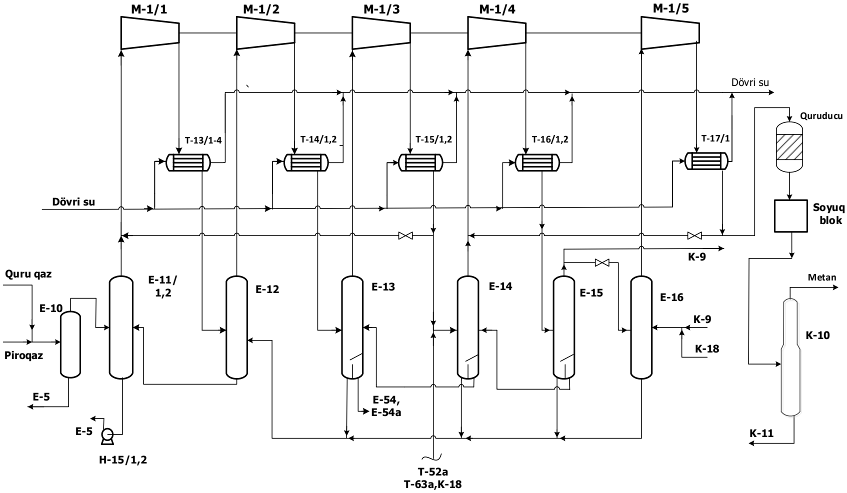

Figure 11. M-1/1÷M-1/5- compressor stages; T-13/1-4, T-14/1-2, T-15/1-2, T-16/1-2, T-17/1 heat exchangers; E-10- separator; E-11/1,2 ÷ E-16; K-10 calon, H-15/1,2- pump.

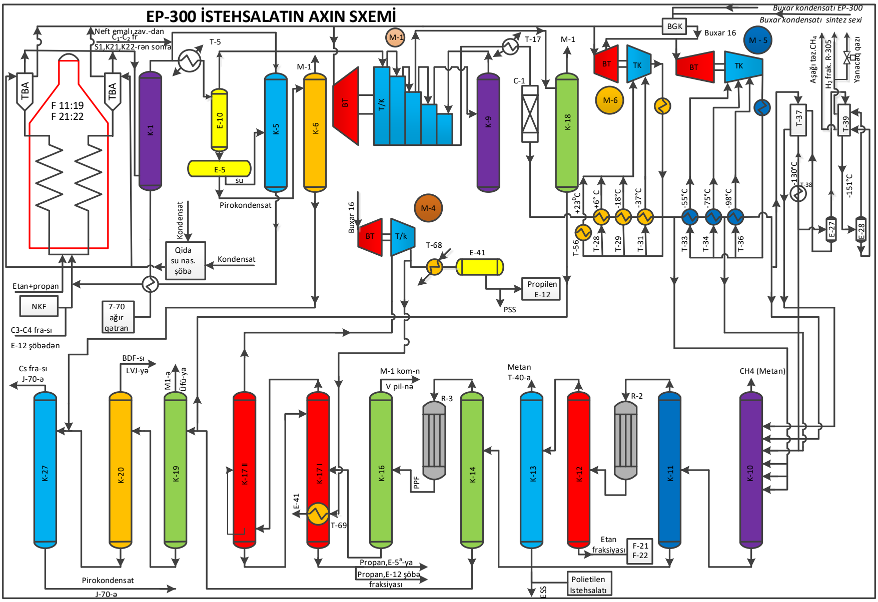

Figure 12. The principle scheme of the EP-300 complex.

Processes of pyrolysis of raw materials, removal of sulfur compounds, separation of C_1-C_4 gases, separation of ethane-ethylene, butylene-butadiene, light and heavy pyrolysis resins in the EP-300 unit are schematically shown in Fig. 12.

Optimum design of ethane and propane fractions in dry gas in pyrolysis process

Mathematical model of the process

In solving the problem of optimal design, it is taken into account that the parameters of the pyrolysis process are constantly changing when designing the mathematical model of the process, taking into account the heat balance equation and the pressure difference based on the general stoichiometric gross-kinetic equations of the reactions designed in the next 2nd stage.

The fission reaction is endothermic, so the heat balance equation consists of the heat input to the surface of the serpentine tube, G_{gas} for the heating of the gas mixture, and G_{reac} for the heat of the reaction itself.

$$G = G_{par} + G_{reac}, \qquad (8)$$

Here; Gpar. is determined by the following formula.

$$G_{par} = \int_{T_0}^{T} \left(\sum_1^6 n_i C_{pi}\right) dT, \qquad (9)$$

Here n_i is the current mole amount of i component in kmol/sec; T_0– temperature at the reactor inlet; C_{pi} – is the isobaric heat capacity of component i of the mixture in kcal/kmol and is determined by the following formula.

$$C_{pi} = a_i + b_i T + c_i T^2,$$

Here, ai, bi, ci are the constants of the heat capacity equation of the i component.

The heat consumed in the reaction

$$Q_{reac.} = n_{C_2H_4} \Delta H_R = x n^0 \Delta H_R, \qquad (10)$$

Here, $n_{C_2H_4}$– amount of ethylene obtained, kmol/sec; ΔH_R - the thermal effect of the pyrolysis reaction is determined from the Kirchhoff equation.

$$\Delta H_R = \int_{298}^{T} \Delta C_p \, dT + \Delta H_{298}, \qquad (11)$$

ΔH_{298}- standard heat of reaction, kcal/kmol; ΔC_p- the change of the isobaric heat capacity of the system during the course of the reaction is equal:

$$\Delta C_p = \sum_i \nu_i' C_{pi}^{mh} - \sum_i \nu_i C_{pi}^{götür.mad} \qquad (12)$$

We get by inserting equations (10), (11), (12) into (13):

$$Q = \int_{T_0}^{T} \left(\sum_1^6 n_i C_{pi}\right) dT + x n^0 \Delta H_R$$

Let us determine the change in temperature of the mixture along the length of the reactor by taking the total differential of the two parts and dividing both parts by dL.

$$\frac{dT}{dL} = \frac{\frac{dQ}{dL} - n_A^0 (\Delta H_R)_{T0} \frac{dx}{dL}}{n^0[(21{,}14+0{,}02056T) - x(0{,}35+0{,}00109T)]10^{-3}} \qquad (13)$$

In this way, we can give heat to the surface of the pipes from the outside:

$$dQ = dHq = \pi d_x dLq, \qquad (14)$$

Here, dH– elemental surface of the tube m^2; g – the thermal stress of the radiant tubes was equal g=27090 kcal/hour m^2; d_x– outer diameter of the pipe, m. Using equation (14) and also molar velocities, heat capacities, and standard heats of reaction components from Table 3, we can obtain the heat balance equation for the first-stage studies:

$$\frac{dT}{dL} = \frac{\pi d_x q - n^0 \, (\Delta H_R)_{T0} \frac{dx}{dL}}{n^0[(21{,}14+0{,}02056T) - x(0{,}35+0{,}00109T)]10^{-3}}, \qquad (15)$$

Table 3

Thermodynamic parameters of the model

Components	Mol rate, mol/hour	Heat capacity, C_p, kcal/kmolK	n_iC_{pi}	Constant generated heat, ΔH_{298}, kcal/kmol
C_3H_8	$(1–x)n^0$	21,14+0,02056T	$(21{,}14+0{,}02056T)(1–x)n^0$	-24,820
C_3H_6	$0{,}300xn^0$	17,88+0,01645T	$(5{,}36+0{,}00494T)xn^0$	4879
C_2H_6	$0{,}065xn^0$	13,34+0,01589T	$(0{,}87+0{,}00103T)xn^0$	-20236
C_2H_4	$0{,}6675xn^0$	12,29+0,01022T	$(8{,}20+0{,}00682T)xn^0$	12496
CH_4	$0{,}635xn^0$	6,98+0,01012T	$(4{,}43+0{,}00643T)xn^0$	-17889
H_2	$0{,}300xn^0$	6,42+0,00082T	$(1{,}93+0{,}00025T)xn^0$	0
Total	$(1+0{,}9675x).n^0$		$[(21{,}14+0{,}02056T)– x(0{,}35+0{,}00109T]n^0$	

The Darcy-Weisbach equation for a straight tube with a round cross-section was used to derive the pressure variation equation along the length of the tube in a tubular reactor:

$$\Delta P = -\lambda_{fric.} \Delta L \frac{U^2}{2gd_d}\gamma, \tag{16}$$

here $\lambda_{fric.}$– friction coefficient that depends on the flow regime of the stream for 4 and 6 inch pipes: $\lambda_{fric.}$= 0,0044.

The linear velocity of the flow is determined by the formula given below:

$$U = U_0(1+\delta x)\frac{TP_0}{T_0 P}\,, \tag{17}$$

U_0 – the initial linear velocity of the stream, is equal to:

$$U_0 = \frac{\upsilon_0}{F} = \frac{4\upsilon_0}{\pi d_d^2}. \tag{18}$$

Pυ=NRT Klapeyron– we get it from the Mendeleev equation:

$$\gamma = \frac{P\bar{M}}{RT}, \tag{19}$$

here $\bar{M}$ – the average molecular weight of the mixture, R=0,0821 m^3 atm/kmol· degree.

$$\bar{M} = \frac{\sum_i n_i M_i}{\sum_i n_i},$$

here M_i – molecular mass of component i in the mixture. Accordingly, we get the formula (20).

$$\bar{M} = \frac{n^0\left[(1-x)M_{C_3H_8} + 0{,}300xM_{C_3H_6} + 0{,}065xM_{C_2H_6} + 0{,}6675xM_{C_2H_4} + 0{,}635xM_{CH_4} + 0{,}300xM_{H_2}\right]}{(1+0{,}9675x)n^0} =$$

$$= \frac{(1-x)44{,}09 + 0{,}300x42{,}08 + 0{,}065x30{,}07 + 0{,}6675x28{,}05 + 0{,}635x16{,}04 + 0{,}3x2{,}016}{(1+0{,}9675x)} =$$

$$= \frac{44{,}09 + 2{,}12\cdot 10^{-3}x}{1+0{,}9675x} \approx \frac{44{,}09}{1+0{,}9675x}. \tag{20}$$

Using equations (18)–(20) and making appropriate substitutions, we get the pressure loss equation along the length of the reactor for stage I of the considered methodology:

$$\frac{dP}{dL} = -172{,}02\cdot 10^{-4}\,\frac{\lambda_{titr.}\upsilon_0^2(1+\delta x)}{d_d^5}\frac{T}{P}\left(\frac{P_0}{T_0}\right)^2 \tag{21}$$

Equations of kinetics, heat balance and pipe pressure loss (21) provide a complete mathematical model of the process for phase I of the study. The data were solved on IBM-486 using the Runge–Kutt method with the following initial conditions. n^0 = 72,73 kmol/hour, P_0

= 4,2 atm, T_0 = 866 K.

Process Research

According to the given conversion of the raw material (85%), during the research of the process based on the mathematical model developed for pipes of different diameters, it was found that in the required conversion, the output of the four-inch reactor is 180 m long and for the six-inch reactor, it is 117.4 m long. Tables 4 and 5 give the results of the calculated values of the length of the process in the four-inch and six-inch reactors. The calculated results of the process parameters for the length of the six-inch reactor exceed the specified pressure drop in the first two meters of the reactor coil for the two-inch reactor (1.95 atm at the reactor outlet). Here, the conversion of raw materials is less than 1%. 85% of the given conversion is ensured at a length of more than 500 m, which leads to excessive consumption of expensive metal pipes.

Table 4.

Results of calculated process values along the length of the four-node reactor

L, м	X	T	P	dx/dL	dT/dL	dP/dL
10,2	0,006	915,7	4,16	0,0014	49,70	0,041
20,4	0,028	949,9	4,12	0,022	34,17	0,043
30,6	0,072	964,9	4,07	0,044	15,04	0,046
40,8	0,125	971,4	4,02	0,053	6,5	0,050
50,9	0,180	976,0	3,96	0,055	4,6	0,060
61,2	0,237	980,3	3,91	0,057	4,3	0,050
71,3	0,292	984,7	3,85	0,055	4,4	0,060
81,6	0,347	989,3	3,78	0,055	4,6	0,070
90,1	0,394	993,3	3,73	0,047	3,99	0,050
100,3	0,449	998,3	3,66	0,055	5,04	0,08
110,3	0,504	1003,7	3,58	0,055	5,4	0,08
120,6	0,557	1009,5	3,50	0,053	5,8	0,09
130,9	0,611	1015,7	3,41	0,054	6,3	0,09
141,1	0,664	1022,6	3,32	0,053	6,9	0,1
151,3	0,716	1030,2	3,22	0,052	7,6	0,1
161,5	0,766	1038,8	3,12	0,050	8,6	0,08
170,0	0,808	1047,1	3,02	0,042	8,3	0,08
180,0	0,855	1058,5	2,90	0,047	11,42	0,12

Table 5.

Results of the calculated values of the process along the length of

six-inch reactor tubes of pyrolysis

L , м	X	T	P	dx/dL	dT/dL	dP/dL
10,2	0,019	931,2	4,194	0,018	65,16	0,006
20,4	0,085	953,7	4,188	0,066	22,5	0,006
30,6	0,168	960,6	4,182	0,083	6,94	0,006
40,8	0,253	966,3	4,175	0,085	5,72	0,007
50,9	0,337	972,2	4,168	0,084	5,90	0,007
61,1	0,421	978,5	4,160	0,084	6,31	0,008
71,4	0,504	985,4	4,152	0,083	6,85	0,008
81,6	0,587	992,9	4,142	0,083	7,61	0,010
90,1	0,655	1000,2	4,135	0,068	7,17	0,007
100,3	0,734	1010,2	4,124	0,079	9,99	0,011
110,5	0,811	1022,5	4,114	0,077	12,32	0,010
115,6	0,849	1029,9	4,108	0,038	7,49	0,006
117,3	0,855	1032,7	4,106	0,011	2,76	0,002

Therefore, it is appropriate to look at the results of the parameters of the four- and six-inch tubular reactors only. The calculated results show that for a two-inch reactor, the pressure drop in the first two meters of the reactor coil exceeds the specified level (1.95 atm at the reactor outlet). Here, the conversion of raw materials is less than 1%. 85% of the given conversion is ensured at a length of more than 500 m, which leads to excessive consumption of expensive metal pipes. Therefore, it is appropriate to look at the results of the parameters of the four- and six-inch tubular reactors only.

Stoichiometric equations

In the second stage, the equations of parallel and ternary reactions are added to the main equation of pyrolysis, which leads to a decrease in the yield of the target product:

$$1.\ C_3H_8 \xrightarrow{k_1} CH_4 + C_2H_4 \qquad 2.\ C_3H_8 \xrightarrow{k_2} C_3H_6 + H_2$$

$$3.\ C_3H_8 + H_2 \xrightarrow{k_3} C_2H_6 + CH_4 \qquad 4.\ C_2H_6 \xrightarrow{k_4} C_2H_4 + H_2$$

$$5.\ C_3H_8 + CH_4 \xrightarrow{k_5} C_2H_6 + C_2H_4 + H_2 \qquad 6.\ C_3H_6 + H_2 \xrightarrow{k_6} C_2H_4 + CH_4$$

$$7.\ C_2H_4 + 2H_2 \xrightarrow{k_7} 2\ CH_4$$

Kinetic model

A complete kinetic model of the process corresponding to this stoichiometric scheme is proposed by the following equations.

$$\frac{dn_{C_3H_8}}{dl} = -u^{-1} n_{C_3H_8} \left(k_1 + k_2 + k_3 \frac{n_{H_2} P}{\left(\sum\limits_i n_i\right) RT} + k_5 \frac{n_{CH_4} P}{\left(\sum\limits_i n_i\right) RT} \right)$$

$$\frac{dn_{C_3H_6}}{dl} = u^{-1} \left(k_2 n_{C_3H_8} - k_6 n_{C_3H_6} \frac{n_{H_2} P}{\left(\sum\limits_i n_i\right) RT} \right)$$

$$\frac{dn_{C_2H_6}}{dl} = u^{-1} \left(k_3 n_{C_3H_8} \frac{n_{H_2} P}{\left(\sum\limits_i n_i\right) RT} - k_4 n_{C_2H_6} + k_5 n_{C_3H_8} \frac{n_{CH_4} P}{\left(\sum\limits_i n_i\right) RT} \right)$$

$$\frac{dn_{C_2H_4}}{dl} = u^{-1} \left[k_1 n_{C_3H_8} + k_4 n_{C_2H_6} + k_5 n_{C_3H_8} \frac{n_{CH_4} P}{\left(\sum\limits_i n_i\right) RT} + k_6 n_{C_3H_6} \frac{n_{H_2} P}{\left(\sum\limits_i n_i\right) RT} - \right.$$

$$\left. - k_7 n_{C_2H_4} \left(\frac{n_{H_2} P}{\left(\sum\limits_i n_i\right) RT} \right)^2 \right]$$

$$\frac{dn_{CH_4}}{dl} = u^{-1} \left[k_1 n_{C_3H_8} + k_3 n_{C_3H_8} \frac{n_{H_2} P}{\left(\sum\limits_i n_i\right) RT} + k_6 n_{C_3H_6} \frac{n_{H_2} P}{\left(\sum\limits_i n_i\right) RT} - \right.$$

$$\left. - k_5 n_{C_3H_8} \frac{n_{CH_4} P}{\left(\sum\limits_i n_i\right) RT} + 2 k_7 n_{C_2H_4} \left(\frac{n_{H_2} P}{\left(\sum\limits_i n_i\right) RT} \right)^2 \right]$$

Linear speed of flow:

$$u = \frac{v_0}{F} = \frac{\left(\sum\limits_i n_i\right) RT}{FP}$$

Continuation of the comparison of the results of the report on the available and proposed options for four-burner pyrolysis furnaces. However, in the absolutely identical processing of all snake-shaped pipes, the output of the target products will always be less than the ideal option in both cases. The proposed control method consists of a highly accurate assessment of the condition of each coil of the furnace by recording the temperature and pressure differences in each coil. This makes it possible to distribute the load of raw materials between them more thoroughly and thereby increase the productivity of the furnace. Management with the proposed method is carried out as in table 6.

Table 6.

Real option

X_i^{output}=0.5093+ +0.0003814 ($\Delta T_i/\Delta P_i$)				$g_i^0 = g^0$, kg/hour				$g(C_3H_6+C_2H_4)=$ $=g^0\Sigma X_i^{вых}$
I	II	III	IV	I	II	III	IV	
0,5780	0,5665	0,5551	0,5436	3000	3000	3000	3000	6729,5
0,5665	0,5551	0,5436	0,5360	3100	3100	3100	3100	6823,7
0,5589	0,5513	0,5398	0,5322	3200	3200	3200	3200	6982,8
0,5513	0,5436	0,5360	0,5284	3300	3300	3300	3300	7125,5
0,5474	0,5398	0,5322	0,5246	3400	3400	3400	3400	7289,6
0,5398	0,5322	0,5246	0,5207	3500	3500	3500	3500	7410,5
0,5360	0,5284	0,5207	0,5169	3600	3600	3600	3600	7567,3
0,5322	0,5246	0,519	0,5131	3700	3700	3700	3700	7721,1

Table 7.

Suggested option

$g_i^0 = B_i^1 \cdot G$, kg/hour				$g(C_3H_6+C_2H_4)=$ $\Sigma\ g_i^0\ X_i^{output}$	$g(C_3H_6+C_2H_4)_{offer}$ $-g(C_3H_6+C_2H_{real.}$	Income, dollars/ year
I	II	III	IV			
4000,0	3333,3	2666,7	2000,0	6767,6	38,1	182880
4325,6	3460,5	2595,3	2018,6	6864,1	40,4	193920
4378,9	3705,3	2694,7	2021,1	7020,1	37,3	179040
4537,5	3721,5	2887,5	2062,5	7157,0	31,5	151200
4857,1	3885,7	2914,3	1942,9	7326,6	37,0	177600
5333,3	4000,0	2666,7	2000,0	7448,0	37,5	180000
5929,4	4235,3	2541,2	1694,1	7615,0	47,7	228960
6830,8	4553,8	2276,9	1138,5	7785,1	64,0	307200

The calculation block receives 28 data from 3-6 sensors (informers) about the consumption of raw materials from each serpentine pipe, from sensors 12-15 about the pressure at the inlet of the serpentine pipe, from sensors 20-23 about the temperature of the serpentine pipes, from sensors 16-19 about the pressure at the outlet of the serpentine pipes. 24-27 sensors provide information about the temperature at the outlet of the serpentine pipes. It also provides information on the total consumption of raw materials entering the furnace through pipe 2, which is measured by sensor 7. Based on the input information, the calculation block calculates the pressure and temperature differences in each coil, the value of the Bi ratio for each coil, and the given value of the raw material consumption in each coil. At the same time, performing the cleaning function, the calculating block compares the consumption price of raw materials to each serpentine tube with the current values from sensors 3-6 and gives control signals to the executive mechanisms. By multiplying these prices by the cost of the target products (about 600 dollars per ton) and the amount of annual working hours of the furnace (8000 hours), we can get the real income (from one furnace) of using the proposed optimal method of distribution of raw materials to serpentine tubes.

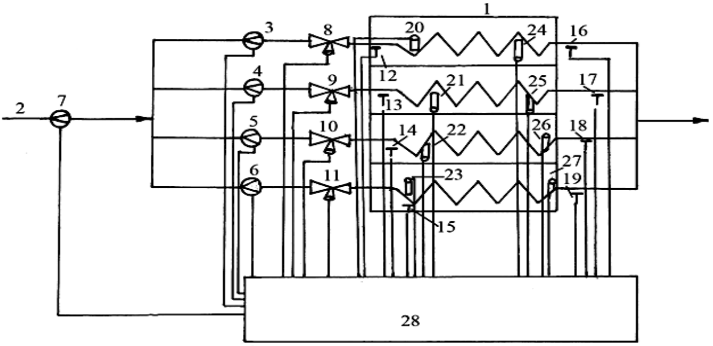

Figure 9. Control scheme of a four-burner pyrolysis furnace

At different loadings of the reactor, the change rates of pyrogas molar content along the length of the serpentine tube (kmol/s) were given.

As can be seen from Figure 10, with the increase of the inlet temperature corresponding to the loading, the propane decomposition rate increases along the length of the reactor and reaches a maximum at the length of 36-72 m and then decreases.

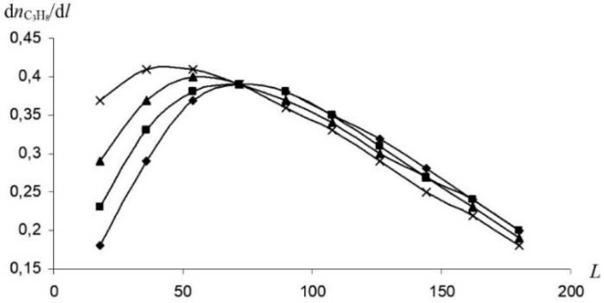

Figure 10. Propane decomposition rate over the length of the serpentine tube at different loadings (♦-3000 kg/h, ■-3200 kg/h, ▲-3400kg/h, x -3600kg/h)

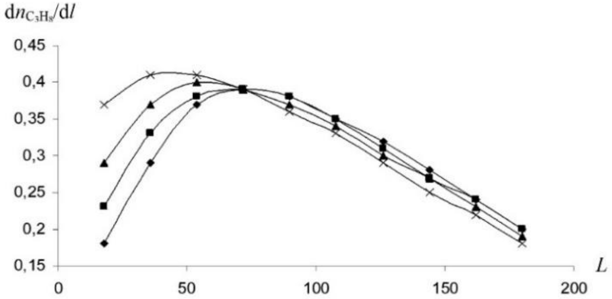

Figure 11. Propylene extraction rate according to the length of the serpentine pipe at different loads (♦-3000 kg/h, ■-3200 kg/h, ▲-3400kg/h, ● -3600kg/h).

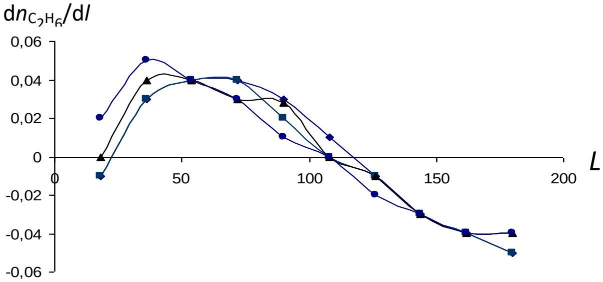

Figure 12. The rate of ethane consumption according to the length of the serpentine tube at different loadings (♦–3000 kg/h, ■–3200kg/h, ▲–3400kg/h, ● –3600kg/h).

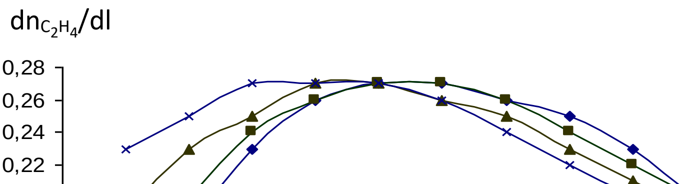

Figure 13. The rate of ethylene extraction according to the length of the serpentine pipe at different loads (♦-3000 kg/h, ■-3200 kg/h, ▲ – 3400kg/h, x – 3600 kg/h).

As the loading increases (short distance from the reactor inlet), the ethane consumption rate and ethylene production reach a maximum sooner. Ethylene production rate is much higher than propylene production rate. Because ethylene is obtained from four reactions and consumed by one. However, propylene is obtained only from the dehydrogenation of propane, combining with hydrogen to form hydrogen ethylene. An analogous situation is observed for methane, the values of its production rates are comparable to the production rates of ethylene, which is explained by the stoichiometric reactions of the process. Up to 54 m length of the serpentine tube, hydrogen uptake rates decrease, then begin to increase at all loadings and remain constant from 100 m length to the end of the reactor. Figures 10–13 show pressure, mixture temperature, conversion, selectivity, and relative yields of propylene and ethylene according to the length of the serpentine tube at different loadings of the reactor (g^0= 3000–3600 kg/h). Figure 14 shows the pressure, temperature, conversion, selectivity and relative yields of propylene and ethylene according to the length of the serpentine tube at the reactor loading g^0 = 3000-3600 kg/h.

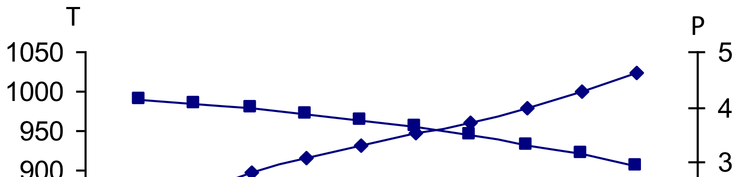

Figure 14. Change of pressure and temperature according to the length of the serpentine pipe at loading g^0= 3000 kg/h

Increasing the load in the furnaces leads to a sharper pressure drop along the tube, which in turn leads to a lower cost of conversion along the entire length of the serpentine tube, because the residence time of the mixture in the reaction zone is reduced. Due to the length of the serpentine tube, the selectivity of propylene in the loading of the conversion decreases, which means that the rate of additional conversions increases.

Ethylene selectivity initially decreases along the length of the serpentine tube, but begins to increase after about one third of the length. In addition, this is achieved more quickly as the loading increases, but less than if the loading is low in each section of the pipe. The fact that the value of the selectivity of ethylene exceeds the minimum is explained by the fact that the first reactions of conversion of propane to propylene and ethane take place first, so the selectivity is lower. Later, propylene and ethane are converted to ethylene by the second and third reactions, and the selectivity to ethylene begins to increase. Relative yields of propylene and ethylene increase monotonically along the length of the pipe due to the total loading (K_1, K_2). The temperature distribution profile along the length of the reaction tube has a significant effect on the pyrolysis results.

Optimization and mathematical modeling of butane-isobutylene (BIF) fractionation and industrial pyrolysis process.

Gasoline pyrolysis process in "Azerikimya" "EP-300" unit is accompanied by a number of series-parallel transformations. As a result of them, a large amount of products are obtained (including the fraction of C_4 hydrocarbons). However, due to the shortage of raw materials, the plant could not work at full capacity, and the butane-butadiene fraction obtained from pyrolysis was simply sent for storage or sale at a low price without finding further rational use. Therefore, in order to use it effectively an industrial experiment was carried out: butane-butadiene fraction (n-butane -10%, α-butylene - 70%, cis -butylene - 5%, trans -butylene - 15%) was added to the pyrolysis gas furnace simultaneously with ethane) was given. Ethylene + propylene was used as raw material for additional purchase of targeted products. The process of thermal decomposition of hydrocarbons consists of a number of elementary reactions that take place in two stages.

At first, the first type reactions of thermal decomposition of alkanes take place with the production of olefins, diolefins and alkanes with less carbon and hydrogen content than the initial reactions. Olefins, diolefins and alkanes obtained in the second stage are subjected to reactions of hydration of alkanes and further decomposition and condensation with the purchase of methane, acetylene, benzene and carbon. Carbon is adsorbed on the surface of the reactor and forms pyrolysis coke.

The decomposition schemes of ethane and propane, including the proposed appropriate formulas, were used in the design of the stochometric scheme of the pyrolysis process of the mixture (ethane + BIF). The stoichiometric formulas of BIF fraction decomposition were added to them.

1) $n\text{-}C_4H_{10} \xrightarrow{k_{B1}} C_2H_4 + C_2H_6$, 2) $n\text{-}C_4H_{10} \xrightarrow{k_{B2}} C_3H_6 + CH_4$,

3) $n-C_4H_{10} \xleftrightarrow{k_{B3}} a-C_4H_8+H_2$ 4) $\alpha\text{-}C_4H_8 \xrightarrow{k_{B4}} 2C_2H_4$,

5) $\alpha\text{-}C_4H_8 \xrightarrow{k_{B5}} CH_4 + C_3H_4$ (PD) ,

6) $\text{cis-}C_4H_8 \xrightarrow{k_{B6}} C_2H_2 + C_2H_6$, (22)

7) $\text{trans-}C_4H_8 \xrightarrow{k_{B7}} C_3H_4$ (MA) + CH_4 ,

8) $\alpha\text{-}C_4H_8 + C_2H_4 \xrightleftharpoons{k_{B8}} C_6H_{12}$,

9) $\alpha\text{-}C_4H_8 + C_3H_6 \overset{k_{B9}}{\rightleftharpoons} C_7H_{14}$,

10) $\alpha\text{-}C_4H_8 \xrightarrow{k_{B10}} C_4H_6 + H_2$,

Here C_3H_4 (PD) –propadiene, C_3H_4 (MA)- methylacetylene (propyne), cis- C_4H_8 cis 2- butylene, trans- C_4H_8-trans-2- butylene, C_6H_{12}-1- hexene, C_7H_{14}-1-heptene, α-C_4H_8- normal butylene. A view of the model according to this kinetic scheme:

$dn\ C_2H_6/dL = dn_{C_2H_6}/dL = (-r_1-r_7+r_{p3}+r_{p5}+r_{в1}+r_{в6})\cdot F$

$dn_{C_2H_4}/dL = (r_1- r_2-r_3-r_4-r_5-r_6-r_7+r_{p1}+r_{p5}+r_{p6}+r_{в1}+2r_{в4}-r_{в8})\cdot F$

$dn_{H_2}/dL = (r_1-2r_2-r_3/8+r_4+r_5+2r_6+93r_7/150+r_9+r_8+r_{p2}-r_{p3}-r_{p6}+r_{в3}+r_{в10})\cdot F$

$dn_{CH_4}/dL = (2r_2+r_{p1}+r_{p3}+r_{p6}+r_{в2}+r_{в5}+r_{в7})\cdot F$

$dn_{C_4H_6}/dL = (r_3/4+r_{в10})\cdot F$

$dn_{C_4H_8}/dL\ (r_3/8+r_{в3}-r_{в4}-r_{в5}-r_{в8}-r_{в9}-r_{в10})\cdot F$

$dn_{C_4H_{10}}/dL = (r_3/8-r_{в1}-r_{в2}-r_{в3})\cdot F$

$dn_{C_6H_6}/dL = (r_4/3)\cdot F$

$dn_{C_2H_2}/dL = (r_5+r_{в6})\cdot F$

$dn_C/dL = (2r_6-r_8)\cdot F$

$dn_{C_3H_6}/dL = (143r_7/150+r_{p2}-r_{p6}+r_{в2}-r_{в9})\cdot F$

$dn_{C_3H_8}/dL = (57r_7/150-r_{p1}-r_{p2}-r_{p3}-r_{p5})\cdot F$

$dn_{CO}/dL = (r_8-r_9)\cdot F$

$dn_{CO_2}/dL = r_9\cdot F$

$dn_{H_2O}/dL = (-r_8-r_9)\cdot F$

$dn_{sis-C4H8}/dL = (-r_{в6})\cdot F$

$dn_{trans\ C4H8}/dL = (-r_{в7})\cdot F$

$dn_{C_3H_4(PD)}/dL = r_{в5}\cdot F$

$dn_{C_3H_4(MA)}/dL = r_{в7}\cdot F$

$dn_{C_6H_{12}}/dL = r_{в8}\cdot F$

$dn_{C_7H_{14}}/dL = r_{в9}\cdot F$,

Here: F – cross-sectional area of the reactor, m^2; $r_1 \div r_9$ – reaction rates in pyrolysis of ethane; $r_{p1} \div r_{p9}$– reaction rates of pyrolysis of propane; The reaction rates of $r_{B1} \div r_{B10}$– (ethane+BIF) pyrolysis are equal:

$$r_1 = k_1 \left[n_{C_2H_6} - (1/k_{p1}) n_{C_2H_4} \cdot n_{H_2} \cdot P/RT \sum_i n_i \right] \cdot P \Big/ \sum RT \sum_i n_i$$

$$r_2 = k_2 \left[n_{C_2H_4} \left(n_{H_2}^2 \cdot P/RT \sum_i n_i \right) - (1/k_{p2}) n_{CH_4}^2 \right] \cdot \left(P \Big/ RT \sum_i n_i \right)^2$$

$$r_3 = k_3 n_{C_2H_4} \cdot P \Big/ RT \sum_i n_i$$

$$r_4 = k_4 n_{C_2H_4} \cdot P \Big/ RT \sum_i n_i$$

$$r_5 = k_5 n_{C_2H_4} \cdot P \Big/ RT \sum_i n_i$$

$$r_6 = k_6 n_{C_2H_4} \cdot P \Big/ RT \sum_i n_i$$

$$r_7 = k_7 n_{C_2H_6} n_{C_2H_4} \cdot \left(P \Big/ RT \sum_i n_i \right)^2$$

$$r_8 = k_8 n_C n_{H_2O} \cdot \left(P \Big/ RT \sum_i n_i \right)^2$$

$$r_9 = k_9 n_{CO} n_{H_2O} \cdot \left(P \Big/ RT \sum_i n_i \right)^2$$

$$r_{p1} = k_{p1} n_{C_3H_8} \cdot P \Big/ RT \sum_i n_i$$

$$r_{p2} = k_{p2} n_{C_3H_8} \cdot P \Big/ RT \sum_i n_i$$

$$r_{p3} = k_{p3} n_{C_3H_8} n_{H_2} \cdot \left(P \Big/ RT \sum_i n_i \right)^2$$

$$r_{p4} = k_{p4} n_{C_2H_6} \cdot P \Big/ RT \sum_i n_i$$

$$r_{p5} = k_{p5} n_{C_3H_8} n_{CH_4} \cdot \left(P \Big/ RT \sum_i n_i \right)^2$$

$$r_{p6} = k_{p6} n_{C_3H_6} n_{H_2} \cdot \left(P \Big/ RT \sum_i n_i \right)^2$$

$$r_{p7} = k_{p7} n_{C_2H_6} n_{H_2}^2 \cdot \left(P \Big/ RT \sum_i n_i \right)^3$$

$$r_{\text{в}1} = k_{\text{в}1} n_{C_4H_{10}} \cdot P \Big/ RT \sum_i n_i$$

$$r_{\text{в}2} = k_{\text{в}2} n_{C_4H_{10}} \cdot P \Big/ RT \sum_i n_i$$

$$r_{\text{в}3} = \left[k_{\text{в}3} n_{C_4H_{10}} - k_{\overline{\text{в}3}} n_{H_2} n_{\alpha-C_4H_8} \cdot P \Big/ RT \sum_i n_i \right] \cdot P \Big/ RT \sum_i n_i$$

$$r_{\text{в}4} = k_{\text{в}4} n_{\alpha-C_4H_8} \cdot P \Big/ RT \sum_i n_i$$

$$r_{\text{в}5} = k_{\text{в}5} n_{\alpha-C_4H_8} \cdot P \Big/ RT \sum_i n_i$$

$$r_{\text{в}6} = k_{\text{в}6} n_{H_2O} \cdot P \Big/ RT \sum_i n_i$$

$$r_{\text{в}7} = k_{\text{в}7} n_{\text{цис}-C_4H_8} \cdot P \Big/ RT \sum_i n_i$$

$$r_{\text{в}8} = \left[k_{\text{в}8} n_{\alpha-C_4H_8} n_{C_2H_4} \cdot P \Big/ RT \sum_i n_i - k_{\overline{\text{в}8}} n_{C_6H_{12}} \right] \cdot P \Big/ RT \sum_i n_i$$

$$r_{\text{в}9} = \left[k_{\text{в}9} n_{\alpha-C_4H_8} n_{C_3H_6} \cdot P \Big/ RT \sum_i n_i - k_{\overline{\text{в}9}} n_{C_7H_{14}} \right] \cdot P \Big/ RT \sum_i n_i$$

$$r_{\text{в}10} = k_{\text{в}10} n_{\alpha-C_4H_8} \cdot P \Big/ RT \sum_i n_i,$$

Here, $k_1 \div k_9$ reaction rate constants for ethane pyrolysis, $k_{P1} \div k_{P7}$ – reaction rate constants for propane pyrolysis, $k_{B1} \div k_{B10}$–reaction rate constants for (ethane+BIF) pyrolysis, k_{-B3}, k_{-B8}, k_{-B9} are the rate constants of the reverse reaction in equations (22). In this case, (ethane+BIF) pyrolysis also decomposes propane, so we also take into account its decomposition rate. In order to obtain a complete mathematical model of the (ethane+BIF) pyrolysis process with reverse communication, we add (23) to the kinematic model (24), the heat balance of the recirculation flows (25) and the hydrodynamic equations (26).

$$f_i^o = f_{0i}\left(1 - \alpha_R\right) + f_{Ri}\alpha_R \quad (23); \qquad f_i = f_{mhi}\left(1 - \alpha_R\right) + f_{Ri}\alpha_R \quad (24)$$

$$dP/dl = \pi d_{a.k} q - \sum_j r_j \Delta H_{Rj} \Big/ \sum_i \left\{ \left[\left(1/1 - \alpha_R\right) \sum_i g_{0i} \big/ \bar{M} \right] \sum_i \alpha_i' + \sum_i \Delta n_i \right\} C_{pi} \quad (25)$$

$$dP/dl = -0{,}50962 \cdot 10^{-13} \left[1 + \left(\Psi d_d / L_0\right)\right] \lambda_{titr} \left[\left(\sum_i n_i \right) T \Big/ P d_d^5 \right] \left(\sum_i g_{0i} \Big/ 1 - \alpha_R \right) \quad (26)$$

According to the main components of the process, average deviations from experimental indicators were arranged: H_2– 3,3 %; CH_4– 9,3 %;

C_2H_6– 7,1 %; C_2H_4– 4,0 %; C_3H_8– 6,9 %; C_3H_6– 10,9 %; C_4H_6– 9,6 %; $\sum C_4$(BİF) – 6,6 ; $\sum C_6$ – 10,4%. This shows the full compatibility (adequacy) of the mathematical model.

Study of co-pyrolysis of propane-propylene and butane-butylene ($C_3 + C_4$) fractions obtained from catalytic cracking process with addition of hydrogen

Recently, at a time when the demand for gasoline has increased sharply, it is preferred to increase the yield of ethylene and propylene by using alternative raw materials. One of these types of raw materials is $C_3 + C_4$, which is a compressed liquid gas mixture produced in the catalytic cracking unit of the Oil Refinery, and is supplied to pyrolysis furnaces in an industrial complex. In this case, the output of ethylene is 23% and propylene is 17-19%, and the amount of intermediate products of pyrolysis and coking in furnaces increases. In order to increase the productivity of ethylene + propylene and increase the working time of pyrolysis furnaces, pyrolysis was carried out with $C_3 + C_4$ fractions by supplying hydrogen in different proportions. The pyrolysis process was carried out at temperatures of $830 \div 860^0$C, with a contact time of 0.5 seconds, the ratio of steam to raw materials - 0.5÷1% mass and the ratio of $C_3 + C_4$ fractions and hydrogen in the pyrolysis process was 0,01;0,02; 0,03; 0,04 mass %. The indicators of the conditions of the experiments were selected based on the operating modes of the SRT-II type industrial gasoline stoves at the "EP-300" unit of the "Azerikimya" production unit. In the hydropyrolysis process, hydrogen was supplied to the pyrolysis furnace together with water vapor and the optimal operating modes were determined. The outlet temperature of the pyrolysis furnace is 830 ÷ 8600C, the contact time is 0.5 seconds, the ratio of water vapor to raw materials is 0.5÷1 mass %. At this time, the amount of gas and hydrogen in the pyrolysis furnace increases, while the amount of liquid products decreases (Fig. 15-16).

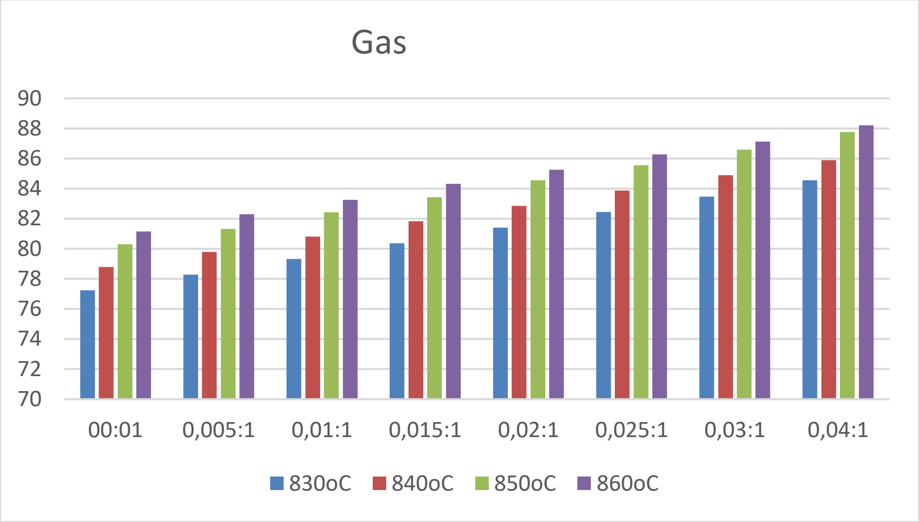

Figure 15. Yield of gaseous products obtained from pyrolysis of hydrocarbon fraction C_3–C_4 depending on the amount of added hydrogen and pyrolysis temperature.

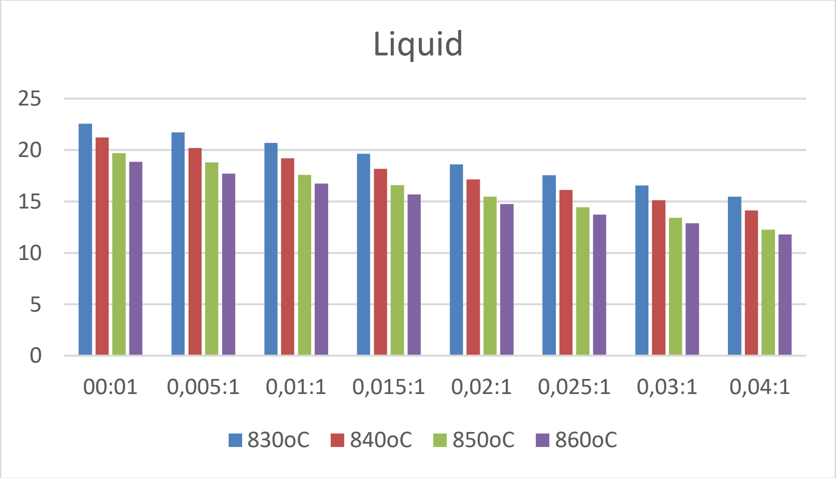

Figure 16. Yield of liquid products obtained from the pyrolysis of the C_3–C_4 hydrocarbon fraction depending on the amount of added hydrogen and pyrolysis temperature.

The analysis of the indicators of Table 8 shows that, the amount of hydrogen provided by the raw material increases from 0 to 0.04 mass %, at the temperatures of the investigated $C_3 + C_4$ fractions of pyrolysis, an increase in the yield of the gas part of the initiated pyrogas products and a corresponding decrease in the yield of the liquid part are observed.

Table 8.

Yields of components obtained from a mixture of hydrogen in different proportions with the C_3–C_4 fraction supplied to pyrolysis furnaces at a temperature of 860^0C, mass %

Hydrogen/ raw mat. Compo-nents	0:01	0,005:1	0,01:1	0,015:1	0,02:1	0,025:1	0,03:1	0,035:1
H_2	1,4	1,6	1,95	2,3	2,65	3,0	3,35	3,7
CO	0,57	0,55	0,53	0,51	0,49	0,47	0,45	0,43
CO_2	0,16	0,15	0,14	0,13	0,12	0,11	0,1	0,09
CH_4	20,54	21,09	21,64	22,19	22,7	23,4	24	24,6
C_2H_6	3,06	3,22	3,38	3,44	3,56	3,68	3,8	4,0
C_2H_4	23,75	24,82	25,94	27,06	28,2	29,3	30,42	31,2
C_2H_2	0,52	0,5	0,48	0,46	0,44	0,42	0,4	0,3
C_3H_8	2,25	2,28	2,31	2,34	2,39	2,44	2,49	2,54
C_3H_6	19,46	19,0	18,6	18,3	18	17,7	17,0	16,36
MA+allen	1,06	1,01	0,96	0,91	0,86	0,81	0,76	0,71
C_4	5,04	4,9	4,6	4,32	3,9	3,32	2,9	2,63
Butadiene-1,3	3,32	3,12	3,0	2,85	2,7	2,65	2,4	2,26
C_5	6,27	5,48	4,47	3,78	3,14	2,35	1,62	0,93
Benzene	6,8	6,68	6,88	7,08	7,28	7,48	7,68	8,0
Toluene	1,2	1,09	1,0	0,9	0,8	0,7	0,6	0,5
C_8-C_9	0,35	0,33	0,31	0,30	0,28	0,26	0,24	0,22
Heavy resin	4,2	3,95	3,7	3,45	3,8	2,95	2,7	2,45
Coke	0,35	0,33	0,32	0,3	0,28	0,26	0,24	0,22
Gas	81,13	82,29	83,26	84,32	85,2	86,27	87,22	88,2
Liquid	18,85	17,71	16,74	15,68	14,7	13,73	12,78	11,8
Special weight	0.882	0.860	0.838	0,816	0.787	0.752	0.725	0.700
Hardness	0,84	0,79	0,73	0,69	0,64	0,60	0,56	0,52
Selectivity	2,13	2,11	2,07	2,05	2,03	1,99	1,96	1,93

As can be seen from Table 8, at the temperature of 860^0C of the pyrolysis process, the ratio of hydrogen : C_3 + C_4 fractions was 0.005:1% by mass, ethylene was 24.82% by mass, propylene was 19.0% by mass, at that temperature, hydrogen : C_3 + C_4 fractions ratio is 0.01:1 mass ratio, ethylene-25.94% mass, propylene 18.6% mass, hydrogen : C_3 + C_4 fractions ratio is 0.015:1% by mass, ethylene is

27.06% by mass, propylene is 18.3% by mass, hydrogen : C_3 + C_4 fractions ratio 0.02:1 mass ratio ethylene-28.18% mass, propylene 18.0% mass, hydrogen : C_3 + C_4 fractions ratio 0.025:1 mass ratio ethylene-29.3% mass, propylene 17.7% mass, hydrogen : C_3 + C_4 fractions ratio 0.03:1 mass ratio ethylene-30.42 mass %, propylene 17.0 mass % and hydrogen: C_3 + C_4 fractions ratio is 0.035:1% by mass, ethylene-31.2% by mass, propylene is 16.36% by mass.

Modeling and optimization of the combined pyrolysis process of gasoline, ethane and propane in a gasoline pyrolysis furnace

The pyrolysis gases produced during the pyrolysis of gasoline at the Sumgayit "Ethylene-Polyethylene" Plant contain ethane and propane, which are used as raw materials for the production of valuable olefins widely used in industrial production, such as ethane and propane. In [266], an optimal design method, as well as a scheme and calculation of a chemical-technological complex (CTC) for the processing of cracking and pyrolysis gases are proposed. Both ethane and propane, after being released, enter the CTC reactor element where they undergo pyrolysis to obtain ethylene and propylene.

It was determined that if ethane and propane are returned to the gasoline furnace for recycling before entering the CTC, the process of obtaining the main products can be significantly intensified. To solve this problem, three possible options were considered: 1) the procedure is repeated until the non-degradable product leaving the furnace is completely returned to the re-furnace and transformed into final products (ethylene + propylene); 2) to carry out a similar procedure with propane by recirculating the non-degraded part coming out of the furnace; 3) in the third case, jointly, in the variant, recycle both unreacted products (ethane and propane) at the same time. The objective of this work is the selection of the most used raw materials of the gasoline refining scheme in all three cases, ethylene and propylene are considered as optimization criteria of the final products.

Only ethane or propane were recycled, as these are the reagents that were converted to the target products during the initial reactions. Primary and other reactions that occur during the pyrolysis of gasoline or are accompanied by parallel-sequential reactions. For this reason, the acquisition of by-products continues or reaches an equilibrium state corresponding to a sufficiently deep decomposition of raw materials. Complete conversion with reduced by-product yields and increased target products can only be achieved using recycling. The essence of the method is to return the unreacted substance to the furnace in a mixture with fresh raw materials after passing through the separation system. For each subsequent cycle, enough feedstock is added to the pyrolysis furnace to add the amount recycled to the furnace's yield load. After a certain number of cycles, recirculation becomes insignificant, which indicates complete conversion of hydrocarbons to the target products.

A large number of reactants are involved in the decomposition of gasoline fractions, it is impossible to describe all transformations. Therefore, taking into account the most important chemical transformations, the generalized stoichiometric pyrolysis scheme of gasoline, including 4 primary and 3 secondary reaction equations of pyrolytic transformation of raw materials with fourteen current components are given:

$$P^j \xrightarrow{W_j} \nu_{1j}H_2 + \nu_{2j}CH_4 + \nu_{3j}C_2H_4 + \nu_{4j}P_{2-4} + \nu_{5j}C_3H_6 + \nu_{6j}C_4H_6 + \nu_{7j}C_4H_8,\ j = 1,2,3$$

$$H \xrightarrow{W_4} \nu_{1,4}H_2 + \nu_{2,4}CH_4 + \nu_{3,4}C_2H_4 + \nu_{4,4}P_{2-4} + \nu_{5,4}C_3H_6 + \nu_{6,4}C_4H_6 + \nu_{7,4}C_4H_8 + \nu_{8,4}A$$

$$C_2H_4 \xrightarrow{W_5} \nu_{2,5}H_2 + \nu_{1,5}C_2H_2$$

$$\nu_{1,6}C_2H_4 + \nu_{2,6}C_3H_6 + \nu_{3,6}C_4H_8 \xrightarrow{W_6} \nu_{4,6}A + \nu_{5,6}H_2$$

$$\nu_{1,7}C_4H_6 + \nu_{2,7}A \xrightarrow{W_7} C,$$

Here, Pj=1, Pj=2 и Pj=3 — respectively normal, monomethyl and polymethyl substituted paraffinic hydrocarbons; P2–4 —C_2 – C_4 paraffin hydrocarbon atoms; H — naphthenic hydrocarbons; A — aromatic hydrocarbons; C — high-molecular compounds; νij — mass coefficients equal to the mass fraction of the product formed during the complete decomposition of the raw materials.

Table 9.

Calculation results of the joint pyrolysis process of gasoline, ethane and propane in a gasoline furnace

Temperature, ^{0}C	Total load of gasoline, t/s	Water vapor consumpti-on, t/s	Yield of ethylene, t/s	Yield of propylene, t/s	Ethane returned to gas stove, t/s	Propane returned to gas stove t/s	Constant of circulating ethane	Constant of circulating propane
820	13	9	3,47	2,09	0,849	0,130	1,978	1,667
830	13	9	3,73	2,02	0,854	0,159	1,887	1,447
840	13	9	3,95	1,94	0,833	0,156	1,754	1,333
850	13	9	4,11	1,76	0,786	0,174	1,612	1,220
820	14	9	3,63	2,3	0,892	0,210	1,979	1,671
830	14	9	3,89	2,18	0,885	0,243	1,889	1,451
840	14	9	4,18	2,05	0,855	0,233	1,759	1,338
850	14	9	4,26	1,95	0,815	0,239	1,621	1,226
820	15	9	3,72	2,49	1,006	0,213	1,981	1,675
830	15	9	3,97	2,39	0,889	0,217	1,891	1,455
840	15	9	4,21	2,30	0,774	0,270	1,763	1,342
850	15	9	4,38	2,1	0,667	0,274	1,628	1,219
820	16	9	3,45	2,82	0,886	0,320	1,983	1,678
830	16	9	4,15	2,68	0,891	0,370	1,899	1,463
840	16	9	4,48	2,52	0,870	0,405	1,774	1,348
850	16	9	4,65	2,39	0,838	0,390	1,632	1,225

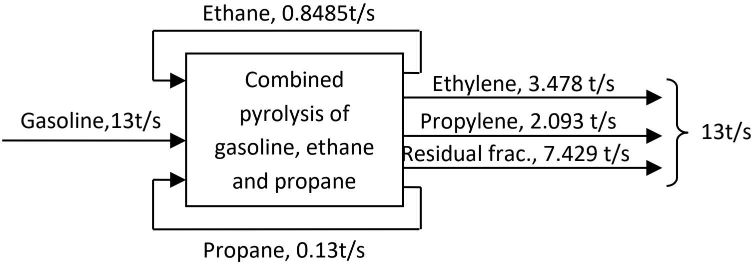

Figure 17. Combined pyrolysis of gasoline, ethane and propane in an industrial pyrolysis furnace

Establishing a steady state in the system is a long process, therefore, when drawing up the material balance of the process in a steady state, the concept of the recycling coefficient introduced by M.

F. Naghiyev is used, multiplying it by the values of the yields of the reaction products in one cycle according to the raw materials, we obtain the values of the product yields:

$$K_R = \frac{g^0}{g_0}$$

Then for ethane, propane and gasoline pyrolysis processes, respectively:

$$K_{R_1} = \frac{0,429}{0,2169} = 1,9779$$

$$K_{R_2} = \frac{0,078}{0,0468} = 1,667$$

$$K_{R_3} = \frac{0,429}{0,429} = 1(g^0 = g_0) \cdot a$$

It is of great importance to integrate dry gas, propane-propylene and butane-butylene fractions obtained as by-products in "Catalytic cracking" and "Gradual coking" units into the "EP-300" unit. For this reason, the "EP-300" unit of by-products has wide possibilities for gasification and pyrolysis. In Figure 1, dry gas from "Catalytic cracking" - 10 t/h, dry gas from "Gradual coking" unit - 10 t/h, and the amount of gasoline supplied as raw material to a pyrolysis furnace was taken as 10 t/h. As can be seen from Figure-18, ethane and propane contained in dry gas and pyrogas obtained from pyrolysis are separated and returned to the pyrolysis furnace as recirculation.

As is known from dry gas analysis, light components have different properties. Methane and hydrogen are cracking products, but nitrogen is added to the dry gas from the air supplied during the regeneration of the cracking catalyst and then makes the gas separation technology very difficult. Dry gas obtained from "catalytic cracking" contains 17.5% ethylene, 19.54% ethane, 8.52% propylene, 3.82% propane.

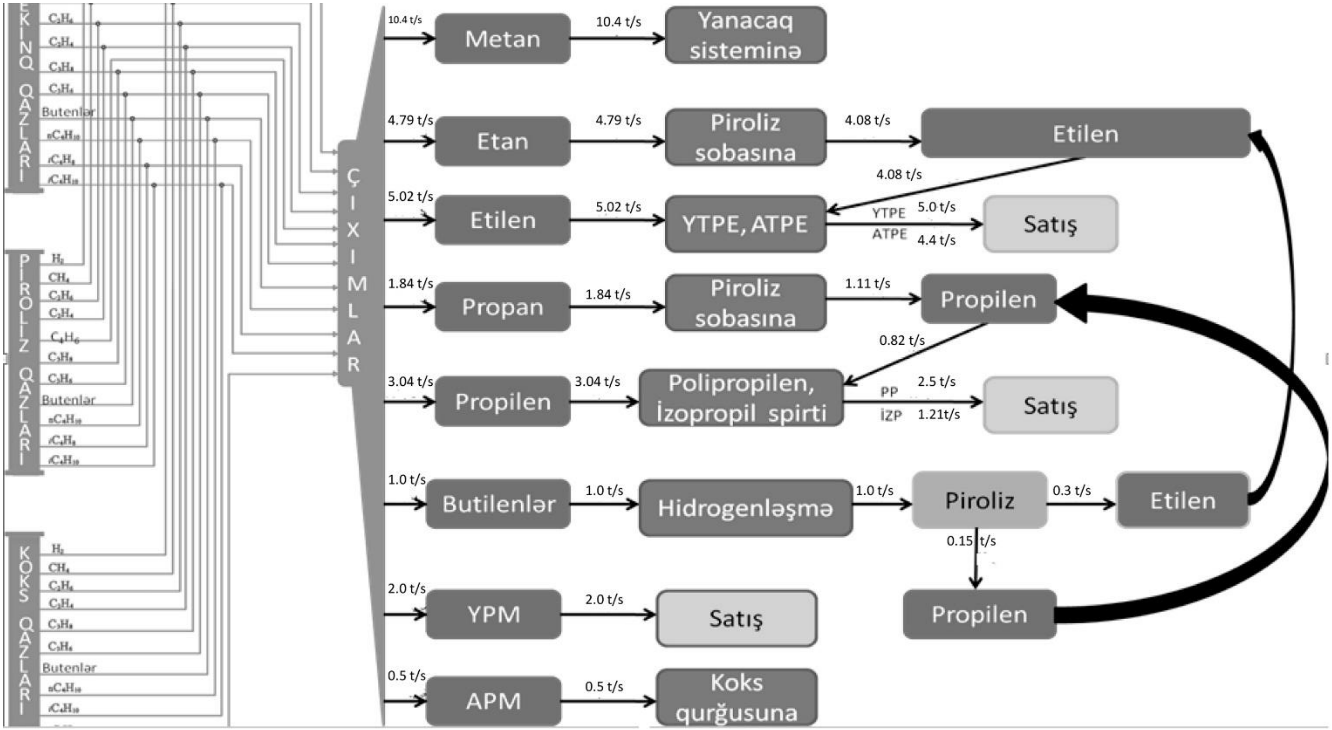

Figure 18. Catalytic cracking, complex processing scheme of coke dry gases with pyrolysis gases

According to the information taken from the regulations of the oil refinery, the output of dry gas in the "Catalytic Cracking" unit, which operates with a productivity of 1944.85 thousand tons/year, is 3.44% by mass, that is, 66.25 thousand tons/year of dry gas is obtained. 12352.9 tons of ethylene and 6403.7 tons of propylene can be bought from the obtained dry gas. At the same time, the amount of dry gas obtained from the "Gradual coking" facility is 82.23 thousand tons/year and contains 3.7% ethylene, 23.8% ethane, 6.3% propylene, 12.7% propane. It is possible to obtain 19,232.3 tons of ethylene and 6,728 tons of propylene from the dry gas obtained from the "Gradual Coking" facility during the year.

It is possible to buy 32330.5 tons of ethane and 12935.23 tons of propane from "Catalytic cracking" and "Gradual coking" facilities. Thus, 45265.73 tons of ethane and propane are obtained from dry gas.

Thus, the application of dry gas to the "EP-300" unit not only increases the production of ethylene and propylene, but also prevents environmental pollution, and the plant gets enough profit. According to the given amount of C_1-C_4 hydrocarbons supplied from the oil refinery and the current value of the products received in manats is given in table 10.

Table 10.

Yields and prices of products obtained from the processing of C_1-C_4 hydrocarbons from the oil refinery in the EP-300 complex

Raw mat.	t/y	With %	Price man.	Obtained	t/y	With %	Price man.
Dry gas	66250	13,26	22392500	Methane	146869,2	29,4	14417058
Coke gas	82290	16,46	27814020	Ethylene	111000	22,22	89244000
PPF	99000	19,52	50985000	Propylene	109000	21,82	87636000
BBF	252000	50,45	129780000	BDF	27720	5,55	2494800
Total	499480		230971520	Pyrocon-densat	89906,4	18	102043310
				Heavy pyrolysis resin	14984,4	3,01	6428136
				Total	499480		302263304

CONCLUSIONS

1. The material, kinetic and thermodynamic parameters of the process were developed to increase the productivity of ethylene and propylene by intensifying the pyrolysis of low-octane gasoline with ethane in industrial pyrolysis furnaces [3, 25, 31].

2. Technological schemes have been developed for increasing the productivity of ethylene and propylene using dry gas from catalytic cracking and coking plants, making maximum use of the potential of the EP-300 unit [14,15,37].

3. A mathematical and kinetic model of the process for selective hydrogenation of acetylene, methylacetylene, propodiene and allenes contained in ethane-ethylene and propane-propylene fractions has been developed in order to increase the production of ethylene and propylene, reduce their losses to a minimum and reduce the consumption rate [24, 27, 28, 35, 42, 43,48].

4. In the production of EP-300, two SRT I type ethane furnaces were designed to work with 13 t/h of ethane each. However, in the current conditions, taking into account the operation of only one furnace at 50-60% capacity, the technology of the possibility of producing ethylene and propylene by additionally giving the butane-isobutylene fraction has been developed [8,16,29,32, 36,50].

5. The influence of the length of the serpentine tube on the productivity of ethylene and propylene in different loadings of the raw materials supplied to the reactor in the industrial pyrolysis process was determined. Raw material:water vapor ratio, convection, total selectivity S, reaction residence time τ were determined as optimal parameters [5,34,39,40,45].

6. The use of C_1-C_4 hydrocarbons obtained from catalytic cracking and coking plants as raw materials in the EP-300 complex makes up 50.43% of the total raw materials, which means the production of 150 thousand tons of ethylene and 100-110 thousand tons of propylene [1,33,38,44].

7. 80,000 tons of butane-isobutylene fraction obtained from catalytic cracking and coking plants were mixed with 40,000 tons of butylene butadiene fraction obtained from pyrolysis, hydrogenated with the presence of a Pd catalyst, converted into n-butane and applied

as raw materials to the pyrolysis process. (The application act is shown in the attachments) [41].

8. It is recommended to remove CO_2, H_2S and mercaptans from C_1-C_4 fractions obtained from catalytic cracking and coking plants and use them as raw materials for dry ice, urea production and sulfuric acid production [4,10,17,18,20,26,46].

9. In order to profitably use the propane-propylene fraction obtained from the catalytic cracking unit, using various types of adsorbents, 70% of the raw material was given directly to the EP-300 propylene boiler to produce quality propylene and the separated propane was applied as a pyrolysis raw material to the SRT I type ethane furnace. (The application act is shown in the attachments) [13,21,22,23].

10. Patented for recovery and extension of working life of spent Pd catalyst used in the process of selective hydrogenation of acetylene and its homologues in EEF and PPF to increase ethylene and propylene by 2-2.5% during the production process and minimize losses [].

11.On the basis of experimental results in the "EP-300" complex, full mathematical models of pyrolysis of ethane, propane and ethane with butane-butylenes (BBF) have been built, taking into account the recirculation characteristics of industrial processes. The annual profit obtained as a result of maintaining the optimal operating modes found on the basis of the inlet temperature and recirculation of the propane pyrolysis process is 6.2 million dollars. Compared to the option of equal distribution of raw materials between streams of the pyrolysis furnace, in the option of optimal distribution, the profit is from 151 thousand to 307 thousand dollars per year [2,6,7,9,11,12, 19,47,53].

12. By processing the C_1-C_4 hydrocarbons from the oil refinery in the "EP-300" complex, products worth 302263304 manats are produced, of which 71291784 manats are net income [51,52,54,55].

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following scientific works:

1. Aliev, A.M., Babayev, A.I, Tairov, A.Z., Mamedov, Z.A. Develoment of the mathematical model of process of pyrolysis of dearomatized distilled gasoline in the presence of fuel qas // Athens-Crete, Greece. Chemreaktor-17, – may15-19, – 2006, – p.698-700.
2. Алиев, А.М., Керимов, М.З., Гасанов, М.А., Таиров, А.З., Мамедов, З.А. Исследование кинетики газофазного гидрирования фракции C_2 печей гидролиза на промотированном катализаторе G-58C // Материалы конференции «ФАРГАН-2006», – Воронеж, – 2006, – 8-14 сентябрь, – том 1, – с. 286-288.
3. Бабаев, А.И., Мамедов, З.А., Таиров, А.З. Разработка математической модели процесса пиролиза прямогонных бензинов в присутствии топливного газа // Международная Научная Конференция. «Математические методы в течнике и технологиях», ММТТ-19, Сборник трудов ТОМ 9, секция 10, – Воронеж, – 2006, – с. 23-24.
4. Qadjiyeva, S.R., Kerimov, M.Z., Mamedov, Z.A., İsmailov, N.R., Tairov, A.Z., Safarov, A.R. Regeneration and utilization fulfilled zeolites in drying proses // Minth Baku International Conqres Energy Ekology Ekonomy, – Baku, –7-9 june, – 2007, – p.631-633.
5. Алиев, А.М., Керимов, М.З., Таиров, А.З, Гусейнова, А.М., Исмаилов, Н.Р., Мамедов, З.А. Математическое моделирование процесса пиролиза этан с рециркуляцей // "Riyaziyyatın tətbiqi məsələləri və yeni informasiya texnologiya". Respublika Elmi Konfransının materialları. – Sumqayıt, –26-27 noyabr, –2007, –s.34-36.
6. Kərimov, M.Z., Əliyev, A.M., Tahirov, A.Z, Həsənov, M.Ə., Məmmədov, Z.A. Piroliz qazının etan-etilen fraksiyasının selektiv hidrogenləşdirilməsi prosesinin riyazi model əsasında optimallaşdırılması // "Riyaziyyatın tətbiqi məsələləri və yeni informasiya texnologiya". Respublika Elmi Konfransının materialları – Sumqayıt, 26-27 noyabr, –2007, – s.36-37.
7. Tahirov, A.Z. Etan-etilen fraksiyasının hidrogenləşdirilməsi

reaksiyasının kinetik modelinin qurulması / A.Z.Tahirov, A.M.Əliyev, M.Z.Kərimov, M.Ə.Həsənov, Z.A.Məmmədov // Azərbaycan Kimya jurnalı, – 2007. №2, – s.12-15.

8. Исмаилов, Н.Р. Результаты оптимизации процесса пиролиза пропана с обратной связью и расчет экономической эффективности газовой пиролизной печи / Н.Р.Исмаилов, А.З.Таиров, А.М.Алиев, М.З.Керимов, М.А.Гасанов, А.М.Гусейнова. З.А.Мамедов // Химические проблемы – 2007. № 2, – с.213-218.
9. Tahirov, A.Z. Piroliz qazının propan-propilen fraksiyasının hidrogenləşmə prosesinin mexanizminin seçilməsi / A.Z.Tahirov, A.M. Əliyev, M.Z. Kərimov, M.Ə. Həsənov, Z.A. Məmmədov, İ.İ. Quliyeva // Kimya problemləri jurnalı, – 2007. № 2, – s.276-279.
10. Керимов, М.З. Регенерация цеолитов, отработанных в процессе осушки газовых потоков пропиленовых производств / М.З.Керимов, М. А. Гасанов, Н.Р. Исмаилов, З.А. Мамедов, А.З. Таиров // Azərbaycan Kimya jurnalı, – 2007. №4, s.170-175.
11. Tahirov, A.Z., Əliyev, A.M., Kərimov, M.Z., Həsənov, M.Ə., Məmmədov, Z.A., Qulieva, Z.A. Piroliz qazının C_2,C_3 fraksiyalarının hidrogenləşdirilməsi prosesinin riyazi modeli // AMEA-nın müxdir üzvü H.X.Əfəndiyevin 100 illik yubleyinə həsr olunmuş konfrans, – Bakı, – 2007, – s.190-191.
12. Гасанов, М.А. Исследование кинетики селективного гидрирования ацетилена в этан-этиленовой фракции / М.А.Гасанов, З.А.Мамедов, А.М.Алиев, А.З.Таиров // Журнал, «Химическая промышленность», – 2011. № 3, – с.6-10.
13. Бабаев, А.И. Разработка математической модели и оптимизация процесса получения белых масел / А.И. Бабаев, А.З.Таиров, З. А. Мамедов, А.М. Гусейнова, А.Г. Ахмедов // Журнал «Химия и технология топлив и масел», – 2011. № 1 – с.32-35.
14. Neft-Kimya sənayesində istifadə olunan kimyəvi analiz metodları. I hissə / R.Ə.Əliyeva, S.R. Hacıyeva, F.M.Çıraqov, Z.A. Məmmədov. – Bakı: ELM, – 2012. – 330 s.
15. Neft-Kimya sənayesində istifadə olunan kimyəvi analiz metodları.

II hissə / R.Ə.Əliyeva, S.R. Hacıyeva, F.M. Çıraqov, Z.A. Məmmədov. – Bakı: ELM, – 2012. – 268 s.

16. Babayev, Ə.İ. Etilen-propilen istehsalının alınma texnologiyası və ekoloji problemin həlli yolları / Ə.İ. Babayev, S.R.Hacıyeva, Z.A. Məmmədov. – Sumqayıt: “Bilik”, – 2014. – 315 s..
17. Məmmədov, Z.A., Cəfərov, A.A., İbrahimov, H.C., Rüstəmov, M.İ., Qasımova, K.M., Əliyeva, A.Ə. Katalitik krekinq qurğusunun C_1-C_2 karbohidrogenləri EP-300 qurğusu üçün xammal mənbəyi kimi // Akademik S.C. Mehdiyevin 100 illik yubileyinə həsr olunmuş Respublika elmi-praktiki konfransının materialları. II cild, – Baku, – 2-3 dekabr, – 2014, – s.18-20.
18. Hacıyeva, S.R., Əminbəyov, Ə.F., İsmayılov, N.R, Cəfərov, A.A, Məmmədov, Z.A., Cəfərov, V.C. H.Əliyev adına Neft emalı zavodunda alınan C_1-C_2 (Quru qaz) fraksiyasının tərkibində olan hidrogen-sulfidin təmizlənməsi və onunla bağlı ekoloji problemin aradan qaldırılması // AR Təhsil Nazirliyi SDU “Ekologiya və Həyat fəaliyyətinin mühafizəsi” üzrə Sənaye ilinə həsr olunmuş VIII ənənəvi Beynəlxalq elmi konfrans, – Sumqayıt, – 2014, – s.480-481.
19. Babayev, Ə.İ., İsayev, X.Q., Alıyev, N.Ə., Cəfərov, A.A., İsmayılov, N.R., Məmmədov, Z.A. Yüngül piroliz qatranından hidropiroliz üsulu ilə təmiz benzolun alınması // AR Təhsil Nazirliyi SDU “Ekologiya və Həyat fəaliyyətinin mühafizəsi” üzrə Sənaye ilinə həsr olunmuş VIII ənənəvi Beynəlxalq elmi konfransı. II cild, – Sumqayıt, – 2-3 dekabr, – 2014, – s.128-130.
20. Hacıyeva, S.R., Əminbəyov, Ə.F., Məmmədov, Z.A. Sənayedə texnoloji qazların tərkibindəki nəmin sintetik seolitlərdə tutulması və işlənmiş seolitlərin yenidən bərpa olunaraq prosesə qaytarılması // Bakı Dövlət Universitetinin 95 illik yubleyinə həsr olunmuş Elmi Konfransın materialları. – Bakı, – 10 dekabr, – 2014, – s.96-97.
21. Hacıyeva, S.R., Babayev, Ə.İ., Əminbəyov, Ə.F., Əzizova, N.Q., Məmmədov, Z.A. Piroliz prosesi zamanı alınan piroqazın tərkibində kükürdlü birləşmələrin və asetaldehidin müasir texnologiyalar tətbiq etməklə ekoloji problemlərin həlli yolları // BDU, H. Əliyevin anadan olmasının 92-ci il dönümünə həsr

olunmuş elmi konfrans. – Bakı, – 7-8 may, – 2015, – s. 47-49.

22. Babayev, Ə.İ., Əzizova, N.Q., İsmailov, N.R., Cəfərov, A.A., Məmmədov Z.A. Polietilen istehsalı üçün Propan-propilen fraksiyasından alınan hidrogenləşdirilmiş propilen oliqomerinin kompressor yağı kimi tətbiqi // Akademik Ə. Quliyev adına AKİ yaradılmasının 50 illiyinə həsrolunmuş “Sürtkü materialları, yanacaqlar, xüsusi mayelər, aşqar və reagentlər” mövzusunda Respublika elmi konfransı. – Bakı, – 13-14 oktyabr, – 2015, – s.57.
23. Məmmədov, Z.A., Hacıyeva, S.R., Alıyev, N.Ə., Səfərov, A.R. Propan-propilen fraksiyasının tərkibində olan kükürdlü birləşmələrdən təmizlənməsi prosesinin tədqiqi. Материалы Респуб. Науч. конф. посвящ. 80-летному юб. Института Катализа и Неорганической химии им. М. Нагиева, – Баку, – 15-16 ноября, – 2016, – с.400 - 401.
24. Məmmədov, Z.A., Hacıyeva, S.R., Alıyev, N.Ə., Səfərov, A.R. Hidrogen əlavə etməklə C_3 və C_4 (maye qaz) fraksiya qarışıqlarının piroliz prosesinin tədqiqi // Материалы Респуб. Науч. конф. посвящ. 80-летному юб.инст. Катализа и Неорганической химии им. М.Нагиева, – Баку, – 15-16 ноября, – 2016, – с.398-399.
25. Mammadov, Z.A. Investigation of regularities of hydropyrolysis process of petroleum fraction on EP-300 // Processes of petrochemistry and oil-refining, – 2016. Vol 17, №2 (66), – p. 90-97.
26. Мамедов, З.А. Технология очистки фракции C_1–C_2 от кислого газа и сернистых соединений и подготовка сырья для получения этилена и пропилена // Конференция по работе производств этилена и бензола. ВНИИОС-наука, – г.Звенигород, – 12-13 октября, – 2016, – сертификат.
27. Алиев, А.М. Моделирование и оптимизация совмещенного процесса пиролиза бензина, этана и пропана / А.М. Алиев, З.А. Мамедов, А.Р. Сафаров, И.И. Османова, А.М. Гусейнова. // Журнал «Химия и технология топлив и масел», – 2017. № 3, – с.27-32.
28. Алиев, А.М. Интенсификация процесса пиролиза бензина с учетом рециркуляции / А.М. Алиев А.Р. Сафаров, И.И.

Османова, А.М.Гусейнова, З.А. Мамедов, О.А. Исмаилов // Азербайджанский химический жунал, – 2017. № 1, – с.20-29.

29. Алиев, А.М. Применение методики оптимального проектрования процессов пиролиза парафиновых углеводородов к процессу пиролиза пропана / А.М. Алиев, А.М. Гусейнова, С.Р. Гаджиева, З.А.Мамедов // Журнал «Нефтехимия и нефтепереработка», – 2017. № 6, – с. 37-41.
30. Mammadov, Z.A. Mathematical simulation and optimization of industrial pyrolysis process of etane together with buthane-buthyliane fraction(BBF) taking into account of feedback // Azərbaycan kimya jurnalı, – 2017. № 4, – c 30-40.
31. Мамедов, З.А. Очистка ППФ и модернизация колонны разделения ППФ на заводе «Этилен-Полиетилен» ПО Азерихимия SOCAR // Этиленовой конференции. ВНИИОС-наук. г. – Звенигород, – 17-19 октября, – 2017, – сертификат.
32. Мамедов, З.А. Оптимальная организация теплопередачи в этановой пиролизной печи // «Kimya problemləri» jurnalı, – 2017. № 4, – s. 435-441.
33. Мамедов, З.А. Опыт переработки фракции C_2-C_3 от установок каталитического крекинга на установке получения этилена и пропилена / З.А.Мамедов, И.П.Семенов, А.И.Абсаттаров // Журнал «Химическая техника», – 2017. № 11, – с. 32-39.
34. Алиев, А.М. Кинетические исследования процесса пиролиза парафиновых углеводородов C_2-C_4. / А.М.Алиев, А.М.Гусейнова, С.Р.Гаджиева, З.А.Мамедов // Журнал «Нефтехимия и нефтепереработка» – 2017. № 7, – с. 3-5.
35. Məmmədov, Z.A., Hacıyeva, S.R., Alıyev, N.Ə, İsmailov, N.R., Cəfərov, A.A., Nəcəfov, F.İ. Benzin və kerosin fraksiyalarındakı aromatik karbohidrogenlərin desen-1 ilə alkilləşməsi prosesinin kinetik modeli // ARTN SDU və AMEA PMİ-nun Birgə keçirdikləri “Funksional monomerlər və xüsusi xassəli polimer materiallar: Problemlər, perspektivlər və praktiki baxışlar” Beynəlxalq elmi konfransın materialları, – Sumqayıt, – 15-16 noyabr, – 2017, – s. 70-72.
36. Məmmədov, Z.A., Hacıyeva, S.R., Alıyev, N.Ə., İsmailov, N.R., Cəfərov, A.A, Nəcəfov, F.İ. Katalitik krekinqdən alınan C_1-C_4

fraksiyalarını piroliz qazı ilə birgə istifadə etməklə turbokompressorun qaz-dinamik xassəərinin tədqiqi // ARTN SDU və AMEA PMİ-nun Birgə keçirdikləri "Funksional monomerlər və xüsusi xassəli polimer materiallar: Problemlər, perspektivlər və praktiki baxışlar" Beynəlxalq elmi konfransın materialları, – Sumqayıt, – 15-16 noyabr, – 2017, – s.229-231.

37. Мамедов, ЗА., Гаджиева, С.Р., Алиев, Н.А., Джафаров, А.А., Наджафов, Ф.И. Методы очистки и выделения этилен-пропилена из сухих газов каталитического крекинга // Akademik Rəfiqə Əlirza qızı Əliyevanın 85 illik yubleyinə həsr olunmuş Beynəlxalq elmi konfransın materialları, – Bakı, – 16-17 noyabr, – 2017, – s. 100-101.
38. Мамедов, З.А., Гаджиева, С.Р., Бабаев, А.И., Аллахвердиева, Х.В. Перспективы использования сухого газа каталитического крекинга // Материалы научной конференции «Нагиевские чтения», посвященной 110-летию академика М. Нагиева. – Баку, – 2018, – с. 93.
39. Алиев, А.М. Оптимальное проектирование химико-технологического комплекса по совместной переработке газов крекинга и пиролиза / А.М. Алиев, А.Р. Сафаров, И.И. Османова, А.М. Гусейнова,. З.А. Мамедов. // Журнал ТОХТ, – Москва, – 2018. № 6, – с.628-635.
40. Мамедов, З.А. Оптимизация без рециркуляционного процесса пиролиза этана с бутан-изобутиленовой фракцией в промышленной печи // Журнал Вестник Пермского Национального Исследовательского Политехнического Университета «Химическая Технология и Биотехнология», – 2018. № 1, – с.77-85.
41. Аббасов, В.М. Исследование процесса гидрирования смеси C_3-C_4 фракций газов каталитического крекинга и бутилен-бутадиеновой фракции пиролиза с последующим их использованием в качестве сырья для процесса пиролиза / В.М.Аббасов, Г.А.Гусейнова, С.Р.Гаджиева, Х.Д.Ибрагимов // Журнал «Химическая технология», – Москва, – 2018. №5, – с.203-208.
42. Мамедов, З.А., Гаджиева, С.Р., Бабаев, А.И., Гусейнова, Г.А.

Валиева, З.Т. Разработка химико-технологической схемы выделения этилена из сухого газа // AR TN Gəncə Dövlət Universiteti. Beynəlxalq Elmi Konfrans, – Gəncə, – 04-05 may, – 2018, – s. 323-325.

43. Бабаев, А.И. Влияние деароматизации сырья на процесс пиролиза / А.И.Бабаев, З.А.Мамедов, С.Р.Гаджиева, Л.З.Мамедова // Azerbaijan Journal of Chemical News, – 2019. №1(1), – p.72-79.
44. Məmmədov, Z.A., Hacıyeva, S.R., Məmmədova, L.Z. Heydər Əliyev adına Neft emalı zavodunun “Koks” qurğusundan alınan C_1-C_4 qazlarının “EP-300” istehsalatına inteqrqasiya olunma texnologiyası. //The Internstional Scientific Conference Actual Problems of Modern Chemistry. Dedicated to the 90th Anniversary of the Academican Y.H. Mammadaliyev Institute of Petrochemicalт Processes. – 2019, – October 2-4, – s.34.
45. Мамедов, З.А. Ограничения на рециркуляционные потоки химических процессов // Журнал Вестник Пермского Национального Исследовательского Политехнического Университета «Химическая Технология и Биотехнология», – 2019. № 1, – с.22-34.
46. Семенов, И.П. Технология очистки фракции $\sum C_1$-C_2 от кислого газа и сероорганических соединений и подготовка сырья для получения этилен-пропилена / И.П. Семенов, З.А. Мамедов. // Журнал «Химическая технология», – Москва. – 2019. № 8, – с. 361-367.
47. Tairov, A.Z. İşlənmiş palladium ktalizatorunun regenerasiya üsulu, İxtira İ 2019 0007. Azərbaycan Respublikası / A.Z.Tairov, M.Ə.Həsənov, E.F.Rüstəmov, Z.A.Məmmədov, A.N.Səmədli, M.O.Hümbətov.
48. Əliyev, A.M. Etilen və propilenin alınma üsulu, Ixtira İ 2020 0066. Azərbaycan Respublikası / Əliyev A.M., Səfərov A.R., Quseynova A.M., Alıyev N.Ə., Hacıyeva S.R., Məmmədov Z.A., Əliyev F.V.
49. Neft-Kimya sənayesində istifadə olunan kimyəvi analiz metodları. III hissə / R.Ə.Əliyeva, S.R. Hacıyeva, F.M. Çıraqov, Z.A. Məmmədov, L.Z. Məmmədova. – Bakı: “Elm”, – 2022. – 348 s.
50. Mammadov, Z., Babayev, A., Karimli, F., Mammadova, L. Use

heavy pyorolysis resin as raw material in “Delayed coker” unit // Devoted to the 90 th anniversary of academician Rafiqa Alieva, Baku State University. – Baku, – 29-30 september, – 2022. – p. 300-301.

51. Məmmədov, Z.A. Sənaye sobalarında propanın piroliz prosesinin tətbiqi // Akademik Sahib Müseyib oğlu Əliyevin 90 illik yubleyinə həsr olunmuş konfrans. “Neft kimyası, polifunksional monomerlər, oliqomerlər və polimerlərin sintezi”, – Bakı, – 23 iyun, – 2023, – s. 94-95.
52. Məmmədov, Z.A. // The Use of C_1-C_4 fractions obtalned in catalytic cracking and gradual coking units as raw materials for the production of ethylene and propylene in EP-300 complex // Processes of petrochemistry and oil refining. – 2023. № 3, – p.535-541.
53. Сафаров, А.Р., Мамедов, З.А. Определение усреднённых значений компонентного состава газов установки замедленного коксования // Журнал Нефтепереработка и Нефтехимия, – 2023. №2, – с. 17-22.
54. Алиев, А.М. // Способы окислительного превращения метана в ценные продуктов органического синтеза на модифицированных цеолитных катализаторах / Алиев А.М., Сафаров А.Р., Ализаде Г.А., Алиева М.Г., Агаева Р.Ю., Мамедов З.А., Яриев В.М. // Журнал Нефтепереработка и Нефтехимия, – 2023. №5, с. 33-38.
55. Məmmədov, Z.A., Neft-kimya proseslərində alınan yan məhsulların kompleks emal texnologiyası / Z.A.Məmmədov, Ə.İ.Babayev, L.Z.Məmmədova // ADNSU Azərbaycan Ali Texniki Məktəblərinin xəbərləri. – 2023. Cild 25, №4, – s.35-38.

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