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INDUSTRIAL OPTIMIZATION OF ETHYLENE RECOVERY FROM PYROLYSIS GAS: YELLOW-OIL SEPARATION AND POLYMERIZATION INHIBITION

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Abstract. This study presents an integrated approach to improving the efficiency of ethylene recovery from pyrolysis gas by optimizing key process parameters and mitigating “yellow oil” formation and polymerization-related equipment fouling. The effects of feedstock composition, conversion degree, temperature, steam dilution, and hydrocarbon residence time in the reaction zone were evaluated under laboratory and industrial conditions. Pyrolysis gas samples were analysed by gas chromatography at the central laboratory of the Shurtan Gas Chemical Complex. Laboratory results showed that the maximum ethylene content of 33.3% was achieved at 750–850 °C with a residence time of 6–12 s. The technological system was further improved by installing a 35 m³ vessel for separating “yellow oil” from the spent alkaline solution and applying a Petroflow polymerization inhibitor to the streams entering the reboiler and leaving the lower section of the column. The larger separation vessel reduced the required separation time to approximately 2 h, while inhibitor application limited undesirable polymerization and deposit formation. Following process optimization and equipment modification, the ethylene content increased from 32.65 to 33.466 mol%, corresponding to an absolute increase of 0.816 percentage points. The proposed measures also reduced product losses, minimized equipment fouling, and improved operational stability. These results demonstrate that combining process-parameter optimization, improved “yellow oil” separation, and polymerization inhibition provides a practical approach to enhancing industrial ethylene recovery from pyrolysis gas.

Keywords: gaz chemical compleks. monomer, polymerization, yellow oil, inhibitor, polyethylene, ethylene.

Аннотация. В данном исследовании представлен комплексный подход к повышению эффективности извлечения этилена из пиролизного газа путем оптимизации ключевых параметров процесса и уменьшения образования

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“желтого масла” и загрязнения оборудования, связанного с полимеризацией. В лабораторных и промышленных условиях оценивалось влияние состава исходного сырья, степени конверсии, температуры, разбавления водяным паром и времени пребывания углеводородов в зоне реакции. Образцы пиролизного газа были проанализированы методом газовой хроматографии в центральной лаборатории Шуртанского газохимического комплекса. Лабораторные результаты показали, что максимальное содержание этилена в 33,3% было достигнуто при температуре 750-850°C и времени выдержки 6-12 с. Технологическая система была дополнительно усовершенствована за счет установки емкости объемом 35 м3 для отделения “желтого масла” от отработанного щелочного раствора и применения ингибитора полимеризации Petroflow к потокам, поступающим в ребойлер и выходящим из нижней секции колонны. Большая емкость для разделения сократила требуемое время разделения примерно до 2 часов, в то время как применение ингибиторов ограничило нежелательную полимеризацию и образование отложений. После оптимизации процесса и модификации оборудования содержание этилена увеличилось с 32,65 до 33,466 мол.%, что соответствует абсолютному увеличению на 0,816 процентных пункта. Предложенные меры также позволили снизить потери продукта, свести к минимуму загрязнение оборудования и повысить стабильность работы. Эти результаты демонстрируют, что оптимизация технологических параметров, улучшение отделения “желтого масла” и ингибирование полимеризации в сочетании обеспечивают практический подход к увеличению извлечения промышленного этилена из пиролизного газа.

Ключевые слова: газохимический комплекс. мономер, полимеризация, желтое масло, ингибитор, полиэтилен, этилен.

Annotatsiya. Ushbu tadqiqotda asosiy texnologik parametrlarni optimallashtirish va "sariq moy" hosil bo'lishini va polimerizatsiya bilan bog'liq uskunalarning ifloslanishini kamaytirish orqali piroliz gazidan etilenni qayta tiklash samaradorligini oshirishga kompleks yondashuv keltirilgan. Laboratoriya va sanoat sharoitida xomashyo tarkibi, konversiya darajasi, harorat, bug 'bilan suyultirish va uglevodorodlarning reaksiya zonasida qolish vaqtining ta'siri baholandi. Shurtan gaz-kimyo majmuasining markaziy laboratoriyasida piroliz gazi namunalari gaz xromatografiyasi usuli bilan tahlil qilindi. Laboratoriya natijalari shuni ko'rsatdiki, 750–850 °C haroratda 6–12 s yashash vaqti bilan maksimal 33,3% etilen tarkibiga erishilgan. Texnologik tizim “sariq moy”ni sarflangan ishqoriy eritmadan ajratish uchun 35 m³ hajmli idish o‘rnatish va

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reboilerga kiradigan va ustunning pastki qismidan chiqadigan oqimlarga Petroflow polimerizatsiya inhibitori qo‘llash orqali yanada takomillashtirildi. Kattaroq ajratuvchi idish kerakli ajratish vaqtini taxminan 2 soatgacha qisqartirdi, inhibitorni qo'llash esa kiruvchi polimerizatsiya va cho'kma hosil bo'lishini chekladi. Jarayonni optimallashtirish va uskunani o'zgartirish natijasida etilen miqdori 32,65 dan 33,466 mol% gacha oshdi, bu mutlaq o'sish 0,816 foiz punktga to'g'ri keladi. Taklif etilgan chora-tadbirlar, shuningdek, mahsulot yo'qotishlarini kamaytirdi, uskunaning ifloslanishini minimallashtirdi va ish barqarorligini yaxshiladi. Ushbu natijalar shuni ko'rsatadiki, jarayon parametrlarini optimallashtirish, "sariq moy" ni yaxshiroq ajratish va polimerizatsiya inhibisyonini birlashtirish piroliz gazidan sanoat etilenini qayta tiklashni yaxshilashga amaliy yondashuvni ta'minlaydi.

Kalit so'zlar: gaz kimyo majmuasi. monomer, polimerizatsiya, sariq moy, ingibitor, polietilen, etilen.

INTRODUCTION.

Ethylene is one of the most important petrochemical monomers in the global chemical industry, serving as a fundamental building block for polymers such as polyethylene, ethylene glycol, polyvinyl chloride and various high-value chemicals. It is estimated that current world ethylene production capacities exceed 185 million tonnes per year, with a continuing growth trend driven by demand for plastics and derivatives in diverse industrial sectors [1].

Traditionally, ethylene is predominantly produced via steam cracking (pyrolysis) of hydrocarbon feedstocks, especially ethane, propane and naphtha fractions. In this high-temperature endothermic process, carbon–carbon bonds are cleaved to form low-molecular-weight olefins, with ethylene as the major product. However, conventional pyrolysis processes are energy intensive and produce a range of by-products that complicate downstream separation and reduce process selectivity.

The efficient separation of ethylene from pyrolysis gas streams remains a considerable challenge due to the thermodynamic similarity between ethylene and ethane, the presence of secondary hydrocarbons, and the formation of heavy by-products such as “yellow oils” and coke precursors. These by-products not only reduce ethylene yield but also contribute to equipment fouling, increased operational costs, and complex purification demands [2-3].

In recent years, researchers have sought innovative strategies to address these limitations. For example, novel adsorption-based separation methods using porous materials have been shown to improve ethylene/ethane selectivity and

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enable more energy-efficient downstream product purification. Other approaches explore the integration of membrane engineering and modular reactor designs to reduce overall energy consumption and enhance ethylene productivity in steam cracking processes.

In addition to conventional pyrolysis optimization, sustainable and carbon-neutral production pathways, including electrification of cracking furnaces and plasma-assisted mechanisms, have been proposed to mitigate greenhouse gas emissions and enhance environmental performance of ethylene plants.

Despite these advances, the optimization of pyrolysis operational parameters such as temperature profile, residence time, steam dilution, and reactor design still plays a pivotal role in maximizing ethylene output. Classical studies have shown that careful control of feedstock composition and reactor conditions can significantly influence product distribution and minimize unwanted side reactions.

In Uzbekistan and related regional contexts, experimental investigations into pyrolysis gas processing have focused on improving ethylene yield and reducing side-product formation through process modifications and inhibitor addition. These efforts aim to align industrial practice with global research trends while addressing local raw material characteristics and operational constraints.

Thus, this study builds upon established global research by targeting the enhancement of ethylene monomer production efficiency from pyrolysis gas through improved separation strategies, optimized reaction conditions, and mitigation of polymerization and by-product formation. The outcomes are intended to contribute both to scientific understanding and practical advances in the petrochemical sector [4-7].

EXPERIMENTAL RESEARCH.

Selection of Alternative (Optimal) Parameters for the Separation of Ethylene from Pyrolysis Gas. The selection of alternative (optimal) parameters for the process of separating ethylene from pyrolysis gas is a critical task. The amount of ethylene monomer released during the pyrolysis process is influenced by the following technological parameters [8-9]:

- composition of the feedstock supplied to pyrolysis;
- degree of conversion;
- temperature;
- saturated steam pressure;
- residence time of hydrocarbons in the reaction zone.

Composition of the feedstock supplied to pyrolysis. In the pyrolysis process, the yield of products per unit mass depends on the mass fraction of components in the feedstock. Product yields were determined using the example of: 1 – ethylene, 2 – propylene, and 3 – liquid-phase products. It was found that

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when the ethylene hydrocarbon content in the feedstock increased from 0 to 0.7, its share in the product composition increased from 0.17 to 0.50. Thus, the proportion of ethylene in the product relative to propylene increased by 1.2 to 2.1 times. At the same time, under these conditions, the formation of liquid-phase products decreased from 0.26 to 0.15 mass units.

Temperature. The dependence of pyrolysis product yields on temperature and time was analyzed. Under laboratory conditions, the residence time of the feedstock in the reaction zone was maintained within 6–12 seconds at temperatures of 500–550 °C, 550–650 °C, 650–750 °C, and 750–850 °C, and the results were summarized in a table. Based on the results, the maximum ethylene monomer yield of 33.3% was achieved at temperatures of 750–850 °C with a residence time of 6–12 seconds.

Industrial operation. In industrial conditions, the dependence of pyrolysis product yields on temperature and residence time was analyzed. According to the analysis, at temperatures of 650–750 °C, the residence time of the feedstock in the reaction zone was 0.7–1.0 seconds, whereas at 750–850 °C it was 0.3–0.5 seconds.

Saturated steam. In the process, saturation of the hydrocarbon feedstock supplied to pyrolysis with water steam was identified as one of the most important factors. It was determined that the optimal steam addition is 34–35% relative to the feedstock amount.

Residence time of hydrocarbons in the reaction zone. The residence time of the feedstock in the reaction zone is also a key parameter in the pyrolysis process. Studies were conducted by passing the feedstock through the reaction zone for up to 12 seconds at temperatures of 550–850 °C and analyzing the volume of ethylene monomer formed. In order to reduce coking of the pyrolysis furnace tubes, it was determined that maintaining a residence time of 6–12 seconds and a temperature range of 600–850 °C is optimal. According to the existing regulations, the residence time is up to 0.3 seconds and the temperature is 1000–1100 °C. Under such conditions, furnace tubes undergo intensive coking, leading to a decrease in product yield and a drop in pressure difference between the tubes [10-14].

Based on the above-mentioned parameters, laboratory analyses yielded the following positive results.

Table 1.

Dependence of pyrolysis product yields on temperature and residence time.

Products	Product output level			
	500-550 °C 6-1,2 s	**550-650 °C 6-12 s**	**650-750 °C 6-12 s**	**750-850 °C 6-12 s**
CH_4	15,6	16,6	16,8	16,7

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C_2H_4	23,0	25,9	29,3	33,3
C_3H_6	13,6	12,7	12,2	11,7
C_4H_6	2,2	3,8	4,2	4,8
C_5 and above	32,8	29,7	27,8	23,9
CH_4/ C_2H_4	0,678	0,641	0,575	0,501
C_3H_6/ C_2H_4	0,591	0,490	0,418	0,351

Saturation of the hydrocarbon feedstock supplied to the pyrolysis process with water steam is considered one of the most important factors, since a decrease in the partial pressure of hydrocarbons due to steam dilution leads to an increase in the yields of ethylene, 1,3-butadiene, and butenes. At the same time, the formation of aromatic hydrocarbons and methane is reduced, and the rate of secondary reactions directed toward the formation of high-molecular-weight compounds decreases, thereby ensuring a reduction in coke formation within the reactors. The indicators of feedstock saturation with water steam are presented in Table 2.

Table 2.

Degrees of Feedstock Saturation with Water Steam

	Ethane	**Butane**	**Light naphtha**	**Heavy naphtha**	**Gasoil**
Water Steam Saturation (relative to feedstock amount, %)	35	50	50-60	60-70	80-100

The presence of water steam reduces the rate of coke deposition on the inner surfaces of pyrolysis process tubes and prevents excessive increases in pressure and temperature. As a result, it becomes possible to extend the operating cycle between tube decoking operations. Therefore, saturating the feedstock subjected to pyrolysis with water steam leads to milder operating conditions of the process and makes it possible to increase the ethylene yield without reducing process selectivity [14-15].

RESEARCH RESULTS.

In order to further improve production efficiency, a method for reducing the formation of “yellow oil,” which is considered a globally relevant issue, was developed. As a result of the conducted studies, it was determined that the use of a storage vessel with a capacity of 35 m³ in the process of separating “yellow oil” makes it possible to reduce the time required to separate this type of oil from the alkaline solution in separators to up to 2.0 hours and to ensure the dissolution of “yellow oil” in the ethane–ethylene fraction. This method was subsequently implemented in industrial practice. As a result, in the separators used to separate

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the gas–liquid flow, the spent alkaline solution is effectively separated from the yellow oil.

The pyrolysis gas, purified from acidic gases and oils, is withdrawn from the top of the alkaline column under elevated pressure and fed to the demethanizer, where methane is separated; hydrogen is removed in the separators, and the ethane–ethylene fraction is then directed to the deethanizer column DA-1402.

The hydrocarbon 1,3-butadiene, formed as a result of the dimerization reaction of two acetylene molecules, is considered the primary representative of "yellow oils." The oil consists of a mixture of hydrocarbons with carbon numbers ranging from C_4 to C_{28}, with C_6–C_8 hydrocarbons constituting the major fraction. "Yellow oil" is an oily liquid that coats the surfaces of column trays, packings, demisters, compressor impellers, and molecular sieves, significantly reducing their activity and efficiency. Therefore, it is expedient to separate it from ethylene monomer as quickly and as completely as possible.

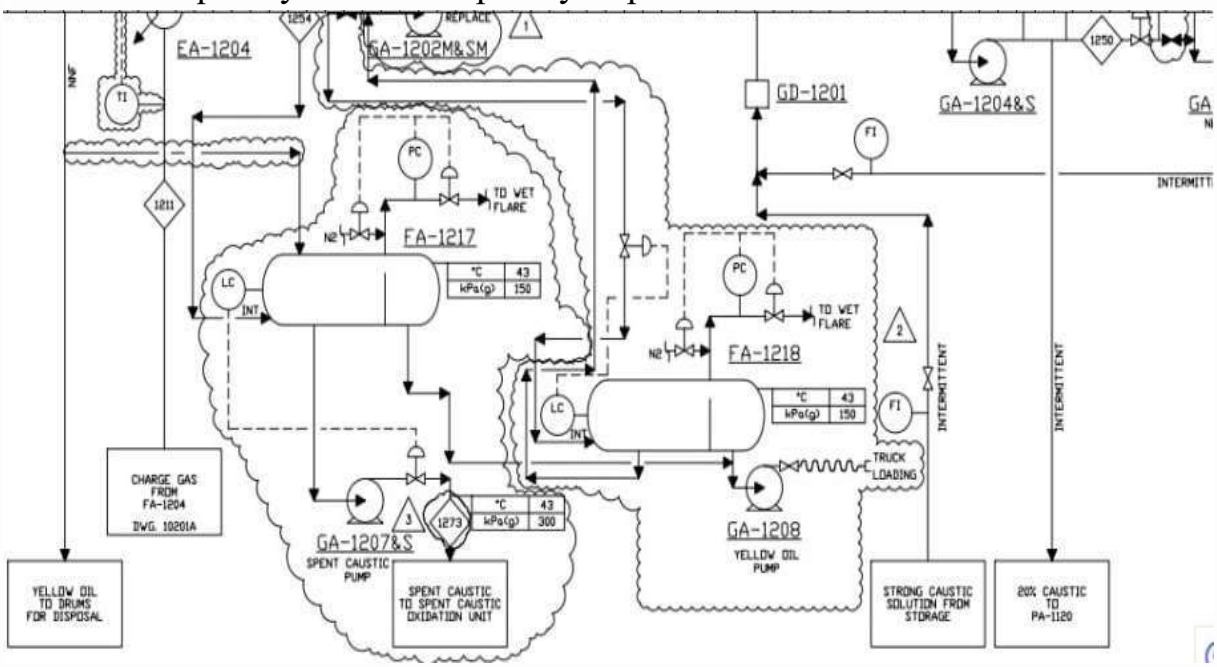


Figure 1. Method for Reducing the Formation of "Yellow Oil" during the Separation of Ethylene Monomer from Pyrolysis Gas

The selection and application of polymerization inhibitors is also an important factor in increasing the yield of ethylene monomer.

During the pyrolysis of hydrocarbons, two acetylene molecules undergo a dimerization reaction to form 1,3-butadiene, which is highly prone to polymerization. Even trace amounts of oxygen present in the pyrolysis feedstock convert butadiene into peroxides. This condition, under normal circumstances, significantly accelerates the onset of the polymerization reaction.

Thus, polymerization reactions occurring during the pyrolysis process are considered undesirable and must be minimized.

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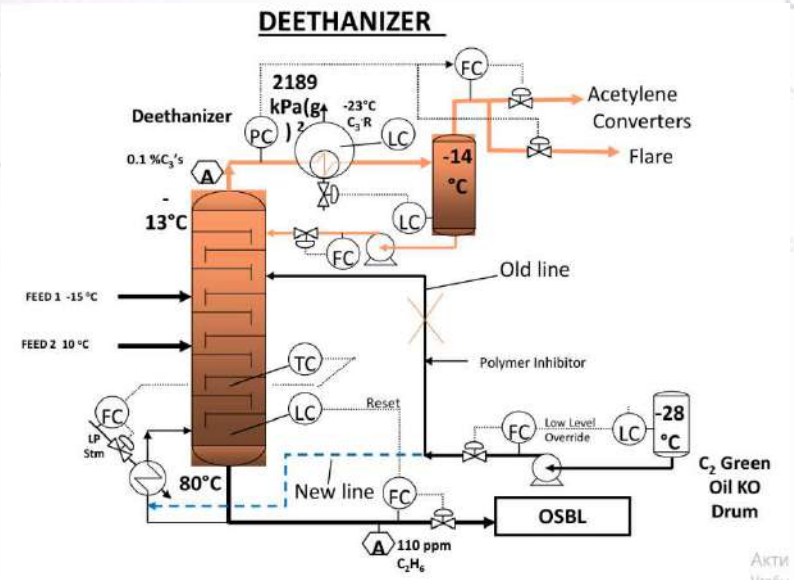


Figure 2. Application of Polymerization Inhibitors to Increase Ethylene Monomer Yield

To reduce the rate of polymerization reactions and minimize fouling of the reboiler, a polymerization inhibitor of the Petroflow brand was selected and recommended to be sprayed into the streams entering the reboiler of the product cube and into the flows leaving the lower part of the column. This method was implemented in industrial practice [16-18].

In general, it is advisable to add the inhibitor in amounts of 0.5–1.5% for these purposes.

Based on the selection of optimal parameters and upgraded process equipment, the pyrolysis process was organized, and the substances formed in the composition of pyrolysis gas were analyzed under laboratory conditions using gas chromatography.

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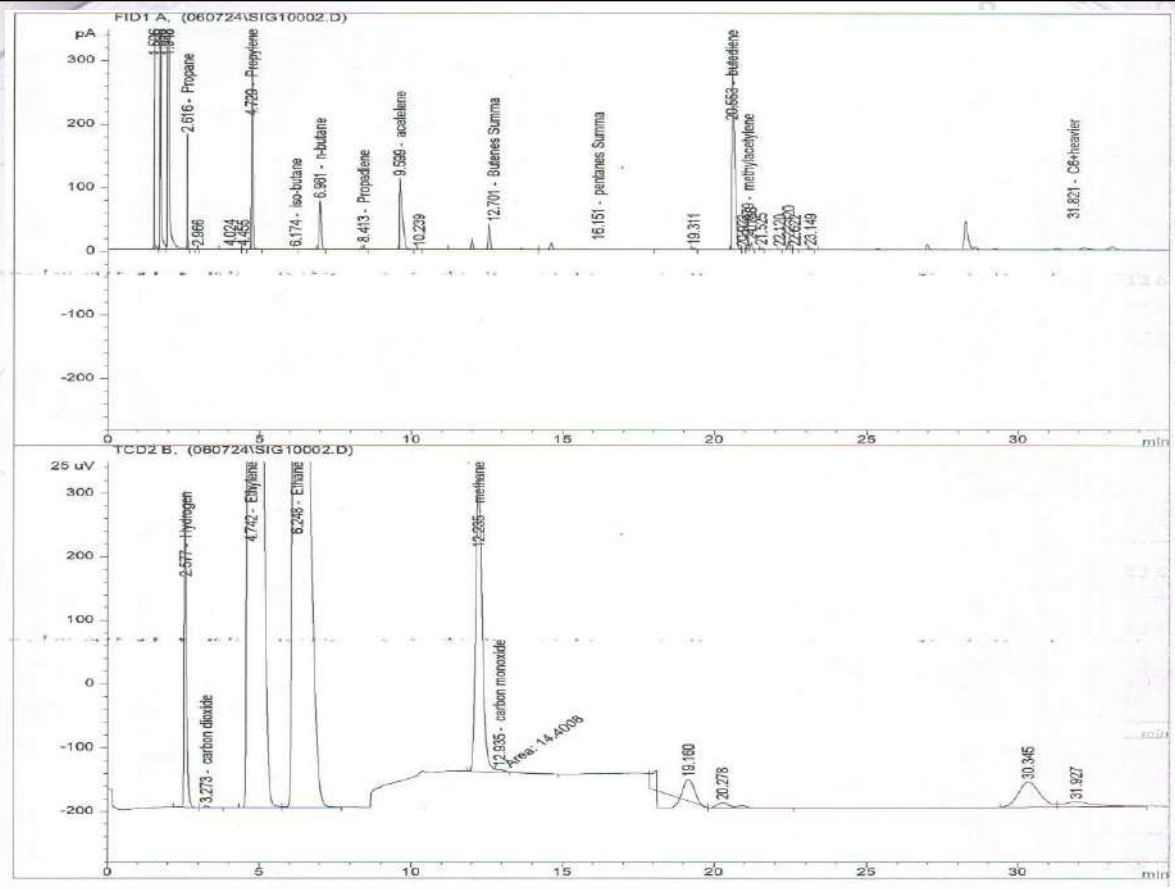


Figure 3. Chromatographic Analysis of Pyrolysis Gas Samples with Modified Furnace Operation (FID Detector)

Due to the fact that the thermal conductivity of many compounds is significantly lower than that of helium or hydrogen, when the analyzed gases reach the detector, the thermal conductivity of the detector decreases, generating a detectable signal [19-20].

The conducted study, based on the selected optimal parameters and modifications in the upgraded technological system, analyzed the ethylene monomer content (mol%) at the Shurtan Gas Chemical Complex central laboratory. The results are as follows: according to the standard regime, the initial ethylene monomer content was 32.65%. After optimizing technological parameters—such as feedstock composition, degree of conversion, temperature, saturated steam pressure, and hydrocarbon residence time in the reaction zone—the ethylene monomer content in the resulting pyrolysis gas increased to 33.32%. Further improvements in the technological system resulted in an increased monomer content of 33.466% [21-23].

Table 3.

Ethylene content (mol%) separated under modified conversion conditions in pyrolysis furnaces.

Compound Name	Ethylene Content under Modified	Ethylene Content According to Project

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	Conversion Conditions (mol%)	Documents and Regulations (mol%)
Hydrogen	38,304	32,92
Carbon monoxide (CO)	0,0049	0,11
Carbon dioxide (CO_2)	0,0069	0,03
Methane	4,539	3,56
Acetylene	0,32	0,23
Ethylene	**33,466**	**32,65**
Ethane	22,049	24,02
Iso-butane	0,000141	0,07
n-Butane	0,074	
Propadiene / Methylacetate	0,0095	0,2
Propylene	0,46	0,39
Butenes	0,066моль	0,06
Propane	0,0627	0,08
Butadiene / C_4 Acetylene	0,536	0,29
Methylacetylene	0,000193	-
C_6 Hydrocarbons	0,0959	0,06
Benzene	-	0,05
Toluene	-	0,01

Based on the modifications in the upgraded technological system, the ethylene monomer content was determined to be 33.466 mol%. The increase in ethylene content compared to the project value is calculated as:

F=33,466моль%- 32,65моль%=0,816 моль%

This shows that the technological improvements led to an increase of 0.816 mol% in ethylene monomer yield.

CONCLUSIONS.

This study analyzed innovative technologies and methods for improving the efficiency of ethylene monomer production from pyrolysis gas. Key process parameters, including feedstock composition, degree of conversion, temperature, saturated steam pressure, and hydrocarbon residence time in the reaction zone, were optimized. Proper adjustment of these parameters led to an increase in ethylene monomer content from 32.65 mol% to 33.466 mol%, representing an enhancement of 0.816 mol%.

Undesirable reactions, such as “yellow oil” formation and polymerization, negatively affect process efficiency. To address these issues, the feedstock was saturated with steam, the separation capacity for “yellow oil” was increased to

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35 m³, and a Petroflow brand polymerization inhibitor was applied. These measures minimized product loss, reduced fouling of process equipment, and enhanced operational stability.

The results demonstrate that careful control of pyrolysis process parameters significantly improves both the yield and quality of ethylene monomer. Moreover, the developed methods for reducing "yellow oil" formation and polymerization have practical applicability in industrial-scale production, ensuring efficient operation of gas-chemical complexes.

Scientifically, this study contributes to the optimization of pyrolysis processes and modernization of separation equipment, providing a foundation for higher-yield ethylene production. These advancements can further support the production of high-molecular-weight polymers and petrochemical products in both national and international industrial contexts.

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