DEPENDENCE OF THE OUTPUT OF THE MAIN PYROLYSIS PRODUCTS OF n-PARAFFIN HYDROCARBONS C$_6$-C$_{15}$ FROM THE LENGTH OF THE CHAIN

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ABSTRACT

In this work, we studied the dependence of the yield of the main pyrolysis products on the chain length of n-paraffin hydrocarbon in the series n-hexane, n-octane, n-decane, n-dodecane, n-pentadecane at temperatures of 620-780 $^\bullet$ C and conversions of 2-65%. It was shown that the nature of the dependence of the yield of the main pyrolysis products on the chain length of n-paraffin hydrocarbon changes with a change in the degree of conversion. A method for calculating the composition of the pyrolysis product of the studied hydrocarbons based on the radical chain mechanism of their decomposition taking into account the unequal isomerization of primary alkyl radicals into secondary ones through alkyl radicals through five-, six-, seven- and eight-membered cyclic transition complexes is proposed.

KEYWORDS: *Pyrolysis, pyrolysis products, olefin, n-paraffin, polycyclic aromatic hydrocarbons, ethylene, propylene, heavy distillates, α-olefin, conversion, conversion depth, thermal decomposition.*

1. INTRODUCTION

Every year in the world, the demand for ethylene and propylene, which are the basic raw material for petrochemical synthesis processes, is increasing. Despite the active use of light hydrocarbons as a raw material for pyrolysis, the use of gasoline fractions still occupies a leading position. Pyrolysis in tube furnaces is widely used in industry today. Although the ways to improve this process are being implemented, in general, its possibilities are limited. The expansion of the initial raw material base with a possible reduction in the specific consumption of raw materials, as well as all heat and energy and material costs, requires the development of new modifications of the pyrolysis process. In this regard, the development of the pyrolysis process, which allows to increase the yields of low molecular weight alkenes, in particular propylene, while reducing operating costs for their production is an urgent task.

This paper presents the results of a study of the pyrolysis of higher n-paraffin hydrocarbons with different chain lengths in a flow reactor with a fluidized bed of powdered quartz.

The best raw materials for pyrolysis in order to obtain lower olefins are paraffin hydrocarbons. The yield of lower olefins during the pyrolysis of hydrocarbons of various classes kills n-paraffins, iso-paraffins, substituted naphthenes, unsubstituted naphthenes, substituted polycyclic aromatic hydrocarbons, monocyclic aromatic hydrocarbons in the series. Currently, from an economic point of view, the most promising types of raw materials for the production of lower olefins are heavy distillates and residual oil fractions, including various types of hydrocarbons [1]. According to recent studies of the structural-group composition of the vacuum residues of a number of oils, the heaviest fractions contain aliphatic chains with an average chain length of about 12 carbon atoms. Moreover, even the aromatic and resinous fractions extracted from the vacuum residue of heavy sour Iranian oil have alkyl substituents with an average chain length of 5-7 carbon atoms, and individual chains include 14 carbon atoms. The total carbon content in the aliphatic part of these fractions reaches approximately 50% [2]. In this regard, it is of interest to study the patterns of variation in the yield of the main pyrolysis products with a change in the chain length of n-paraffin hydrocarbons, which are part of the oil fractions from gasoline to fuel oil and characterize mainly the quality of the pyrolysis feedstock.

The study of the laws of thermal transformations of higher n-paraffin hydrocarbons with a detailed study of not only gaseous, but also liquid products has been the subject of a relatively small number of works [3-8]. Typically, these studies

relate to low temperatures (400-600 degrees °C). In addition, based on the literature data obtained using various techniques, it is impossible to formulate patterns of variation in the yield of pyrolysis products from the length of the hydrocarbon chain.

2. THE EXPERIMENTAL PART OF THE WORK

In this work, we studied the pyrolysis of higher n-paraffin hydrocarbons with various chain lengths in a flow reactor with a fluidized bed of powdered quartz. Pyrolyzed n-hexane, n-octane, n-decane and n-pentadecane having a purity of 98%. Pyrolysis was carried out in a stream of argon at temperatures of 620-780 degrees °C, atmospheric pressure and a molar ratio of hydrocarbon / argon equal to 0.08-0.60. The experimental technique is described in [9]. The pyrolysis products were analyzed chromatographic. The table shows the compositions of the products of typical experiments on the pyrolysis of hydrocarbons C_6-C_{15}. As follows from the table, the main gaseous products of pyrolysis are hydrogen, methane, ethane, ethylene, propylene and butylenes. Significantly smaller amounts of propane and divinyl are present. The content of butane and C_3H_4 hydrocarbons is negligible. Liquid pyrolysis products consist mainly of α-olefins. Diene hydrocarbons are also present in small amounts.

t,^{0}C	Concentration	H$_2$	CH$_4$	C$_2$H$_6$	C$_2$H$_4$	C$_3$H$_6$	α-C$_4$H$_8$	C$_4$H$_6$	α-C$_5$	α-C$_6$	α-C$_7$	α-C$_8$	α-C$_9$	α-C$_{10}$	α-C$_{11}$	α-C$_{12}$	α-C$_{13}$	α-C$_{14}$	Source n-para-fin
n - Hexane																		
620	1.9	0.01	0.26	0.09	0.63	0.58	0.25	-	0.03-	-	-	-	-	-	-	-	-	-	97.38
650	10.3	0.05	1.01	0.40	2.78	2.36	1.51	0.07	0.47	-	-	-	-	-	-	-	-	-	88.76
720	27.7	0.25	4.07	1.22	12.37	6.70	1.97	0.48	0.66	-	-	-	-	-	-	-	-	-	71.76
n - Octane																		
620	3.4	0.01	0.25	0.43	0.89	0.52	0.33	-	0.25	0.22	0.11	-	-	-	-	-	-	-	95.53
680	16.5	0.15	2.09	1.48	5.91	2.64	1.44	0.13	1.12	0.93	0.52	-	-	-	-	-	-	-	82.84
720	35.9	0.11	1.93	2.95	16.14	6.81	2.31	0.29	2.02	2.00	0.86	-	-	-	-	-	-	-	63.42
n - Dean																		
646	9.4	0.03	0.83	1.01	3.18	1.47	0,70	0,04	0,51	0,62	0,54	0,58	0,30	-	-	-	-	-	88,64
670	13.5	0.05	1.22	1.23	4.14	2.14	1,07	0,08	0,81	0,97	0,77	0,77	0,36	-	-	-	-	-	84,72
689	26.8	0.11	2.64	2.21	8.72	4.26	1,41	0,18	1,37	1,72	1,49	4,67	0,67	-	-	-	-	-	71,73
n - Dodecan																		
647	8.0	0.01	0.33	0.37	1.17	0.53	0,38	0,02	0,69	1,63	1,30	1,17	1,02	0,90	0,18	-	-	-	89,69
680	23.2	0.10	1.77	1.31	6.44	2.84	1,34	0,17	1,39	1,89	1,41	1,36	1,26	1,20	0,77	-	-	-	75,05
700	34.7	0.14	2.33	1.87	8.48	3.63	1,83	0,14	3,17	3,73	2,45	2,09	1,74	1,59	0,88	-	-	-	63,71
n - Pentadecane																		
626	10.3	0.03	0.70	0.65	1.90	1.14	0,45	0,06	0,35	0,73	0,63	0,60	0,59	0,62	0,55	0,49	0,42	-	89,73
662	18.2	0.04	1.13	1.02	3.80	1.79	0,63	0,10	0,80	1,58	1,20	1,09	1,08	1,09	1,05	0,96	0,73	-	81,79
719	65.1	0.37	7.36	3.49	21.38	8.78	2,83	0,57	3,31	3,67	2,22	1,72	1,56	1,54	1,38	1,33	1,20	0,61	34,93

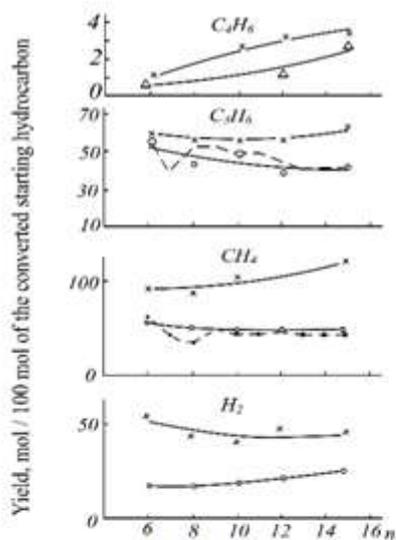**The distribution of the pyrolysis products of the studied hydrocarbons. mass %**
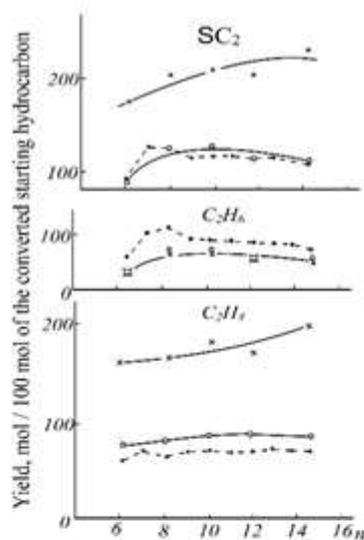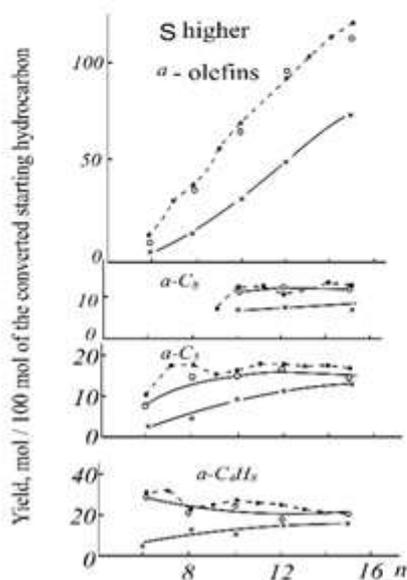
Fig. 1.

Fig. 2.

Fig. 3.

Fig. 1. Dependence of the yield of hydrogen, methane, propylene, and divinyl on the chain length of n-paraffin carbon. Designations in fig. 1.2: Experiment; ----payment; ○ - extrapolation to zero conversion; X-50% conversion; Δ-10% conversion.

Fig. 2. Dependence of the yield of ethylene, ethane, and ΣC_2 on the chain length of n-paraffin hydrocarbon.

Fig. 3. Dependence of the yield of α-butylene, α-butylene, α-pentane, α-octene and the sum of the higher α-olefins on the length of the n-paraffin carbon chain. Designations are the same as in Fig. 1.

In fig. Figure 1-3 shows the dependences of the yield of the main pyrolysis products on the length of the n-paraffin chain, obtained by extrapolation to a zero degree of conversion and at a degree of conversion of 50%. The hydrogen yield at the zero conversion degree slightly increases with increasing chain length of n-paraffin from 15 (for n-hexane) to 23 mol / 100 mol of the converted hydrocarbon (for n-pentadecane).

At 50% conversion, the hydrogen yield is practically independent of the chain length of n-paraffin and amounts to 45-40 mol / 100 mol of the converted starting carbon. The methane yield, on the contrary, remains almost constant for all C_6-C_{15} hydrocarbons studied at zero conversion and is approximately 50 mol / 100 mol of converted hydrocarbon, and at 50% conversion they increase with increasing n-paraffin chain length. Moreover, in the case of pyrolysis of each of the studied hydrocarbons, the yield of methane and hydrogen increases with the conversion depth.

At a zero degree of conversion, the ethylene yield remains almost unchanged with increasing carbon chain length and is about 90 mol / 100 mol of the converted starting hydrocarbon. For each n-paraffin, with an increase in the conversion depth, the ethylene yield increases. Moreover, at a 50% conversion, a monotonic increase in ethylene yield is observed with an increase in the chain length of n-paraffin from about 160 (for n-hexane) to 210 mol / 100 mol of the converted hydrocarbon (for n-pentadecane). The yield of ethane at the zero degree of conversion increases somewhat upon transition from n-hexane to n-octane, and then it does not practically change with increasing chain and amounts to about 40 mol / 100 mol of the converted hydrocarbon. In this case, there is no significant change in the yield of ethane during the pyrolysis of the studied hydrocarbons slightly lower than its yield at zero degree of conversion.

The yield of propylene at zero conversion decreases slightly with increasing chain length. With the conversion depth, the propylene yield during the pyrolysis of n-hexane varies very slightly. With increasing hydrocarbon chain length, the propylene yield increases with increasing degree of conversion. The yield of propylene at zero and 50% conversion of n-hexane is almost the same and is about 55 mol / 100 mol of converted n-hexane, and in the case of n-pentadecane it differs significantly and carries out 40 and 62 mol / 100 mol of converted n-pentadecane, respectively .

At a zero degree of conversion, the yield of α-butylene slightly decreases with increasing chain length of n-paraffin and is approximately 30 and 20 mol / 100 mol of the converted hydrocarbon in the case of n-hexane and n-pentadecane, respectively. With an increase in the degree of conversion, the yield of a-butylene decreases. In this case, the sharpest dependence of the α-butylene yield on the conversion depth is observed during the pyrolysis of n-hexane: 30 and 60 mol / 100 mol of the conversion of n-hexane at zero and 50% conversion, respectively. The yield of α-butylene during the pyrolysis of n-pentadecane weakly depends on the conversion depth and is about 21 and 45 mol / 100 mol of converted n-pentadecane at zero and 50% conversion, respectively. In general, at a 50% conversion, a slight increase in the yield of α-butylene with increasing chain length is n-low and increases with the conversion depth. When extrapolating to a zero degree of conversion, the yield of butadiene tends to zero. With increasing chain length of n-paraffin, the yield of butadiene increases. At a 50% conversion upon pyrolysis of n-hexane and n-pentadecane, the yield of C_4H_6 is 1 and 3 mol / 100 mol of the converted hydrocarbon, respectively.

During pyrolysis of the studied n-paraffins, the yield of each subsequent α-olefin, starting from pentene, decreases monotonically. The exception is hexene, the yield of which is higher than that of pentene during the pyrolysis of n-decane and higher molecular weight n-paraffinic hydrocarbons. The yield of each of the higher α-olefins (α-olefins C_5 and higher) weakly depends on the chain length of the pyrolyzable n-paraffin, and their total yield increases sharply. With an increase in the degree of conversion of the initial hydrocarbon, the yield of higher α-olefins decreases.

Thus, during the pyrolysis of C_6-C_{15} n-paraffin hydrocarbons under the studied conditions, with an increase in the degree of conversion, the yield of H_2, CH_4, C_2H_4, C_3H_6 increases, the yield of higher α-olefins decreases, and the yield of $C2H6$ remains almost constant. Moreover, at a zero degree of conversion, the yield of ethylene and methane very weakly depends on the chain length of n-paraffin, the yield of hydrogen and higher α-olefins increases, and the yield of propylene and α-butylene decreases. At 50% conversion with enthusiasm, the chain length of n-paraffin, the yield of ethylene, divinyl and propylene methane increases, the yield of ethane and α-butylene practically does not change, and the yield of hydrogen decreases slightly.
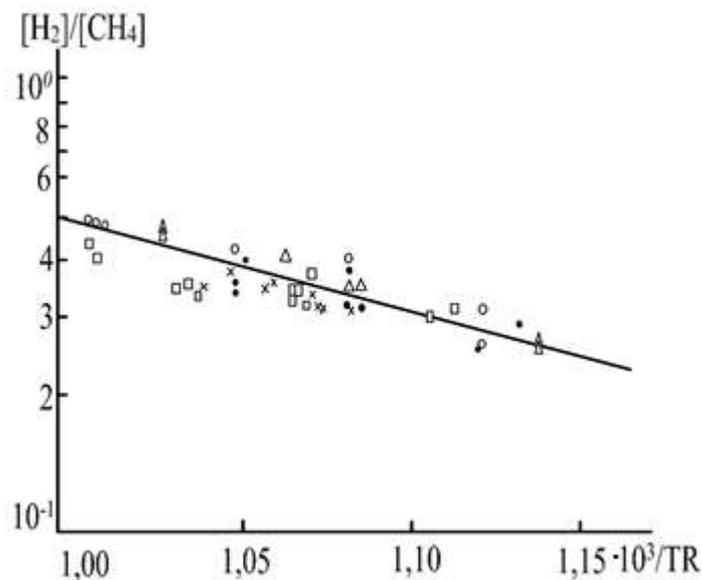
Fig. 4. Dependence of the ratio of the concentration of hydrogen and methane in the pyrolysis products of the studied n-paraffin hydrocarbons on temperature: -n-hexane; n-octane; x-n-decane, Δ-n-dodecane; n-pentadecane.

Therefore, with a change in the conversion depth, the character of the dependence of the composition of the pyrolysis products of n-paraffin hydrocarbons on the chain length changes.
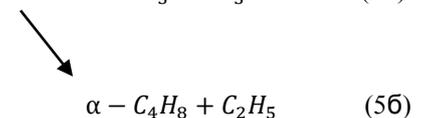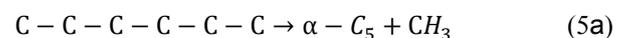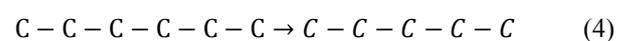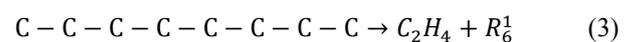
The thermal decomposition of n-paraffin hydrocarbons proceeds via a radical chain mechanism. The main radicals leading the chain are hydrogen atoms and methyl radicals. The formation of hydrogen and methane occurs only with the participation of atoms. Hydrogen and CH_2 radicals according to reactions of the type:

$$H+RH \rightarrow H_2+R$$
$$CH_2+RH \rightarrow CH_4+R$$
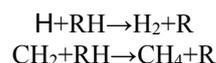
From the literature it follows that the ratio of the rate constants of reactions of type (1), (2) is practically independent of the type of hydrocarbon [11,12]. In this case, the ratio of the concentrations of hydrogen and methane in the pyrolysis products characterizes the ratio of the concentrations of atoms. Hydrogen and methyl radicals formed in the process. In the pyrolysis products of the studied n-paraffin hydrocarbons, the ratios of the concentrations of hydrogen and methane are almost identical and depend little on temperature (Fig-4). Consequently, the studied paraffin hydrocarbons formed in the pyrolysis zone also have close values and are little dependent on temperature.
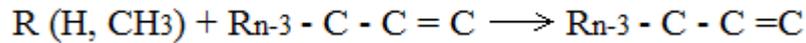
In the decomposition mechanism of higher n-paraffin hydrocarbons, an important role is played by the reactions of isomerization of primary alkyl radicals through various cyclic transition complexes [12]. The fact that the pyrolysis of the studied n-paraffin hydrocarbons with a chain length of more than eight C atoms yields α-hexane higher than the yield of α-pentene, can be explained by the relatively higher concentration of alkyl radicals with free valency at the fifth carbon atom, which is created due to preferred isomerization higher primary alkyl radicals through a six-membered cyclic transition complex [12]. In the case of n-octane, the radical $R_8^{5\,1}$ formed during isomerization through a six-membered cyclic transition complex further decomposes with equal probability to form α-hexene and α-pentene. At the same time, there are no additional sources of the formation of α-hexene, while α-pentene can be formed during the decomposition of the radical R_6^3, the appearance of which in this case is possible only as a result of the isomerization of the radical R_6^1 through a five-membered cyclic transition complex.

$$C-C-C-C-C-C-C-C \rightarrow C_2H_4 + R_6^1 \qquad (3)$$

$$C-C-C-C-C-C \rightarrow C-C-C-C-C \qquad (4)$$

$$C-C-C-C-C-C \rightarrow \alpha-C_5 + CH_3 \qquad (5a)$$
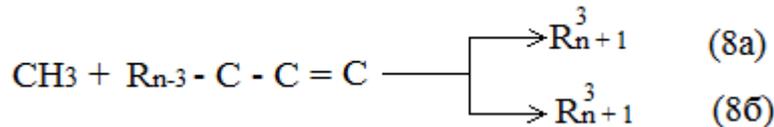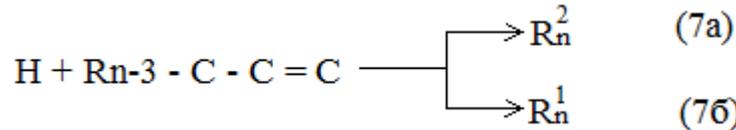
$$\alpha-C_4H_8 + C_2H_5 \qquad (5б)$$

However, the concentration of radicals R_6^3 is not large and the excess of the yield of α-pentene over α-hexene is equal to 2-3 mol / 100 mol of converted n-octane.

The observed decrease in the yield of higher α-olefins with a conversion depth is associated with the occurrence of secondary processes of their conversion mainly with the participation of hydrogen atoms and methyl radicals. The main directions of the conversion of higher α-olefins are the reactions of detachment of hydrogen atoms from carbon in the β-position to a double bond:
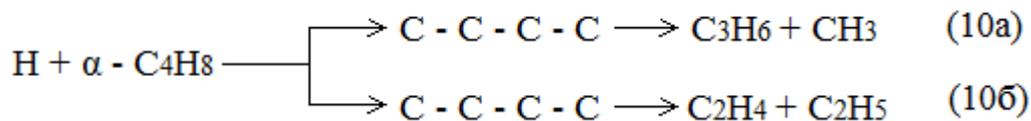
$$R\,(H, CH_3) + R_{n-3} - C - C = C \longrightarrow R_{n-3} - C - C = C$$

and connections at the double bond location:

$$H + R_{n-3} - C - C = C \longrightarrow
\begin{cases}
R_n^2 & (7a) \\
R_n^1 & (7б)
\end{cases}$$

$$CH_3 + R_{n-3} - C - C = C \longrightarrow
\begin{cases}
R_{n+1}^3 & (8a) \\
R_{n+1}^3 & (8б)
\end{cases}$$

The alkyl radicals formed by reaction (6) lead to the formation of butadiene-1,3 and primary alkyl radicals from CH_3 in the case of α-pentene to R_{10} in the case of α-tetradecene. (Since the "heaviest" of the investigated n-paraffin hydrocarbons is n-pentadecane, the most "heavy" α-olefin present in the pyrolysis products is α-tetradecene). The decomposition of the alkyl radicals formed by reactions (7) and (8) leads to the formation of ethylene, propylene, butylene and primary alkyl radicals R_2-R_{12} which decompose further according to general rules with the formation of various lighter products.

Propylene and α-butylene are one of the main products of the pyrolysis of n-paraffin hydrocarbons, which have relatively low stability in the pyrolysis zone. Their conversion in the process of pyrolysis proceeds mainly with the participation of hydrogen atoms by the addition reaction at the double bond site:
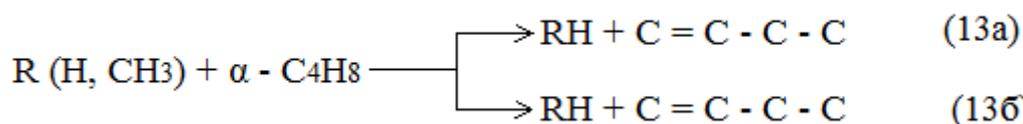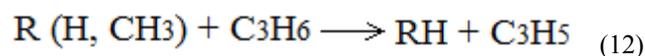
$$H + C_3H_6 \rightarrow C-C-C \rightarrow CH_3 - C_2H_4 \quad (9)$$

$$H + \alpha - C_4H_8 \longrightarrow
\begin{cases}
C - C - C - C \longrightarrow C_3H_6 + CH_3 & (10a) \\
C - C - C - C \longrightarrow C_2H_4 + C_2H_5 & (10б)
\end{cases}$$

In the case of α-butylene, the addition of methyl radicals also proceeds

$$CH_3 + \alpha - C_4H_8 \rightarrow C-C-C-C-C \rightarrow C_2H_5 + C_3H_6 \quad (11)$$

In addition, with the participation of hydrogen atoms and methyl radicals, detachment reactions of the hydrogen atom from propylene and α-butylene molecules occur:

$$R\,(H, CH_3) + C_3H_6 \longrightarrow RH + C_3H_5 \quad (12)$$

$$R\,(H, CH_3) + \alpha - C_4H_8 \longrightarrow
\begin{cases}
RH + C = C - C - C & (13a) \\
RH + C = C - C - C & (13б)
\end{cases}$$

In the case of α-butylene, the formation of a secondary butenyl radical is most likely. However, this resonance-stabilized radical in the studied temperature range mainly enters into a substitution reaction, leading again to α-butylene.

With an increase in conversion, the conversion rate of propylene and α-butylene increases, but at the same time, the rate of their formation in secondary processes also increases mainly during the decomposition of higher α-olefins. In the case of heavy n-paraffin hydrocarbons, a sharper increase in the yield of propylene with a conversion depth is observed, which is associated with a higher concentration of higher α-olefin in the pyrolysis products.

The relatively weak dependence of the α-butylene yield on the conversion depth during the pyrolysis of n-pentadecane and the sharp decrease in the α-butylene yield on the conversion depth in the case of n-hexane are also due to the difference in the total concentrations of higher α-olefins in the pyrolysis products of the studied hydrocarbons. During the pyrolysis of n-hexane, the only source of additional formation of α-butylene is α-pentene, the yield of which is insignificant. Therefore, at deep conversions during the pyrolysis of n-hexane, the decomposition rate of α-C_4H_8 exceeds the rate of its formation due to the secondary conversion of the pyrolysis products. As the chain length of n-paraffin hydrocarbon increases, the heavier α-olefins appear in the pyrolysis products, which upon decomposition lead to the formation of an additional amount of α-butylene.

Thus, a change in the nature of the dependence of the yield of products on the chain length of n-paraffin hydrocarbon with deep conversion is associated with the occurrence of secondary reactions of conversion of propylene α-olefins. Since the total

concentration of α-olefins in the pyrolysis products increases with increasing chain length of n-paraffin hydrocarbon, the role of these reactions in the process of conversion of n-paraffins increases.
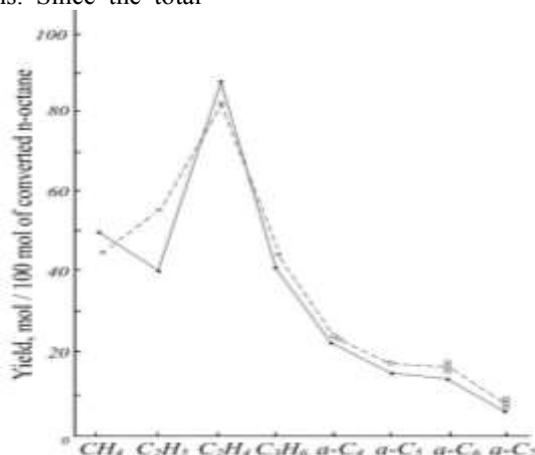
Fig. 5. The yield of n-octane pyrolysis products at 650 ° C, extrapolated to zero conversion. – Experiment: --- calculation; ΔE, kJ / mol: ○ -16.2; Δ-12.6; x-8.4; -2.1.

The yields of the primary pyrolysis products of n-paraffin hydrocarbons extrapolated to the zero degree of conversion can be calculated on the basis of the Reis-Kostyakov assumption about the probability of formation of primary and secondary radicals from the initial n-paraffin molecule taking into account their subsequent isomerization. Such a calculation of the yield of the primary products of the thermal conversion of each of the C_6-C_{15} n-paraffin hydrocarbons was performed at a temperature of 650 ° C under the assumption that the primary alkyl radicals are isomerized through five-, six-, seven- and eight-membered cyclic transition complexes. When calculating the primary distribution of radicals, the difference in the activation energies of the detachment of the hydrogen atom of the primary and secondary carbon atoms was assumed to be 5.0 kJ / mol (ΔEvt), and the difference in the energies of the intramolecular transfer of free valence from the primary C atom to the secondary one was equal to 16.8 kJ / mole (ΔEp). At the same time, it was assumed that the rate constants of the isomerization reactions of primary alkyl radicals through five-, six-, seven- and eight-membered cyclic transition complexes are related as 0.4: 1.0; 0.4: 0.3. The accepted relations were substantiated earlier in [12]. Assuming also that all C_4-C_8 radicals enter only substitution reactions leading to ethane, and C_3-C_7 radicals only decompose to form CH_3 and C_2H_4. In the case of secondary alkyl radicals with a free valence at the third carbon atom, it was assumed that the probability of decomposition of such radicals with a cleavage of the terminal C — C bond and the C — C bond inside the molecule (through one from the carbon atom with a free valence) is treated as 1: 3. For secondary alkyl radicals with free valency, the fourth carbon atom and the subsequent ones were equally

likely to decay on both sides of the carbon atom with free valency.

As follows from Figs. 1-3, the agreement between the calculated and experimentally found yields of the main primary pyrolysis products of n-paraffin hydrocarbons is quite good. The experimentally observed lower yield of ethane and a higher yield of ethylene are due to the fact that at the temperatures studied, ethyl radicals partially decompose to form ethylene, which was not taken into account in the calculation.

3. DISCUSSION OF THE RESULTS

The experimentally found total yield of C_2 agrees well with the calculated one. It should be noted that the convergence of the calculated and experimentally found yields of the main products of pyrolysis in studies of n-paraffin hydrocarbons is better for n-paraffins with a longer chain. This is apparently due to the fact that with an increase in the chain length, the diversity of the formed alkyl radicals increases and the yield of each product is more averaged. The most discrepancy between the calculated and experimental yields is observed for n-octane. On the curve of the dependence of the calculated yields of pyrolysis products on the chain length at point C_8, extremes are observed for CH_4, C_2H_6, C_2H_4, C_3H_6. In this case, the calculated yield of C_2H_4 is lower, and the propylene is higher than experimentally determined. This may be due to the fact that, during the calculation, the proportion of primary radicals leading to the formation of ethylene was underestimated. In order to verify this proposal, calculations of yields of n-octane products at ΔEp equal to 12.6, 8.4, and 2.1 kJ / mol were presented. As follows from fig. 5, the best agreement between the calculated and experimentally found yields of the main products of n-octane pyrolysis is achieved at ΔE = 8.4

kJ / mol and also gives good agreement with the experiment.

Thus, the proposed method for calculating the initial yield of pyrolysis products of n-paraffin hydrocarbons in the proposal for the isomerization of only primary alkyl radicals into secondary ones through five-, six-, seven- and eight-membered cyclic transition complexes at $\Delta Ep = 8.4$ and $\Delta Est = 5$, 0 kJ / mol gives values that are in good agreement with the experiment. The methods for calculating the initial distribution of the products of the pyrolysis of n-paraffin hydrocarbons proposed in [13, 14] also take into account the isomerization of alkanes.

4. CONCLUSION

1. The dependence of the yield of the main pyrolysis products on the chain length of n-paraffin hydrocarbon in the series n-hexane, n-octane, n-decane, n-dodecane, n-pentadecane at temperatures of 620-780 °C and conversions of 2-65% was studied.

2. It has been shown that the nature of the dependence of the yield of the main pyrolysis products on the chain length of n-paraffin hydrocarbon varies with a change in the degree of conversion.

The yield extrapolated to the zero degree of conversion remains almost unchanged with a change in the chain length of n-paraffin hydrocarbon, the yield of ethylene and hydrogen grows weakly, and the yield of propylene decreases. At a 50% conversion, the methane yield is insignificant, and ethylene increases sharply with increasing chain length of n-paraffin hydrocarbon, the yield of hydrogen and propylene practically does not change.

(3) A method is proposed for calculating the composition of the pyrolysis product of the studied hydrocarbons based on the radical chain mechanism of their decomposition, taking into account the unequal isomerization of primary alkyl radicals into secondary ones through alkyl radicals via five-, six-, seven- and eight-membered cyclic transition complexes.

4. The calculated and experimentally determined product yields extrapolated to the zero degree of conversion are in fairly good agreement.

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