

**ORGANIC SYNTHESIS
AND INDUSTRIAL ORGANIC CHEMISTRY**

**The Effect of Hexene-1 in Feedstock
on the Yield of Target Products
during Thermal Pyrolysis of *n*-Hexane**

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Abstract—The effect of the α -olefin addition in the pyrolysis feedstock on the yield of ethylene, propylene, and divinyl (butadiene-1,3) was studied using the *n*-hexane–hexene-1 model system under conditions of a laboratory flow-type thermal pyrolysis setup. It was found that the total yield of unsaturated hydrocarbons $C_2=C_4=$ depends on the ratio of *n*-hexane : hexene-1 in the initial mixture and is characterized by a maximum value at a 0.36 molar fraction of hexene-1 in feedstock. The main directions of reactions in the presence of an α -olefin are discussed.

Keywords: thermal pyrolysis, ethylene, propylene, divinyl, lower olefins, *n*-hexane, hexene-1

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The main process for the production of lower olefins C_2-C_4 and divinyl in industry remains pyrolysis [1, 2]. The composition of the feedstock significantly determines the yield of ethylene, propylene and divinyl, key products, as well as the amount of pyro-condensate and coke, by-products. In recent years, installations for the production of propylene and butenes by catalytic dehydrogenation of the corresponding alkanes, Catofin, Oleflex processes, have been actively introduced into the industry. A significant advantage of the dehydrogenation process over pyrolysis is the absence of the formation of heavy by-products—pyrocondensate. The production capacities and feedstock potential of pyrolysis plants far exceed the capabilities of the production of olefins by the dehydrogenation method. This balance will be maintained for many years, therefore, the search for the process mode, adjustment of the qualitative and quantitative composition of hydrocarbons in the pyrolysis feedstock in order to increase the yield of target products is an urgent task.

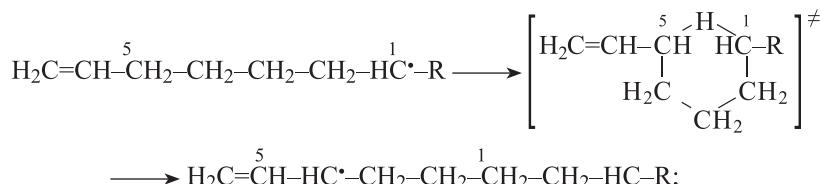
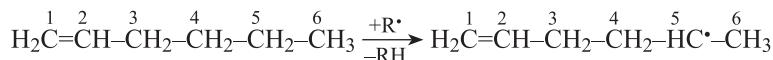
The pyrolysis occurs in accordance with the laws of the radical chain mechanism of chemical reactions. The rate and yield of radical reaction products can be controlled by introducing substances of different

reactivity into the pyrolysis feedstock,. Among these substances are olefinic hydrocarbons.

Various olefin-containing fractions of petrochemical processes for the deep processing of hydrocarbons can be considered as additives to the pyrolysis feedstock. First of all, these are processes whose feedstock material are the target pyrolysis products, for example, the production of α -olefins from ethylene and, to a lesser extent, propylene. The effect of olefin in feedstock materials on the yield of pyrolysis products is reported in patents [3–7]. However, in these patents there is no quantitative data on the effect of a particular alkene on the yield and distribution of the target pyrolysis products—lower olefins and divinyl.

At elevated temperatures, the thermodynamic probability of the formation of radical particles from C_{5+} olefins is higher than from alkanes [8, 9]. The radicals formed during the thermal decomposition of alkenes pass into stable molecular products, mainly, into lower olefins and dienes (ethylene, propylene, divinyl) [8]. The thermal decomposition of unsaturated hydrocarbons is characterized by some features [10]:

- the presence in the olefin molecule of weakened C–C and C–H bonds in the β position to the double bond;

Scheme 1.**Scheme 2.**

– the possibility of intramolecular isomerization of radicals through unstressed 1,4-1,5- and 1,6-transition states, i.e., the conversion of primary alkenyl radicals to substituted allyl radicals (Scheme 1);

– double addition of the H atom with the formation of an olefin and an alkyl radical with a lower molecular weight;

– weakening of the bond C–C between the double bond and the radical center. For example, in the case of hexene-1, the formation of a radical (hexen-1-yl-5) the bond between 3 and 4 carbon atoms weakens (Scheme 2).

The noted features of the decomposition of unsaturated hydrocarbons largely determine the composition of the final pyrolysis products [11].

The choice in this work of the model mixture formed by C₆ hydrocarbons is due to the fact that the straight-run light gasoline fraction (bp 103°C), which is the feedstock material of the pyrolysis plants, contains mainly paraffins of normal structure and is characterized by an average molecular weight of 84 g mol⁻¹ (molecular weight of hexane 86 g mol⁻¹).

This work is a continuation of the studies carried out by the authors in the field of pyrolysis of a light fraction [12], a product of the processing of gas condensate, in order to search for conditions and modes of the process that contribute to an increase in the yield of ethylene, propylene, and divinyl.

The purpose of the work is to obtain quantitative data on the effect of the addition of normal structure α-olefins on the yield of unsaturated hydrocarbons C₂–C₄= under conditions of pyrolysis of a mixture of n-hexane–hexene-1.

EXPERIMENTAL

Thermal pyrolysis. The pyrolysis conditions for mixed hydrocarbon compositions were chosen close to the industrial parameters of the process [13], taking into account the reduced probability of secondary reactions leading to the formation of products of decomposition and condensation of hexene-1.

Thermal pyrolysis of n-hexane and binary mixtures of n-hexane–hexene-1 with different molar ratios was carried out at a temperature of 800°C, a conditional contact time of 0.2 s, and a mass ratio of water vapor : feed = 0.8 : 1.0 in a laboratory setup with a tube furnace, flow reactor (Fig. 1).

The volume of the working zone of the quartz reactor was 60 mL; the height of the heated isothermal high-temperature zone was 300 mm. Temperature was measured over the entire height of the reactor by a TXA(K) thermocouple installed in a quartz pocket located on the axis of the reactor.

Qualitative and quantitative analysis of the composition of gaseous pyrolysis products was carried out by gas chromatography. To determine the C₁–C₅ hydrocarbons, a TsVET-800 gas chromatograph with a flame ionization detector was used. The content of H₂, CO, and CO₂ was determined on a TsVET-100 chromatograph with a thermal conductivity detector. Descriptions of gas chromatographic analysis techniques are given in [12].

RESULTS AND DISCUSSION

The experimental data characterizing the composition of the pyrogas and the yield of pyrolysis products of the hexane/hexene mixture depending on the concentration

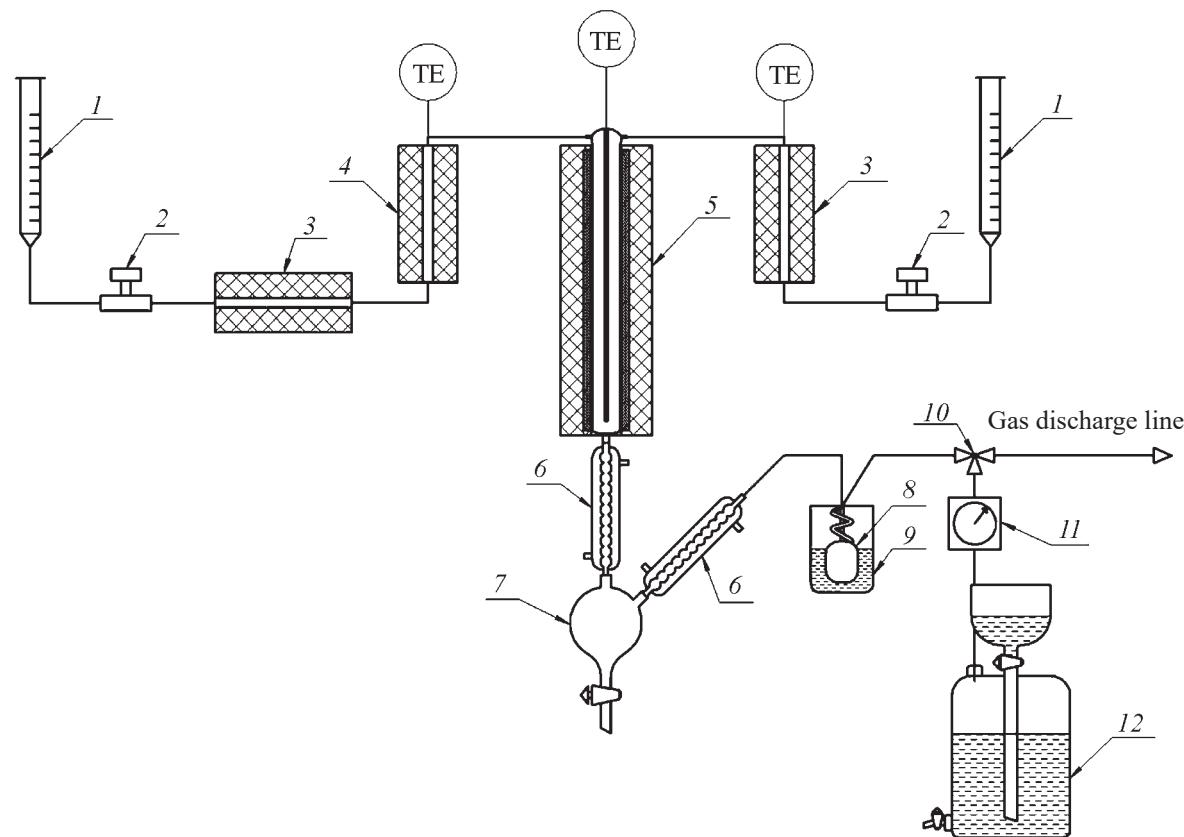


Fig. 1. Scheme of a laboratory setup for thermal pyrolysis of hydrocarbons. (1) Burette, (2) metering pump, (3) evaporator, (4) water vapor superheater, (5) reactor furnace, (6) reflux condenser, (7) receiving flask, (8) receiving trap, (9) Dewar vessel, (10) three-way valve, (11, 12) gas meters

of hexene-1 are presented in Tables 1 and 2. The trend in the total yield of the target products: ethylene, propylene, and divinyl, is illustrated by the curve in Fig. 2. The curve in Fig. 2 has the form of a parabola

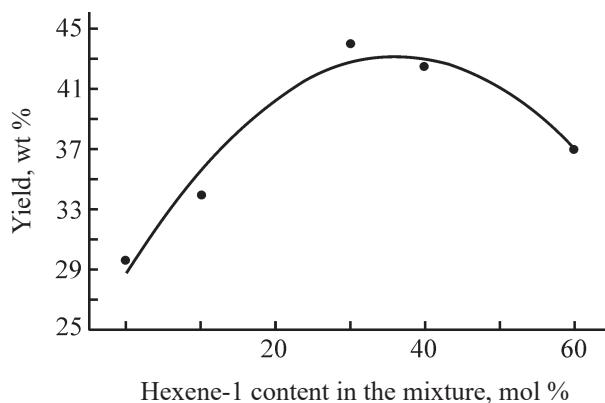


Fig. 2. The total yield of ethylene, propylene, and divinyl vs. the composition of the *n*-hexane–hexene-1 mixture.

with a pronounced maximum point. The maximum total yield of C₂–C₃ olefins and divinyl 43.0 wt % is achieved when the concentration of hexene-1 in the initial reaction mixture is about 36 mol %.

As already noted above, the process of hydrocarbon pyrolysis proceeds in accordance with the basic principles of the radical chain reactions. The diagram shows the expected directions of the reactions leading to the formation of pyrolysis products in a mixture of *n*-hexane–hexene-1, in the region of low and high concentrations of hexene-1, respectively, the sections before and after the extremum point in Fig. 2.

The rate of radical nucleation and their structure will depend on the content of the hydrocarbon component in the mixture, which will ultimately determine the composition of the molecular products of the radical chain decomposition of hydrocarbons in the initial mixture. In the case of a low concentration of hexene-1 in a mixture with *n*-hexane, the source of the formation of radical

Table 1. Composition of gaseous products of thermal pyrolysis of *n*-hexane–hexene-1 mixtures

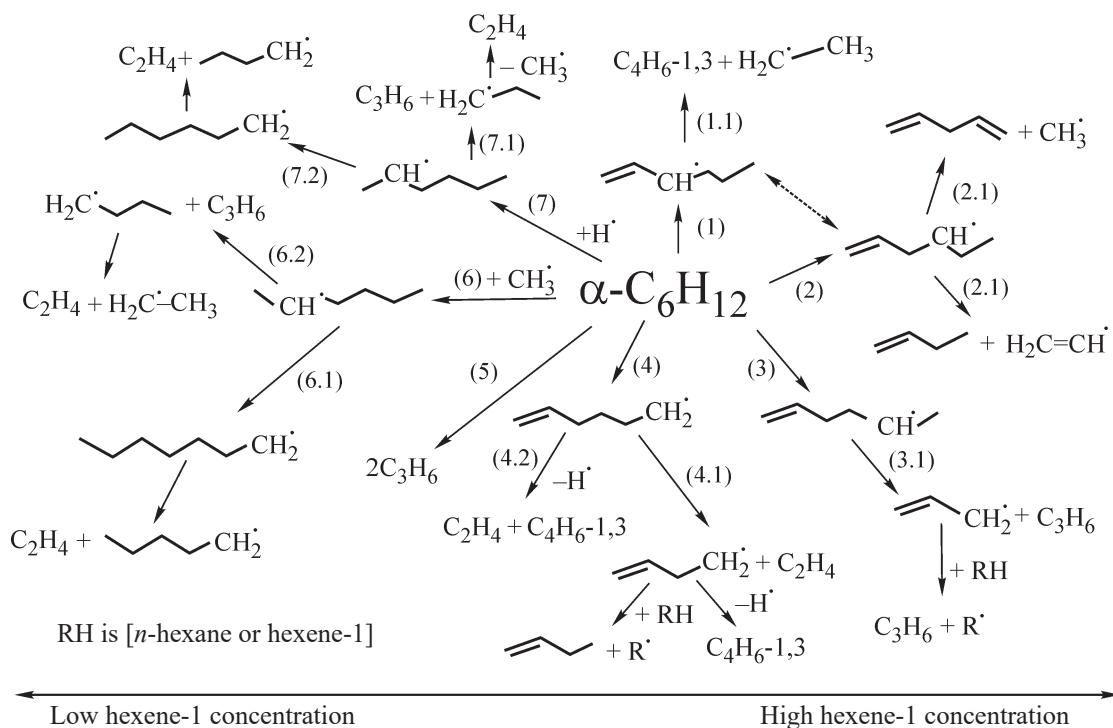
Component of pyrogas	Composition of the pyrogas, wt %/mol % at the initial concentration of hexene-1 in feedstock materials, mol %				
	0	10	30	40	60
Hydrogen [H ₂]	1.46/17.38	1.10/13.97	0.74/10.05	0.70/9.74	0.51/7.55
Methane [CH ₄]	11.30/16.82	11.16/17.72	10.14/17.21	9.94/17.29	8.23/15.23
Ethane [C ₂ H ₆]	3.30/2.62	2.71/2.29	2.14/1.94	2.82/2.62	3.55/3.50
Ethylene [C ₂ H ₄]	37.60/32.01	40.72/36.94	39.03/37.85	36.91/36.69	33.20/35.11
Propane [C ₃ H ₈]	0.92/0.50	0.78/0.45	0.70/0.43	0.51/0.32	0.62/0.45
Propylene [C ₃ H ₆]	18.10/10.27	20.25/12.25	21.04/13.60	22.11/14.65	24.50/17.27
Isobutane [C ₄ H ₁₀]	0.10/0.04	0.02/0.01	0.02/0.01	0.03/0.01	0.03/0.02
<i>n</i> -Butane [C ₄ H ₁₀]	0.42/0.17	0.15/0.07	0.13/0.06	0.12/0.06	0.15/0.08
Propane diene [C ₃ H ₄]	0.05/0.03	0.08/0.05	0.09/0.06	0.34/0.24	0.51/0.38
Acetylene [C ₂ H ₂]	0.26/0.24	0.26/0.25	0.34/0.36	1.55/1.66	1.60/1.82
<i>trans</i> -2-Butene [C ₄ H ₈]	0.13/0.06	0.17/0.08	0.24/0.12	0.56/0.28	0.69/0.36
Butene-1 [C ₄ H ₈]	8.05/3.43	8.67/3.93	8.50/4.12	8.44/4.19	9.12/4.82
Isobutylene [C ₄ H ₈]	0.02/0.01	Traces	Traces	0.02/0.01	0.03/0.02
2,2-Dimethylpropane [C ₅ H ₁₂]	0.06/0.02	0.04/0.01	0.11/0.04	0.20/0.08	0.14/0.06
<i>cis</i> -2-butene [C ₄ H ₈]	0.12/0.05	Traces	0.21/0.10	0.30/0.15	0.36/0.19
Divinyl [C ₄ H ₆]	1.84/0.81	2.70/1.27	4.28/2.15	6.00/3.09	7.15/3.92
Cyclopentane [C ₅ H ₁₀]	0.02/0.01	0.05/0.02	0.03/0.01	0.10/0.04	0.06/0.03
Isopentane [<i>i</i> -C ₅ H ₁₂]	Traces	0.02/0.01	0.02/0.01	0.02/0.01	0.02/0.01
<i>n</i> -Pentane [<i>n</i> -C ₅ H ₁₂]	0.02/0.01	0.11/0.04	0.02/0.01	0.05/0.02	0.04/0.02
Carbon monoxide [CO]	0.96/0.82	0.50/0.45	0.75/0.73	1.12/1.11	1.18/1.25
Carbon dioxide [CO ₂]	1.09/0.59	0.76/0.44	0.85/0.53	1.13/0.71	1.20/0.81

Table 2. Yield of the products per the passed feedstock of thermal pyrolysis of *n*-hexane–hexene-1 mixtures

Product	Yield of pyrolysis products, wt %, at an initial concentration of hexene-1 in feedstock materials, mol %				
	0	10	30	40	60
Ethylene	19.35	21.80	26.70	24.20	18.60
Propylene	9.30	10.80	14.40	14.40	14.20
Divinyl	0.95	1.40	2.90	3.90	4.20
Pyrogas	51.40	53.50	68.40	65.00	56.10
Condensate, including unconverted feed	48.60	46.30	30.60	32.10	38.90
Coke	—	0.20	1.00	2.90	5.00

particles, namely, hydrogen atoms and methyl radicals [8], is mainly *n*-hexane. In the presence of hexene-1, the formed hydrogen atom is attached at the site of the double bond of hexene-1 [in the diagram, directions

(6), (7)] [10]. This is evidenced by experimental data showing a marked decrease in the yield of molecular hydrogen in the presence of hexene-1 compared with the pyrolysis of individual *n*-hexane (Table 1).

Scheme 3. The main directions of thermal decomposition in the presence of hexene-1.

The participation of α -olefin in the nucleation of radical particles cannot be ignored under conditions of pyrolysis with an increased content of hexene-1. The reactions proceeding in directions (1)–(4) in the hexene-1 transformation scheme (Scheme 3) describe the formation of molecular products just in the case when the concentrations of hexene-1 and *n*-hexane in the initial mixture are comparable. Apparently, an increase in the yield of propylene and divinyl is a consequence of the formation of isomeric alkenyl radicals. The weakened C–H bond at the third carbon atom (353 kJ mol^{-1}) [14] determines the predominant formation of an alkylallyl radical, the decay of which leads to divinyl. The yield of divinyl increases with increasing hexene-1 content (Table 2). It should be noted that the yield of ethylene is somewhat reduced.

However, the addition of hexene-1 does not affect the yield and distribution of saturated hydrocarbons in the products. During the pyrolysis of the *n*-hexane–hexene-1 mixture, the yield of propane and *n*-butane is practically independent of the alkane/alkene molar ratio. Apparently, this is due to the fact that propane is formed at the stage of chain development, and *n*-butane, at the stage of termination by the reaction of recombination of ethyl radicals [10].

CONCLUSIONS

In the thermal pyrolysis of *n*-hexane in the presence of hexene-1, the yield of ethylene, propylene, and divinyl (butadiene-1,3) depends on the ratio of *n*-alkane : α -olefin in the initial mixture and takes the maximum value of 43 wt % at a temperature of 800°C , a conditional contact time of 0.2 s, and the mass ratio of water vapor : feedstock materials = 0.8 : 1.0, when the molar fraction of hexene-1 in the initial mixture is 0.36. In the presence of hexene-1, the yield of molecular hydrogen decreases compared to pyrolysis in an individual *n*-hexane medium, and the yield of saturated C₃–C₄ hydrocarbons to the passed feedstock is practically independent of the hydrocarbon ratio of the initial mixture. C₆–C₁₀ α -olefins, both individual and their mixtures, can be considered as an additive in pyrolysis feedstocks based on light naphtha from gas condensate to increase the yield of divinyl.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

REFERENCES

- Amghizar, I., Laurien, A.V., Van Geem, K.M., and Marin, G.B., *Engineering*, 2017, vol. 3, no. 2, pp. 171–

178. <https://doi.org/10.1016/J.ENG.2017.02.006>
2. Levin, V.O., Potekhin, V.M., and Kudimova, M.V., *Neftepererab. Neftekhimiya*, 2017, no. 6, pp. 28–36.
3. US Patent 3529032 (Publ. 1970). *Cracking of Olefins*.
4. CN Patent 103788989 (Publ. 2014). *Steam Cracking Method*.
5. CN Patent 103588608 (Publ. 2014). *Butadiene Preparation Method*.
6. DE Patent 1233846 (Publ. 1967). *A process for the Thermal Cracking of Olefins*.
7. CN Patent 103788989 (Publ. 2012). *A Kind of Steam Cracking Method*.
8. Shevelkova, L.V., Guselnikov, L.E., Bach, G., and Zimmermann, G., *Russ. Chem. Rev.*, 1992, vol. 61, no. 4, pp. 433–445.
<https://doi.org/10.1070/RC1992v06n04ABEH000955>
9. Magaril, E.R. and Magaril, R.Z., *Izv. Vuzov. Neft' Gaz*, 2018, no. 3, pp. 131–137.
<https://doi.org/10.31660/0445-0108-2018-3-131-137>
10. Yampol'skii, Yu.P., *Elementarnye reaktsii i mehanizm piroliza uglevodorodov* (Elementary Reactions and the Mechanism of Hydrocarbon Pyrolysis), Moscow: Khimiya, 1990.
11. Magaril, R.Z., *Mekhanizm i kinetika gomogennykh termicheskikh prevrashchenii uglevodorodov* (The Mechanism and Kinetics of Homogeneous Thermal Transformations of Hydrocarbons), Moscow: Khimiya, 1970.
12. Levin, V.O., Potekhin, V.V., Potekhin, V.M., Kholodnov, V.A., Meshkov, A.V., *Russ. J. Appl. Chem.*, 2019, vol. 92, no. 11, pp. 1537–1548.
<https://doi.org/10.1134/S1070427219110119>
13. Litvintsev, I.Yu., *Chem. J.*, 2006, no. 5, pp. 42–46.
14. Yang, F., Fuquan, D., Peng, Z., Erjiang, H., Yu, C., Zuohua, H., *Energy & Fuels*, 2016, vol. 30, no. 6, pp. 5130–5137. <https://doi.org/10.1021/acs.energyfuels.5b02910>