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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;

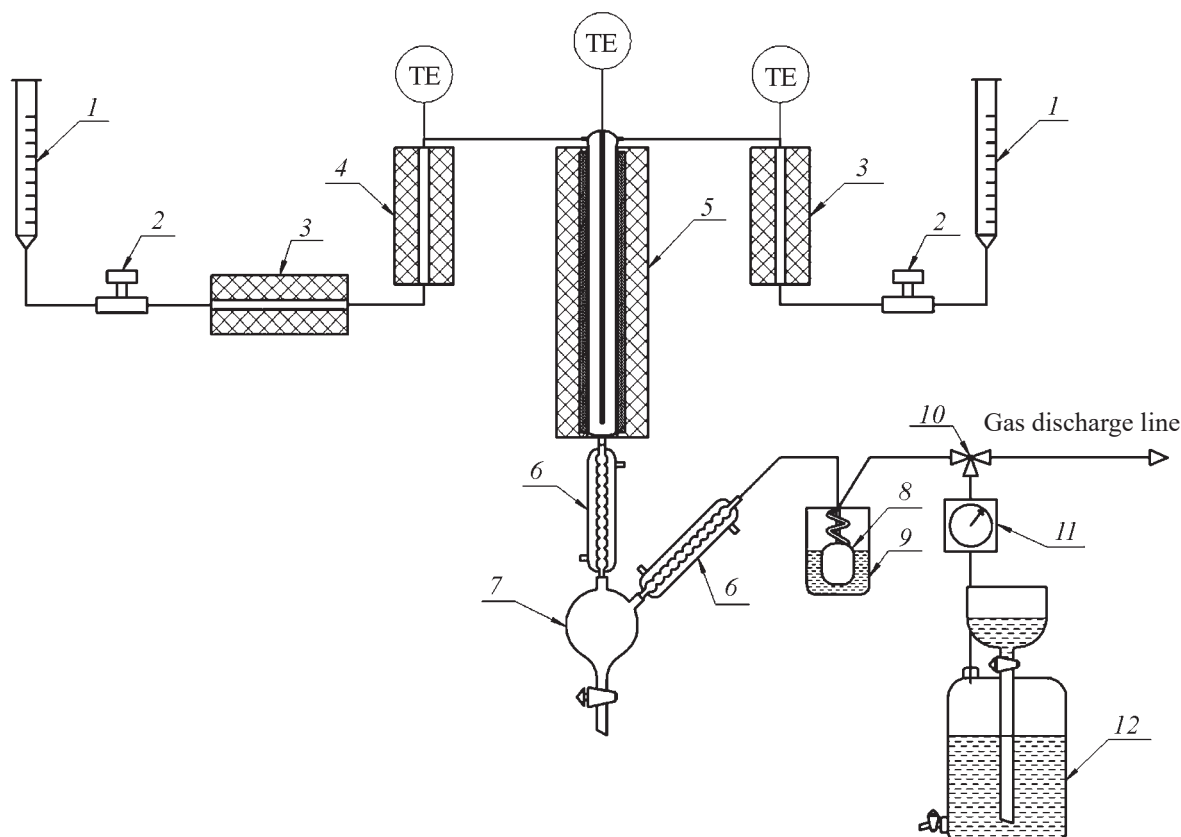


Fig. 1. Scheme of a laboratory setup for thermal pyrolysis of hydrocarbons. (1) Burette, (2) metering pump, (3) evaporator, (4) water vapor superheater, (5) reactor furnace, (6) reflux condenser, (7) receiving flask, (8) receiving trap, (9) Dewar vessel, (10) three-way valve, (11, 12) gas meters

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

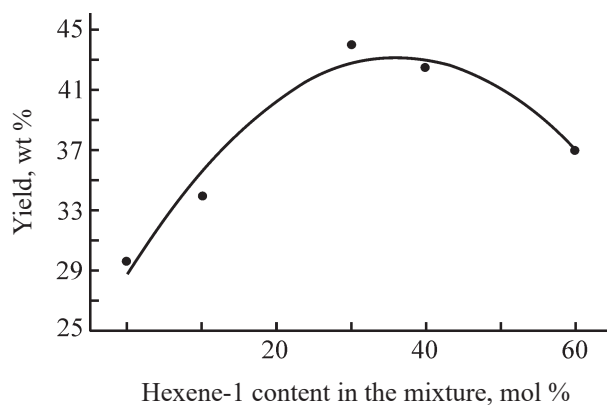


Fig. 2. The total yield of ethylene, propylene, and divinyl vs. the composition of the *n*-hexane–hexene-1 mixture.

with a pronounced maximum point. The maximum total yield of C_2 – C_3 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).

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