# Effect of Governing Parameters on Pyrolysis of Liquefi Petroleum Gases in the High-Temperature Heat Carrier

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**Abstract**—Detailed measurements of temperature and product distributions are carried out during the pyrolysis of liquefied petroleum gases in a model reactor where the inlet conditions of the feedstock/heat carrier fast mixing are realized. The developed theoretical process model involves the detailed kinetic scheme that is tested by the reference data and our experiments. The yield of the most valuable product of petrochemistry, ethylene, substantially increased as compared to the conventional furnace-pyrolysis method is the specific feature of the performed experiments results. By the results of the numerical simulation, the effect of temperature, pressure, and residence time in the reactor on the pyrolysis product composition is determined. The calculation results enable to optimize operation conditions for the fast-mixing reactor.

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# **INTRODUCTION**

Basic products of the modern petrochemical industry are lower olefins (ethylene, propylene) used in the production of plastics, synthetic filaments, rubber, etc. Ethylene and the most part of propylene are produced during the thermal decomposition of a number of high-molecular organic matters to the more useful products with the lower (generally) molecular weight. As a feedstock for pyrolysis production, liquid and gaseous hydrocarbons are used, namely, straight-run gasoline (naphtha), gas oils, ethane, propane, and butane. The feedstock mixture heated up to a temperature of  $\sim 820-900$  K with the water steam enters the inlet of a reaction coil mounted in a radiant section of a furnace. Due to heat supplied in from the coil walls, the temperature of the reacting flow increases up to 1100-1200 K at the outlet, where the maximum concentration of the most valuable petrochemistry product, ethylene, is attained. Next, the reacting flow rapidly cooled, after which the mixture enters into the fractioning, compressing, and gas separation units. The feedstock residence time in the reaction area depends on the maximum temperature of process and usually is a range of 0.1-0.5 s.

The efficiency of pyrolysis process is generally determined by consumptions of energy and feedstock. Papers [1, 2] cite typical specific energy consumption, and papers [3-5] cite the compositions of pyrolysis products. It follows from [3-5] that the efficiency of a pyrolysis unit (characterized by the yield of ethylene and propylene) is insignificant different despite the defined differences in the general process flow dia-

gram. Because the possibilities of intensifying the process in the framework of the conventional pyrolysis flow scheme are almost exhausted, interest is growing in alternative methods, of which the most prospective are, in our opinion, are the catalytic method and the feedstock pyrolysis in the high-temperature heat carrier. The first of them was recently realized in the highcapacity units [6, 7]; at the same time, the temperature level in a reactor decreased, the ethylene yield remained almost invariable, and the propylene yield significantly increased.

The other way for pyrolysis intensification that is generally directed to the ethylene yield increasing is associated with the temperature increase in the reaction area, which is impossible in frames of the method because of limitation in the heat resistance of coil tubes. However, this limitation can be overcome if heat to feedstock is supplied not from tube walls, but supplied directly by mixing the feedstock with the highenthalpy heat carrier, in which the heat storage is sufficient for the realization of pyrolysis at high temperatures. The key problem in this method is the mixing of the feedstock with the heat carrier that must occur very fast in order for the residence time of the feedstock in the high-temperature section of a mixer to be extremely small. Thus, one can to prevent or minimize the reactions role under uncontrolled (and nonoptimal) conditions before the reactor inlet.

Literature gives various methods of mixing the feedstock with the heat carrier [8-11]. For example, the mixing completely [10, 11] or partially [9] occurs in the supersonic flow at temperatures lower than the



Fig. 1. Flow diagram of pyrolysis process.

initial reaction temperature. When the mixing is over, the flow in the shock waves transits into the subsonic flow, and the temperature quickly increases up to a preset value. The All-Russian Research Institute of Organic Synthesis experiments [8] were carried out by the mixing the feedstock stream injection along the reactor axis.

In [12], we proposed another method for the feedstock pyrolysis in the high-temperature flow of the heat carrier. The method is based on the possibility for the short-term mixing of the feedstock with the heat carrier. The mixer geometry for operation in the mode of the impinging jets with the transverse flow was determined in a series of experiments [13] on a gasdynamic setup. The short-term mixing of the feedstock with the heat carrier made it possible to investigate liquefied petroleum gases pyrolysis at reactor inlet temperatures that exceed the maximum values in the conventional methods by 200 K. In this case, the ethylene yield increases significantly [14, 15].

The present work continues our study of liquefied petroleum gases pyrolysis in the fast-mixing reactor. Because conditions for the operation of the model setup do not completely correspond to the proposed flow diagram, process characteristics for conditions corresponding to real ones were determined with the use of a theoretical model tested by experimental results. The effects of main factors that determine the efficiency of the process on pyrolysis products, such as as temperature, pressure, and residence time, were also investigated.

#### **EXPERIMENT**

Figure 1 represents the flow diagram of the pyrolysis of hydrocarbons in the fast-mixing reactor, and Fig. 2 shows the schematic of the model setup. The combustion products of the stoichiometric fuel—oxygen mixture diluted by superheated steam, were used as the heat carrier in the proposed method. The pyrolyzed feedstock streams are injected into the subsonic flow along normal to the setup axis. The feedstock may be gas or preliminary evaporated liquid and, as the need arises (for enhancing the mixing quality), is injected into the reactor with superheated steam. The mixer geometry is chosen by the condition of the fast and qualitative mixing of the feedstock with the heat carrier, and the feedstock residence time in the reactor corresponds to obtaining the optimum pyrolysis product composition at the reactor outlet. Next, the pyrogas—steam mixture is quickly cooled in a heat exchanger.

The model experimental setup described in [14, 15] is intended for the investigation of hydrocarbon pyrolysis in the fast-mixing reactor. Its desin generally allows for the main features of the proposed process flow diagram. The general device units are the burner, combustion chamber, mixer, and reactor composed of two sections (40 and 80 mm in diameter and 1.15 and 1.52 m in length, respectively). The combustion chamber was cooled by water, and reactor walls were covered by a mullite wool layer 10 mm in thickness. All parts of the device are made of stainless steel. The diameter of the mixer is 15 mm. The feedstock stream was injected through eight orifices 0.75 mm in diameter. Thermocouples and water-cooled samplers were arranged along the reactor. The reactor pressure was close to atmospheric.

To choose the mixing chamber geometry, we use the results of an investigation of the mixing quality of jets with the transvers flow in a cylindrical channel [13]. The base was the mixer variant with a high uniformity of the resulting flow that is attained at a short distance, namely, at the relative length L/D = 1, where L and D are the length and diameter of the mixer channel. The mixer diameter was decreased compared with the before investigated variant [14] of the mixing chamber from 40 to 15 mm, and the relative mixer sizes (d/D and S/d), where d and S are the diameter and the orifice spacing) remained invariable. At the same time, we proceed based on the following considerations. The decrease in the channel diameter D for geometrically similar mixers at the same parameters of the main and injected flow makes it possible to shorten the mixing time because the absolute length of the mixing area (at invariable L/D) decreases and the average flow rate in the mixer channel increases.

The second circumstance also taken into account when selecting the geometry of the mixer was the need to provide the momentum ratio of the jet and the main



Fig. 2. Schematic of experimental fast-mixing reactor.

flow under mixer operation in the pyrolysis device so that streams impinged at the channel axis. As was shown in [13], this condition has been necessary for all investigated mixer variants when there has been a need to shorten the extent of the mixing area. The area-weighted mean-square deviation of the injected substance concentration from the average value was ~4% at h/D = 0.5 and continued to decrease with a rise in h/D [13]. Here, h/D is considered to be a "jet penetration parameter", where h is the jet penetration depth in the unconfined transverse flow that is calculated by the known empirical relationship [16].

Thus, it was believed that the flow ununiformity for geometrically similar mixers at the equal "jet penetration parameters" was also equal at a distance equal to L/D.

The h/D parameter under the conditions of reactor operation was in the range of 0.45–0.55. In order to verify the validity of our approach to the mixer geometry choice, we investigated the degree of uniformity for the flow at the mixer outlet, which was mounted to the combustion chamber. The temperature at the mixer inlet was approximately the same as in the main experiment series, but the injected gas was nitrogen instead of the feedstock. Measurements were carried out in the plane L/D = 1 from the injection point. The nitrogen stream parameters corresponded to the jet penetration parameter h/D = 0.45. Thus, we provided the geometrical and dynamic similarity of processes in mixers, one of which was investigated on the gasdynamic setup, while the second one was used on the model pyrolysis setup. In this case, the injected substance concentration fields in the cross section of the channel at a distance of L/D = 1 were found to be close, as well as the mean-square deviations from the mean value, i.e., 4.5% on the gas-dynamic model and 2.5% in the reactor mixer. Taking (assumed) the mixing area dimension L/D = 1, one can evaluate the mixing time using the average flow rate in the mixer channel. This value under conditions of these experiments is approximately 0.05 ms. The feedstock heating rate determined by the ratio of the temperature difference at the mixer outlet and inlet to the mixing time is around  $10^7$  K/s. The experiments described below were carried out with a mixture of liquefied petroleum gases as the pyrolized feedstock with the following composition:  $C_3H_8$ , 71.3%; *n*- $C_4H_{10}$ , 4.1%; *iso*- $C_4H_{10}$ , 4.2%;  $C_2H_6$ , 19.7%;  $C_3H_6$ , 0.3%;  $C_4H_8$ , 0.4%. The pyrolysis product composition was determined by a Crystall-2000 H chromatograph equipped by a thermal conductivity detector. The flow temperature was measured by type K thermocouples with a thermojunction diameter of 0.7 mm. The thermocouple readings were corrected for thermojunction emission.

# EXPERIMENT RESULTS AND COMPARISON WITH SIMULATIONS

Let us further consider results of the experiment in which the highest ethylene yield was revealed. The design temperature at the mixer inlet was  $T_0 = 1750$  K in the experiment. The flow temperature at the mixer outlet was determined by heat balance on the assumption of the inert mixing of the feedstock with the heat carrier. Its value under conditions of this experiment was  $T_{\text{inert}} = 1400$  K; at the same time, the heat carrier/feedstock ratio was 13.3.

The distribution of mass concentrations for main products and flow temperature along the reactor axis is shown in Fig. 3. The coordinate x = 0 on the upper axis corresponds to a distance of 15 mm (x/D = 1) from the place of the injection of feedstock streams; the lower axis shows the mixture residence time in the reactor. The total composition of the pyrolysis products in the point where the ethylene concentration is maximal is listed in the table. The CO<sub>2</sub> mass concentration in the same section is 0.007, and the CO presence in the mixture is not revealed. Apart from experimental data, the table lists the total content of components undetermined by chromatograph, but was found by calculations.

The data of Fig. 3 demonstrate the extremely fast pyrolysis rate determined by the high temperature at the reactor inlet. The main change in the pyrolysis product composition is observed in a temperature range of 1400-1200 K for  $\sim 20$  ms and, next, the

Components	Mass fraction
H <sub>2</sub>	0.033
CH <sub>4</sub>	0.114
$C_2H_2$	0.065
$C_2H_4$	0.473
$C_2H_6$	0.079
$C_3H_6$	0.073
$C_3H_8$	0.058
$C_4$	0.014
Residual*	0.091

Pyrolysis products composition

\* Calculation.

dependences  $C_i(t)$  becomes distinctly smooth. It should be noted that the temperature distribution along the reactor axis is affected by the relatively small flow ununiformity at the mixer outlet and the heat boundary on the walls. However, in this case, because the main processes in the reacting flow occur in the initial part of the reactor, heat to the wall, which results in a decrease in the axial temperature, is favorable to the deceleration of the reaction in the lower temperature region.

Apart from the experimental investigation, the numerical simulation of process was carried out. The



**Fig. 3.** Distribution of temperature and mass concentrations of products along reactor axis at  $T_{\text{inert}} = 1400 \text{ K}$ , g = 13.3: (1, e) temperature (points are experiment; and line, approximation); (2–5, a–d) concentrations (lines is calculation; and points, experiment: (2, a) C<sub>2</sub>H<sub>4</sub>; (3, d) CH<sub>4</sub>; (4, b) C<sub>3</sub>H<sub>6</sub>; and (5, c) C<sub>3</sub>H<sub>8</sub>.

kinetic scheme was chosen by the results of testing three models and included 80 [17], 776 [18], and 689 [19] reactions with 30, 99, and 155 particles, respectively. The simulation results were compared with experimental date on pyrolysis of ethane within a shock-wave reactor [11], in which the temperature and pressure profiles used in our calculations were also given in addition to the distribution of the concentration of the pyrolysis product along the reactor axis. The best results were obtained with the kinetic scheme [19]. The comparison of simulation with experimental data [11] shows agreement [12]. In further calculations, we used this kinetic model.

The calculation began from the distance x/D = 1 (15 mm) from the feedstock injection point. The flow in this cross-section was considered to be completely mixed. In addition, it is believed that the reactions do not have time to begin during mixing. With allowance made for these assumptions, one can determine the initial design temperature ( $T_{inert}$ ) by the heat balance equation subject to the experimentally measured heat flux to the combustion chamber walls. The further temperature history corresponds to the measuring results. For simulation we used the CHEMKIN-II software package [20].

The data in Fig. 3 make it possible to analyze the correctness of the calculation method used. Its accuracy is determined not only by the reliability of the chosen kinetic model, but also by that assumptions of the inert mixing and the flow uniformity at the reactor inlet are to what extent correct. Based on a comparison of the experimental data and the numerical simulation of the process, it follows that the calculation method used as a whole fairly well describes the change in the concentrations of the main components, the content of which in the mixture changes in a wide range. To a great extent, this is true with regard to ethylene and methane; the experimental propane concentration is somewhat higher than the calculated concentration, while and the concentration of propylene is somewhat lower. The difference is also observed for C<sub>4</sub> components, but their content in the mixture is small. As a whole, taking into account the simplicity of the calculation method, the accepted assumptions, and the uncertainty of some constants of the kinetic scheme, one can consider the agreement of the design model with the calculation to be reasonable. Furthermore this theoretical model is used to analyze the effect of governing parameters upon the efficiency of the pyrolysis process.

#### PARAMETRIC ANALYSIS

Let us first estimate the effect of heat transfer to the experimental reactor wall (and the temperature history transforming with that) upon the pyrolysis product composition. For the purpose of that, we carried out calculations with the assumption of the complete heat insulation of walls (adiabatic reactor) under the



**Fig. 4.** Comparison of calculation results for adiabatic reactor (dotted lines) and calculation with the experimental temperature profile (solid lines) at  $T_{inert} = 1400$  K, g = 13.3: (1, 2, e) temperature (1)  $T_{ad}$ , (e)  $T_{exp}$ , (2) approximation); (3–6, a–d) concentrations (lines are calculation; and points, experiment: (3, b) C<sub>2</sub>H<sub>4</sub>; (4, c) CH<sub>4</sub>; (5, a) C<sub>2</sub>H<sub>2</sub>; and (6, d) C<sub>3</sub>H<sub>6</sub>.

conditions of the experiment, the results of which were shown in Fig. 3. As before it was believed that the instantaneous mixing the feedstock with the heat carrier and the initial data (composition and mixture mass flow and temperature  $T_{inert}$ ) were the same as in the calculations with the experimental profile T(x). A comparison of the results of calculating the adiabatic reactor and the calculations with the temperature distribution represents in Fig. 4, which shows the corresponding profiles of temperatures and concentrations for some reacting mixture components. The graph also contains the results of measurements taken under our experimental conditions. The data of Fig. 4 reflect a significant difference in the experimental temperature profile from the profile in the adiabatic reactor, and this difference increases downstream. The difference in temperature profiles is relatively small in the initial stage, in the region of high temperatures; this is the region of parameters where the main amount of ethylene forms. Here, the calculation results for the ethylene concentration nearly coincide, and the experiment well agrees with the calculation data. Next, over time,  $T_{ad}$  remains at a high level, as a result of which the ethylene concentration in the adiabatic reactor gradually begins to decrease. The effect of the temperature history on the profiles of other mixture components is more significant. Because of the higher temperature in the adiabatic reactor, the methane and acetylene concentrations are higher, and the propy-



**Fig. 5.** Temperature history in real heat carrier flow at  $T_{\text{inert}} = 1500 (I)$ , 1400 (2), and 1300 (3) K.

lene concentration level lower than in the reactor with heat losses. On the other hand, a decrease in the temperature level relative to  $T_{ad}$  at  $t \ge 0.01$  s favors to the deceleration of reaction rates, which is found in both the experiment and the calculations with the experimental temperature profile.

Let us consider further the effect of governing parameters on the hydrocarbon pyrolysis in the heat carrier flow. For furnace pyrolysis, these parameters are the feedstock composition, temperature (or more exactly the temperature history), pressure, ratio of dilution steam/feedstock, and residence time in the reactor. In the case of pyrolysis in the heat carrier flow by our proposed flow diagram (see Fig. 1), in addition to the aforementioned parameters (substituting the heat carrier/feedstock ration for the dilution steam/feedstock one), the mixing time  $t_r$  for the feedstock with the heat carrier assumes the significance.

In turn, the optimum value must depend on the temperature at the mixer inlet and the temperature at its outlet, i.e., on some characteristic temperature in the mixing area. For the more severity process conditions, the less the value of  $t_r$  needed to prevent reactions or minimize the role of reactions in high-temperature zones of the mixing area. Ideally, one should tray to achieve an inert character of mixing the feed-stock with the heat carrier.

To perform the parametric analysis of the efficiency of the considered pyrolysis method, except for the experimental study on the model facility (the results are presented in [15]), a series of calculations were done for the conditions of the facility operation with the real heat carrier, i. e. products of combustion of the stoichiometrical methane-oxygen mixture diluted by



**Fig. 6.** Calculation results for propane pyrolysis in real heat carrier flow at  $T_{\text{inert}} = 1300 \text{ K}$ , g = 2.3: (1) (C<sub>2</sub>H<sub>4</sub> + C<sub>3</sub>H<sub>6</sub>)<sub>rec</sub>, (2) C<sub>2</sub>H<sub>4</sub> + C<sub>3</sub>H<sub>6</sub>, (3) C<sub>2</sub>H<sub>6</sub>, (4) C<sub>3</sub>H<sub>8</sub>, (5) C<sub>3</sub>H<sub>6</sub>, and (6) C<sub>2</sub>H<sub>4</sub>.

superheated steam. The dilution steam temperature is accepted to be 500 K. The steam mass flow rate supplied into the combustion chamber was chosen from the condition of achieving a temperature of  $T_0 = 1900$  K at the mixture inlet. Propane as feedstock was chosen with an initial temperature of 300 K, and the oxygen temperature is also 300 K. As was done previously, mixing the feedstock with the heat carrier was assumed instantaneous. The propane mass flow rate corresponds to the inert mixing temperature  $T_{inert} = 1200$ , 1300, 1400, and 1500 K for the feedstock/ heat carrier mass flow ratio of g = 1.7, 2.3, 3.4, and 4.4, respectively.

It should be noted that the value of  $T_0$  accepted for calculations appears to be as a limiting case by experimental results on the model setup because a further increase in  $T_0$  at the actual value  $T_{inert}$  does not result in an increase in the olefin yield. Thereby, the mixture temperature at the mixer inlet determines the steam/combustion product ratio; and  $T_{inert}$  determines the heat carrier/feedstock ratio. The accepted range of  $T_{\text{inert}}$  corresponds to the investigated range on the model setup operating condition. At the same time, the mixer geometry used in the experiment makes it possible to achieve conditions close to inert mixing. At  $T_0$  and  $T_{\text{inert}}$  accepted for calculations, the conditions of mixer operation are more favorable for achieving fast and qualitative mixing because the jet penetration parameter greater than in the experiment with the maximum olefin yield ( $T_0 = 1750$  K,  $T_{inert} = 1400$  K, g = 13.1). As was shown by our experiments [13], at invariable mixer geometry, an increase in the jet penetration parameter, which is resulting from in the actual case by an increase in the ratios of flow rates (momentum) of injected streams to the main flow results in an



**Fig. 7.** Calculation results for propane pyrolysis in real heat carrier flow at  $T_{\text{inert}} = 1400 \text{ K}$ , g = 3.1: (1) (C<sub>2</sub>H<sub>4</sub> + C<sub>3</sub>H<sub>6</sub>)<sub>rec</sub>, (2) C<sub>2</sub>H<sub>4</sub> + C<sub>3</sub>H<sub>6</sub>, (3) C<sub>2</sub>H<sub>6</sub>, (4) C<sub>3</sub>H<sub>8</sub>, (5) C<sub>3</sub>H<sub>6</sub>, and (6) C<sub>2</sub>H<sub>4</sub>; points are experiment with model hear carrier at  $T_{\text{inert}} = 1400 \text{ K}$ , g = 13.3: (a) C<sub>2</sub>H<sub>4</sub> + C<sub>3</sub>H<sub>6</sub>, and (b) (C<sub>2</sub>H<sub>4</sub> + C<sub>3</sub>H<sub>6</sub>)<sub>rec</sub>.

improved mixing quality. In this case, the mixing time is ~0.05 ms in our experiment [15], which is sufficient to achieve conditions for mixing the feedstock with the heat carrier, at which the effect of reactions in the mixing area on the pyrolysis process flow can be neglected (at a first approximation). Thus, the mixer geometry used in our experiments must provide the realization of the accepted assumption on the inert mixing character and the flow uniformity at the reactor inlet.

Let us consider at first effect of the temperature  $T_{\text{inert}}$  on the pyrolysis process flow. In these calculations, the pressure in the reactor is accepted to be



**Fig. 8.** Calculation results for propane pyrolysis in real heat carrier flow at  $T_{\text{inert}} = 1500 \text{ K}$ , g = 4.4: (1) (C<sub>2</sub>H<sub>4</sub> + C<sub>3</sub>H<sub>6</sub>)<sub>rec</sub>, (2) C<sub>2</sub>H<sub>4</sub> + C<sub>3</sub>H<sub>6</sub>, (3) C<sub>2</sub>H<sub>4</sub>, (4) C<sub>2</sub>H<sub>6</sub>, (5) C<sub>3</sub>H<sub>8</sub>, and (6) C<sub>3</sub>H<sub>6</sub>.



**Fig. 9.** Maximum olefin yields vs. temperature: (1)  $(C_2H_4 + C_3H_6)_{rec}$ , (2)  $C_2H_4 + C_3H_6$ , and (3)  $C_2H_4$ .

0.1 MPa. The residence time dependences of the reacting flow temperature at various temperatures at the reactor inlet are shown in Fig. 5. All of the calculation variants reveal a rapid decrease in the temperature. Furthermore, the rate of the temperature change decreases and, and at large value of t, the pyrolysis process proceeds under almost isothermal conditions.

Figures 6–8 represent calculation results that illustrate the effect of the initial temperature on the yield of the most valuable pyrolysis products, i.e., ethylene and propylene. In addition, the graph demonstrates the concentration profiles for propane and ethane, which are considered to be the recycle flow components, as well as using the conventional pyrolysis method. Figures 6–8 also show the history of the total ethylene and propylene concentration, as well as with allowance made for the recycling of  $C_2H_6$  and  $C_3H_8$ . At the same time, the efficiency of ethane was considered the same as for propane, i.e., it is believed that  $(C_2H_4 + C_3H_6)_{rec} =$  $(C_2H_6 + C_3H_6)/(1 - C_2H_6 - C_3H_8)$ .

In addition to the calculation data, Fig. 7 presents the total concentrations of  $C_2H_4$  and  $C_3H_6$ , including with regard to the recycling of  $C_2H_6$  and  $C_3H_6$ , which were obtained in the experiment with the model heat carrier (combustion products of the air-hydrogen mixture). In this case, the effect of the heat carrier composition on the total concentration of lower olefins is relatively small.

As in experiments with the model heat carrier, calculations predict an abrupt increase in the concentration of ethylene and propylene at the initial range of the pyrolysis process, and the maximum concentration of  $C_3H_6$  is attained far earlier than the maximum concentration of  $C_2H_4$ . The initial temperature of the flow strongly affects on the time of attaining the maximum of ethylene concentration, i.e., from ~700 ms at  $T_{inert} = 1300$  K up to ~5 ms at T = 1500 K. At the same time, the time for attaining the maximum concentra-



**Fig. 10.** Olefin yield at P = 0.1 MPa (solid lines) and 1.0 MPa (dotted lines) at  $T_{\text{inert}} = 1300$  K, g = 2.3: (1) C<sub>2</sub>H<sub>4</sub> + C<sub>3</sub>H<sub>6</sub>, (2) C<sub>2</sub>H<sub>4</sub> and (3) C<sub>3</sub>H<sub>6</sub>.

tions of the olefins sum varies in a narrower range, i.e., from ~1 ms at T = 1500 K up to ~120 ms at T = 1300 K. A reduction in the contribution of the recycle flow in the total concentration of lower olefins should be noted with an increase in the residence time in the reactor because the propane conversion degree increases quickly, and the ethane concentration is small and varies weakly over time.

The data in Fig. 9 generalize the calculation results represented in Figs. 6–8 and show the effect of the initial temperature on the main characteristics of the pyrolysis process. Maximum yields of  $C_2H_4$  and  $C_2H_4 + C_3H_6$  are mismatched because of the different character of the history of  $C_2H_4$ ,  $C_3H_6$ ,  $C_2H_6$ , and



Fig. 11. Maximum olefin yields vs. pressure at  $T_{\text{inert}} = 1300 \text{ K}$ : (1)  $(C_2H_4 + C_3H_6)_{\text{rec}}$ , (2)  $C_2H_4 + C_3H_6$ , and (3)  $C_2H_4$ .

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 $C_3H_8$  concentrations at different temperatures. The total olefin concentration increases almost linearly with a rise in temperature. The data in Fig. 9 make it possible to determine the optimum initial temperature  $T_{\text{inert}} \approx 1400$  K, which corresponds to the maximum of the olefin sum concentration (0.577). With allowance made for the recycle of ethane and propane, this value increases to 0.641.

In addition to temperature, the pressure effect on the pyrolysis process for propane was studied. Calculations were carried out at a pressure of 0.1, 0.5, and 1.0 MPa in the reactor. The initial temperature is accepted to be 1300 K. Figure 10 shows the change in concentration for ethylene, propylene, and their sum in the wide range of the residence time in the reactor. As is evident, the ethylene concentration is stronger dependent on pressure, which increases as the residence time increases. However, the data difference at P = 0.1 and 1.0 MPa is small in the range of t, where the total olefin concentration is close to maximum. Data in Fig 11, which shows the change in concentrations of  $C_2H_4$ ,  $C_2H_4 + C_3H_6$ , and olefin sum with the consideration of recycle (in the point of the maximum of  $C_2H_4 + C_3H_6$  sum), show the weak effect of pressure upon the total olefin concentration.

# **CONCLUSIONS**

The present paper represents results of the experiment and modeling of the pyrolysis process for propane in the high-temperature flow at the ultra-short time of mixing the feedstock with the heat carrier. The effect of the heat carrier composition, temperature, pressure, and residence time in the reactor on the pyrolysis product yields was investigated.

The calculation results based on the method tested by experimental data predict the high efficiency of the pyrolysis process in the fast-mixing reactor for realistic conditions of the practical realization. The presence of maximums on the dependences of the ethylene and propylene concentrations on the initial mixture temperature is shown. The calculation at this optimum temperature of 1400 K predicts the high selectivity of the process in the fast-mixing reactor with a total ethylene and propylene concentration of 0.571 and with allowance made for the propane and ethane recycle in a concentration of 0.641. According to the calculations, the effect of pressure on the olefin yield in the pressure range of 0.1-1.0 MPa is small.

# NOTATION

- *C*—mass concentration;
- *D*—mixer channel diameter, m;
- *d*—mixer orifice diameter, m;
- *g*—heat carrier/feedstock;
- h—jet penetration depth, jet penetration parameter, m;
- *L*—mixer channel length, m;

P—pressure, MPa; S—orifice spacing, m; T—temperature, K; t—time, ms;

*x*—coordinate, m.

# SUBSCRIPTS AND SUPERSCRIPTS

0—corresponds to conditions at the mixer inlet; ad—adiabatic process;

i—mixture component;

inert—corresponds to conditions of inert mixing the

feedstock with the heat carrier;

r-chemical reaction;

rec-recycle.

# REFERENCES

- Ren, T., Patel, M.K., and Blok, K., Steam cracking and methane to olefins: energy use, CO<sub>2</sub> emission and production costs, *Energy*, 2008, vol. 33, p. 817.
- 2. Ren, T., Patel, M.K., and Blok, K., Olefin from conventional and heavy feedstock: energy use in steam cracking and alternative processes, *Energy*, 2006, vol. 31, p. 425.
- 3. Bowen, C.P., Stone and Webster ethylene technology, in *Handbook of Petrochemicals Production Processes*, Meyers, R.A., Ed., New York: McGraw-Hill, 2005, p. 6.21.
- Borsos, S. and Ronczy, S., KBR Score<sup>TM</sup> ethylene technology, in *Handbook of Petrochemicals Production Processes*, Meyers, R.A., Ed., New York: McGraw-Hill, 2005, p. 6.51.
- 5. Zimmermann, H. and Walzle, R., Ethylene. http://media.wiley.com/product\_data/excerpt/55/352 73038/3527303855.pdf
- VNIIOS, Catalytic pyrolysis of petroleum fractions to produce ethylene and propylene, 2003. http:// www.vniios.ru/english/1.htm
- Tallman, M., ACO<sup>TM</sup>, The Advanced Catalytic Olefin Processes. http://technologyconference.kbr.com/ 2009/Dubai/conference
- 8. Mukhina, T.N., Barabanov, N.L., Babash, S.B., Men'shchikov, V.A., and Avrekh, G.L., *Piroliz uglevodorodnogo syr'ya* (Pyrolysis of Hydrocarbon Feddstocks), Moscow: Khimiya, 1987.
- 9. Baldwin, R.L. and Kamm, G.R., Make ethylene by ACR process, *Hydrocarbon Process.*, 1982, vol. 61, no. 11, p. 127.
- 10. Hertzberg, A., Mattick, A.T., and Russel, D.A., US Patent 5300216, 1993.
- 11. Mattick, A.T., Knowlen, C., Russel, D.A., and Hertzberg, A., Pyrolysis of hydrocarbons using a shock wave reactor, *Proc. 21st Int. Symp. on Shock Waves*, Great Keppel Island, Australia, 1997.
- 12. Ktalkherman, M.G. and Namyatov, I.G., Pyrolysis of hydrocarbons in a heat-carrier flow with fast mixing of the components, *Combust., Explos. Shock Waves*, 2008, vol. 44, p. 529.

- 13. Ktalkherman, M.G., Emel'kin, V.A., and Pozdnyakov, B.A., Influence of the geometrical and gasdynamic parameters of a mixer on the mixing of radial jets colliding with a crossflow, *J. Eng. Phys. Thermophys.*, 2010, vol. 83, p. 539.
- 14. Ktalkherman, M.G., Namyatov, I.G., Emel'kin, V.A., and Pozdnyakov, B.A., Investigation of high-temperature pyrolysis of propane in a fast-nixing reactor, *High Temp.*, 2009, vol. 47, p. 707.
- 15. Ktalkherman, M.G., Namyatov, I.G., and Emel'kim, V.A., High-temperature pyrolysis of lique-fied petroleum gases in fast-mixing reactor, *Int. J. Chem. Reactor Eng.*, 2011, vol. 9, paper A69.
- 16. Ivanov, Yu.V., *Principles of Calculation and Design of Gas Burners*, Moscow: Gostoptekhizdat, 1963.
- 17. Marinov, M., Pitz, W.J., Westbrook, C.K., Vincitore, A.M., Castaldi, M.J., and Senkan, S.M., Aromatic and polycyclic aromatic hydrocarbon forma-

tion in a laminar premixed *n*-butane flame, *Combust. Flame*, 1998, vol. 114, p. 192.

- Westbrook, C.K., Pitz, W.J., Herbinet, O., Curran, H.J., and Silke, E.J., A detailed chemical kinetic reaction mechanism for *n*-alkane hydrocarbons from *n*-octane to *n*-hexadecane, *Combust. Flame*, 2009, vol. 156, p. 181.
- Pitz, W.J., Naik, C.V., Mhaolduin, T.N., Westbrook, C.K., Curran, H.J., Orme, J.P., and Simmie, J.M., Modeling and experimental investigation of methylcyclohexane ignition in a rapid compression machine, *Proc. Combust. Inst.*, 2007, vol. 31, p. 267.
- Kee, R.J., Rupley, F.M., and Miller, J.A., CHEMKIN-II: A Fortran Chemical Kinetics Package for the Analysis of Gas-Phase Chemical Kinetics, Livermore, Calif.: Sandia Nat. Lab., 1989.

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