STUDY OF THE HIGH-TEMPERATURE PYROLYSIS OF PROPANE IN THE FAST-MIXING REACTOR

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We studied the hitherto proposed method of hydrocarbons pyrolysis in a flow of a high-temperature heat carrier, wherein the pyrolyzed feedstock jets are injected by the normal to the reactor’s axis. The fundamental schematic of the process is presented. The experimental facility developed in accordance with the proposed concept is described. The experiments were performed with the propane as pyrolyzed feedstock, and products of hydrogen-air mixture combustion used as the heat carrier. The results of experiments and numerical simulation demonstrated the promising future of the developed method of pyrolysis. As the initial mixture temperature was increased up to 1400 R, the yield of ethylene increased essentially comparing to the traditional pyrolysis method. The required length of reactor reduced about one order.

In [1, 2] the new model of the high-temperature pyrolysis of hydrocarbons in the high-temperature heat carrier flow is proposed. The heat accumulated in the heat carrier should be enough to enable endothermic reactions (producing lower olefins) within the high temperatures range, which is unattainable in the traditional furnace-pyrolysis method [3 – 5] due to the temperature limitations of furnace tubing materials. According to the available data [5 – 8], the transition into the high-temperature region (T ≥1200 K) combined with the shorter residence time results in the higher yield of the major desired product – ethylene.

The present investigations differ from the known researches [5 – 8] by the method of working medium formation, namely, this medium forms due to the mixing of feedstock jets injected transversally to the reactor’s axis, and the heat carrier. Because of the higher temperature, the reaction time reduces dramatically. In these conditions, the mixing problem becomes critically important for the developed method, since the mixing time must be extremely small – much less than the time of maximum ethylene yield achievement.

Special attention was focused on the solution of this problem. The process of mixing of impacting jets with the transversal gas stream was studied on the model gas-dynamic facility within the wide range of governing parameters. The experimental results [9] showed the possibility of fast formation of the uniform feedstock-heat carrier mixture in the assumed parameters range.

The fundamental schematic of the process considered in the present paper is shown in Fig. 1. The products of fuel-oxygen mixture combustion diluted with water steam are used as a heat carrier gas. The mixture components in the stoichiometric ratio are supplied into the burner in the combustion chamber. The temperature at the combustion chamber output is controlled by the injected water steam. Gas jets of the pyrolyzed feedstock are injected into the heat carrier flow by the normal to the reactor’s axis. The feedstock may be either a gas or pre-evaporated liquid, and, if necessary, may be inserted into the reactor mixed with the water steam. The injection unit geometry should guarantee fast and qualitative mixing of the feedstock and heat carrier, and reactor’s channel geometry should satisfy the requirement of such a mixture residence time which corresponds to the maximum yield of the desired product. Similarly to the tradition method of furnace tubing pyrolysis, the mixture of pyrogas and water steam should be cooled quickly to avoid the desired
products losses. The way of utilization of the heat remaining in the flow is the same as in the traditional method of pyrolysis. Gas separation model also remains the same.

Fig. 1. Fundamental schematic of the process

To study the realizability of the proposed method of pyrolysis, we manufactured an experimental facility – a reactor of fast feedstock and heat carrier mixing. The main units of the facility which is schematically shown in Fig. 2 are: a burner, combustion chamber, mixer, reactor and system of gases injection. The fuel (hydrogen) and oxidizer (air) are injected separately into the burner (a cylinder of 40 mm in diameter and with a semispherical end-face). The mixture is ignited with a spark plug. Hydrogen flow rate in each experiment was 5 – 6% higher than the stoichiometric value, to provide full oxygen expenditure in the reactions with hydrogen. To control the temperature, either nitrogen or oxygen can be supplied into the air line. The combustion chamber is made as a cylinder with the inner diameter of 40 mm and length of 170 mm. Between the burner and combustion chamber there is a hollow diaphragm with the inner diameter of 19 mm. Its role is twofold. First, it is a peculiar “flame holder”. In the extended recirculation zone, where the flow turbulence degree is high, the reacting mixture components are extra mixed, which stimulates higher fuel combustion efficiency. Second, such a device enables to equalize the gas-dynamic parameters distribution at the channel cross section owing to the flow turbulization below the reattachment region. As a result, the temperature profile nonuniformity at the distance of 35 mm from the combustion chamber exit (outside the boundary layer) did not exceed ± 5%.

The mixing chamber is made with 8 nozzles, their axes are perpendicular to the main stream axis. The output diameter of the nozzles is 1.8 mm. The inner diameter of the mixing chamber is 35 mm. The gas was supplied to the mixer’s nozzles from a collector by individual pipes. To provide the uniform gas injection by the nozzles, there was a critical orifice in each line. In some experiments, to improve the mixing quality (to increase the jet penetration parameter), the pyrolyzed gas was diluted with nitrogen.

![Fig. 2. Schematic of the experimental facility to study the high-temperature pyrolysis of hydrocarbons](image-url)
The reactor presented a tube of 40 mm in diameter and 1,500 mm in length. The sealed inlets set over the whole reactor’s length were intended to locate the thermocouples and samplers. All units of the facility are made of stainless steel. The burner, diaphragm, and combustion chamber were cooled with water. The mixer was not cooled. The reactor’s walls were thermally insulated with a layer of mullite wool.

The mixture of the heat carrier and combustion products was exhausted into atmosphere through an exhaust pipe. The pressure in the reactor approached to atmospheric.

During the experiment, the temperature distribution along the reactor’s axis was measured, as well as the flow rates of the gases entering into the burner and combustion chamber. Gas samples were collected from six stations along the reactor. The flow rates of air, hydrogen, nitrogen, and pyrolyzed gas were determined with the critical orifice flow meters. Samples were analyzed in gas chromatograph Kristall-2000H. The sampler was a copper tube of 6 mm in diameter, with a capillary of stainless steel insider, its diameter was 1 mm. The nose of the capillary was square-bent and entered in the hole in the tube and then was soldered flush with the wall. The capillary orifice was directed toward the flow. The sampler was entered into the reactor’s channel through two sealed inlets situated on the opposite channel’s sides. The capillary was cooled with the water flowing by the tube. Hence, the pyrogas content was frozen in the capillary. The samples were taken into medical syringers of 150 ml. Concentrations of the following pyrogas components: CH₄, C₂H₆, C₂H₄, C₃H₆, i-C₄H₁₀, n-C₄H₁₀, C₄H₈, CO, CO₂, H₂ were determined.

The flow temperature was defined with the chromel-alumel thermocouples coated with a ZrO₂ film. The diameter of the thermocouple (with the coating) joint was 0.7 mm.

To find the actual flow temperature, the correction for the joint emission was introduced. The correction factor was computed by the heat-balance equation for the thermocouple joint. The values of zirconium oxide emissivity, needed for the computation, are given in [10].

At the first stage of researches, the mixture chosen mainly consisted of propane. The mass content of the mixture was such: C₃H₈ – 86.8%, C₂H₆ – 2.8%, C₄H₁₀ – 10.4% (later on this mixture will be called the propane). Such a choice results from, on the one hand, relative simplicity of the pyrolysis kinetics, and, on the other hand, – no experimental data in the literature for the propane pyrolysis at high temperatures.

The experiment was performed as follows. First, nitrogen was supplied into the mixer. It was necessary to prevent the thermocouples damage, since the temperature at the combustion chamber input was above the top limit of a chromel-alumel thermocouples effective range. Then, the components of the fuel-air mixture were injected into the combustion chamber and, upon the ignition, the pre-determined flow-rates of hydrogen, air, and nitrogen were set-on. The stationary regime onset was monitored by the thermocouples data and was usually of about 10 minutes. Within this time, the reactor’s wall and heat insulation layer were heated up. Then, the required flow-rates of propane and nitrogen through the mixer were established, and in 2 – 3 minutes we began pyrogas sampling. The temperature distribution along the reactor’s axis at this period was constant. The cooling water flow rate was also constant within the whole experiment, as well as the temperature difference at the input and output of the cooling contour, which provided the constant heat fluxes into the combustion chamber walls and burners.

Besides the experimental investigation, we carried out the numerical simulation of the propane pyrolysis in the fast-mixing reactor. The kinetic model was chosen from the tested three models which included 80 [11], 776 [12], and 689 reactions [13] involving 30, 99, and 155 particles correspondingly. For the computations, we used the package “CHEMKIN-II” [14]. Computation results were compared to the experiments of the ethane pyrolysis in the shock-wave reactor [8]. The best results were obtained with the kinetic mechanism [13]. The computation by this model describes successfully the ethylene and thane concentration distribution along the reactor’s length (see [1, 2]). But, since at the ethane pyrolysis, the concentration of the other hydrocarbons in the pyrogas content is not big, it was impossible to specify the correctness of the model in respect to the
reaction constants involving, in particular, propylene and methane, which play an important role in the propane pyrolysis. Nevertheless, the kinetic model from [13] was used in our subsequent computations.

The calculations began at the distance $x/D = 1$ from the point of pyrolyzed feedstock injection. In this cross section, according to the experiment (see [1, 2]), the flow was almost uniform, and hence was assumed to be completely mixed in the computations. Moreover, since the mixing time in the experimental conditions ($\approx 1$ ms) was much shorter than the characteristic reaction time ($\approx 30$ ms), it was suggested that the reactions have no time to begin during the mixing process. This assumption, together with the assumption of the flow uniformity, enabled to determine the initial temperature of the process $T_{\text{inert}}$ by the flow rates and enthalpies of the mixture components, with due regard to the heat losses in the combustion chamber and burner measured in the experiment. Further distribution of the flow temperature on the reactor’s axis corresponded to the measured results, and the temperature profile in the computations was approximated with the straight lines which connected the experimental points. The dependence $T(x)$ between cross sections $x/D = 1$ and $x/D = 1.7$ (there the first thermocouple is located) was also considered as linear one.

Several experiments with different initial temperature and different feedstock/heat carrier ratio were performed. The conditions and results of one experiment are given below. This test features the fact that the process of feedstock decomposition was almost finished within the limits of a short (1.5 m) experimental reactor. This fact, in particular, enables to specify the reliability of the computation method within the wide range of varying concentrations of the reacting mixture. The experiment described below was repeated two times. The results of both tests are in good agreement with each other.

In these tests, no nitrogen was supplied into the burner; nitrogen was only added to propane, to increase the mixer jets penetration parameter, which, as is shown in [1, 9], improves the mixing quality. Air flow rate was 10.1 g/s, hydrogen – 0.318 g/s, the flow rate of nitrogen added to the feedstock – 2 g/s. Hence, the heat carrier (combustion products and nitrogen) flow rate was 13 times higher than the feedstock flow rate.

Let us present the characteristic process temperatures. Adiabatic temperature of the combustion products $T_{\text{ad}} = 2403K$ ($p = 0.1$ MPa). The nominal temperature at the combustion chamber exit (regarding the heat losses measured in the experiment) $T_n = 1809K$ differed significantly from $T_{\text{ad}}$, which indicates the intensive heat exchange between the flow and combustion chamber and burner walls. The temperature of the mixed heat carrier and feedstock ($T_{\text{inert}}$) plays a key role in the experimental data analysis, on the assumption of the inert character of the jet mixing with the flow from the combustion chamber. According to the thermodynamic computation in this experiment, $T_{\text{inert}} = 1400K$.

The flow in the reactor was essentially subsonic: the flow velocity computed by the inert mixing parameters was about 46 m/s.

High mixing quality should guarantee a rather high value of the jet penetration parameter. In this experiment this value was $h/D = 0.5$.

The experimental data are shown in Fig. 3. The coordinate $x = 0$ corresponds to the jet injection cross section. The mass fraction of the pyrogas components $C_i$ and nominal residence time $t_r(x)$ are laid off on the left ordinate axis, on the right axis – the flow temperature on the reactor’s axis. The leftmost point on the dependence $T(x)$ is the temperature $T_{\text{inert}}$ in the cross section $x/D = 1$, where the flow was assumed to be inert and completely mixed. The experimental points on the dependence $T(x)$ are connected with straight lines.
The relationship $T(x)$ in these experimental conditions is governed by two factors: the influence of reactions endothermics and heat fluxes to the reactor’s walls. Since the relative length of the reactor was large ($L/D = 37.5$), the regime approaching to the hydrodynamically stabilized flow in the tube at Reynolds number $9 \times 10^3$ realized within the biggest part of the reactor. In these conditions, the temperature difference on the channel axis and wall was of $200 – 300$ K in the biggest part of the reactor.

In the mixing region, the feedstock temperature changed from 295 K at the mixer input to 1400 K at the distance of $x = 40$ mm from the jets injection point. Hence, the rate of temperature change in the mixing region was about $10^6$ K/s.

The flow temperature on the reactor’s axis reduces dramatically at the reactor’s inlet, where we observe the significant change of the pyrolysis components concentration. Then the rate of temperature drop decreases, whereas more essential change of the temperatures between two last points (at the reactor output) is seemingly caused by the end effect. In general, the flow temperature reduced to 300 K regarding $T_{\text{inert}}$.

Patterning the dependencies $C_i(x)$ in Fig. 3 it was regarded that not any mixture component was determined with the chromatograph. Their content ($\Delta C_i$), according to the modelling, varies from 0.085 at $x = 68$ mm to 0.12 at the distance of $x = 1480$ mm. Correspondingly, the data of the chromatographic analysis were multiplied by the factors $(1 - \Delta C_i)$. The presence of excess hydrogen in the pyrogas, which had not reacted in the combustion chamber, was also taken into account.

The data in Fig. 3 show fast feedstock breakdown in the high-temperature region and also the high feedstock conversion within the reactor’s length. According to the chromatographic analysis, even in the section of 6.8 cm from the injection point, half of the initial feedstock was decomposed. In the cross section $x = 42$ cm, the mass content of the propane in the mixture is 0.091, at the output – 0.055, which correlates with the conversion degree of 94%. In accordance with the $C_3H_8$ consumption rate, ethylene concentration rises and reaches the maximum of $C_{C_2H_4} = 0.45$ in the section $x = 73$ cm, in the first station, where the sampler was set ($x = 6.8$ cm), its content in the composition is 0.25. Experimental values of the propylene concentration are much smaller than ethylene, and vary weakly over the reactor’s length. In the cross section of $C_{C_2H_4}$ maximum, the content of $C_3H_6$ in the pyrogas composition is 0.06.

Analyzing the experimental data in general, it can be stated that the proposed method of high-temperature pyrolysis in the fast-mixing reactor permits to realize the process conditions which stimulate the high yield of the most valuable product – ethylene. Its amount (under these
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Experimental conditions) is much higher than the values typical for the traditional method of propane pyrolysis – 31 – 36% [15 – 17]. Because of the reactions acceleration, the required residence time shortens essentially: in these tests (see Fig. 5) the optimum value was $t_r = 15$ ms. The needed length of the reactor reduces correspondingly. In this case, as was mentioned above, the maximum $C_2H_4$ yield was observed at the distance of $x = 73$ cm, which is more than one order less than the pyrolysis coil in the traditional method of pyrolysis.

The data in Fig. 3 enable also to analyze the reasonableness of the applied quasi-one-dimensional computation method. Its accuracy depends not only on the reliability of the chosen kinetic model, but also on the correctness of the assumptions on the mixing character and temperature variation in the reaction area beginning. Comparing the experimental and simulation results, one can see that in general the applied computation method describes quite successfully the dependencies $C(x)$ for most components, whose concentration in the pyrogas changes significantly during the process, namely, $C_3H_8$, $C_2H_4$, and $CH_4$. Note the good agreement between the computation and experiment for ethylene in the biggest part of the $C_{C_2H_4}(x)$ dependence, whereas the measured concentrations of propylene are lower than computed ones. The difference is also observed for the $C_4$ components, but their content in the mixture is not high.

Fig. 4 shows the comparison between the measurement results and computation of the process in the adiabatic reactor. As before, it was assumed that the uniform propane – heat carrier mixture was formed in the cross section $x/D = 1$, the temperature of this mixture being of 1400 K. The ratio propane/heat carrier corresponds to the experimental value. It is seen that, beginning from $x = 22$ cm ($x/D = 5.5$), the imperfection of the reactor’s wall thermal insulation tells upon the situation: thermal boundary layers joint, and the temperature on the reactor’s axis deviates gradually from the temperature of the adiabatic reactor’s wall. Excluding the last point, this difference does not exceed 50K. Correspondingly, the experimental distributions of the pyrogas components concentrations are in satisfactory agreement with the computation for the adiabatic reactor.

The data of Fig. 4, which shows the computation results for the reactor 500 mm length, enable to observe the evolution of the thermal and concentration profiles at longer residence time (longer reactor’s length). Evident that at $x \geq 100$ cm, $T_{ad}$ does not practically change, similarly to the ethylene concentration. The content of methane, propylene, and acetylene changes the most...
significantly. Thus, it can be stated that the reactor’s length approaches to the optimum one under these experimental conditions.

So, the results of the performed investigation have shown the advance of the proposed model of the fast-mixing reactor applied to the process of high-temperature pyrolysis of hydrocarbons. The designed facility produced in compliance with the developed concept, is relatively simple and allows working at the temperatures unachievable in the furnace-pyrolysis method. In the experiments with the propane used as the pyrolyzed feedstock, the initial flow temperature was 200K higher than the maximum temperature in the traditional method. In these conditions, the ethylene yield has increased 1.2 – 1.3 times, whereas the required reactor length has reduced one order.

In general, the approximate computational model, developed during the investigations, describes quite successfully the results of measurement of the main components concentrations, which permits to optimize the process parameters.

The challenge of utilization of the heat remaining in the flow assumes a great importance. Basically, this problem can be solved by the same methods as it is done in the traditional method. It is much more complicated to reduce the ratio of the heat carrier/feedstock. This can be reached, in particular, by means of the higher temperature in the combustion chamber. In this case, the requirements to the mixing rate will increase significantly (due to the kinetics). This will call for the very precise approach to the choice of the mixer geometry. We are planning to continue the work in these directions.

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