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Experimental Study of Oil Non-Condensable Gas Pyrolysis in a Stirred-Tank Reactor for Catalysis of Hydrogen and Hydrogen-Containing Mixtures Production

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Abstract: The present study is focused on improving the technology for deep oil sludge processing by pyrolysis methods, considered to be the most promising technology for their environmentally friendly utilization, in which a significant yield of fuel products is expected. The technology developed by the authors of this study is a two-stage process. The first stage, pyrolysis of oil sludge, was investigated in previous papers. A significant yield of non-condensable gases was obtained. This paper presents a study of the second stage of complex deep processing technology—pyrolysis of non-condensable gases (purified propane) using a stirrer with the help of the developed experimental setup. The expected benefit of using the stirrer is improved heat transfer due to circumferential and radial-axial circulation of the gas flow. The effect of a stirrer on the yield of final target decomposition products—H_2-containing mixtures and H_2 generated during non-catalytic (medium-temperature) and catalytic pyrolysis of non-condensable gases obtained by pyrolysis of oil sludge are estimated. Ni catalyst was used for catalytic pyrolysis. The study shows that the application of the stirrer leads to increasing in H_2-containing mixtures and H_2 concentrations. In particular, during the whole reaction time (10 h), the average H_2 concentration in pyrolysis gas during catalytic pyrolysis increased by ~5.3%. In this case, the optimum reaction time to produce H_2 was 4 h. The peak H_2 concentration in the pyrolysis gas at reaction temperature 590 ± 10 °C was: 66.5 vol. % with the stirrer versus 62 vol. % without the stirrer with an error of ±0.4 %. A further increase in reaction time is cost-effective in order to obtain H_2-containing mixtures.

Keywords: stirred-tank reactor; hydrogen production; propane pyrolysis; industrial waste; non-condensable gases; oil sludge; waste-to-energy

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1. Introduction

The oil and gas industry produces a huge amount of waste—oil sludge. The refining industry probably accounts for the largest share. According to the published report from OPEC, in the past three quarters of 2022, global refinery capacity for crude oil averaged

about 79 million barrels per day (3.934 million tonnes per year) [1]. For Russia, the figure is 5.23 million barrels per day (260 million tonnes per year). According to [2], there is about one tonne of this waste for every 500 tonnes of crude refined, i.e., 158.000 tonnes in 2022 globally and 10.500 tonnes in Russia.

On the one hand, oil sludge contains a lot of toxic substances which are potentially dangerous to human health and the environment [3–5]. Due to the toxic potential of oil sludge, they cannot be disposed of without processing. Disposal of oil sludge without treatment can reduce hydraulic conductivity, hygroscopic humidity, and wetting capacity of the soil and cause soil degradation if its water-air regime and soil matrix profile are disturbed [6,7]. Petroleum hydrocarbons can percolate from soil to groundwater, posing a serious threat to aquatic ecosystems [8]. In addition, improper disposal of oil sludge poses a serious risk to human and animal health due to the genotoxicity of petroleum and polycyclic aromatic hydrocarbons [9]. As a consequence, environmentally sound management of oil sludge is necessary to reduce its harmful effects on the environment.

On the other hand, oil sludge contains from 10 to 60 hydrocarbon weight percent [10], which can be regarded as a potential energy resource [11,12]. Thermal processes such as pyrolysis and gasification are considered the most promising methods of oil sludge utilization where significant production of fuel gases and hydrocarbon-rich liquids with Physico-chemical characteristics comparable to low-grade oil distillates is expected [13,14]. The formed liquid hydrocarbons can be used as fuel or raw material for the petrochemical industry [12]. Non-condensable gas and coke residue, in their turn, can be recycled into the thermal oil sludge refinery cycle as a secondary source of energy [15]. Thermal methods can be used to obtain methane-hydrogen, propane-hydrogen and other hydrogen-containing mixtures, as well as hydrogen, from non-condensable gases whose combustion produces less hazardous substances in comparison with traditional fuels [16]. Hydrogen is called "the fuel of the future" and the most promising alternative to fossil fuels because of its remarkable properties, including extremely high energy content per unit mass, lightness, prevalence and environmental friendliness [17,18].

Research by Ktalherman et al. on propane pyrolysis using water steam is known [19]. However, the energy intensity of steam pyrolysis (or steam gasification) is extremely high because of heat loss due to moisture [20], and high temperatures require special approaches for equipment and materials. The pyrolysis method is practical in terms of the ability to control the quality of the output product. In particular, research by Cheng et al. [21] carried out catalytic pyrolysis of oil sludge in the stirred-tank reactor with the addition of ash consisting of Al_2O_3, Fe_2O_3 and CaO. This increased the saturated fraction of the oil product and decreased the mobility of S, N, and O (their migration from the oil sludge to the oil product) and the value of the carbon residue of the oil product. Abbas-Abadi et al. studied the pyrolysis process of polyethylene in the stirred-tank reactor [22], which showed that stirring significantly accelerated the heat exchange process and promoted better energy conservation and homogeneous temperature distribution in the reactor.

At the same time, literary data analysis testifies to a lack of research on the energy products produced by pyrolysis methods of non-condensable gases obtained by oil sludge thermal destruction when using stirrers. Thus, the purpose of this study is to determine the influence of the stirrer on the yield of energy products at medium-temperature and catalytic pyrolysis of non-condensable gases obtained by oil sludge thermal destruction.

2. Materials and Methods

The integrated technology for deep processing of industrial organic wastes developed by the authors of this study and partially disclosed in previous publications [15,23] can be briefly described as follows. The processing line contains two main operating stages (Figure 1). The essence of the stages is the sequential controlled thermal decomposition of hydrocarbons into their component parts. The first stage includes the formation of hydrocarbon substances (liquid, solid and gaseous). In the second stage, hydrogen-containing mixtures, hydrogen, as well as carbon nanomaterials [24] are obtained.

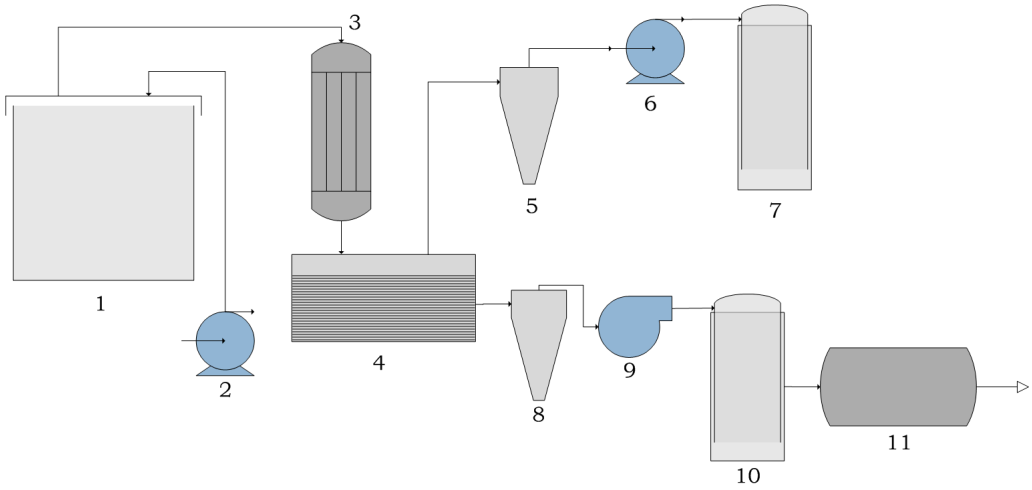


Figure 1. Schematic diagram of a reactor line for oil sludge disposal, where: 1—type 1 pyrolysis reactor; 2, 6—pump; 3—refrigerator; 4—mud tank; 5—liquid product rectifier; 7—receiver; 8—gaseous product rectifier; 9—fan; 10—gas tank; 11—type 2 pyrolysis reactor.

In order to investigate the influence of the stirrer on the yield of the final target product in the pyrolysis of non-condensable gases of oil-containing sludge (second stage), an experimental setup was developed. Its process flow diagram is shown in Figure 2. This unit can operate in two modes corresponding to the mentioned stages of the reactor line (Figure 1). The first mode consists of waste processing to produce gaseous (light hydrocarbons, non-condensable gases), liquid (saturated, unsaturated, cyclic and aromatic hydrocarbons) and solid (coke, ash) pyrolysis products. The second mode is to process previously obtained non-condensable gases with the formation of hydrogen-containing mixtures and hydrogen.

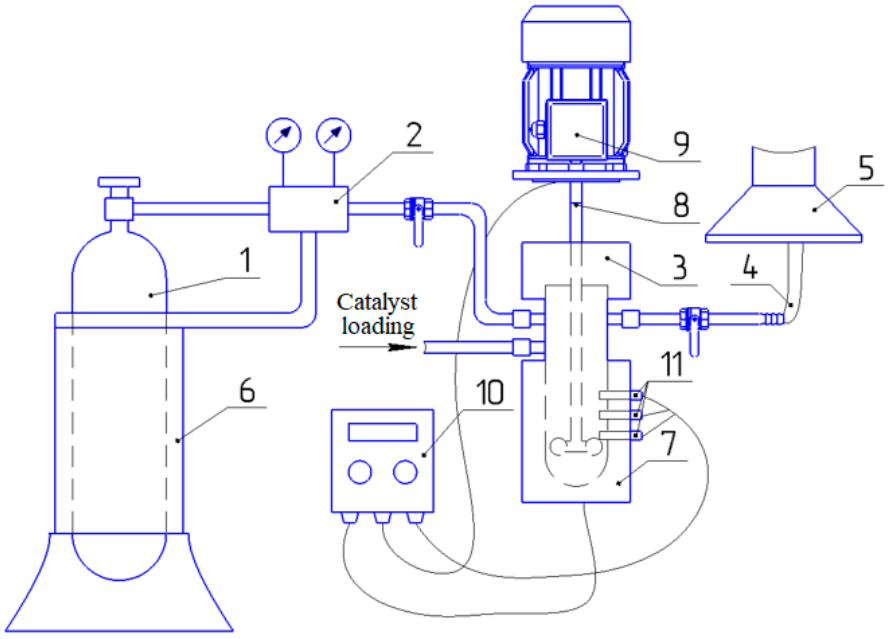
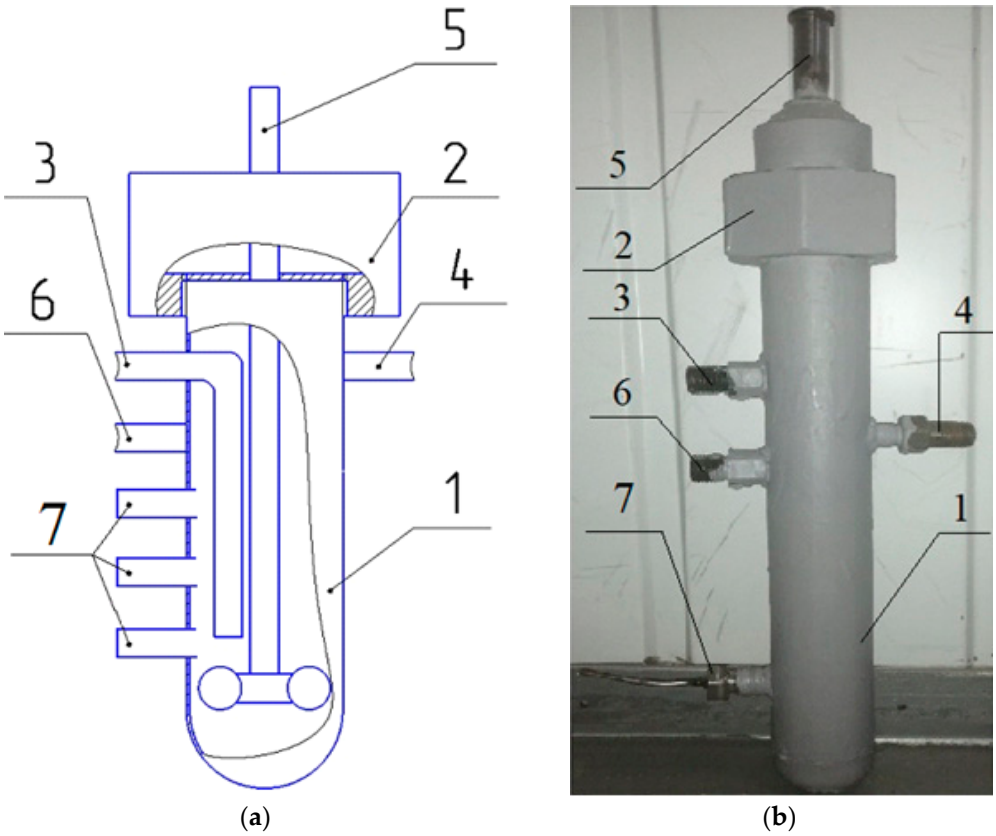


Figure 2. Flow diagram of an experimental pyrolysis unit for organic products, where: 1—feed gas cylinder; 2—control and feed gas system; 3—pyrolysis reactor; 4—air duct; 5—extractor hood; 6—thermostatic volume; 7—electric furnace; 8—stirrer; 9—electric motor; 10—meter-controller; 11—thermocouple.

The principle of the experimental setup (Figure 2) is as follows. The catalyst (in the case of catalytic pyrolysis) was placed in a pyrolysis reactor (3), and then the reactor was heated by an electric furnace (7). A split lid (2) was used to load a catalyst into the reaction zone of a reactor. The process can be briefly described as follows: unscrewing the lid—loading the catalyst—screwing and sealing the lid. When the necessary temperature was reached, hydrocarbon gas was fed from cylinder (1), the content of which was maintained at room temperature. The feed gas came into contact with the catalyst and formed a gas mixture, part of the gas was sampled for research. The hydrocarbon gas flow rate was set at 100 $l/h \cdot g_{cat}$ according to research [25]. In non-catalytic pyrolysis, the hydrocarbon gas volume flow rate was set to 1 l/h. The increase of gas flow rate without a catalyst will not change the percentage of concentration but only increase the volume of produced gases, i.e., it does not make sense for this research. The catalyst mass was 0.1 g. The pyrolysis process was controlled by a two-channel meter controller (10), OVEN 2TRM1 type, with an accuracy class of 0.5/0.25. To control the temperature in the reactor, three thermocouples (11) of THA (K) type were used, located in the thermocouple pocket evenly at the height of the reactor.

The pyrolysis reactor of the experimental setup and its actual design is shown in Figure 3. The flask (1), made of heat-resistant AISI 310S stainless steel, is hermetically connected to the metal lid (2) by means of a threaded connection. PENOSIL Premium +1500 °C Sealant was used to seal the metal lid (2). The reactor flask diameter is 100 mm, and the height is 300 mm.



(**a**) (**b**)

Figure 3. Schematic diagram (**a**) and actual design (**b**) of the pyrolysis reactor, where: 1—metal flask; 2—metal lid; 3—inlet pipe for hydrocarbon gas; 4—outlet pipe for gaseous pyrolysis products; 5—stirrer; 6—inlet pipe for catalyst; 7—thermocouple.

The stirrer (5) of the reactor (Figure 4) is a shaft made of AISI 321 steel, along the entire length of which there are technological holes at regular intervals to enable installation and fixation of the stirring elements (in the particular case of blades). The geometry and number of the stirring elements can be varied. The ability to control these features (shape, number)

allows us to establish optimum ratios to achieve maximum efficiency of the stirring device in future research. At this stage of research, we used the stirrer with ten flat blades, which is justified by the high degree of completeness of flow interaction with a flat blade (its high hydraulic resistance). The number of revolutions of the stirrer in the experimental propane pyrolysis studies was 300 ± 10 rpm.

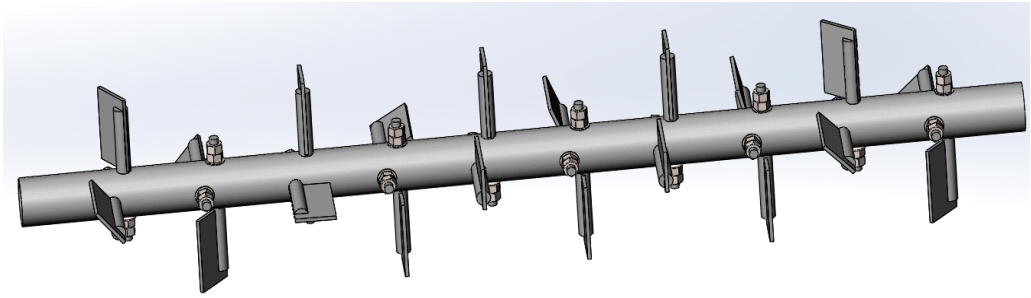


Figure 4. Pyrolysis reactor stirrer.

The pyrolysis reactor and pipework system were purged with an inert gas—carbon dioxide (CO_2), followed by a visual inspection of the compounds before the experiment started. The reactor temperature was kept at 590 ± 10 °C. As mentioned earlier, the temperature was monitored by means of an OVEN 2TRM1 measuring and control device connected to thermocouples located along the height of the reactor. The reactor was heated in a volumetric-type electric furnace. Both pyrolysis modes were performed at near atmospheric pressure (~0.1 MPa) with an upward deviation of no more than 5%. The reactor with the catalyst was heated immediately after pressurization in an inert gas environment. Upon reaching the specified temperature, the process of supplying hydrocarbon gas—purified non-condensable gas of oil sludge thermal destruction took place.

Proven in hydrogen production high-percentage nickel catalyst was used [26]. The following catalyst was used in the present study: 70Ni–20Cu–10Al_2O_3. Here, the coefficients in front of the elements and compounds show their percentages in the catalyst. Nickel catalysts are characterized by high product yield efficiency and low cost compared to catalysts containing noble metals. The catalyst was prepared by mixing a suspension of pseudobemite gel (texture promoter) and nitric acid, followed by the addition of $Ni(NO_3)_2 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ salts and stirring thoroughly until a paste-like consistency was achieved. The last stage in catalyst preparation was the addition of concentrated ammonia solution (as precipitator) followed by oven drying to 750 °C. The heating rate was 1 °C/min, and the dwell time was 3 h. The transformation formula, in general terms, can be represented as follows:

$$\begin{aligned} &\mathrm{Me(NO_3)}_y \cdot x\mathrm{H_2O} + \mathrm{AlOOH} \cdot n\mathrm{H_2O} + \mathrm{NH_4OH} + \mathrm{HNO_3} \xrightarrow{t\,^0C} \\ &\xrightarrow{t\,^0C} \mathrm{NO_2} + \mathrm{O_2} + (n+x)\mathrm{H_2O} + \mathrm{MeO/Al_2O_3} \end{aligned} \quad (1)$$

The authors of this study [27] established that texture promoter (Al_2O_3) in catalyst composition should be 10 wt. % and active metal (Ni) particles should have a size in the range from 10 to 40 nm. According to [28,29], the data obtained from [27] agree well with the catalytic pyrolysis of propane and methane. Although Ni demonstrates the highest catalytic activity among conventional transition metals [30], it is rapidly deactivated at temperatures above 600 °C due to coking [31]. This explains the choice of catalytic pyrolysis reaction temperature (590 ± 10 °C). Catalyst regeneration was carried out in a hydrogen stream at 550 °C for 3 h.

There were three experiences with a reactor without a stirrer and three experiences with a rector including a stirrer. The total reaction time of each experiment was 10 h. Five samples of gaseous products were taken every hour. The yield error of the gaseous products was estimated by the procedure presented in the study by Klinger et al. [32].

The components of the gas mixture obtained were analyzed using a "Clarus 600 GC/MS" chromatograph with a flame ionization detector manufactured by PerkinElmer Inc., USA. The tolerance limit of the relative standard deviation of the flame ionization detector output signal is 2%. The limit of variation of the flame ionization detector output signal over a measurement cycle of 48 h is ±5%.

Based on the analysis of fifteen samples, the average value of product concentration was found. The average concentration curves of gaseous pyrolysis products were plotted based on the obtained average values. The obtained hydrogen concentration curves were approximated and analyzed using mathematical analysis tools, in particular, the well-known formula for finding the mean value of the function y_{avg} (2).

$$y_{avg} = \frac{1}{b-a}\int_a^b y(x)dx \tag{2}$$

where $y(x)$ is the approximating function of the average concentration of pyrolysis hydrogen; a and b are the analyzed start and end times of the reaction, respectively.

The original methodology proposed and applied in this study to evaluate the efficiency of the stirrer in a non-condensable gas pyrolysis process is to compare the added input energy of the pyrolysis process with the additional output work (energy) produced in hydrogen yield. The added input energy through the use of a stirrer was estimated by the introduced coefficient k_{Ein} according to formula (3). The additional "work" on the hydrogen yield was estimated by the introduced coefficient k_{Eout} according to formula (4). The stirrer efficiency can be determined by the coefficient of energy transformation k_E, which describes the difference between k_{Eout} and k_{Ein} (5).

$$k_{Ein} = (100\% - \frac{N_p}{N_p + N_{st}}100\%) \cdot h \tag{3}$$

$$k_{Eout} = \int_a^b (y_{st}(x) - y_p(x))dx \tag{4}$$

$$k_E = k_{Eout} - k_{Ein} \tag{5}$$

where N_p is the power consumption of the pyrolysis reactor; N_{st} is the power consumption of the stirrer; $h = b - a$ is the analyzed reaction time; $y_{st}(x)$ is the approximating function of the average hydrogen concentration in pyrolysis with stirring; $y_p(x)$ is the approximating function of the average hydrogen concentration in unstirred pyrolysis.

Non-condensable gases formed in the course of oil sludge pyrolysis were treated by a low-temperature rectification method [33] with the separation of propane. Thus, propane (C_3H_8) obtained by pyrolysis of oil sludge was used as the initial gas. The caloric value of propane was determined using "STA 449 Jupiter" calorimeter.

General processes and mechanisms of propane pyrolysis reaction without a catalyst can be represented schematically in the form of a reaction Equation (6). The total reaction of propane pyrolysis with a catalyst is presented in the form of a reaction Equation (7).

$$2C_3H_8 \rightarrow \begin{cases} 2C_3H_6 + 2H_2 \\ 2C_2H_4 + 2CH_4 \\ CH_4 + C_2H_6 + C_3H_6 \end{cases} \tag{6}$$

$$C_3H_8 \rightarrow 2C + CH_4 + 2H_2 \tag{7}$$

"Hobbit-T" stationary gas analyzer was used to measure the concentration of harmful substances in the generated gases.

3. Results and Discussion

3.1. Non-Catalytic Pyrolysis

The formation of propane pyrolysis products depending on the reaction temperature without a catalyst and a stirrer is shown in Figure 5. In all the graphs shown, the concentration is expressed in a molar fraction multiplied by 100%.

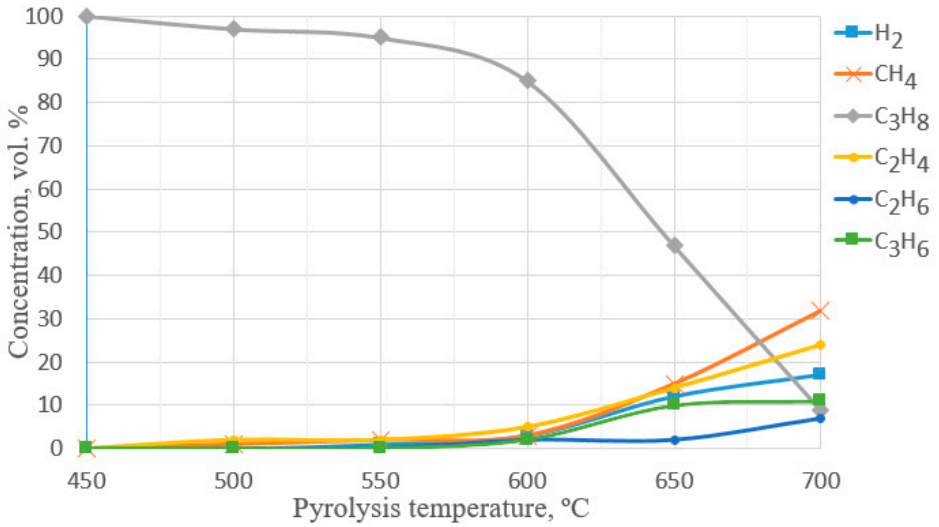


Figure 5. Temperature dependence of the concentration of non-catalytic propane pyrolysis products without a stirrer, the contact time was around 1 s.

It is clear from the data presented that propane degradation (C_3H_8) starts from a temperature of 500 °C. At 450 °C and below, its concentration is virtually indistinguishable. The decomposition products at 500 °C are methane (CH_4) and ethylene (C_2H_4). From 550 °C, hydrogen (H_2) is added to the reaction products and from 600 °C, ethane (C_2H_6) and propylene (C_3H_6). When increasing temperature, an increase in the reaction products is observed, and hydrogen concentration does not exceed that of the other reaction products throughout the temperature range. Propane conversion approaches 91% at temperatures around 700 °C. Hydrogen concentration at the maximum temperature was 17 vol.%. Thus, in order to obtain high hydrogen concentrations, the reaction temperature should be higher than 700 °C.

The temperature dependence of the formation of non-catalytic propane pyrolysis products using a stirrer is shown in Figure 6.

Analyzing the data in Figures 5 and 6, it can be concluded that the use of the stirrer does not reduce propane decomposition temperature (C_3H_8), which is 500 °C. The decomposition products at 500 °C are also methane (CH_4) and ethylene (C_2H_4). From 550 °C, hydrogen (H_2) is added to the reaction products and from 600 °C, ethane (C_2H_6) and propylene (C_3H_6). However, the use of the stirrer leads to an increase in the concentrations of the reaction products. This suggests an increase in conversion, which reaches its maximum value of 96% at 700 °C. The hydrogen concentration at the maximum temperature was 19 vol.%.

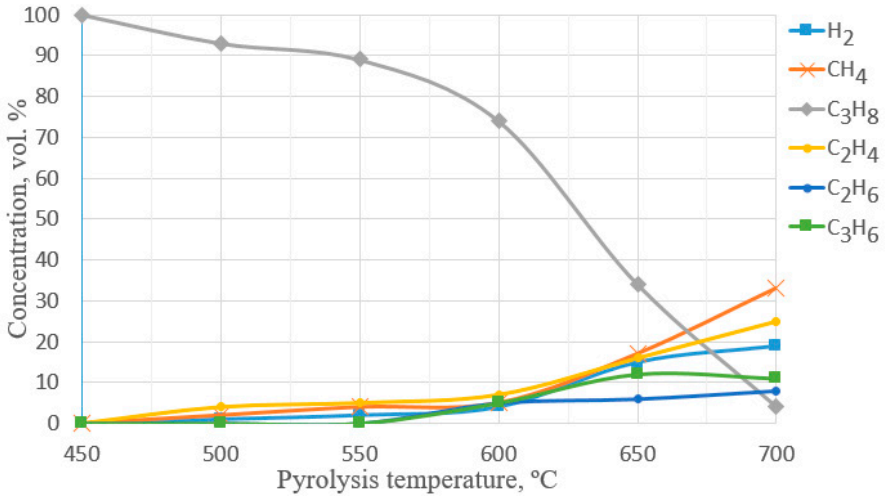


Figure 6. Temperature dependence of non-catalytic propane pyrolysis products concentration using a stirrer, the contact time was around 1 s.

The analysis of concentrations of harmful substances revealed that maximum permissible concentrations of harmful substances (CO, CO_2) according to hygienic regulations of the Russian Federation GN 2.2.5.3532-18 and GN.2.1.6.3492-17 do not exceed established standards.

3.2. Catalytic Pyrolysis

As described previously, the average pyrolysis yield was calculated based on the analysis of three experiments and five product samples taken every hour of the experiment. As an example, Figure 7 shows the hydrogen concentration individually for the fourth hour of the propane pyrolysis reaction of both the reactor with and without the stirrer.

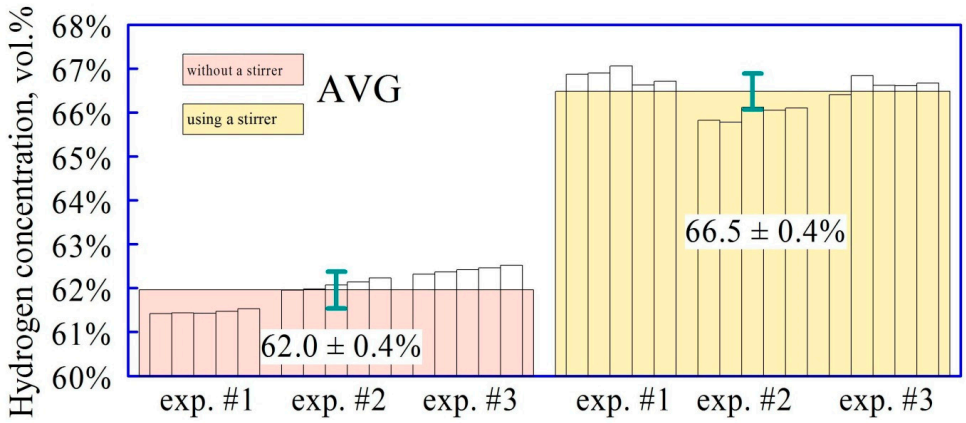


Figure 7. Pyrolysis hydrogen concentration during the fourth hour of reaction for reactor without stirrer (left) and reactor with a stirrer (right) in a catalytic propane pyrolysis study. The error bars represent $\pm 1\sigma$ of the average.

Average concentration curves of obtained propane catalytic pyrolysis products without a stirrer and with it are shown in Figures 8 and 9, respectively. The specific heat propane combustion was ~93 MJ/m^3.

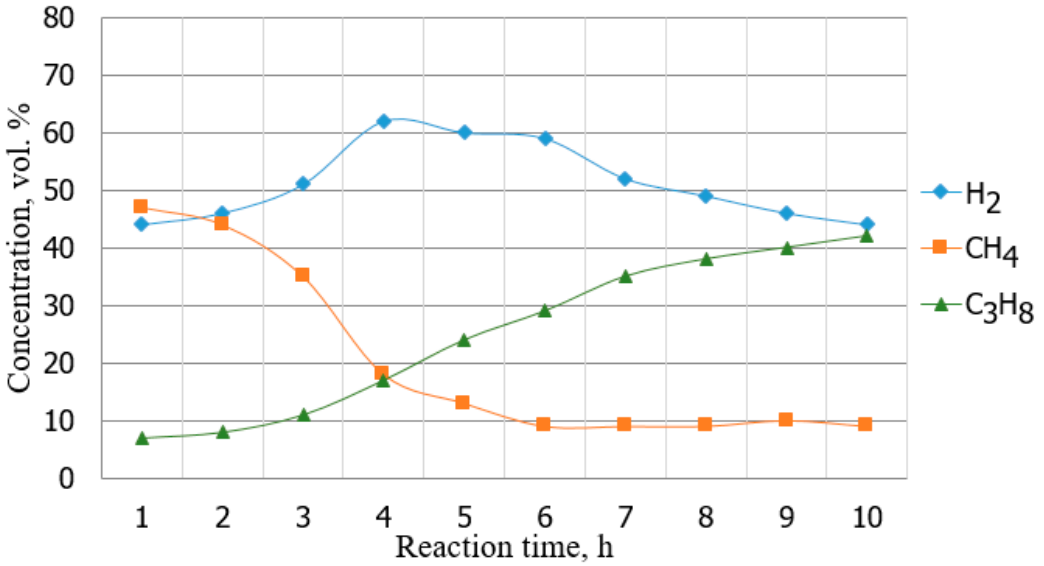


Figure 8. Reaction time dependence of the concentration of catalytic propane pyrolysis products without using a stirrer at reactor temperature 590 ± 10 °C; curves of the average concentration of propane pyrolysis products based on 150 samples are presented.

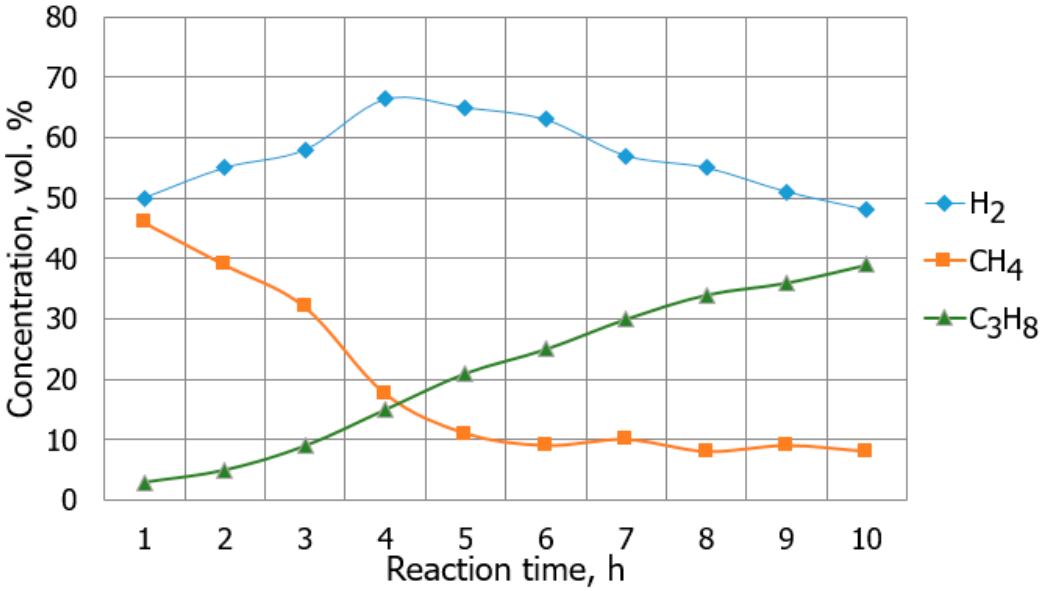


Figure 9. Reaction time dependence of catalytic propane pyrolysis products concentration using a stirrer at reactor temperature 590 ± 10 °C; curves of the average concentration of propane pyrolysis products based on 150 samples are presented.

In both the first and second cases, the formation of hydrogen (H_2), methane (CH_4) and propane (C_3H_8) are observed according to the previously presented reaction Equations (6) and (7). The increase in propane concentration after 4 h of reaction indicates a gradual deactivation of the catalyst. The main reason for deactivation is the blockage of the active carbon center. The carbon, in this case, is the resulting nanofibre carbon and carbon nanotubes ("carbide cycle mechanism") [34,35]. A further reaction time of 10 h or more will lead to a gradual decrease in methane and hydrogen yields with a simultaneous increase in propane yields until the catalyst is completely deactivated. In addition to these substances, the presence of ethylene (C_2H_4) and ethane (C_2H_6) was also observed, the total concentration of which in both cases was less than 1 vol. % up to 6 h and was below 5 vol. % from 7 to 10 h (not shown in Figures 8 and 9).

The decrease of propane (C_3H_8) concentration in the stirred-tank reactor indicates an intensification of the hydrocarbon thermal degradation reaction (Figure 9). The decrease in methane concentration (CH_4) is observed up to 4 h with a further curve to a stable level, as in a reactor without a stirrer. At the same time, it can be assumed that a further increase in reaction temperature leads to a decrease in propane concentration due to its complete decomposition with a gradual decrease in the amount of hydrogen emitted and sharply increasing values of methane and ethylene + ethane group. The stirrer plot (Figure 9) shows a decrease in methane and propane concentrations over almost the entire reaction time period, indicating an increase in conversion.

Figure 10 shows the polynomial approximation functions of the average pyrolysis hydrogen concentration curves presented in Figures 8 and 9.

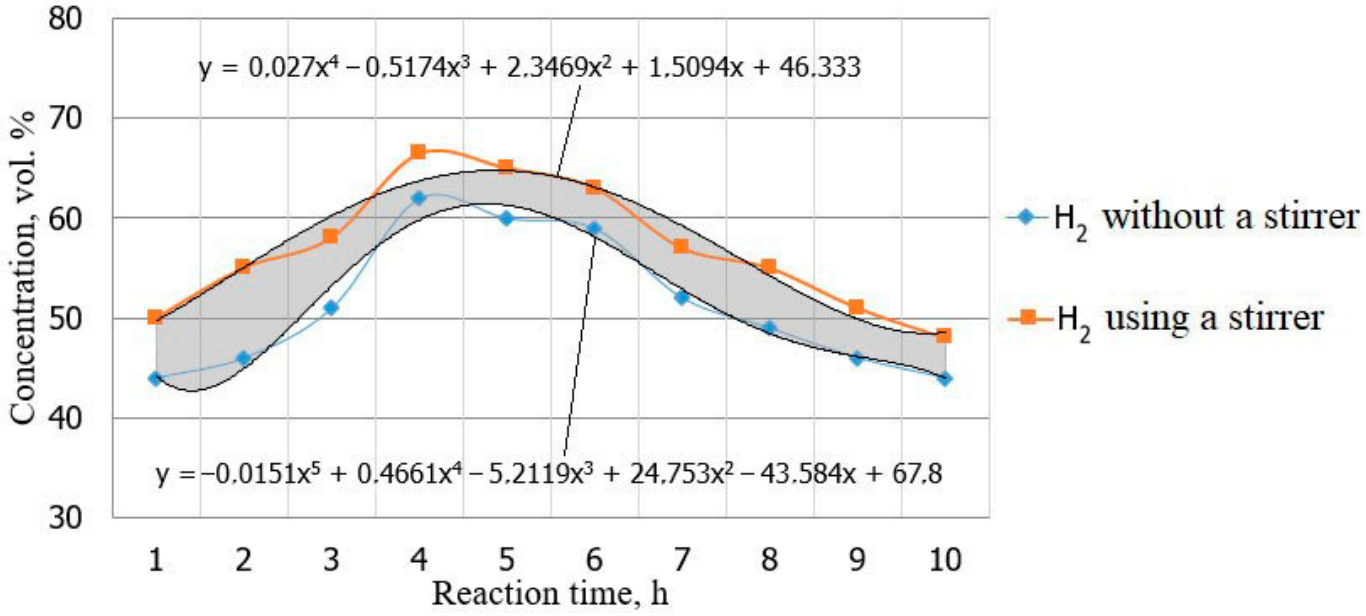


Figure 10. Approximation plots of average pyrolysis hydrogen concentration curves.

The grey area in Figure 10 clearly illustrates the "work" added by the stirrer to produce hydrogen. Quantitative evaluation of stirrer influence on hydrogen yield in catalytic pyrolysis of non-condensable gases (pyrolysis of oil sludge) is presented in Table 1.

Table 1. Quantitative evaluation of stirrer influence on hydrogen yield in catalytic pyrolysis of non-condensable gases.

Option/ Parameter	Approximation Function $y(x)$	Mean of a Function y_{avg} (Formula (2)), vol. %			"Work" on the Hydrogen Yield (Area under the Function), vol. %·h		
		for All the Reaction Time	in 4 h of Reaction	4 to 10 h	for All the Reaction Time	in 4 h of Reaction	4 to 10 h
Without a stirrer	$y_p(x) = -0.0151x^5 + 0.4661x^4 - 5.211x^3 + 24.753x^2 - 43.584x + 67.8$	52.48	49.71	53.87	472.33	149.13	323.20
Using a stirrer	$y_{st}(x) = 0.027x^4 - 0.5174x^3 + 2.3469x^2 + 1.5094x + 46.333$	57.76	57.38	57.95	519.85	172.14	347.71
Proportional ratio of values, $\%(100\% - \frac{\text{Without a stirrer}}{\text{Using a stirrer}}\ 100\%)$		9.14	13.37	7.05		—//—	
Value difference (formula (4)), %		5.28	7.67	4.08	47.52 *	23.01	24.51

* k_{Eout} (grey area in Figure 10).

According to the original methodology mentioned above, using Table 1, we can determine the difference between the "work" produced in hydrogen yield and the energy consumed when using a stirrer. According to our estimates, the total power consumption of the pyrolysis reactor used is about 7.5 kW, excluding heat losses. The power consumption of the stirrer used is 0.25 kW. Given formula (3), the ratio of the rector's 10-h energy consumption values will be k_{Ein} = 32.23 %·h. As already noted, the energy produced (the extra "work" of hydrogen extraction) by the stirrer is characterized by the difference of areas indicated by the grey area in Figure 10, calculated and shown in Table 1 (k_{Eout} = 47.52 %·h). Thus, the positive effect, characterized by the difference in k_{Eout} and k_{Ein} (formula (5)), over the whole reaction time between the hydrogen yield "work" produced and the energy consumed when using a stirrer is k_E = +15.29 %·h (coefficient of energy transformation). According to this proposed methodology, the effectiveness of a particular stirrer or its improved features can be further evaluated.

By analyzing the obtained graphs (Figures 8 and 9), it can also be concluded that the most optimal reaction time to produce hydrogen is 4 h, as the concentration of hydrogen is maximum, and the concentration of methane and propane is minimum. A further increase in the reaction time is cost-effective to produce methane-hydrogen and propane-hydrogen mixtures. The increase in the concentration of the pyrolysis target products using the stirrer is due to the continuous maintenance of the set reaction temperature throughout the reactor reaction chamber. This phenomenon is achieved by creating a vortex motion of the incoming gas by the stirrer resulting in more efficient extraction of heat energy by gas from heated reactor walls. Another reason for this increase in total concentration is the mixing of gas and catalyst due to the increased diffusion of molecules to and from the catalyst surface.

3.3. Heat and Mass Transfer Processes When Using a Stirrer in Pyrolysis of Non-Condensable Gases

Based on experimental results, we have some insight into the heat and mass transfer processes when using a stirrer in the pyrolysis process of hydrocarbon gases. The stirrer obviously promotes both circumferential gas flow circulation associated with the rotation of the mass around the axis of rotation of the stirrer and radial-axial flow circulation associated with the pumping action of the stirrer.

It is known that as the number of revolutions of the stirrer increases, the resistance of the medium increases. The stirrer interferes with the stratification of gas. At the chosen stirring mode (300 $\pm$ 10 rpm), we expected intensification of radial-tangential gas flows or, in other words, strengthening of convective heat transfer in the direction from the side wall to the central part of the reactor. We can indirectly judge the validity of this assumption due to the visually observed reduced coking of the reactor walls in the stirrer, which generally has a positive effect on the continuity and scalability of the process. In addition to stirring, radial-tangential flows also contribute to temperature equalization.

The hydrogen concentration peaks in the catalytic pyrolysis plots (Figures 8 and 9) occur at the same reaction time. This allows the hypothesis that the stirrer does not seem to influence the deactivation of the catalyst. Perhaps this is due to the peculiarities of the paddle stirrer used and may be the subject of future research. At this stage of research, it is rather difficult to draw more in-depth conclusions about the effect of the stirrer on heat and mass transfer processes since no experiments with changes in stirring speed and temperature have been conducted. These studies are much more effective through numerical methods of analysis, such as computer modeling, which is planned for the future.

3.4. Comparing Results

Comparing catalytic pyrolysis data according to Figures 8 and 9 with propane pyrolysis data without catalyst (Figures 5 and 6), it can be concluded that at reaction temperature 600 °C maximum hydrogen yield is observed in catalytic propane pyrolysis using 70Ni–20Cu–10Al_2O_3 catalyst. To achieve high hydrogen yields in the case of pyrolysis without a

catalyst, it is necessary to increase the reaction temperature, which may not be feasible due to high energy requirements.

The results obtained were also compared with those of other studies [28,36,37] in the thermal destruction of hydrocarbon gases to produce pyrolysis hydrogen. The main findings are summarised in Table 2.

Table 2. Influence of different catalyst types and other pyrolysis process conditions on the hydrogen yield in the thermal destruction of propane.

Feature of the Process	Catalyst (Reaction Time)	Reaction Temperature (°C)	Molar Concentration of Hydrogen in the Pyrolysis Gas (Peak), vol. %
Current study results			
Pressure near atmospheric pressure	Not present, ~1 s.	600 700	~12 ~17
Pressure near atmospheric pressure, with a stirrer	Not present, ~1 s.	600 700	~15 ~19
Pressure near atmospheric pressure	Ni–Cu, 1 to 10 h	590 ± 10	~62.0 (4 h)
Pressure near atmospheric pressure, with a stirrer	Ni–Cu, 1 to 10 h	590 ± 10	~66.5 (4 h)
Results of other studies			
Pressure near atmospheric pressure [36]	70Ni–20Cu; 63Ni–23Cu; 50Ni–40Cu, 1 to 40 h	500 600 700	~30 (1.5 h, 70Ni–20Cu); ~35 (less than 1 h, 63Ni–23Cu); ~17 (0.5 h, 50Ni–40Cu) ~62.5 (4 h, 70Ni–20Cu); ~43 (less than 1 h, 63Ni–23Cu); ~59 (1–2 h, 50Ni–40Cu) ~68 (1 h, 70Ni–20Cu); ~80 (1.5 h, 63Ni–23Cu); ~75 (1 h, 50Ni–40 Cu)
Pressure change 0.1 to 0.5 MPa [28]	Ni–Cu; Ni–Fe	600	~53 (5 h, 0.1 MPa, 50Ni–40Cu); ~52 (12.5 h, 0.3 MPa, 50Ni–40Cu); ~50 (14 h, 0.5 MPa, 50Ni–40Cu) ~53 (4 h, 0.1 MPa, 50Ni–40Fe); ~57 (6 h, 0.3 MPa, 50Ni–40Fe); ~50 (9.5 h, 0.5 MPa, 50Ni–40Fe)
Pressure near atmospheric pressure, adding oxidizer [37]	Pt; Ni–Al_2O_3, 1 to 60 min.	600 700 800 900	~27 ~36 ~39 ~40

The gaseous yield results obtained by the authors of this study without a stirrer agree well with the data obtained by Solov'ev et al. in the paper [36] when using Ni–Cu-based catalysts (Table 2). The difference in hydrogen yield at 600 °C is ~0.5%. The effect of catalyst composition on hydrogen yield was also shown in Ref. [36]. As the composition changes, the hydrogen concentration peak shifts in time. Analyzing the available data, it can be concluded that increasing the content of Cu in the catalyst will not significantly increase the selectivity and hydrogen yield during the reaction. An increase in temperature leads to a high molar concentration of hydrogen, but after a few hours, the concentration decreases sharply (after 3–4 h). An increase in temperature leads to an increase in the concentration of the excipients—ethylene and ethane. At 700 °C, the formation of propylene is observed.

Thus, the reaction temperature of 600 °C and 70Ni-20Cu catalyst are optimal in terms of the hydrogen-excipient ratio as well as the energy input.

Popov and Bannov [28] found that higher pressure shifts the hydrogen concentration in the pyrolysis gas during the propane thermal degradation reaction. When using a 50Ni-40Fe catalyst with increasing pressure (Table 2), there was a decrease in hydrogen concentration in the first hours of the reaction and a gradual increase in concentration from 8 h onwards. At a pressure of 0.1 MPa, in particular, there was a sharp increase in hydrogen concentration during the first hours of the reaction and a drop from 4 h onwards. At a pressure of 0.5 MPa, the situation is reversed: at the beginning of the reaction, the concentration decreases, and then, from 6 h onwards, it increases. A pressure of 0.3 MPa has been found to be optimum, as the process is characterized by a smooth flow; the concentration increases smoothly and holds throughout the reaction without sudden spikes. It can therefore be concluded that the pressure when using Ni-Cu based catalyst reduces the hydrogen concentration. However, it contributes to an increase in methane concentration, which can be useful in the production of methane-hydrogen mixtures. Thus, in order to produce hydrogen, it is preferable to thermally decompose propane at close to atmospheric pressure, as confirmed by the research carried out in this article.

Finally, a comparison was made with the results obtained by Corbo and Migliardini [37] using catalytic pyrolysis technology with the addition of an oxidant (air). The data of this study (Table 2) show that less hydrogen is produced during the reaction than in catalytic pyrolysis without an oxidizer. However, the resulting gas mixture consists of fewer components (H_2, CO and CO_2) which can be an advantage in the situation when hydrogen is separated from the original mixture, as less expense is required.

4. Conclusions

In order to study the processes of deep, complex processing of industrial organic wastes, the experimental setup was developed and presented. Its distinctive feature is the possibility to test pyrolysis processes in the stirred-tank reactor to assess its efficiency in terms of the yield of final target decomposition products—hydrogen and hydrogen-containing mixtures. Experimental studies were conducted for non-catalytic (medium-temperature) and catalytic pyrolysis processes of thermal decomposition product of oil sludge—non-condensable gas (purified propane). 70Ni–20Cu–10Al_2O_3 catalyst was used for catalytic pyrolysis. An original methodology has been proposed and applied to evaluate the effectiveness of the stirrer in the pyrolysis process of non-condensable gases. It consists in comparing the energy added to the pyrolysis process through the stirrer with the additional work produced in hydrogen yield, that is, in evaluating the transformation of the stirrer energy into gas conversion work.

The results of experimental studies of non-catalytic pyrolysis demonstrate that the use of the stirrer does not decrease propane decomposition temperature but leads to increasing concentrations of reaction products (hydrogen-containing mixtures and hydrogen). This suggests an increase in conversion, which reaches its maximum value of 96% at 700 °C. The peak hydrogen concentration in the pyrolysis gas at a reaction temperature of 600 °C was 15 vol. % with the stirrer versus 12 vol. % without the stirrer.

From the results of experimental studies of catalytic pyrolysis, it also follows that the use of the stirrer leads to an increasing concentration of reaction products (hydrogen-containing mixtures and hydrogen). In particular, over the entire reaction time (10 h), the average concentration of hydrogen in the pyrolysis gas increased by ~5.3%. The most optimal reaction time to produce hydrogen was 4 h, as the concentration of hydrogen is at its maximum while the concentration of methane and propane is at its minimum. A further increase in reaction time is cost-effective to produce methane-hydrogen and propane-hydrogen mixtures. The peak hydrogen concentration in the pyrolysis gas at reaction temperature 590 ± 10 °C was: 66.5 vol. % with the stirrer vs. 62 vol. % without the stirrer with an error of ±0.4 %. The gaseous yield results obtained without the stirrer are in good agreement with those obtained by other researchers using Ni-Cu-based catalysts.

Using the above-mentioned methodology, we obtained an energy transformation ratio of +15.29 %·h. This indicator can be used in further studies to compare the effectiveness of specific stirrers or their features.

Thus, the use of the stirrer in the pyrolysis of non-condensing gas can increase the catalysis of hydrogen and hydrogen-containing mixtures production. The increased yield of hydrogen and hydrogen-containing mixtures is due to the creation of vortex motion of incoming gas by the stirrer resulting in a more efficient extraction of thermal energy by gas from the heated walls of the reactor. Another reason for this increase in total concentration is the mixing of gas and catalyst due to the increased diffusion of molecules both to and from the catalyst surface.

It should also be noted that the use of a nickel catalyst in propane pyrolysis significantly increases the hydrogen and methane-hydrogen mixture yields and reduces the reaction temperature.

Further research is planned to analyze the effect of the stirrer configuration on the pyrolysis of hydrocarbon gases in the presence of different catalysts. These studies will make it possible to evaluate the influence of the stirrer features on the qualitative-quantitative parameters of the pyrolysis process, including such chemical process indicators as conversion rate and selectivity.

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