A NEW METHOD OF OBTAINING NANOCARBON AND HYDROGEN FROM THE PROPANE-BUTANE FRACTION

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Abstract.
In the work, the kinetic laws of the process of obtaining nanocarbon and hydrogen from the propane-butane fraction were studied under differential reactor conditions. Experiments were conducted in a differential-mode, flow-through laboratory setup consisting of a vertical stainless steel reactor with a 32 mm internal diameter and a length of 500 mm. The initial period (≈10 min) is the stage of reduction of Ni, Co, Fe and Mo oxides to metal, accumulation of free carbon and formation of carbon nanotube particles, the active phase of synthesis lasts 9÷10 min and ensures η within 22 gc/gcat.
The effect of temperature on the specific yield was studied in the temperature range of 550÷700 °C with a step of 10 °C. The thickness of the catalyst layer was hk≈0.2 mm (m=12 mg), the consumption of carbon-retaining gas was 9±0.1 l/hour, and the time of the process was 12 minutes. According to the results of experimental research, starting from 620 °C, the process temperature does not affect the specific yield of carbon nanotubes, it was . Evaluation of the influence of technological parameters of the process on the relative yield of the product and the properties of the obtained materials was carried out by the gravimetric method under isothermal conditions. During the process, the relative yield of carbon nanotubes was determined using the formula . Experimental studies to determine the dependence of carbon nanotube-specific yield η on process time were conducted at 550 to 700 °C and hydrocarbon flow rates of 15 to 20 l/h. The structural characteristics of the original HSZ and the modified samples before their processing and subsequent processing, acidic properties of the catalysts - temperature-programmed desorption of ammonia - were studied by IR-spectroscopy, X-ray phase analysis, benzene adsorption methods. The qualitative and quantitative composition of the reaction products was studied by the gas-liquid chromatographic method in the "Chromatek - Kristall 7000" chromatograph. The dimensions and morphology of the catalyst were determined by illumination electron microscopy, scanning electron microscopy and adsorption (BET) methods. Based on the study of textural characteristics, mesoporosity was estimated.
The purpose of the work consists of studying the kinetic laws of the process of obtaining nanocarbon and hydrogen from the propane-butane fraction.
Keywords: carbon storage compounds, catalyst, contact time, hydrogen, nanocarbon, temperature

INTRODUCTION

A sharp increase in demand for hydrogen is expected in the near future. The major contributors to global hydrogen demand are expected to be automotive and energy supply systems, where hydrogen serves as an energy carrier that can be stored and transported like natural gas. The growing needs of the chemical industry and the energy industry will help to increase the production of hydrogen. For example, during the last decade, the annual growth of world hydrogen production was 4.5%, and the current production level exceeds 100 million tons per year. Hydrogen has no resource limits and does not produce greenhouse gases. At the same time, the use of carbon nanotubes is increasing in various fields, such as the development of water purification filters, the synthesis of multipurpose hydrogels, drug delivery, and biosensors. Multi-walled carbon nanotubes [1, 2] are promising materials with low toxicity and adsorption capacity. Multi-walled carbon nanotubes are preferred in the production of biosensors with lower costs and higher electrical conductivity. [3-6] Many results have focused on the successful use of carbon nanotubes in many fields of science, such as energy, construction, cleaning and environmental protection. [4-9]

Currently, hydrogen is a valuable chemical product and is widely used in several important industrial processes, such as the production of ammonia [10], methanol [11, 12], hydrazine [13], and synthetic hydrocarbons. [14] Hydrogen is of great importance in the food industry, and it is used in the hydrogenation of vegetable oils. [15,16] On the other hand, hydrogen is one of the most environmentally friendly sources of thermal energy. [17] On an industrial scale, hydrogen is produced by methane steam reforming, heavy oil oxidation, coal gasification, and water electrolysis [18–20]. It should be noted that biomass is also a potential source of hydrogen. [21] In general, the process can be represented by the following equation:

$$C_nH_m \rightarrow nC + (m/2)H_2 \qquad (1)$$

This process is widely used [22] to obtain carbon nanotubes. Pure hydrogen is obtained by catalytic decomposition of carbon compounds into carbon and hydrogen. [23-31]

Materials and Methods

The Experiments were conducted in a differential-mode, flow-through laboratory setup consisting of a vertical stainless steel reactor with a 32 mm internal diameter and a length of 500 mm. A mixture of gases is sent from the bottom of the reactor. To uniformly heat the gas mixture supplied from the bottom of the reactor and to distribute the gas flow over the cross-section of the reactor, the bottom of the catalyst is filled with nozzles (quartz pieces) from 150 mm below. A substrate dusted with a catalyst was placed at the bottom of the reactor and its sealing was carried out. During the heating of the reactor, it was filled with argon.

The propane-butane mixture of gases was fed into the reaction zone and heated to operating temperature, and the reactor heating circuit was driven with an inert gas, which allowed atmospheric air to be expelled from the reaction zone. Torsion balance indicators, which record the change in the mass of the substance in the boat, were measured with a periodicity of 15 s. After the formation of carbon nanotubes stopped, the hydrocarbon was expelled from the reactor with an inert gas. A catalyst containing $15\%Ni*5\%Co*5\%Fe*5\%Cu*2\%Mo/HSZ$ was used in the experimental studies of obtaining carbon nanotubes. The thermal decomposition method was used in the preparation of the catalyst. The thermal decomposition method is one of the most effective methods for the preparation of catalysts. Catalyst powder was obtained by thermal decomposition of metal nitrates.

The essence of the method is that the catalyst contains ($Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_2 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $(NH_4)_2 MoO_4 \cdot 24H_2O$) consists of the interaction of a mixture of metal

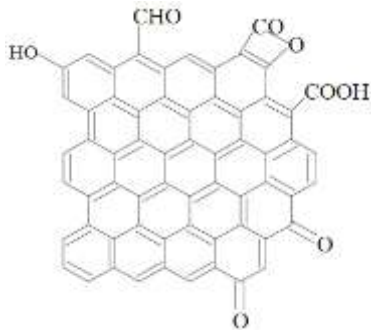
nitrates, ammonium molybdate and high-silica zeolite (HSZ) obtained from bentonite from Navbahor district, Navoi region, Republic of Uzbekistan, and an organic substance (for example, a mixture of glycine and citric acid) in the air at temperatures ≥500 °C. At temperatures above 500 °C, thinly dispersed oxides of metals are formed. The physicochemical and textural characteristics of HSZ have been studied [32–33] and used in the aromatization of natural gas, petroleum satellite gases, and propane-butane fractions [34–37] and the Fischer–Tropsch process and the production of olefins from dimethyl ether. [38–39] HSZ forms a well-developed porous structure, with Ni, Co, Fe, Cu, and Mo particles distributed over its surface.

During the experimental studies of the carbon nanotubes synthesis process, propane-butane mixture ($C_3H_8 / C_4H_{10} = 50\% / 50\%$) and inert gas - argon (Ar) stored in a cylinder were used. The removal of catalyst particles from the synthesized carbon nanotubes was carried out by the acid washing method.

Pyrolysis of the propane-butane mixture (C_3H_8 – 30%, C_4H_{10} – 70%) was carried out at atmospheric pressure and temperature of 600-650 °C, on the fixed bed of the catalyst in laboratory and pilot reactors operating periodically. A filter based on zeolite was used to clean gas mixtures from additives and dry them from moisture. The waste gas was analyzed in the "Chromatek - Kristall 7000" chromatograph.

Catalytic synthesis of carbon nanostructures by catalytic pyrolysis of carbon-containing organic and inorganic compounds in the absence of air was carried out at atmospheric pressure in the temperature range of 400-1000 °C. To speed up the synthesis of nanocarbon in the centre of the reactor, powders of metals and intermetallics were placed in a thin layer at the bottom of a quartz boat. In the same way, the placement of catalysts incorporated in different holders was carried out. The heating of the reactor was carried out in a flow of hydrogen or argon. As soon as the working temperature was reached, a mixture of gases in the required ratio was sent to the reactor. The composition of the gas phase was changed by changing the volumetric velocities of the gas streams. The flow rate of each of the gases was selected depending on the amount of catalyst, pyrolysis temperature and process duration in the range of 5-100 cm^3/min. The pyrolysis time varied from 1.5 hours to 4 hours.

It is known that the functional properties of the obtained carbon nanofibers and nanotubes are required. For this, it is necessary to clean the obtained carbonaceous material from catalysts and by-products of pyrolysis. Catalyst removal of carbon nanofibers and nanotubes was treated with concentrated sulfuric acid in an ultrasonic bath by drying at 65-70 °C for 3-3.5 hours to neural medium and then washing and air drying at 140-150 °C for 7 hours. Further treatment was carried out by boiling in concentrated nitric acid for one hour to remove amorphous carbon and encapsulated metal particles. After purification, according to atomic absorption spectrometry and chromatographic analysis, the dry residue content of the sample was less than 0.1%, which corresponds to the measurement error. Boiling in nitric acid also causes partial oxidation of carbonaceous material:



This facilitates further use of nanofibers and nanotubes. If oxygen groups are not needed on the surface of carbon nanostructures, additional treatment of carbon material is carried out in hydrogen flow at 900 °C for one hour.

Evaluation of the effect of technological parameters of the process on the relative yield of the product and the properties of the obtained materials was carried out by the gravimetric method under isothermal conditions. The method made it possible to quickly select the conditions in which the largest specific yield of carbon is achieved.

The specific yield of carbon nanotubes, η, was determined by the following ratio:

$$\eta = \left(m_{prod} - m_{cat.}\right) / m_{cat}. \qquad (2)$$

here, η - the specific yield of the nanomaterial, $g_C/g_{cat.}$; $m_{cat.}$ - the catalyst mass loaded into the reactor, g; $m_{prod.}$ - the mass of the obtained product.

Results and Discussion

Experimental studies to determine the dependence of carbon nanotube-specific yield η on process time were conducted at 550 to 700 °C and hydrocarbon flow rates of 15 to 20 l/h (Figure 1).

The initial period (≈10 min) describes the stage of reduction of Ni, Co, Fe and Mo oxides to metal, accumulation of free carbon and formation of carbon nanotube particles. The active phase of synthesis lasts 9÷10 minutes and ensures that η is within the limits of 22 g_C/g_{cat}. Then the growth of nanostructures stops.

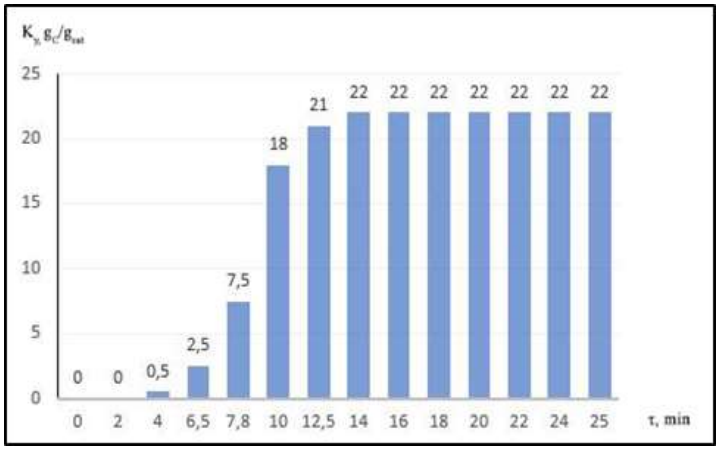


Fig. 1 Dependence of specific yield of carbon nanotubes (η) on pyrolysis time (τ).

To determine the influence of the thickness of the catalyst layer on the productivity of the product, different weights of the catalyst were placed in the "boat" (average bulk density $\rho_к \approx 480$ kg/m^3) and spread evenly over the entire surface (S_{boa}=0.1·10-3 m^2). The thickness of the catalyst layer was changed in the range of h_k=0.1÷2 mm, and the loaded catalyst mass was determined as $m_k=\rho_k S_{boa} h_k$. Experiments were conducted for 10 minutes at 550 to 700 °C and

15 to 20 l/h hydrocarbon flow rate. The duration of the procedure was selected based on previous experience.

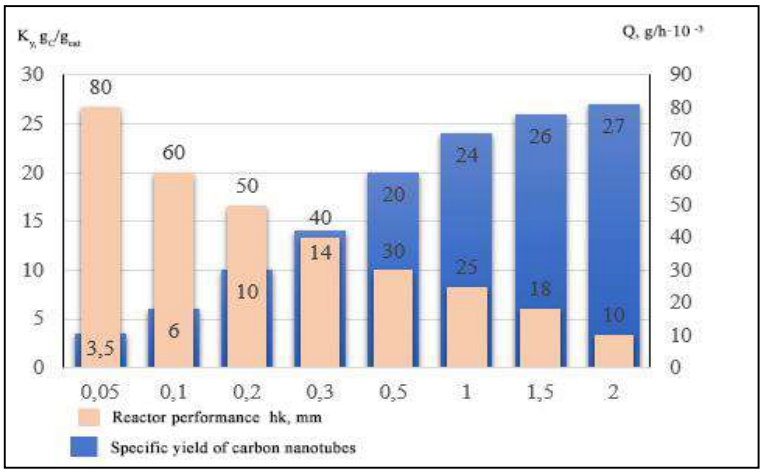


Fig. 2 Dependence of the specific yield of carbon nanotubes (K_y) and reactor productivity (Q) on the thickness of the catalyst layer (h_k)

The thickness of the catalyst layer $h_k \approx 0.2 \div 0.3$ mm was determined for conducting experiments and setting the calculation parameters of the experimental-industrial device for the synthesis of carbon nanotubes. The effect of temperature on the specific yield was studied in the temperature range of 550÷700 °C with a step of 10 °C. The thickness of the catalyst layer was $h_k \approx 0.2$ mm (m=12 mg), the consumption of carbon-retaining gas was 9±0.1 l/hour, and the time of the process was 12 minutes. The results of experimental studies (Figure 5) showed that from 620 °C, the process temperature does not affect the specific yield of carbon nanotubes, which was $\eta \approx 22\ g_C / g_{cat}$.

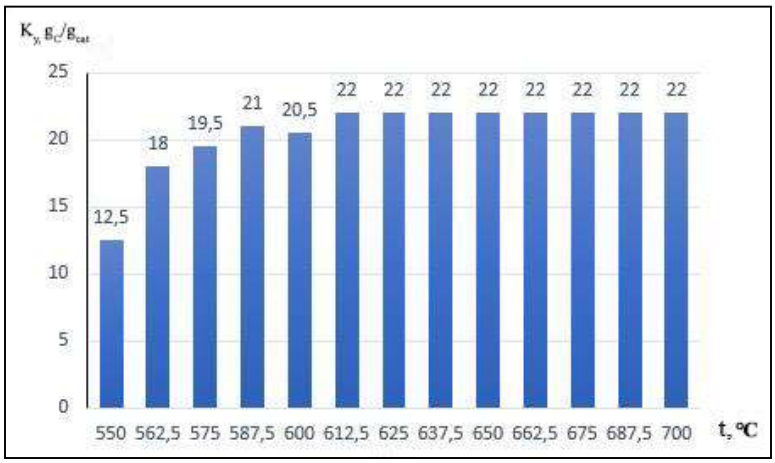


Fig. 3 The graph of the temperature (T) dependence of the specific yield of carbon nanotubes (η)

The conducted experiments made it possible to determine the laws of the kinetics of carbon nanomaterials (CNM) synthesis, establish the exact conditions of its transfer in a flow-type reactor, and determine the dependence of η on the parameters of the main regime. These studies, carried out at the initial stage of the work, made it possible to make sure that using a propane-butane mixture, the synthesis of carbon nanotubes is possible with this catalyst and its production technology.

A method based on measuring the electromagnetic properties of the synthesized material. To study the kinetics of the carbon nanotube formation process, an original method was

developed based on measuring the complex dielectric absorption of the catalyst and carbon nanotubes placed in the reaction zone called electrographic. Depending on the size of the catalyst, carbon nanotubes, as well as the material placed in the reactor, the complex dielectric absorbance of the catalyst, carbon nanotubes, and the corresponding signal coming to the counting device and reflected on the monitor screen also change.

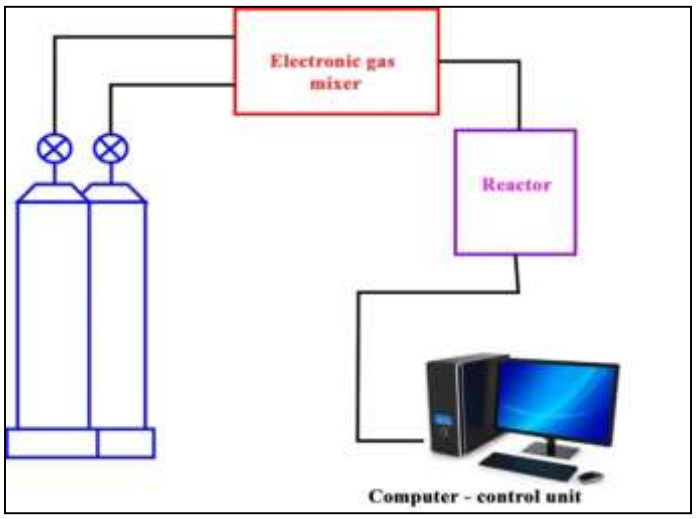


Fig. 4 The scheme of the device for determining the kinetics of the carbon nanotube formation process

To implement this method of researching the kinetic characteristics of the carbon nanotube synthesis process, an original design of the device was created and worked out, its scheme is shown in Fig. 4.

By catalytic pyrolysis of organic and inorganic compounds containing carbon in the device, it is possible to change the conditions of the carbon nanotube production process, monitor the reaction mass change in the reactor cell, and monitor the information obtained on the monitor screen in real-time.

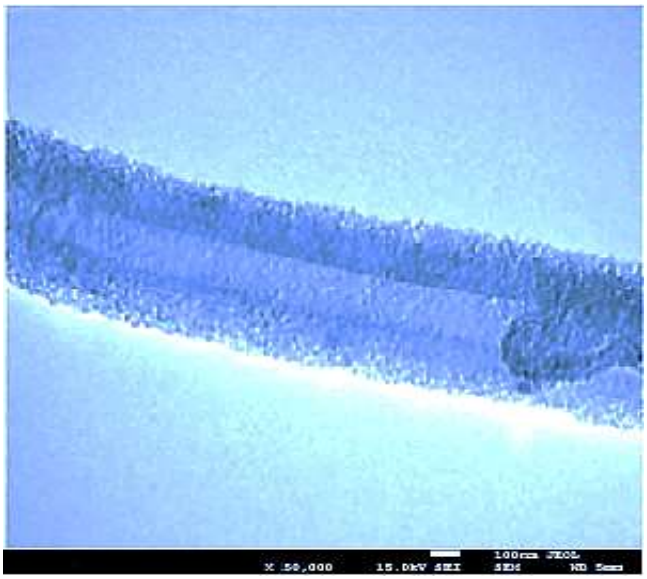


Fig. 5 Microstructure of the obtained materials

Timely stopping of the synthesis at the end of the growth of nanostructures, which was carried out within the framework of this experiment, allowed not only to significantly optimize the processing time but also to obtain carbon nanotubes with high-quality properties. Scanning

microscopy data (Fig. 5) show that the synthesized material consists almost entirely of tubular nanocarbon with a narrow range of diameters (15-20 nm) with a minimal amount of amorphous carbon (<3-5 %). The conducted studies allow us to conclude that carbon nanotubes can be synthesized by catalytic pyrolysis of the propane-butane mixture ($C_3H_8 / C_4H_{10} = 50 / 50\%$) using this type of catalyst ($15\%Ni * 5\%Co * 5\%Fe * 5\%Cu * 2\%Mo / HSZ$). The known mode parameters and the obtained relationships are the basis of the recommendations for the design of laboratory reactors for the synthesis of carbon nanotubes by catalytic pyrolysis with a fixed bed of catalyst. The synthesis was carried out at atmospheric pressure in the temperature range of 500÷700 °C, the pyrolysis time was changed to the range of 5÷30 min. At the end of the process, the reactor was cooled in a stream of argon. The processing of the obtained data allows getting the relationships that evaluate the impact of the processing time on the relative productivity of the product (Fig. 6). The maximum η was reached approximately 35 min after the start of the process.

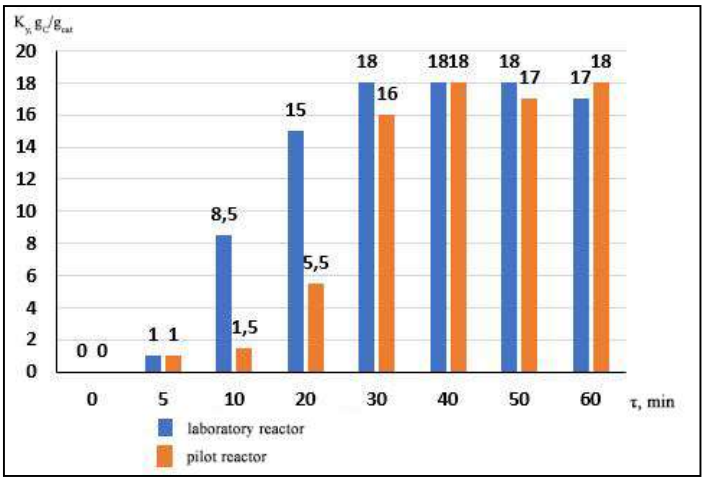


Fig. 6 The graph of dependences of CNM η specific yield on pyrolysis time (τ)

Despite the different nature of the mass growth curves of the carbon nanotubes used in the reactors, $\eta \approx 18 g_C / g_{cat}$. was approximately the same magnitude.

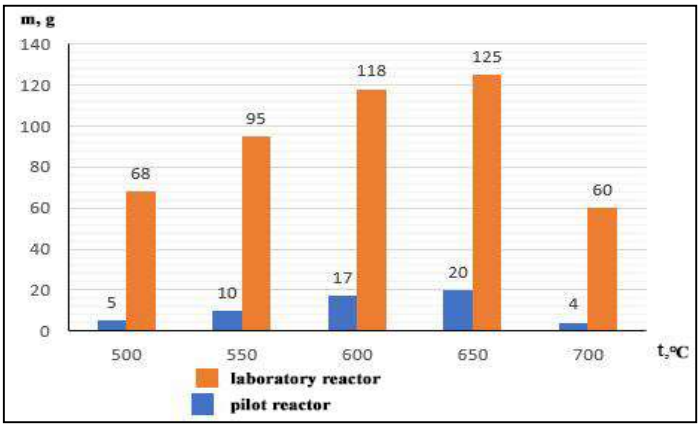


Fig. 7 The graph of dependence of mass (m) of obtained CNM on pyrolysis temperature (T)

The results of the study of the efficiency of the synthesis depending on the temperature allow recording 640-650 °C as the optimal range. A further increase in temperature causes an acceleration of pyrolysis and the subsequent accumulation of excess free carbon. These carbon nanotubes screen the surface of the active centres of the formation of bubbles, causing the

accumulation of its amorphous constituent. As a result, the activity of the catalyst decreases, and the amount of synthesized carbon nanotubes decreases dramatically.

Correlations showing the effect of catalyst layer thickness on η and reactor productivity are shown in Figures 8 and 9 for laboratory and pilot reactors, respectively. Different amounts of catalyst (layer thickness varied from 0.05 to 2 mm) were placed in the reactor. Experiments were conducted at 650 °C and gas consumption of 85 l/h - laboratory reactor and 120 l/h - pilot-industrial reactor. The cycle time was 30 minutes.

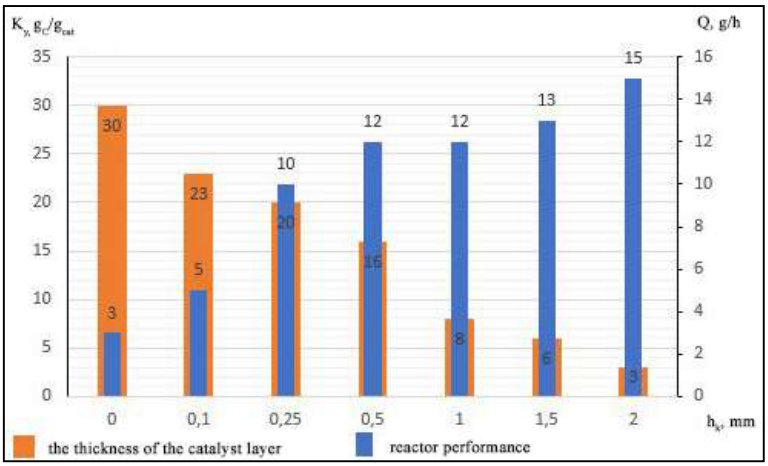


Fig. 8 The graph of dependences of CNM specific productivity (η, $g_C/_{cat}$) and reactor productivity (Q, g/h) on the thickness of the catalyst layer (h_k, mm) in the laboratory reactor

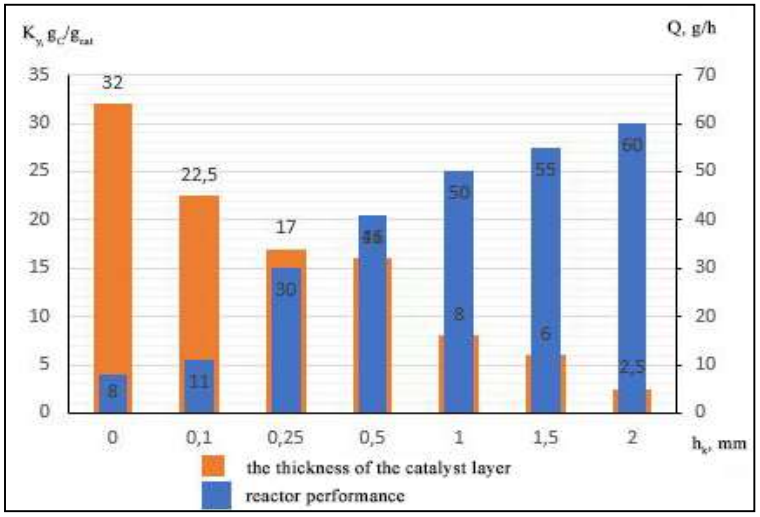


Fig. 9 CNM comparative productivity (η, $g_C/_{cat}$) and reactor productivity (Q, g/h) to the thickness of the catalyst layer in the pilot reactor (h_k, mm) graph of dependencies

Analyzing the relationships obtained, it can be concluded that h_k=0.25-0.4 mm is a reasonable value of the thickness of the catalyst layer in the studied reactors with a fixed layer of the catalyst.

The results of experimental studies of the effect of hydrocarbon consumption on relative productivity are presented in Figure 10. As the hydrocarbon feed rate increases, the relative yield of the product increases. The maximum specific productivity was achieved at consumption values of 80 l/h - laboratory reactor and 100 l/h - pilot-industrial reactor. However, with a further increase in consumption, the amount of stratified carbon decreases. In

this case, the catalytic particles are covered with layers of carbon that cause the deactivation of the catalyst.

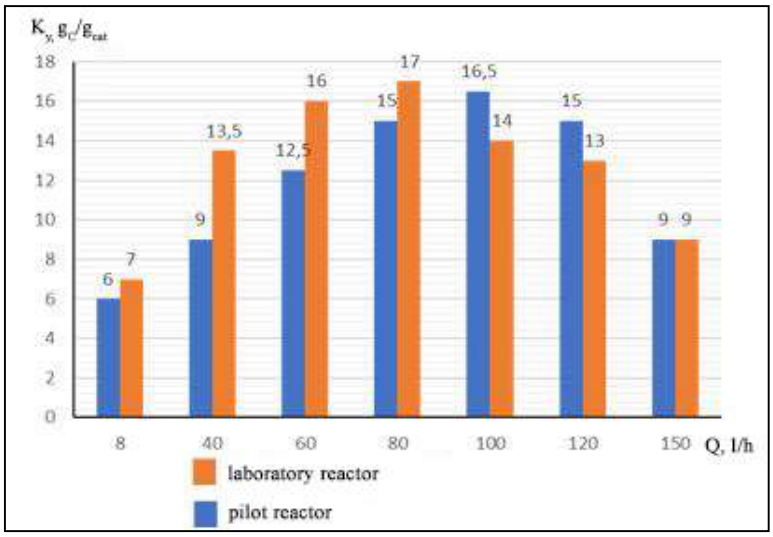


Fig. 10 The graph of dependencies of CNM (η) specific productivity on propane-butane consumption (Q, l/h)

The study of the effects of mode parameters (τ, T, h_k, Q) on the number of synthesized carbon nanotubes allows obtaining initial data for establishing technological modes of operation. A microphotograph of the resulting nanocarbon obtained by scanning electron microscopy is shown in Figure 11 below.

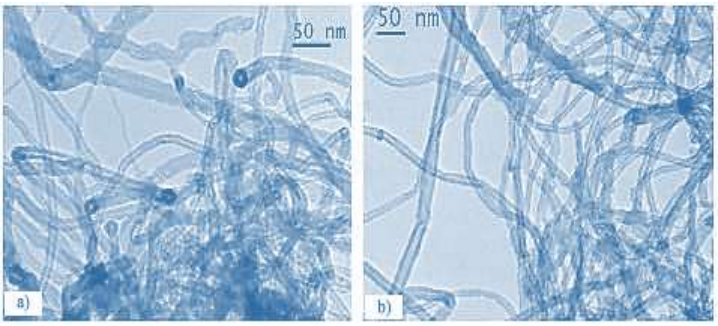


Fig. 11 TEM image of the initial (a) and treated with nitric acid for 8 hours (b) nanocarbon

Conclusion

Thus, the process of obtaining nanocarbon and hydrogen from the propane-butane fraction was studied in the presence of a catalyst containing $15\%Ni*5\%Co*5\%Fe*5\%Cu*2\%Mo/HSZ$ high catalytic activity and selectivity. Experimental studies to determine the dependence of carbon nanotube-specific yield on process time were conducted at 550 to 700 °C and hydrocarbon flow rates of 15 to 20 l/h.

The initial period of time (≈10 min) is the stage of reduction of Ni, Co, Fe and Mo oxides to metal, accumulation of free carbon and formation of carbon nanotube particles, the active phase of synthesis lasts 9÷10 min and ensures η within the limits of $22g_C/g_{cat}$. The effect of temperature on the specific yield was investigated in the temperature range of 550÷700 °C with a step of 10 °C. The thickness of the catalyst layer was h_k≈0.2 mm (m=12 mg), the consumption of carbon-retaining gas was 9±0.1 l/hour, and the time of the process was 12 minutes. According to the

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References:

[1] Chen X, Zhang Q, Li J, Yang M, Zhao N, Xu FJ. Rattle-structured rough nanocapsules with in-situ-formed gold nanorod cores for complementary gene/chemo/photothermal therapy. ACS nano. 12(6) (2018) 5646-56. https://doi.org/10.1021/acsnano.8b01440.

[2] Zhao N, Fan W, Zhao X, Liu Y, Hu Y, Duan F, Xu FJ. Polycation–Carbon Nanohybrids with Superior Rough Hollow Morphology for the NIR-II Responsive Multimodal Therapy. ACS applied materials & interfaces. 12(10) (2020) 11341-52. https://doi.org/10.1021/acsami.9b22373.

[3] Feng L, Yang X, Shi X, Tan X, Peng R, Wang J, Liu Z. Polyethylene glycol and polyethylenimine dual-functionalized nano-graphene oxide for photothermally enhanced gene delivery. Small. 9(11) (2013) 1989-97. https://doi.org/10.1002/smll.201202538.

[4] Naldini L. Gene therapy returns to centre stage. Nature. 526(7573) (2015) 351-60. https://doi.org/10.1038/nature15818.

[5] Ibraheem D, Elaissari A, Fessi H. Gene therapy and DNA delivery systems. International journal of pharmaceutics. 459(1-2) (2014) 70-83. https://doi.org/10.1016/j.ijpharm.2013.11.041.

[6] Taghavi S, Abnous K, Taghdisi SM, Ramezani M, Alibolandi M. Hybrid carbon-based materials for gene delivery in cancer therapy. Journal of Controlled Release. 318 (2020) 158-75. https://doi.org/10.1016/j.jconrel.2019.12.030.

[7] de Menezes BR, Rodrigues KF, da Silva Fonseca BC, Ribas RG, do Amaral Montanheiro TL, Thim GP. Recent advances in the use of carbon nanotubes as smart biomaterials. Journal of Materials Chemistry B. 7(9) (2019) 1343-60. https://doi.org/10.1039/C8TB02419G.

[8] Hu Y, Liu S, Li X, Yuan T, Zou X, He Y, Dong X, Zhou W, Yang Z. Facile preparation of biocompatible poly (l-lactic acid)-modified halloysite nanotubes/poly (ε-caprolactone) porous scaffolds by solvent evaporation of Pickering emulsion templates. Journal of Materials Science. 53(20) (2018) 14774-88. https://doi.org/10.1007/s10853-017-1342-9.

[9] Liu H, Wang ZG, Liu SL, Yao X, Chen Y, Shen S, Wu Y, Tian W. Intracellular pathway of halloysite nanotubes: potential application for antitumor drug delivery. Journal of Materials Science. 54(1) (2019) 693-704. https://doi.org/10.1007/s10853-018-2775-5.

[10] Rouwenhorst KH, Krzywda PM, Benes NE, Mul G, Lefferts L. Ammonia production technologies. Techno-Economic Challenges of Green Ammonia as Energy Vector. Academic Press: Cambridge, MA, USA, 14 (2020) 41-84. https://doi.org/10.1016/C2019-0-01417-3.

[11] Kim S, Kim J. The optimal carbon and hydrogen balance for methanol production from coke oven gas and Linz-Donawitz gas: Process development and techno-economic analysis. Fuel. 266 (2020) 117093-117095. https://doi.org/10.1016/j.fuel.2020.117093.

[12] Monnerie N, Gan PG, Roeb M, Sattler C. Methanol production using hydrogen from concentrated solar energy. International Journal of Hydrogen Energy. 45(49) (2020) 26117-25. https://doi.org/10.1016/j.ijhydene.2019.12.200.

[13] N. X. Musulmonov and N.I. Fayzullaev. Textural characteristics of zinc acetate catalyst, AIP Conference Proceedings 2432, 050015 (2022). https://doi.org/10.1063/5.0090920.

[14] Q. Bukhorov, Sh. Ch. Aslanov, and N. I. Fayzullaev. Direct extraction of dimethyl ether from synthesis gas, AIP Conference Proceedings 2432, 050013 (2022). https://doi.org/10.1063/5.0090210.

[15] Dijkstra, A.J.; van Duijn, G. Vegetable Oils: Oil Production and Processing. In Encyclopedia of Food and Health; Academic Press: Cambridge, MA, USA. (2016) 373–380. https://doi.org/10.1016/B978-0-12-384947-2.00707-8.

[16] Sun, Z.-Y. Hydrogen energy. In Sustainable Fuel Technologies Handbook; Academic Press: Cambridge, MA, USA, 2021 339–365. https://doi.org/10.1016/j.ijhydene.2012.08.125.

[17] Yürüm Y. Department of Chemistry Hacettepe University. Hydrogen Energy System: Production and Utilization of Hydrogen and Future Aspects. (1995) 295:15. https://doi.org/10.1007/978-94-011-0111-0.

[18] Balat M. Hydrogen-rich gas production from biomass via pyrolysis and gasification processes and effects of catalyst on hydrogen yield. Energy Sources, Part A. 30(6) (2008) 552-64. https://doi.org/10.1080/15567030600817191.

[19] Franchi G, Capocelli M, De Falco M, Piemonte V, Barba D. Hydrogen production via steam reforming: A critical analysis of MR and RMM technologies. Membranes. 10(1) (2020) 10. https://doi.org/10.3390/membranes10010010.

[20] Koskin AP, Zibareva IV, Vedyagin AA. Conversion of rice husk and nutshells into gaseous, liquid, and solid biofuels. InBiorefinery of alternative resources: targeting green fuels and platform chemicals. Springer, Singapore. (2020) 171-194). https://doi.org/10.1007/978-981-15-1804-1_8.

[21] Shimamoto D, Muramatsu H, Fujisawa K, Hayashi T, Kim YA, Endo M. Synthesis of catalytic chemical vapor grown carbon fibers: Carbon nanotube and carbon nanofiber. Carbon. 2(49) (2011) 738. http://dx.doi.org/10.1016%2Fj.carbon.2010.09.017.

[22] Docekal J. Hydrogen production from hydrocarbons. International journal of hydrogen energy. 11(11) (1986) 709-14. https://doi.org/10.1016/0360-3199(86)90139-4.

[23] Li Y, Chen J, Qin Y, Chang L. Simultaneous production of hydrogen and nanocarbon from decomposition of methane on a nickel-based catalyst. Energy & Fuels. 14(6) (2000) 1188-94. https://doi.org/10.1021/ef0000781.

[24] Muradov N.Z., Veziroğlu T.N. From hydrocarbon to hydrogen–carbon to hydrogen economy. International journal of hydrogen energy. 30(3) (2005) 225-37. https://doi.org/10.1016/j.ijhydene.2004.03.033.

[25] Rahman, M.S.; Croiset, E.; Hudgins, R.R. Catalytic Decomposition of Methane for Hydrogen Production. Top. Catal. 37 (2006) 137–145. https://doi.org/10.1007/s11244-006-0015-8.

[26] Oensan Z.I. Catalytic processes for clean hydrogen production from hydrocarbons. Turkish Journal of Chemistry. 31(5) (2007) 531-50. https://journals.tubitak.gov.tr/chem/vol31/iss5/14.

[27] Nguyen M.C., Lee H, Ihm J. Hydrogen storage using functionalized saturated hydrocarbons. Solid state communications. 147(9-10) (2008) 419-22. https://doi.org/10.1016/j.ssc.2008.06.009.

[28] Ahmed S, Aitani A, Rahman F, Al-Dawood A, Al-Muhaish F. Decomposition of hydrocarbons to hydrogen and carbon. Applied Catalysis A: General. 359(1-2) (2009) 1-24. https://doi.org/10.1016/j.apcata.2009.02.038.

[29] Ibrahim A.A., Fakeeha A.H., Al-Fatesh A.S., Abasaeed A.E., Khan W.U. Methane decomposition over iron catalyst for hydrogen production. International Journal of Hydrogen Energy. 40(24) (2015) 7593-600. https://doi.org/10.1016/j.ijhydene.2014.10.058.

[30] Tezel E, Figen H.E., Baykara S.Z. Hydrogen production by methane decomposition using bimetallic Ni–Fe catalysts. International Journal of Hydrogen Energy. 44(20) (2019) 9930-40. https://doi.org/10.1016/j.ijhydene.2018.12.151.

[31] Mamadoliev I.I., Khalikov K.M., Fayzullaev N.I. Synthesis of high silicon of zeolites and their sorption properties. International Journal of Control and Automation. 3(2) (2020). 703-9. https://www.elibrary.ru/item.asp?id=43272397.

[32] Mamadoliev I.I., Fayzullaev N.I. Optimization of the activation conditions of high silicon zeolite. International Journal of Advanced Science and Technology. 29(3) (2020) 6807-13. http://sersc.org/journals/index.php/IJAST/article/view/7333.

[33] S.Yu. Bobomurodova., N.I. Fayzullaev., K.A. Usmanova. Catalytic Aromatization of Oil Satellite Gases, International Journal of Advanced Science and Technology, 29(05) (2020) 3031 - 3039. http://sersc.org/journals/index.php/IJAST/article/view/11606.

[34] N. S. Tursunova, N. I. Fayzullaev. Kinetics of the Reaction of Oxidative Dimerization of Methane. International Journal of Control and Automation, 13(02) (2020). 440 - 446. http://sersc.org/journals/index.php/IJCA/article/view/9897.

[35] Fayzullaev, N. I., S. Yu Bobomurodova, G. A. Avalboev, M. B. Matchanova, and Z. T. Norqulova. Catalytic change of C1-C4-alkanes. International Journal of Control and Automation 13(2) (2020) 827-835. http://sersc.org/journals/index.php/IJCA/article/view/11230.

[36] Ibodullayevich, F. N., B. S. Yunusovna, and X. D. Anvarovna. "Physico-chemical and texture characteristics of Zn-Zr/VKTS catalyst. Journal of Critical Reviews. 7(7) (2020) 917-920. http://dx.doi.org/10.31838/jcr.07.07.166.

[37] Aslanov, S.C., Buxorov, A.Q., Fayzullayev, N.I. Catalytic synthesis of C2-C4-alkenes from dimethyl ether. International Journal of Engineering Trends and Technology, 69(4) 2021 67–75. http://dx.doi.org/10.14445/22315381/IJETT-V69I4P210.

[38] F N Temirov, J Kh Khamroyev, N I Fayzullayev, G Sh Haydarov and M Kh Jalilov. Hydrothermal synthesis of zeolite HSZ-30 based on kaolin. IOP Publishing, IOP Conf. Series: Earth and Environmental Science. 839 (2021) 042099. http://dx.doi.org/10.1088/1755-1315/839/4/042099.

[39] H. N. Xolmirzayeva, N. I. Fayzullayev. Obtaining nanocarbon from local raw materials and studying its textural and sorption properties. International Journal of Engineering Trends and Technology. 70(2) (2022) 163-171. http://dx.doi.org/10.14445/22315381/IJETT-V70I2P219.