

# Analysis of an Existing Method of Producing Carbon Fiber

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**ABSTRACT:**The aim of this work is to increase the energy efficiency of furnaces for thermal stabilization of PAN fibers based on the study of heat and mass transfer processes occurring in their working space. To achieve this goal in the work, it was necessary to solve a number of scientific and technical problems: Analyze the current state of the theory and practice of the process of thermal stabilization of PAN fibers and collect the initial data necessary to develop a mathematical model of the object under study.

## I. INTRODUCTION

Carbon Fibers are one of the main types of reinforcing elements used in the creation of composite materials. Various Polymer Fibers used for their production, most often poly-acrylonitrile (PAN Fibers). The prime cost of Hydrocarbon (HC) production is very high, and the main cost item is energy consumption. The existing technology for the production of hydrocarbons consists of three successive stages of heat treatment of the original fiber: thermal stabilization, carbonization and graphitization. After the stage of thermal stabilization, the filaments of polymer fibers acquire the structure necessary to obtain the required quality of hydrocarbons. After carbonization, they acquire strength, and after graphitization, elasticity. The longest time and energy-intensive (more than 70% of the total energy consumption in three stages) is thermal stabilization. In this regard, it is advisable to reduce energy consumption for the production of hydrocarbons, reducing them at the stage of thermal stabilization, improving the design and operating mode of the furnace for this. The thermal stabilization operation consists in heating the initial fiber in the presence of oxygen to a temperature of 300°C. In this case, the structure of carbon molecules changes, approaching that necessary for

obtaining a high-quality hydrocarbon, and impurities removed. The difficulty in implementing heat treatment of PAN is that at temperatures of 230–280°C and exothermic reaction occurs in the fiber with the release of a large amount of heat ( $1.34 \times 10^6$  J/kg). This phenomenon called exo-effect. With an uncontrolled release of the heat of the exo-effect, the processed fiber may burn out, and it will become unsuitable for HC production. To prevent over burning, a stepped temperature regime is maintained in the working space of the furnace. In existing thermal stabilization furnaces, a variable temperature regime is maintained by changing the temperature of the air supplied to the working space, which are a heat carrier and a source of oxygen. The air is heated in an electric heater to a predetermined temperature and heats the processed fibers due to convective heat exchange. Simultaneously removes the air excessive amount of heat released in the fibers during exothermic reactions. This technology of thermal stabilization, implemented all over the world, is extremely ineffective and difficult to control. Over 93% of the total energy consumed spent on heating the air and only about 3% on heating the processed material. Therefore, at present, the problem of increasing the energy efficiency of thermal stabilization furnaces in the production of carbon fibers is urgent.

## II. CARBON FIBERS PROPERTIES AND SCOPE

Composite materials (CM) are modern structural materials that largely determine the level of development of rocket-space and aviation technology. Carbon fibers (HC) are currently one of the main types of reinforcing elements used to create high-modulus high-strength CM, the main of which are carbon fiber reinforced plastics (CFRP) [1-7]. HC are distinguished by high values of strength (up to 7 GPa), elastic modulus (up to 600

GPa) and low, in comparison with metals, density (1.7–1.9 kg / m<sup>3</sup>). UP - polymer composite materials from intertwined threads of carbon fiber located in a matrix of polymer (epoxy, phenolic, etc.) resins. The resin under low stress reinforces the fibers and acts as a means of transferring and distributing the load among the fibers [8]. The fillers introduced into the polymer can lead to an increase in the strength and modulus of elasticity, heat and heat resistance, and a decrease in the specific electrical resistance of the composite material [9-13]. Table 1 shows the properties of Grafil composites, created using HC, in comparison with some metals [14]. The main field of HC application is the aerospace industry, which requires materials with high specific strength and rigidity [1-3]. About 25% of the mass of artificial

satellites made up of elements made of carbon fiber reinforced plastics. The use of hydrocarbons in chemically and corrosion-resistant parts and structures is because they have a very high resistance to concentrated hot aqueous solutions of acids and alkalis. Due to their high electrical conductivity, hydrocarbons, and especially graphitized ones, are used for the manufacture of heating elements. They are used for the manufacture of heaters used both at low temperatures in spacecraft and in furnaces operating at high temperatures.[15-17]. An important direction in the development of CM from HC is also hydrogen energy, within the framework of which special fuel cells are being developed, which are widely used in many countries of the world in housing [18-21].

Table 1

Properties of Various Grafil Composites and Metals

Material	Specific weight, (g/cm <sup>3</sup> )	Tensile strength, GPa	Module Jung, GPa	Specific ultimate tensile strength, GPa	Young's modulus, GPa
Grafil made from quality HC	1.5	1.5	110	1.00	74
Grafil made of highly elastic UV	1.5	1.9	125	1.27	83
Grafil made of high strength HC	1.5	1.9	130	1.27	87
Grafil from high modulus HC	1.6	1.5	190	0.94	119
Steel	7.8	1.0	210	0.13	27
Titanium	4.5	0.96	110	0.21	25
Aluminum	2.7	0.47	75	0.17	28

HC, in addition to high strength and rigidity, have a low X-ray absorption coefficient and excellent compatibility with living tissues. These properties determine the use of HC in medicine in the manufacture of prostheses of the musculoskeletal system. HC they are used almost everywhere where, when a weight reduction is required, it is necessary to maintain the strength and rigidity of

the material. In addition, high thermal stability allows the use of HCs for the manufacture of heat-protective means. Thus, HC fabrics provide excellent heat shields. Two types of carbon fiber are been developed - high-strength and high-modulus [14, 22]. High modulus fiber is obtained by subjecting high strength fiber to graphitization. In this case, the modulus of elasticity increases, but

the strength decreases. The thermal properties of hydrocarbons substantially depend on the nature of the surrounding atmosphere [23-26]. In air, hydrocarbons are oxidized at elevated temperatures. Therefore, the temperature of their long-term operation does not exceed 300–400°C. In an inert environment, the temperature of long-term operation of the fibers is 400–600°C. Under conditions of short-term heating in an inert or reducing environment, they can withstand temperatures of 1500–2000°C and even up to 2500–3000°C. Carbon fibers were first produced in 1880 and used in incandescent lamps as light-emitting elements. Such fibers were obtained because of pyrolysis of cotton or hydrated cellulose fibers and were characterized by fragility and high porosity [1]. Therefore, the light emitting elements were unreliable. Later, in incandescent lamps, they began to use tungsten wire, with the result that the production of carbon fibers has practically ceased. Interest in carbon fibers appeared again in the middle of the 20th century, when the search for materials suitable for use as components of composites for the manufacture of rocket engines was carried out. HC on their own qualities turned out to be one of the most suitable reinforcing materials for this. Currently, the use of carbon fibers is very wide. They are successfully used in the aerospace industry, the defense industry, in the manufacture of sports and leisure products, in nuclear power engineering, mechanical engineering, petro-chemistry, construction and other industries [3][15][16][27][28]. The technology of HC application in aircraft structures has progressed rapidly and now many components are mass-produced. In fact, all progress in military aviation programs in both the United States and Europe has been achieved through the use of carbon fiber reinforced plastics, which contribute to

reducing the weight of the structure and, thereby, saving money and reducing emissions of carbon dioxide into the atmosphere. The governments of developed countries consider the presence of their own industrial base in the field of HC and CM production on their basis as a necessary condition for ensuring national security, technological independence and mobilization readiness. The production of carbon fibers is characterized by high production costs. Their price, according to sources [29-32], depending on the assortment, ranges from \$50 to \$300 / kg. Until 1972, the use of hydrocarbons was very insignificant - less than 10 tons per year, and they were used exclusively in the aviation and space industries, but even there, mainly, only for the most advanced models of technology. This situation changed dramatically in 1973, when 500,000 HC golf clubs were produced in the United States. Then, in Japan, the consumption of hydrocarbons began to rise, after which the demand for carbon fibers suddenly jumped. Huge investments in hydrocarbon production make it possible to annually increase their production in the world. [29][30] From 2008 to 2013. The consumption of hydrocarbons in the world has grown almost 1.6 times and reached 48 thousand tons. The leaders in HC production are the Japanese companies Toray, Toho and Mitsubishi; their subsidiaries are located in the USA, Germany and France. The share of HC production in Russia does not exceed 1.5% of the world level, the amount of which is insufficient to meet the demand of consuming industries. Table 2 shows the range of domestically produced carbon fibers, their properties and field of application [14]. Table 3 presents comparative data on the properties of carbon fiber-reinforced plastics produced in Russia and Japan

Table 2

Properties of domestic hydrocarbons

Material	Specific Gravity , g/cm <sup>3</sup>	Linear Density tex	Ultimate tensile strength GPa	Young's Modulus GPa	Industry Application
structural carbon thread UKN / 5000	1.72	410	2.0	210	Rocket science
Carbon thread UKN-M, grade 1	1.73	190, 380, 760	3.5	225	Aviation and missile engineering
Thread for sewing Argon UKN-3 / NM	1.72	170	3.0	250	Rocket science

HARNESS Graphite GZ, grade A	1.82-1.96	90, 120, 280, 480, 450	1.4	350	Atomic industry
Carbon fiber material GRAPAR-27	1.72	200, 400, 500, 740	2.5	270	Rocket science
Carbon fiber of UK brand	1.75	27000	2.0	200	Aircraft construction

Table 3

Comparative data on the properties of carbon fiber-reinforced plastics produced in Russia and Japan.

Parameter	Russia	Japan		
	Filler			
	ELUR-P	T-300	T-800	T-1000
Tensile strength, GPa	1.0	1.7	3.0	3.5
Compressive strength, GPa	0.9	1.4	1.7	1.7
Elastic modulus, GPa	140	125	150	170

The modernization of the industrial production of CMs with reaching a modern level in the quality of products in Russia is impossible without a multiple increase in the production of hydrocarbons and a significant increase in their quality [33-34]. HC is obtained by thermal treatment of artificial or natural organic fibers, after which mainly carbon atoms remain in the fiber material. [2]. Fibers can be made in the form of endless yarns, tows, felts, fabrics, knitwear, etc. Raw materials intended for processing into hydrocarbons must meet the following basic requirements [17]:

- do not melt during heat treatment.
- give a high yield of coke residue or carbon fiber.
- processed into carbon fiber with high physical and mechanical properties.
- have an extremely low price.

As such materials, cellulose hydrate (GTZ) and poly-acrylonitrile (PAN) fibers, pitches, polyesters, polyamides, and other polymers can be used [35-37].

### III. PRODUCTION OF CARBON FIBERS FROM POLY-ACRYLONITRILE

#### 3.1 Obtaining PANS Fibers

The main raw material for the production of high-strength high-modulus hydrocarbons is PAN fiber [30, 38]. Its advantages are a high carbon yield (about 40-50% of the polymer mass) [23] and pre-cyclized macromolecules, which are a pre-material, located parallel to each other and to

the fiber axis. Stretching during heat treatment and the formation of intermolecular bonds helps to maintain the orientation of macromolecules. Due to this, in the future, the formation of an organized form of carbon is facilitated and the technological process for obtaining carbon, especially high-strength fiber [17] is simplified. The production of hydrocarbons with high strength is also inherent in the peculiarities of the chemical composition and the supra molecular structure of the original fiber [39]. The cost of PAN fibers in the world in 2007 varied in the range of 2300-2850USD/t [40]. According to sources [41, 42], the world production of PAN fibers in 2007 was about 2400 thousand tons. Then there was a certain decline and in 2012-2013 the volume of production of PAN fibers did not exceed 2000 thousand tons per year [43, 44]. In Russia, this figure was significantly lower - 0.4 thousand tons, while consumption was 8 thousand tons [45]. This result in Russia is associated with lagging behind the world level in all indicators: volumes, assortment, quality of fibers, industry structure, innovations, etc. [46]. Currently, the only manufacturer of PAN fibers in the country is Kompozit-Fiber LLC, whose production is located on the territory of the Saratovorgsintez plant. Poly-acrylonitrile is linear, difficult to crystallize, carbon chain polymer of white color. Its structure is shown in Figure 1[1][47][48]. The presence of nitrile groups provides a relatively strong intermolecular interaction, which is expressed in a rather high

glass transition temperature of PAN (about 120 °C) [1].

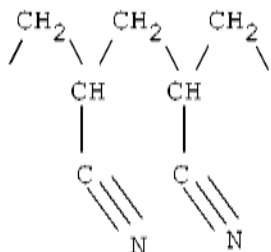
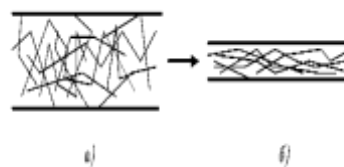


Figure 1 - The structure of the PAN macromolecule

The main stage in the production of PAN fibers is spinning, the task of which is to impart such a physical structure to the polymer that would provide the required physical and mechanical properties of the fiber. The structure of the polymer begins to form even in the spinning dope. When the solution flows through the holes of the die, the structure of the polymer undergoes significant changes that partially remain fixed in the fiber. One of the main aspects of fiber spinning is the precipitation of the polymer from the solution. In this case, several interrelated processes take place. The fiber (thread) freshly planted from the solution is subjected to orientational stretching, washing from the solvent, drying, heat treatment and finishing with various preparations

[1][49][50]. In all these operations, a change in the structure of the polymer occurs, and therefore all of them, to one degree or another, affect the properties of the finished fiber. When forming PAN fibers from solutions, dry, dry-wet, and wet methods of producing fibers can be used [51]. The most common industrial method is the wet spinning of PAN fibers. In this case, it is possible to use dies with a large number of holes (more 100,000). During the flow of the dope through the capillaries of the spinneret, a significant change in the structure of the dissolved polymer occurs. In addition to the properties of PAN and the solvent, the decisive role in changing the structure of the polymer in the capillary is played by the conditions of the solution flow: the size of the capillary, the rate of forcing of the solution, the duration of the stay of the solution in the capillary, and, of course, the temperature conditions. In addition, the conditions at the inlet and outlet of the solution from the capillary also have a significant effect. The jet of spinning solution when flowing out of the orifice of the spinneret into the settling bath expands significantly. Simultaneously with the expansion on the surface of the liquid stream, the polymer begins to precipitate. In accordance with

the law of phase equilibrium, the spinning jet transforms into a gel-like state. Under the action of water as a precipitant, the spinning stream as a system passes into a non-equilibrium state and decomposes into two phases: the first phase with a high polymer concentration is a dense framework, determining the mechanical properties of the gel thread; the second (liquid) phase is distributed in the form of micro-regions within the framework of the gel. The resulting gel thread goes through the stages of washing, drawing and drying. Stretching is necessary to increase the degree of orientation of macromolecules in the fiber, which further contributes to the formation of graphite planes in the hydrocarbon. The exhaust scheme is shown in Figure .2 [1].



a - the original structure; b - elongated fiber

Figure 2 - Effect of stretching on Fibrillar structure PAN fibers

The properties of hydrocarbons largely depend on the defectiveness and textile form of the PAN fiber [52][57]. The textile form of PAN is determined by the purpose and method of HC production. It also, largely, determines the production costs and the cost of hydrocarbons. PAN fibers used in HC production differ from commercial fibers used in the textile industry in chemical composition, type, commoner content, and physical and mechanical characteristics [47]. Special PAN Fibers contain carboxylic acids, vinyl bromide, acrylic as commoners, meth-acrylic and itacanoic acids. Commoners act as catalysts for the processes taking place during HC production; therefore, special types of commoners are selected. Special PAN Fibers, which usually used for the production of hydrocarbons, have a round cross-sectional shape, a diameter of up to 15µm, a cross-sectional area of up to 180µm<sup>2</sup> and a low linear density of up to 0.17tex. Among the large number of defects inherent in PAN fibers, the most strongly influencing the quality of hydrocarbons are porosity and uneven diameter of filaments (filaments). Since the structure of the HC retains the structural features of the original PAN fiber, the porosity is also retained, causing uneven internal stresses of the HC, which leads to an increase in its fragility and a decrease in strength [17][47][58],

thereby lowering the quality of the product. The pores also serve as embryos or centers of the onset of PAN fiber thermolysis. In their presence, the thermal stability of the PAN fiber decreases; the value of the thermal decomposition temperature decreases polymer. The non-uniformity of filaments along the diameter is characterized by the coefficient of variation of the linear density of the filaments  $K_v$ . With its high value, PAN bundles contain a large number of filaments with a diameter of 18–20 $\mu$ m and a linear density of 0.3tex, which are difficult to process using a technology designed for the use of filaments with a lower linear density [55][56].

### 3.2 Modification of PAN Fibers before heat treatment

Pretreatment or modification of PAN fiber has a strong effect on many properties of the raw material itself and carbon fibers obtained from it [59][68]. It is known[2] that in order to reduce the combustibility of PAN fibers, it is necessary to prevent de-polymerization, which leads to the formation of flammable volatile compounds, and to create conditions for the cyclization reaction, which promotes coke formation. For the initial unmodified PAN fiber, the cyclization processes providing the formation of a polymer structure capable of forming a carbonized residue begin in

the temperature range 210–270 °C. However, as the temperature rises, the processes of de-polymerization become predominant, and the rate of fiber weight loss increases significantly [69]. In order to lower the temperature of the onset of cyclization, flame-retardants (BC) are introduced into the fiber composition. The most effective MHs for PAN fibers are itaconic acid (IR), pyrofix (PF), urea (MO), and polysaccharides (PSCD). When using MH, the loss of fiber mass decreases, and the energy of the cyclization process and the total yield of volatile products in the copolymer decrease. Fiber, thermo-oxidative processes precede deeper, all other things being equal. The thermal effects of these processes and the temperatures of the onset of the exothermic effect decrease [70]. Consequently, with an increase in the content of IR, the rate of cyclization reactions increases, leading to a higher degree of completion of the cyclization process in fibers [71]. This is demonstrated by the example of several fiber samples (A, B, C, and D), differing in pretreatment, the mechanical properties of which are given in Table 4.[14]. Sample A is the original unmodified PAN fiber from which carbon fibers with a strength of only 1.38GPa and Young's modulus of 144.82GPa were obtained. These are very low values by modern standards.

Table 4  
Mechanical properties of modified poly-acrylonitrile and carbon fibers

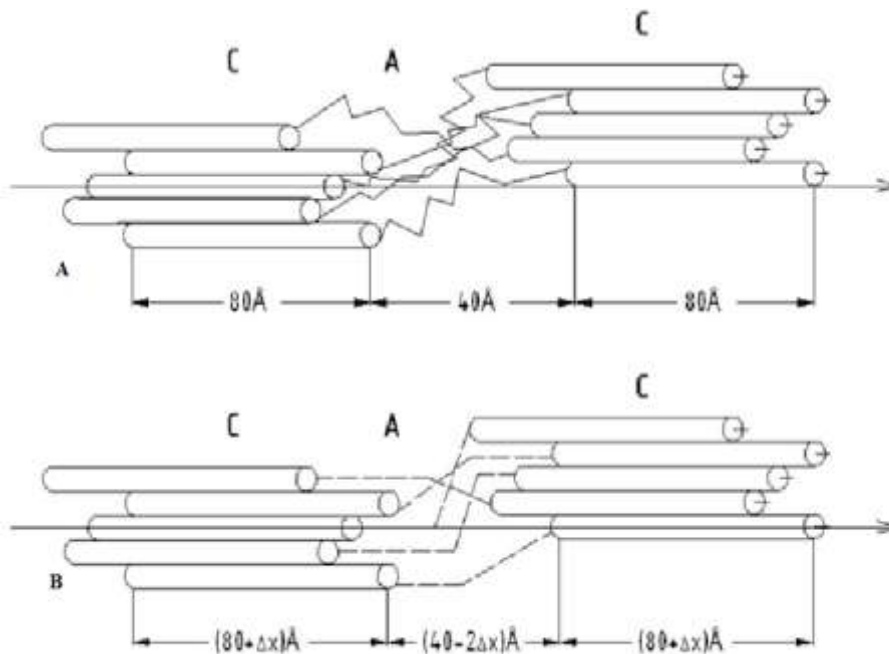
Type Modified Fiber	Sample	PAN fiber		Carbon fiber	
		Strength, Sample GPa	Elastic modulus, GPa	Strength, GPa	Elastic modulus, GPa
Nil (raw source sample)	A	0.51	4.96	1.38	144.82
Sample stretched by 10% in N <sub>2</sub> at 220 °C	B	0.57	9.93	2.75	206.89
Sample stretched 10% in air at 230 °C	C	0.51	8.62	1.88	144.82
Sample stretched in a CuCl solution at 100 °C	D	1	16.2	1.89	165.51

Sample B - modification of sample A by stretching 10% in nitrogen at a temperature of 220°C. As follows from the data in Table 4, although the strength of the raw material increased by only 12%, the value of the primary Young's modulus relative to sample A increased by 100%. Accordingly, the strength of carbon fibers increased from 1.38 to 2.75GPa and the modulus of elasticity from 144.82 to 206.89GPa. If such a

modification is carried out in air instead of nitrogen (sample C), then completely different results will be obtained. The initial Young's modulus will increase in comparison with sample A by 70%. In this case, the Young's modulus of carbon fibers will not increase. In comparison, raw materials modified by pulling in CuCl solution (sample D) significantly improved their properties: when the strength was doubled, Young's modulus increased

threefold. Although the carbon fibers obtained from sample D, have much better properties in comparison with sample A, they do not exceed the level reached for sample B. To explain the reasons for the improvement in the physical and mechanical properties of PAN fibers in the process of modification, Bonn, Warner and others [72][73] proposed a model of the morphological structure of PAN fibers, depicted in Figure 1.3, where the lamellar-like structure is composed of rods that are

in ordered regions (region C), like liquid crystals, are laid perpendicular to the axis of the fibril. The improvement in the properties of carbon fibers based on PAN fibers drawn in nitrogen and CuCl can be explained by the alignment of molecular chains along the fiber axis, the partial distribution of amorphous regions between two well-ordered regions, and an improvement in the orientation of molecules.



a) - before modification; b) - after modification

Figure 3 - Schematic representation of the morphological structure of PAN fibers

Such stretching of PAN in the presence of air does not improve the properties of carbon fibers. Unlike stretching in an inert atmosphere, oxygen, when heated, acts as a catalyst for the cyclization reaction. During stretching in air, the following changes in the structure occur instantly: cyclization, destruction of chains, and elongation of amorphous regions. While elongation will improve the degree of crystallinity and orientation, the cyclization exo effect will cause chain degradation. In this case, the usefulness of elongation will be much less, since simultaneously with the improvement of texture, defects are introduced into the molecular structure of the polymer. The use of modified PAN fiber provides [74]:

- Reduction of heat consumption for carrying out chemical processes;
- Reduction of defectiveness and hairiness of cyclized fibers;

- The possibility of refueling the technological line without a significant decrease in temperature;
- Reduction of waste for refueling.

However, at the same time, an additional link appears in the technological line - a modifying bath. A possible disadvantage of the modification can also be the presence of additional chemical elements in the fiber, which can affect the properties of the finished hydrocarbon both positively and negatively (injury). Thus, it has been argued that the modification of the PAN fiber structure leads to an improvement in the quality of raw materials for the production of carbon fibers and the PAN fibers themselves.

### 3.3 Obtaining carbon fibers from PAN Fibers

The modified PAN fiber is used for HC production. HC production technology is shown in Figure 4. It consists of three sequential processes:

- thermal stabilization by heating the fiber to 200–300 °C in air under tension (oxidation stage);  
 - carbonization when the fiber is heated to 1500 °C in an inert gas atmosphere;  
 - graphitization when the fiber is heated to 3000 °C in an inert gas atmosphere. The thermal stabilization process (TC) of PAN fiber is a complex technological process that includes a large number of parallel, sequential, chemical and

physical processes with the transformation of molecular and supramolecular structures, heat release, processes in the amorphous and crystalline phases, at phase boundaries and in the volume of micro-reactors, the formation of network structures and their relaxation, cyclization, destruction etc. [2][52][75][78]. All these processes must take place inside each elementary fiber of the PAN bundle without injury or destruction [79].

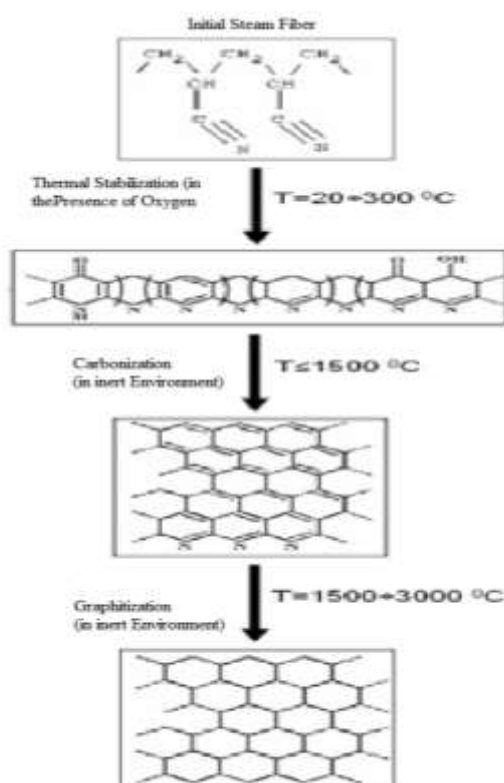


Figure 4 - Flow diagram of the technological process Thermal stabilization of PAN fibers is used to form a heat-resistant HC pre-structure, as well as to increase the resistance of polymers to the effects of various factors under conditions of storage, processing and operation [80]. In the process of thermal stabilization, the original fiber becomes fire resistant, thereby allowing further heat treatment without melting and changing its shape during carbonization. The duration of the process is 1–2 hours, while the strength of the fiber decreases and it loses about 16% in mass. Thermal stabilization of PAN fiber is called the oxidation stage because of the oxygen binding process that occurs during its course, the content of which in the fiber increases to 6–12%. According to Biryukov's data [81], in the process of thermal stabilization, reactions of the

first and second orders occur simultaneously. These types of reaction are shown in Figure 5. In the course of thermal stabilization, cyclization reactions convert the polymer into a ladder polymer by polymerization. To obtain a product with properties and chemical composition uniformly distributed over the cross section and constant along the length of the bundle, it is necessary to conduct the process at a strictly controlled temperature [22, 79]. In this case, this process proceeds with the release of water H<sub>2</sub>O, hydrocyanic acid HCN, ammonia NH<sub>3</sub> and other low molecular weight compounds [82–87]. Oxygen in the air is a catalyst for the cyclization process. The cyclized structure is thermally stable and, upon carbonization, turns into turbostratic carbon with minimal weight loss [88][92]. Turbostratic carbon is a perfect flat hexagonal network of carbon atoms



(the smallest distance between atoms is  $1.415 \cdot 10^{-10}$  m (1.415 Å)).

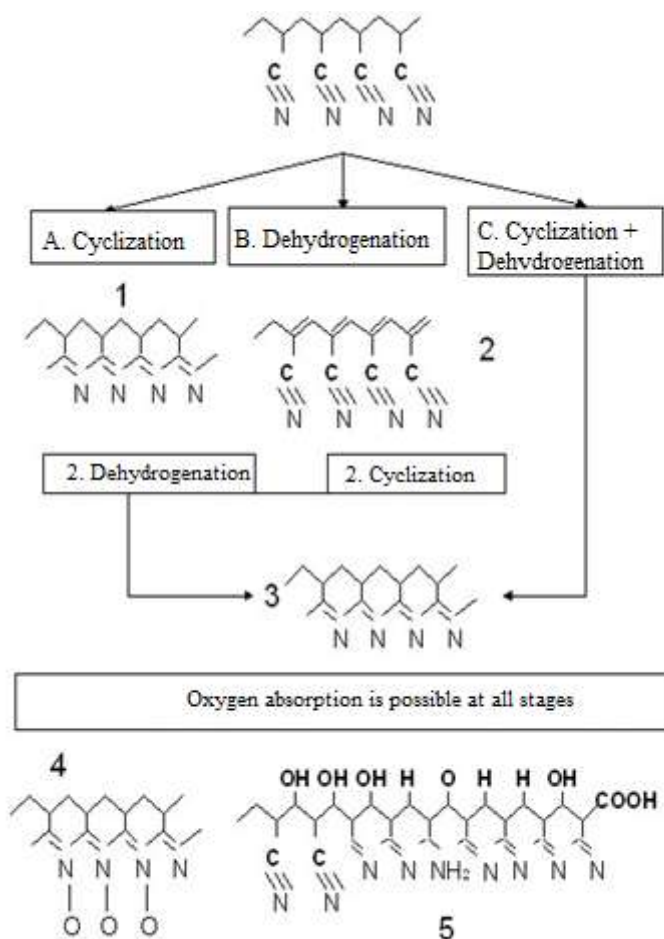


Figure 5 - Schemes of reactions during the heat treatment of PAN at temperatures up to 400°C

The next step in HC production is carbonization of the stabilized PAN fiber. Carbonization is understood as the process of pyrolysis of a stabilized fiber, in which it is converted into carbon fiber. It is at this stage that the necessary properties of the hydrocarbon are achieved. Carbonization is carried out in an inert gas atmosphere at a temperature of 1000–1500 °C. At this temperature, virtually all elements except carbon are removed from the fiber [93][96]. When the temperature is reached 1000°C fiber contains about 94% carbon and 6% nitrogen. At 1300 °C, the nitrogen content decreases to 0.3%. At a temperature of 1600°C, up to 60% of the mass of the initial PAN fiber is lost [1]. The remaining 40–45% is almost pure carbon. This ratio of the masses of the initial and final products is quite high. The duration of the carbonation process can be up to 15 minutes. Source [14] indicates 2-3 minutes. The

next stage is graphitization. This stage is intended to increase the elastic properties of the fiber. Because of graphitization, a high-modulus fiber is obtained, but its strength is somewhat reduced in comparison with carbonized HC. Graphitization is carried out, as a rule, in furnaces with graphite heaters in an inert atmosphere at temperatures of 1500–3000°C. The duration of the process is, depending on the temperature level, from 1 to 10 minutes, while the fiber loses 5–8% in mass. The term graphitization itself is not too strict, since the fiber already has a graphite structure. The increase in elasticity is achieved due to the ordering of the crystal structure and the creation of a preferred orientation of the crystals. Typically, graphite fibers are understood to have a carbon content of about 99%. In the technology of HC production from PAN fibers, the TS process is the most complex and energy-intensive. Thermal

stabilization of the rope is carried out during its movement through the working space of the furnace at an ever increasing temperature of this space up to 300°C [47][52][97]. Due to the complexity of the implementation of the mode of continuous increase in temperature in the working space of the furnace, fiber processing is used in a stepwise mode, when the tourniquet sequentially passes through zones with a certain temperature. Preheated air is used as a hot coolant in all operating furnaces of the vehicle, the temperature of which varies from zone to zone. The main difficulty in the implementation of the thermal

stabilization process is associated with the release of high specific heat upon heating the PAN fiber in the temperature range 200–300°C [98]. This heat is about  $1.34 \cdot 10^6$  J / kg and is called the "exo effect" [14]. As a result, the fiber is burned out and it becomes unsuitable for further processing [1][22]. In this regard, the TS technology is constructed in such a way as to suppress an unacceptably large exo effect. Stepwise heating of one of the samples of unmodified PAN fiber is shown in Figure 1.6. The graph is borrowed from the work of S.A. Podkopaev. [14].

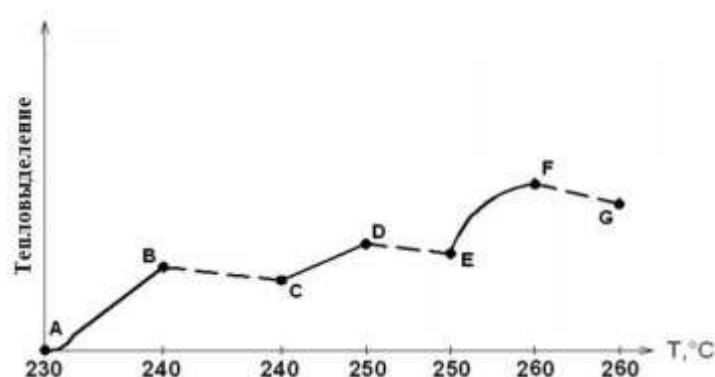


Figure 6 - Influence of step heating on differential thermal analysis of PAN fibers stabilized for 100 min at 230°C

The AB section of the curve shows an increase in the magnitude of the exothermic effect of this sample with an increase in temperature from 230 to 240 ° C in 5 minutes. Isothermal exposure for 10 minutes at 240 ° C is represented by the BC section. A sharp increase in the exo effect in the AB area indicates an intense course of reactions in non-cyclized areas of the sample structure with increasing temperature. The absence of an exothermic effect in the BC region indicates that, under conditions of isothermal holding at 240 ° C, the cyclization rate decreases. With a further increase in temperature to 250 ° C in 5 min, the exo effect appears again (CD region), but in a smaller than for AB region. Isothermal holding at this temperature makes it possible to suppress the exothermic effect (DE region) again. A similar picture is typical for the EF and FG regions. It is possible to carry out controlled heating of the PAN bundle by adjusting the heating rate, the temperature of its processing, the time of isothermal holding of the bundle, the speed of blowing the bundle with air, the composition of the gas mixture in the working space of the furnace, and the degree of bundle tension. The thermal

stabilization furnace must provide stability, reproducibility and controllability of all the listed parameters, and above all the temperature field in its working space. In operating furnaces, these requirements, in addition to changing the air temperature, are fulfilled by regulating the speed of blowing hot air through the harness being processed, and the tensile forces of the rope in the working space of the furnace. In this case, various blowing schemes are implemented. However, the blowing speed of the bundle can vary within small limits - from 2 to 5 m / s, which is associated with the possibility of fluffing the bundle. The author of [81] points out that in order to obtain a high-quality hydrocarbon, it is necessary that exothermic reactions proceed in a zone close to the kinetic one. From the author's experimental data, it follows that the Arrhenius equation can be used to describe the temperature dependence of the kinetic constants of chemical processes. At the same time, it is proposed to describe heat release during thermal stabilization, as the sum of two heat fluxes arising because of heat release during thermal decomposition of PAN components. In this case,

the equation describing the release of the heat of the exo effect will look like this:

$$Q_{cym}^{ekz} = Q_1^{ekz} + Q_2^{ekz}, \quad (1.1)$$

Where  $Q_{cym}^{ekz}$  is the total heat flux resulting from exo-effect, W;  $Q_1^{ekz}, Q_2^{ekz}$  are heat fluxes arising because of heat release during thermal decomposition of sample components according to the first and second mechanisms, respectively, W. As an assumption, it is assumed that the amount of heat released as a result of the exothermic effect during the time  $d_t$  is proportional to the mass reacted during the time  $d_{mass}$ :

#### 4. Methods and designs of furnaces for carrying out thermal

There are various methods and designs of furnaces for carrying out the process of thermal stabilization of PAN. According to one of these methods [99], it was proposed to carry out thermal stabilization according to the following regime. At the first stage, heat the bundle to a temperature of 165–250°C in 1.5–6 minutes and cool it to 20–26°C in 11.7–46.8 minutes. On the second, heating to 180–240°C in 3.3–13.2 minutes and cooling to 165–225°C in 1.5–6 minutes, repeating this cycle

five times, after which additional cooling to 20–26°C in 13, 5–54 min. On the third, heating to 210–250 °C and cooling to 165–235°C, also repeating five times. Then heating to 220–255°C and cooling to 165–245°C three times. Further still three repetitions of heating up to 235–300°C and cooling down to 165–285°C. At the fourth stage, keep the material at 165–265°C for 4–16.2 minutes. In the course of this heat treatment, it was proposed to use air for heating and cooling. As a result, the process was very long and energy intensive, which could not provide sufficient efficiency in the production of carbon fibers. There is a known method for the oxidation of poly-acrylonitrile, when the initial thread is wound on a shell made, for example, of aluminum, then this rigid package is placed in a shaft furnace, where for many hours subjected to heating from 120°C to 280–290°C [54]. With this method of processing, there is no possibility of controlling the drawing of the fiber, which negatively affects the strength of the carbon fibers obtained from this thread. In another setup [100], the cross section and top view of which are shown in Figure 7, it was proposed to isolate the transported PAN filaments from the direct action of a circulating oxidizing medium heated to 230–280°C.

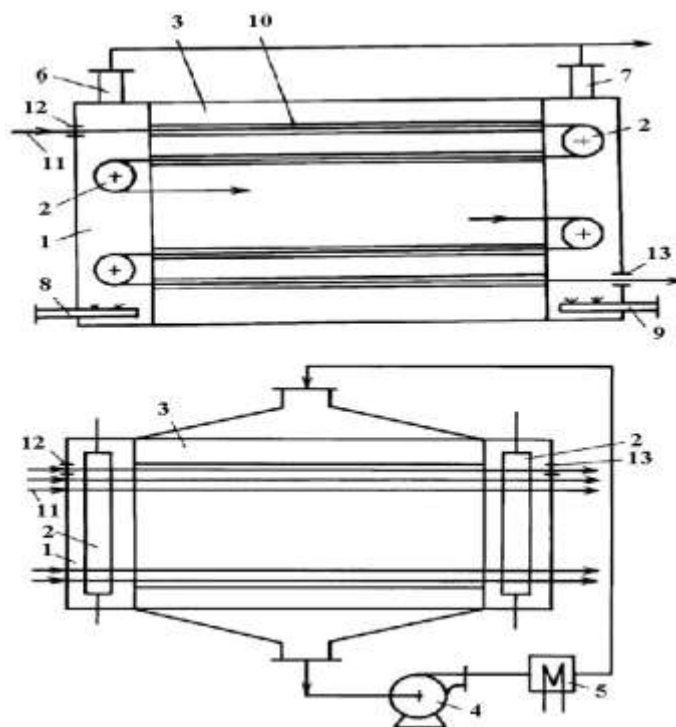


Figure 7 - Cross section and top view of the installation for thermal stabilization of PAN fibers

The installation contains prechambers 1 with transporting rollers 2 and an oxidation

chamber 3, connected through pipelines with a fan 4 and an electric heater 5. The prechambers are

provided with pipes 6 and 7 for suction of gaseous products. Connections 8 and 9 are used to suck in fresh air into the prechambers to compensate for oxygen and dilute the pyrolysis products. The oxidation chamber is equipped with slotted channels 10 for moving the threads. Two flat plates that can be mated at one or both ends form each of them. 11 threads threaded through the hole 12 into the antechamber and further into the slotted canal, pass along the entire length of the canal and leave it. Then they are charged into the next channel in the opposite direction. The number of transporting rollers and channels is selected depending on the set productivity of the apparatus. After multiple passes, the threads through the hole 13 are removed from the installation and sent to carbonization. According to the authors, the use of this installation would reduce the duration of the oxidation process of PAN fibers to 15–30 min and significantly

increase productivity. Then, a method was developed for the thermal stabilization of PAN fibers [101], which provides for the process in a sealed thermostatic chamber at a temperature of 245–255 °C. The cross section and top view of this unit are shown in Figure 1.8. By means of the PAN feeding trio-rollers 2, the fiber (flagellum) 1 is fed through the shutter slit 3 into the thermos-tatted chamber 5. The preset temperature in the chamber is maintained by means of heating elements 6. At the entrance to the heat chamber, when the roller 4, equipped with electric heating, touches, the thread is heated to the preset temperature and enters the working elements 7. In the presence of air oxygen uniformly supplied through the collector 12, under the influence of temperature in the moving fibers, processes characteristic of this stage of heat treatment begin to occur, as a result of which exothermic heat is released.

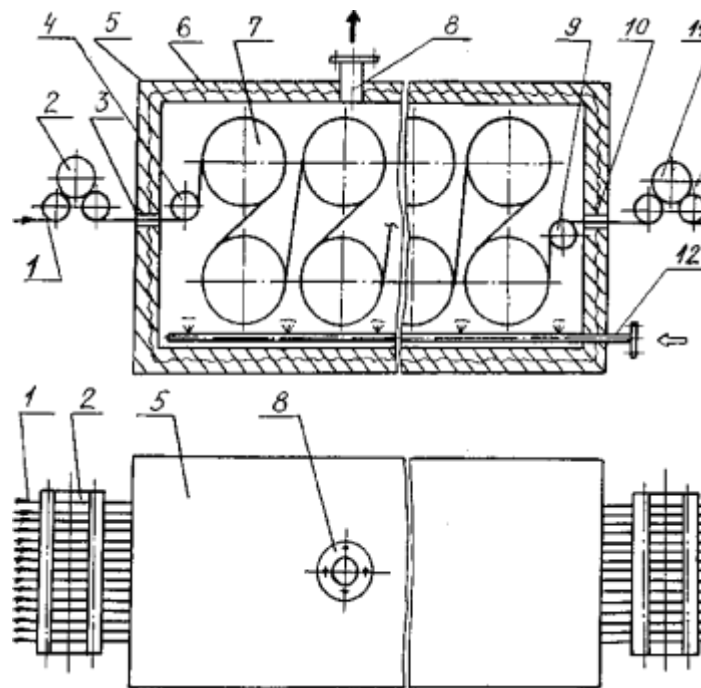


Figure 8 - Cross section and top view of the thermal stabilization unit PAN fibers

Most of the heat is used to conduct the oxidation process, and the excess, leading to overheating (deterioration of the quality) of the material, is removed from the surface of the working elements by heat sinks. The removal of oxidation products is carried out through the fitting 8. The working elements in contact with the fibers inside the chamber can have a different design. They can also be both mobile and stationary. Common to all of them is the presence on their contact surface of a zone with a uniformly

distributed, relatively fibers, and thermal conductivity. The fibers that have passed the process of thermal stabilization through the guide roller 9, the shutter slit 10, are removed from the heat chamber by the receiving trio rolls 11 and fed to the next stage of heat treatment. The complexity of the presented method of thermal stabilization lies in the creation of the same temperature conditions for the oxidation of PAN fibers, because additional metal parts in the workspace installations create temperature inertia of the

working body by increasing the heat capacity. Later, a method was proposed for thermal stabilization of a PAN bundle and a furnace for its implementation [102], providing for the stabilization of the processed material on the heat-

conducting surface of the heater in air. Figure 9 shows a thermal stabilization chamber 1 with transporting rollers 2 and a system of boxes 3 having a surface for contact with the bundles 4.

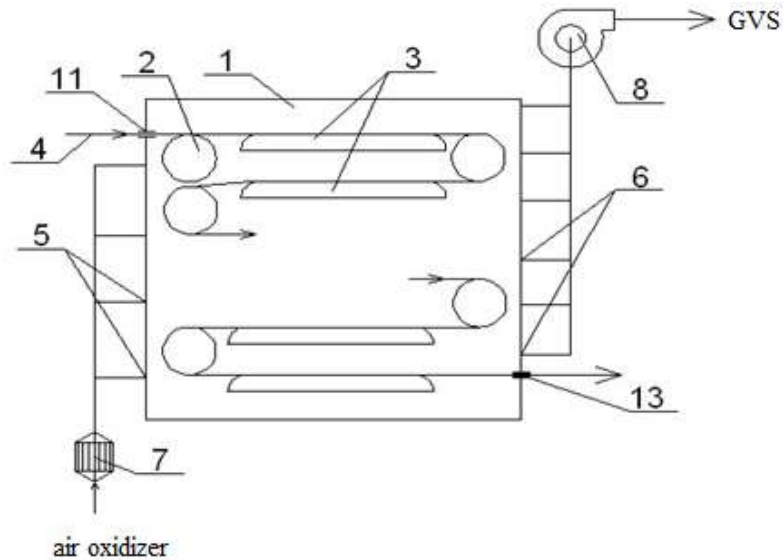


Figure 9 - Diagram of the PAN fiber thermal stabilization chamber

There are holes 6 in the walls of the chamber for removing the gas-air mixture (DHW). Outside the chamber, there are an electric heater 7 and a fan 8, connected by air ducts with openings 5 and 6. Figure 1.10 shows the ducts in which the

coolant circulates. They are made from heat-conducting material and have inside the distribution grid 9 and longitudinal stiffening ribs 10 along the length of the box.

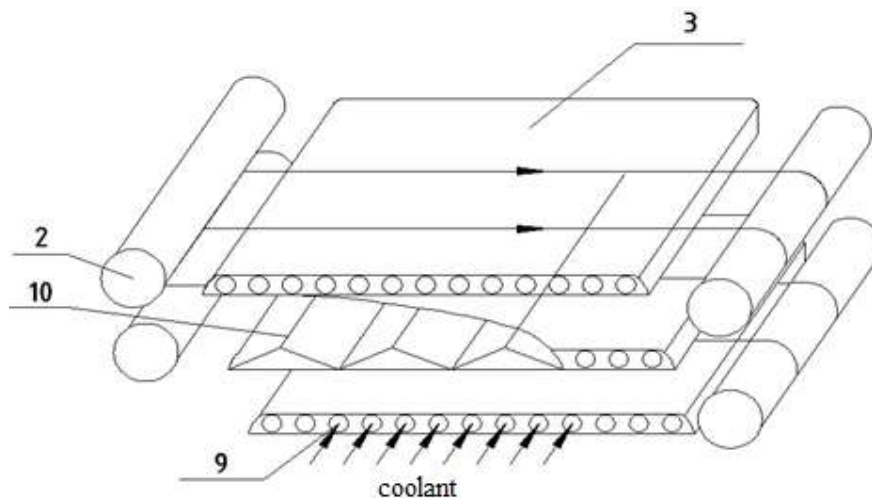


Figure 10 - Scheme of heating ducts

The ducts, the electric heater and the fan are interconnected by air ducts, as shown in Figure 1.11. Figure 1.12 shows a diagram of the regulation of the position of the box 3 relative to the

transporting roller 2 by fixing the box at different heights  $\Delta h$ . The edge sections of the boxes have smooth rounded edges.

The presented furnace works as follows. The bundles through the inlet 11 enter the thermal stabilization chamber and then, during the process,

are transported by rollers along the surface of the boxes (Fig.9).

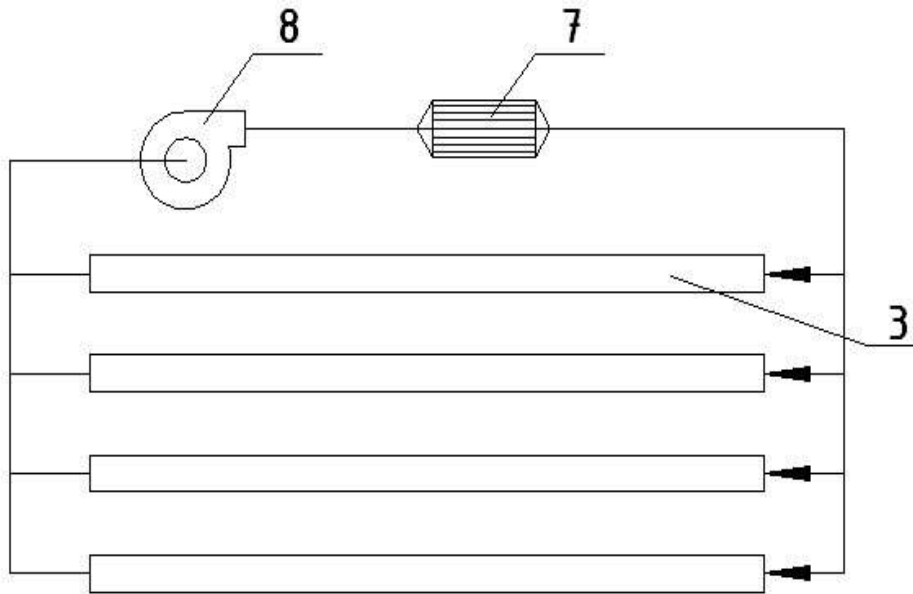


Figure 11 - Duct connection

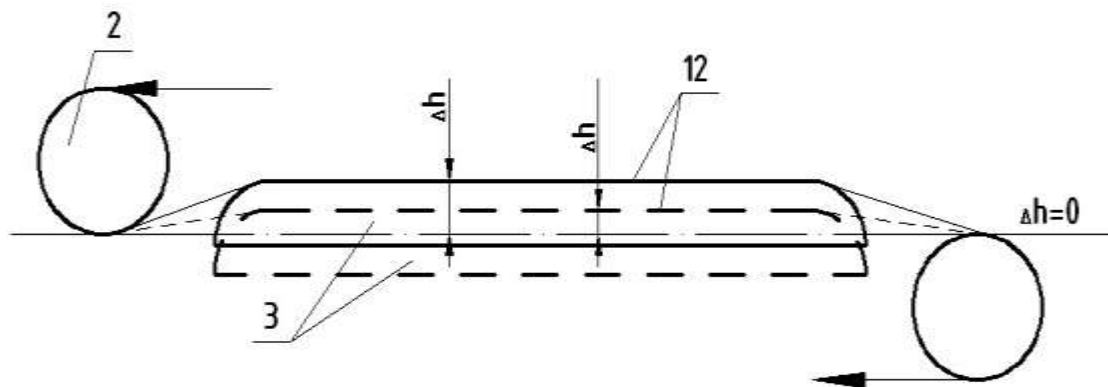


Figure 12 - Adjusting the position of the box

Heating of PAN bundles occurs upon contact with the heat-conducting surface 12 of duct 3 (Fig. 12), in which the coolant circulates in a closed circuit (Fig. 11). Excess exothermic heat is removed through the surface of the box and absorbed by the coolant. Tight contact of PAN harnesses and the surface of the box is achieved by raising the box at a distance from 2 to 10 mm above the trajectory of the harnesses (Fig. 12). The number of boxes depends on the productivity of the furnace, that is, on the required rate of thermal stabilization. After multiple passes of the system of boxes and transporting rollers, the stabilized

bundles are removed from the chamber through holes 13 and subjected to further high-temperature treatment. The air required for oxidation is heated in an electric heater 7 and directed into the thermo-stabilization chamber through holes 5. This process of thermo-stabilization is carried out with the heating of PAN bundles according to the “thermostat” principle, that is, the contact surface has a predetermined temperature with accuracy of  $\pm 1.5^\circ\text{C}$ . According to the authors of the device, the accuracy of the temperature regime is ensured by the implementation of individual circuits for the circulation of the air-oxidizer and coolant

flows. The oxidizing air is heated to a temperature sufficient for oxidation reactions in the polymer, but lower by 10–120°C the exothermic temperature, and blown through the thermal stabilization chamber at a low speed of 0.1–1.0 m / s. Since oxygen is sufficient for oxidation of the polymer, amounting to 8–12% by weight of the fiber mass, there is no need to supply large amounts of oxidizing air, which determines the lower limit of the air velocity range with a margin of 30–50% at the level of 0.1 m / s ... The air speed is in direct proportion to the performance of the thermal stabilization furnace: the higher the productivity, the higher the speed of the oxidizer. For example, with a capacity of 20 kg / h, 1.54 kg / h of oxygen or 11 m<sup>3</sup> / h of air with a temperature of 230–240°C, supplied at a speed of 0.1 m / s, is required. The coolant air circulates in a closed circuit autonomously from the oxidizing air. Its speed significantly exceeds the speed of the oxidizing agent and is determined by the required intensity of heat transfer, which ensures a given temperature regime. The surface of the heater on one side is heated by washing it with air heated to 180–280°C, on the other - it cools by heating the PAN bundle, which is pulled along it. According to the authors, the coolant due to the 50–100-fold excess of the heat transfer rate absorbs the exothermic heat released during the TS process in the "bundle - duct surface" system compared to the rate of convective heat transfer, which occurs when the bundle is blown with oxidizing air. With the closed circuit of the circulation of the coolant, the excess heat released during the thermal stabilization must compensate for the heat loss from suctioned hot water supply, with a stabilized bundle leaving the device, as well as losses through the heat insulation of the furnace. The coolant is not contaminated with toxic oxidation products and is not purified. Thus, there should be energy savings for thermal stabilization of PAN harnesses. When the ratio of the speeds of movement of the oxidizer and the coolant is 0.01–0.25, the speed of the coolant in the duct is maintained within the range of 4–10 m / s, which ensures the optimal nature of heat transfer under conditions of a weakly turbulent coolant flow. At a speed of more than 10 m / s, a turbulent flow regime of the coolant is realized, which creates an increased level of noise and vibration of the furnace structure. The load in the direction normal to the bundle surface affects the rate of heat transfer between the bundles and the heater surface. The area of contact of the bundle with the surface, as well as the uniformity of the thermal stabilization of the polymer over the cross section, depends on its value. At a load of less than

$0.275 \cdot 10^{-5}$  N / tex, only a part of the elementary fibers of the bundle contacts the surface of the heater, and the thermal conductivity in the bundle occurs in the mode of a "thermally massive body", which leads to uneven processing over the section. A load of more than  $1.1 \cdot 10^{-5}$  N / tex contributes to a high rate of thermal conductivity, but creates a risk of breaking of the elementary fibers of the bundle or their mechanical damage due to the increasing frictional force in the "bundle - box surface" system. Thus, the value of the generated load must be between  $0.275 \cdot 10^{-5}$  to  $1.1 \cdot 10^{-5}$  N / tex. In the process of polymer thermal stabilization, secondary gaseous substances are released - HCN, CO<sub>2</sub>, NH<sub>3</sub>, and C<sub>2</sub>H<sub>3</sub>CN. Mixing with the exhaust air-oxidizer, they form hot water supply, which is sucked out of the chamber with the help of a fan through the outlet openings and sent to gas cleaning. WithIn order to prevent the dispersion of toxic gaseous substances through the openings of the furnace, a pressure of 3–6 Pa below atmospheric pressure is created in the thermal stabilization chamber. The undoubted advantages of the design under consideration are the mechanism for implementing and regulating the tension of the bundles during their transportation in the working space of the furnace, as well as preventing poisonous process gases from being knocked out of the furnace by creating a vacuum in its working space. At the same time, the proposed method and the design of the furnace for its implementation have significant disadvantages. Causes serious doubts about the possibility of implementing the described scheme for removing excess heat from the bundle to the heat carrier air. The process of interphase heat transfer is determined by two parameters: the heat transfer coefficient and the temperature difference (the difference between the temperatures of the bundle and the duct surface). The heat transfer coefficient in the "gas - bundle" system has a value of about 20 W / (m<sup>2</sup> · K). There is no apparent reason to assume that this value in the "bundle - duct surface" system will be equal to 2000 W / (m<sup>2</sup> · K), as declared in the cited material. It is all the more difficult to imagine that the temperature difference in the system "bundle - the surface of the box" will be larger than in the system "bundle - air - oxidizer". Also, there are no sufficient grounds to assert that heat losses with gases and heat losses to the environment by radiation and thermal conductivity will compensate for the peak heat release at the moments of exo effects. In addition, there are a number of less serious remarks:

- very complex temperature control of the ducts;

- there is no possibility to smoothly vary the temperature of the processed fiber;
- there are certain strict requirements for the surface treatment of the boxes due to the possibility of fiber damage.

In [103], a method of heat treatment was proposed, which makes it possible to increase the volume of carbon fiber production at the same existing production facilities, using as a starting material a thicker PAN bundle with a linear density of 800 or 1200 tex, obtained by adding 16 or 24 additions of the initial PAN filament to linear density not less than 50 tex. The thermal stabilization of this PAN bundle was proposed to be carried out under isothermal conditions in an air atmosphere according to the following stepwise regime: at a temperature of 180°C - 1 hour, at 200°C - 1 hour, at 220°C - 1 hour, at 240°C - 4 hours. The authors of [104] believe that a certain improvement in the quality of the feedstock makes it possible to reduce the duration of the stage of thermal stabilization of PAN fibers to 8–15 min while maintaining the high operational characteristics of the resulting fiber. For this purpose, to improve the quality of the original PAN fiber, it is proposed to pass the polymer solution through the die additionally introduce into the solution at least one cyclic alkaline carbonate in an amount of 0.2–20 wt% of the solution mass, then the resulting solution must be heated for at least 6 minutes at a temperature ranging from 80 °C to the boiling point of the solvent. After that, the thermal stabilization of the initial PAN fiber obtained with improved properties can be carried out in a wide temperature range from 200 °C to 400 °C and use pure oxygen, air or mixtures of these gases of any composition as an oxidizing agent. Optimal temperature and time conditions for the process of thermal stabilization is proposed to be found in laboratory experiments, where the completion of the stage must be judged by the termination of the exothermic reaction recorded by the differential scanning calorimetry method, by an increase in the fiber density to 1.36–1.4 g / cm<sup>3</sup> and by the termination of fiber ignition in an open gas flame. Burners

In [105], the author describes a method for thermal stabilization of PAN based on a new principle that differs from the known analogs. The difference lies in the fact that heating is proposed to be carried out in a non-equilibrium low-temperature plasma, in which the amount of atomic oxygen and ozone, the chemical activity of which is much higher than that of molecular oxygen. In the author's opinion, this circumstance, together with the specific effect of microwave radiation, will increase the diffusion of oxidants (molecular and

atomic oxygen and ozone) into the central regions of the fiber, which will ultimately lead to its rather rapid oxidation. The author assumes that the use of this PAN TS method will lead to a decrease in the heat treatment time at this stage, which does not exceed 26 minutes, to an increase in the thread pulling speed up to 300 m / h and more. and also to a decrease in material consumption, dimensions and energy consumption of the installation. The disadvantage of this method is that the creation of a non-equilibrium low-temperature plasma and its retention in a fixed zone of the device leads to a technical complication of the process and the device, as a result of which the cost of this method of TS PAN increases. According to the authors of [106], in order to reduce the time of thermal stabilization of PAN fibers and, consequently, to reduce energy consumption and increase the productivity of the process of obtaining carbon fibers, it is necessary to simultaneously heat the working chamber with microwave radiation using any heat sources. which can be used with electric heating devices, inductor, ceramic infrared emitters, etc. The heating of the walls of the working chamber carried out in this way will lead to the heating of the gaseous medium located inside the chamber, which can be used as such conventional working media as molecular oxygen, air, etc. At the entrance to the working chamber and at the exit from it, it is proposed to place means for pulling the fiber (tension rollers or rolls), with the help of which the fiber is fixed and moves inside the working chamber at a given speed, ensuring it is in working chamber during the time required for the stabilization processes to proceed. Depending on the specific design of the working chamber, the location and power of heat sources and microwave radiation sources, a specialist can empirically select the speed of the broach, the amount of heat supplied to the working chamber, and the radiation power. The authors believe that the use of this processing method will accelerate the stabilization of fibers by at least 1.5–2 times in comparison with traditional methods (direct thermal stabilization without microwave treatment). However, in the presence of microwave radiation in the chamber, it can be difficult to measure the exact temperature inside the working chamber and near the fiber. At the same time, it is not possible to control the change in the temperature of the fiber in the event of any deviation from the predetermined temperature regime of heating. As a result of the experiments, it was found that the best results were achieved when the walls of the working chamber were heated to a temperature of 100°C to 300°C at the power supplied to the chamber microwave



radiation from 10 W to 500 W. At a chamber heating temperature of less than 100 ° C and a radiation power of less than 10 W, the stabilization process noticeably slowed down, but did not stop. And when the chamber was heated to a temperature above 300 ° C and the radiation power increased over 500 W, no significant improvements were observed. The Institute NIIgrafit developed, based on the principle of stepwise heating, a technology and a furnace for thermal stabilization of PAN bundles - a VULON furnace [107]. The furnace is continuous, electric, and continuous. It is intended for carrying out the process of thermal stabilization of PAN bundles with linear density from 250 to 54000 tex. Schematic diagram of the installation

the VULON oxidation furnace and its longitudinal section are shown in Figures 1.13 and 1.14, respectively. The frame of the furnace 1 is a welded structure consisting of a frame and a system of rectangular pipes 50 × 100 × 4 mm installed on it. In turn, the frame is a welded structure made of channels. Its dimensions are 1500 × 7240 × 3300 mm. outside, the fences of the rear wall, roof and hearth of the furnace are made of removable steel sheets that are attached to the racks to determine the reaction rates  $m_1$  and  $m_2$ , it is proposed to use the kinetic equations. Frame with screws through seals located along the contour of the sheets. There are holes in the back wall sheets for the heaters outlet.

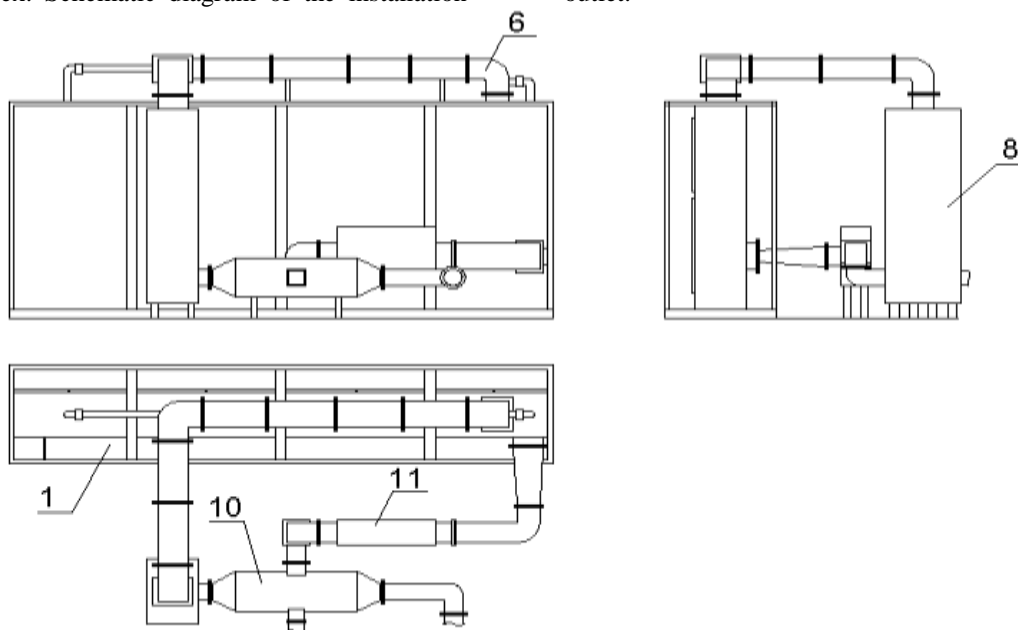


Figure 13 - Schematic diagram of the installation of the VULON oxidation furnace

The front part of the furnace is equipped with a system of eight blocks of doors fixed to the frame through silicone rubber seals, due to which, when closed, the corresponding sections of the furnace are sealed along the front. Along the edges of the oven, there are two small-width blocks, and in the center - four large-width blocks. The door construction is frame, welded. Their surface, facing

the working space of the furnace, framed by a sheet of stainless steel, and the outer surface is made of a sheet of duralumin. Thermal insulation material is placed between the sheets of metal cladding. The doors are secured in the closed position by a screw-clamping strip that simultaneously clamps two doors.

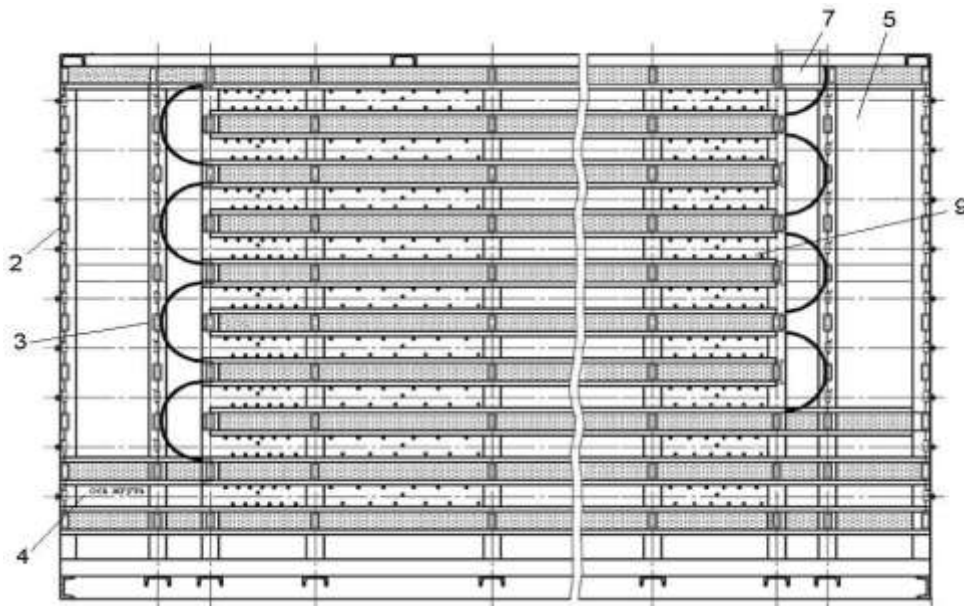


Figure 14 - Longitudinal section of the VULON oxidation furnace

The mend fences of the furnace are made in the form of a system of closures that ensure the sealing of the furnace channels in the nodes of the input and output of the harnesses of the processed material. Two shutters are installed at each end of the channel. The system of external gates 2 represents the external enclosure, and the system of internal gates 3 represents the internal enclosure of the lock chambers. In the walls of the closures there is a slot for the passage of the harnesses 4 and the grooves for the passage of the chain used for threading the harnesses. There are holes in the vaults of the left and right airlock chambers 5, through which the chambers are connected to the evacuation system of the gas-air mixture (GVS) 6 from the furnace. Through them, the suction of hot water supply is carried out, falling from the channels into the airlock chambers. For this, a controlled vacuum ( $10 \pm 1$ ) Pa is maintained at the inlet to the holes. DHW is evacuated from the unit with the help of a centrifugal smoke exhauster at a temperature of about  $280^\circ\text{C}$  through hole 7 in the roof of the outlet section of the upper heating channel. Through the pipeline, the hot water supply enters the neutralizer of toxic impurities 8, in which, during the cleaning, the hot water supply heats up to  $400\text{--}500^\circ\text{C}$ . The working space of the furnace (Fig. 14) consists of nine horizontal channels of rectangular cross-section  $600 \times 200$  mm located one above the other, connected in series along the movement of the bundles. The distance between the channels along the axis is 300 mm. The inner lining of the working space of the channels along the entire perimeter is made of

stainless steel sheets 2 mm thick. Moving the ropes through the furnace is carried out by pulling them through the channels using a multi-roll transport system at a speed not exceeding 100 m / h. Bobbins with bundles are unwound on the creel and through the aerodynamic seal is fed into the lower channel of the furnace, at the beginning of which there is the first unit of the transport system, which provides unwinding of the bundles from the non-powered creel. At the end of the first heating channel, there is a second assembly of the transport system, which ensures the absence of slippage of the bundles when they are pulled with a given tension. The assembly also provides  $180^\circ$  reorientation of the bundles and feed them into the next channel above the previous one. After the bundles exit from the upper ninth channel, they pass through the aerodynamic seal onto the reel. Tension control is carried out using strain gauges on idle reorientation rollers. It is proposed to heat the bundles in the ducts using hot air, which is preheated to the minimum required temperature in the system of autonomous air heaters: recuperator 10 and air heater 11. The heat leaving the DHW neutralizer to the temperature about  $160^\circ\text{C}$  heats the air supplied from the workshop to the recuperator by a centrifugal fan. To avoid overheating of the air entering the oven, The recuperator is provided with a cold air intake pipe and a valve that regulates the proportion of air passing through it. If necessary, the air can be heated in the heater to the technologically set temperature values of the order of  $230^\circ\text{C}$ . The air heated to a predetermined temperature enters the

second and third channels of the furnace through an opening in the middle part of the end wall of the unit. The first heating channel of the furnace does not participate in the DHW circulation and, in fact, is an isothermal thermostat. To provide the possibility of creating a controlled atmosphere in the first channel of the furnace, branch pipes for supplying or withdrawing gas / steam are provided on the side walls of the initial and final sections. The project provides for 2 schemes of air supply to the working space of the furnace. One of them, for the implementation of which the design of the furnace looks as shown in Figure 14, provides for the supply of heated air into the second channel and its further sequential advance through all channels. According to the second scheme, air is supplied to the second and third channels, at the exit from which the DHW flow is connected and, turning by  $180^\circ$ , enters the fourth channel, then into the fifth, etc. To ensure the uniformity of the temperature field in the cross section of the heating of the furnace channels at the air inlet to the channels, turbulizing grids are provided, which ensure the mixing of the air flow and the equalization of its speed and temperature over the section. The project provides for two possible options for heating the furnace channels. In the first version, it is proposed to carry out heating using tubular U-shaped electric heaters (TENs). In the second, using nichrome mesh electric heaters with a wire thickness of 0.32 mm and a cell of 0.63 mm, a width of 100 mm and a length of 550 mm. The ends of the mesh are connected in series to form a single heater. The furnace has 54 heating zones - 6 in each channel. In the case of the first option heating in each zone there are 6 heating elements, three above the bundles and three below them. In the case of the second heating option, each zone will contain two heaters located above and below at the same distance from the axis of movement of the bundles. With the help of electric heaters, the required temperature regime is maintained in accordance with the requirements of the technological process. The authors believe that the use of the VULON oxidation furnace for thermal stabilization of PAN will allow minimizing the cost of manufacturing products and thereby leading to a decrease in cost and an increase in competitiveness of carbon fiber. Thus, the issues of improving the process of obtaining carbon fibers in order to reduce the cost of their production and increase its productivity are highly relevant. In general, it should be noted that the search for the optimal method and design of the furnace for carrying out the thermal stabilization process continues. At the same time, efforts are aimed at separating the functions of heating the

bundle and its supply with oxygen, creating a heating system for the bundle with an adjustable temperature regime in space and time, ensuring the reproducibility of the temperature regime in the working space of the furnace, the creation of a mechanism for the implementation of the controlled tension of the bundles during their thermal stabilization, the reduction of energy consumption for the thermal stabilization process.

#### IV. RESEARCH DISCUSSIONS

A review of the processes for the production of carbon fibers and equipment for their implementation showed that the main raw material for this production now and in the near future is poly-acrylonitrile fibers. The properties of PAN fibers, or, more precisely, the presence of certain copolymers in them, have a significant effect on the properties of carbon fibers and on the parameters of the technological process during their production. In this regard, tools are needed to promptly respond to the composition and properties of specific fibers supplied for processing. It is advisable to correct the hydrocarbon production process at the stage of PAN fiber thermal stabilization, since this is the most complex, long-lasting and energy-intensive stage. The control of the thermal stabilization process involves, first, the regulation of fiber heating in such a way as to avoid a sharp release of a large portion of heat - the exo effect. To do this, it is necessary to regulate the temperature field in the furnace as a function of coordinates and time. A very important condition is the ability to accurately reproduce the required temperature conditions in the operating oven space. An equally important requirement is the requirement to ensure optimal uniform tension in the oven for all strands. In this work, only the thermo-physical side of the indicated problem is considered. In all available sources describing the design of thermal stabilization furnaces and the heat exchange processes that take place in them, preheated air is used as a hot coolant that provides heating of the bundle. In this case, the heating of the bundle occurs due to convective heat exchange, or directly between hot air and a bundle, or between a bundle and an intermediate heat carrier (for example, the surface of the duct), which is heated by hot air. The density of the heat flux transferred to the heated body in this case is determined by the Newton-Richman formula [99]: When the air speed in the working space is limited to no more than 5 m / s, the value of the heat transfer coefficient along the surface of the bundle will not exceed  $20 \text{ W} / (\text{m}^2 \cdot \text{K})$ . If we take into account that the heat transfer coefficient from the outer surface of the

furnace wall to the working space of the shop is usually taken equal to  $19 \text{ W} / (\text{m}^2 \cdot \text{K})$ , then it should be recognized that the heat transfer coefficient from air to the bundle has a very small value and its change in the entire permissible range of speeds air is negligible. The possible range of the temperature difference between the hot air and the surface of the heated bundle, especially in the temperature range of the exothermic effect. Fine regulation of the temperature regime in the working space of the furnace is also hampered by the fact that the temperature of the hot air changes in it due to heat exchange with the bundle rather arbitrarily. It can decrease as a result of heating the bundle, or it can increase as a result of the transfer of the heat of exothermic reactions by the bundle to air. In this case, the amount of heat and the temperature range in which it is released depends on the composition of the fiber, i.e. somewhat unpredictable. The possibilities of regulating the heating mode of the bundle during convective heat exchange are very limited. In addition, in the case under consideration, there is no need to talk about the accuracy and speed of regulation of the heating mode and its repeated reproduction in the working space of the furnace. Thus, in the implementation of traditional methods of heating a bundle in the process of thermal stabilization, in principle, it is impossible to radically improve the quality of the stabilized bundle and the technical and economic indicators of the process of its production. To the greatest extent, the requirements listed above for the rational organization of heating the bundle during its thermal stabilization the radiation mode of heat exchange with the use of electric heaters is responsible. By adjusting the number of heaters installed in the furnace and the power supplied to each heater, it is possible to realize with any necessary accuracy a predetermined temperature regime in the furnace, and also absolutely accurately reproduce it as needed in space and time for an arbitrarily long time. The use of electric heaters creates fundamental opportunities for the use of an automatic control system for the thermal stabilization process, which will improve the quality of the stabilized fiber, process productivity, and reduce scrap yield and energy consumption. From this point of view, the process of thermal stabilization and the VULON furnace for its implementation, developed at the NIIGRAFIT Institute, are of interest. As mentioned in the previous paragraph, in this furnace, equipped with a system of electric heaters, the heating of the bundles is supposed to be carried out with air, which will be heated directly in the channels by electric heaters. It seems to us that the scheme is

more expedient when the heating of the bundle will be carried out due to radiation heat exchange between the electric heaters and the bundle. and the functions of air are reduced to the supply of oxygen to the surface of the bundle and the removal of heat from its surface. This eliminates the preheating of the air. Knowing the temperature of the bundle set by the technology at the exit from each channel, it is possible to determine the amount of heat that the bundle will transfer to the air in each channel. Thus, it becomes possible to create a system for automatic control of the thermal stabilization process. The aim of this work is to increase the energy efficiency of furnaces for thermal stabilization of PAN fibers based on the study heat and mass transfer processes taking place in their working space. To do this, it is necessary to develop a mathematical model of the process of radiation-convective heat transfer in the working space of thermal stabilization furnaces PAN of VULON-type bundles and, on its basis, create a program for calculating the operating mode of each of the heaters installed in the furnace, taking into account the properties of PAN fiber supplied for processing... Such a program is the basis for the subsequent development of an automatic control system for the technological process of thermal stabilization.

## V. CONCLUSION

It has been shown that for the process of thermal stabilization of PAN Fiber in the entire temperature range, the radiation-convective mode of heat transfer is more efficient than the convective one.

## Conflict of Interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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