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**B.T. Ermagambet, M.K. Kazankapova, Zh.Kh.Ermogambetov,**
**A.T. Nauryzbayeva, K.G. Kanagatov, L.D.Abylgazina**

Institute of Coal Chemistry and Technology LLP,Astana, Kazakhstan
bake.yer@mail.ru; maira_1986@mail.ru; zhasik-28@mail.ru; k.koba@bk.ru; asemai_2296@mail.ru;
lelya_1501@mail.ru

# METHODS FOR PRODUCING CARBON NANOFIBERS FROM COAL PITCH

**Abstract.** The article gives a literature review of nanofiber production technologies from coal tar pitch. The basic methods for obtaining carbon nanofibers are considered: the stretching method, the template method, magnetospinning, electrospinning. It presents the advantages and disadvantages of these methods for the synthesis of carbon nanofibers. A technological scheme for the production of carbon fiber based on coal tar pitch has also been proposed. The prospectivity of these studies lies in the possibility of large-scale production of carbon fibers from coal pitch.

**Key words:** nanofiber, coal pitch, nanocomposites,methodof drawing, templating method, electrospinning, magnetospinning.

## Introduction

The new "era" of science throughout the world was marked by the discovery of nanomaterials. Among a wide class of nanomaterials, carbon fibers (CF) occupy a separate position, due to the uniqueness of their physicochemical properties and the prospects for practical application. Carbon fiber is a material consisting of thin filaments with a diameter of 5 to 15 microns, formed predominantly by carbon atoms. The carbon atoms are combined into microscopic crystals aligned parallel to each other. Aligning the crystals gives the fiber more tensile strength. Carbon fibers are characterized by high tension force, low specific gravity, low coefficient of temperature expansion and chemical inertness. Special fibers from phenolic resins, lignin, coal and petroleum pitches can be used to produce hydrocarbons. In this respect, coal precursors are of particular interest, since they are economically viable, and also present in large quantities in various coal deposits.

Coal pitch is a solid product of coal tar processing (yield 50-60% by weight). Coal pitch is a uniform in appearance, a thermoplastic substance of black color with a brilliant wrinkled fracture. The main components of pitch are aromatic and heterocyclic compounds, as well as their polymerization and polycondensation products. About 500 compounds have been identified in the coal tar pitch, including benzoanthracene, benzopyrenes, perylene, benzo-fluorenes, fluoranthene, naphthacene, chrysene, brazan and alkyl brazans, triphenylene, etc. [1].

Carbon fibers are one of the main types of reinforcing elements used to create high-modulus high-strength composite materials.

Materials based on carbon fibers have already been applied in the most significant, knowledge-intensive industries: engineering, nuclear power, aviation and cosmonautics, military-industrial complex, construction, in addition, carbon fibers have the potential to be used in various new applications such as electrodes, substrates catalysts, adsorbents, composites, etc. because of their large surface area and relatively high electrical conductivity [2]. In view of the low cost of the raw materials, the priority goals remain the reduction of energy inputs and the increase in the yield of the target product.

The first developments in the production of carbon fibers from pitch were carried out by Japanese researchers, who are still holding the first place in the world market for the production of carbon fibers.

The technology for producing pitch-based carbon fiber includes several stages: preparation of the substrate, fiber synthesis by spinning from the melt, stabilization in an oxidizing atmosphere, carbonization in an inert atmosphere, graphitization at an elevated temperature.

The conventional technology for the production of carbon fibers is based on the thermal treatment of various organic fibers: hydrate-cellulose, polyacrylonitrile (PAN), pitch, polyesters, polyamides and other polymers [3]. For technological and economic reasons, the most suitable were viscose, PAN and pitches [4].

The authors of [5, 6] considered that all carbon fibers were divided into several types depending on how and from what they are made (Figure 1). However, now the classification is based on their mechanical properties.

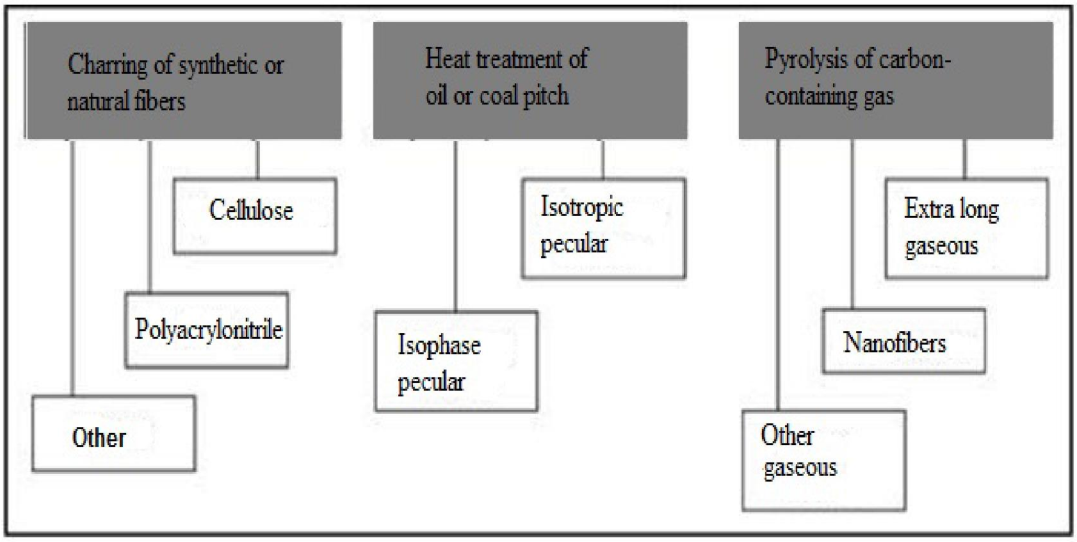


Figure 1 - Types of carbon fibers by origin

The method of drawingis that using a micromanipulator, a thin point is slightly immersed in a drop of the polymer solution near the contact boundary [7] (Figure2). Then the point is extracted from the drop at a speed of ~ $10^{-4}$ m/s, pulling the nanofibers behind it. The method of drawing produces nanofibres of polymers that withstand large deformations while in a viscous-flowing state. The length of the fibers obtained is determined by the speed of curing of the fiber due to the evaporation of the solvent (when forming the polymer solution) or the glass transition of the melt (when forming the polymer melt) [8].

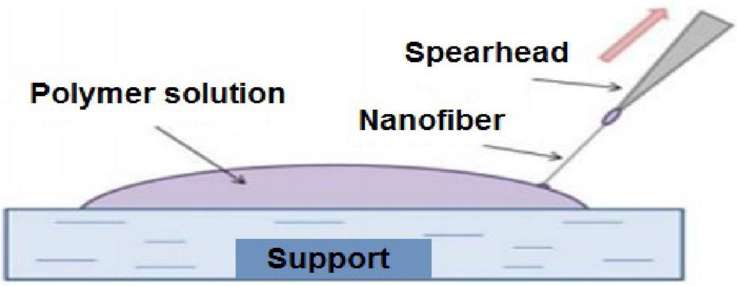


Figure 2 - Schematic representation of the preparation of nanofibers by drawing

The invention [9] relates to a technology for producing carbon fibers from carbon tar. Fibers are drawn by a single gas stream followed by additional drawing when exposed to one additional gas flow creating tension in the fiber, the velocity of at least one additional gas flow exceeding the speed of the fiber. The fiber and the additional gas stream are passed through a Venturi tube and the tensioned fiber is thermoset.

The method [10] for producing nanostructured carbon fibers is that a sprayed catalyst is deposited on the upper surface of a rotating disk through a precipitating chamber of the reactor, heated to a pyrolysis temperature, after which a continuous supply of hydrocarbon gas and the removal of gaseous pyrolysis products are carried out, and upon completion of the process pyrolysis, the finished product together with the catalyst is cooled.

The authors also considered the template method, called the nanofilter method. In this method, a template substrate (a substrate with oriented 1D nanopores) determines the direction of polymer extrusion (Figure3). The polymer solution is pressed through the nanoporous membrane due to the created hydrostatic pressure and the formed nanofibers fall into the curing solution. The diameter of nanopores determines the diameter of nanofibers. As a nanoporous membrane, porous oxides are used, for example anodized aluminum oxide, or metal dies with nanopores formed by laser drilling [11, 12].

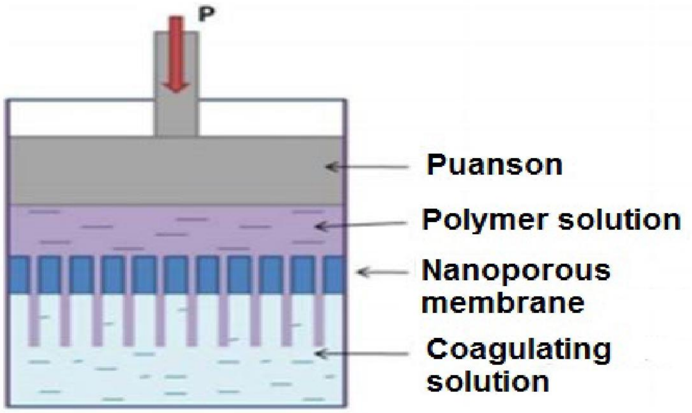


Figure 3 - Diagram of the preparation of nanofibers of polymers by the template method

Electroforming (electrospinning) is the name of a process that leads to the formation of nanofibers as a result of the action of electrostatic forces on an electrically charged jet of polymer solution or a melt [13]. Figure4 shows the scheme of the process of electroforming (EF).

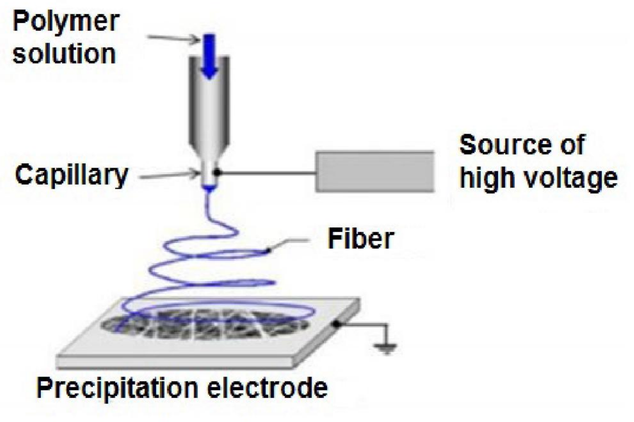


Figure 4 - Scheme of obtaining nanofibers by electroforming process

The essence of the method of electrospinning is that the electrical voltage from one to one hundred kilovolts is applied to a solution (melt), which is fed through a capillary by means of a dispenser [14]. The high voltage induces in the solution the same electric charge, which, as a result of the Coulomb electrostatic interaction, leads to the drawing of the polymer solution into a thin jet [15]. During the electrostatic drawing of a polymer jet, it can undergo a series of successive splittings into thinner jets with a certain ratio of the viscosity values, surface tension and the density of electric charges (or the electrostatic field strength) in the fiber [16]. The resulting jets harden by evaporation of the solvent or as a result of cooling, turning into fibers and under the action of electrostatic forces drift to a grounded substrate having the opposite value of the electric potential. It should be noted that the polarity with the EF can also be reversed when the capillary is grounded, and a high voltage is applied to the depositing substrate. The precipitation electrode (collector) must have good electrical conductivity [17, 18].

The authors of [19] found that by varying the parameters of the electro spinning process, it is possible to vary the thickness of biopolymer threads in the range from hundreds of nanometers to several microns. Figure 5 shows an installation designed to produce biopolymer matrices by the method of electrospinning.

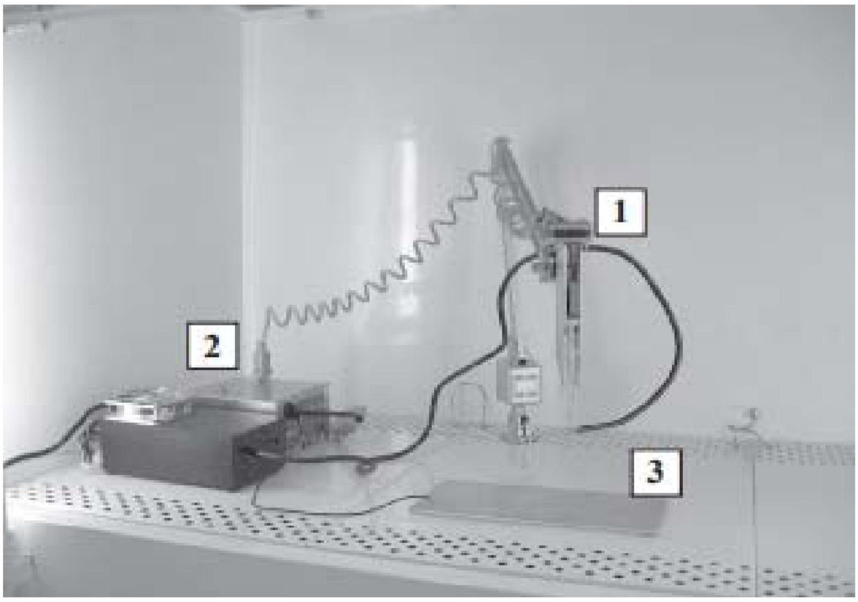


Figure 5-Installation created for manufacturing biopolymer matrices by the method of electrospinning:
1-perfusor (polymer feeding systems); 2- high-voltage power supply; 3- substrate (stationary grounded collector)

The method of electrospinning is good because, unlike usual, mechanical drawing of fibers from a solution, it does not impose high requirements on the chemistry of the process, it does not require high temperatures for solidification of the fiber, and therefore it allows the creation of fibers from long and complex molecules. As a result of the struggle between capillary and electrostatic forces, as well as the processes inside the solution, the charged drop itself lengthens, becomes thinner and dries out in flight. This method has significant drawbacks. It does not allow working with solutions of polymers with a small dielectric constant. In addition, it uses high-voltage equipment, which, firstly, is quite expensive, and secondly, it makes serious demands on safety.

Magnetospinning is a new technique for obtaining nanofibres that lacks these drawbacks. Because it uses magnetic fields to draw the fiber. It looks simpler, and its implementation does not cost as much as an electrospinning. Installation for magnetospinningcan be assembled from a cheap magnet, a simple electric motor and a syringe. This method makes it possible to reduce the cost of production of fibers.

The principle of the magnetospinning method: a permanent magnet is fixed on a rotating disk (Figure6). The point of the syringe is next to the disc. At the end of the syringe hangs a droplet of ferrofluid (polymer solution with magnetic nanoparticles). The speed of rotation of the disk is adjustable in a wide range up to several thousand revolutions per minute. The magnet attracts a droplet, and when it passes in the immediate vicinity of the tip of the needle, the droplet breaks and sticks to the magnet. With a suitable viscosity of the solution between the needle and the magnet, a bridging-constriction occurs. The disc continues to rotate, the distance between the magnet and the needle increases, the constriction stretches out, thins, but does not break. The solvent evaporates at this time, the filament becomes even thinner and solidifies, and as a result, nanofibresare formed. The bobbin, fixed on the opposite side of the disc, ensures continuous winding of the fiber.

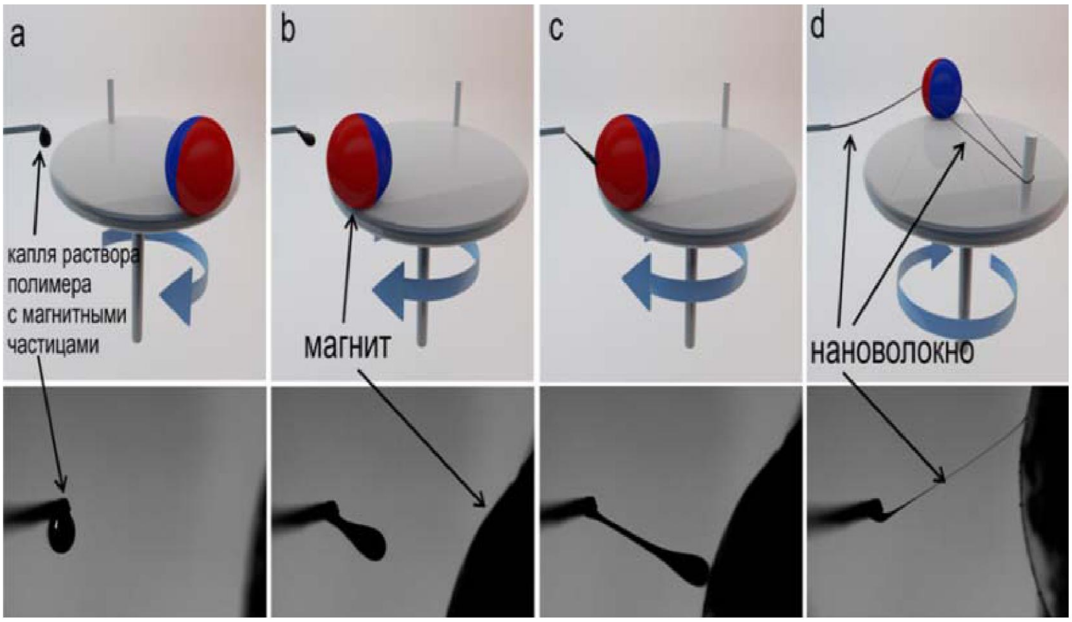


Figure 6 –Scheme of nanofibers synthesis by magnetospinning

Figure 7 represents types of fibers produced by magnetospinning method.

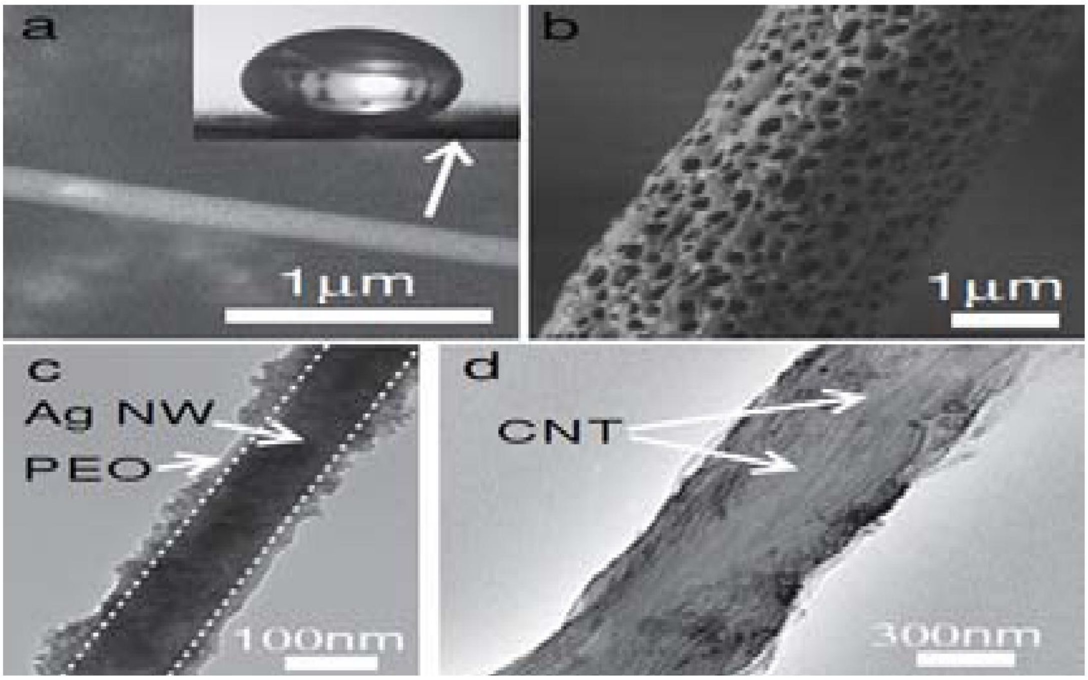


Figure 7 - Fibers produced by magnetospinning method: a- fibers from teflon;
b– porous nanofibres; c- silver wire in polymer shell; d-nanofibers with 10% carbon nanotubes

Technological scheme of carbon fibers production based on coal pitch is presented below(Figure8).