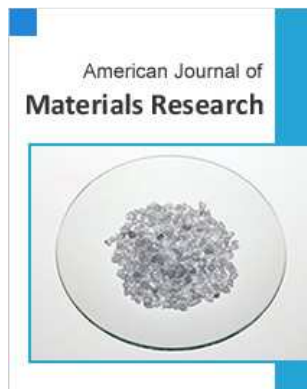




Keywords

Carbon Fibers,
Adsorbents,
Activating Additives,
Solid-phase (Chemical)
Activation,
Sorption Properties

Received: August 27, 2015

Revised: December 18, 2015

Accepted: December 20, 2015

New Carbon Fibers-Sorbents

Fridman L. I.¹, Astashkina O. V.², Rusova N. V.², Lysenko A. A.²

¹Department of Information Technology and Higher Mathematics, Faculty of Management, Autonomous Educational Institution of Higher and Professional Education of Leningrad Region State Institute of Economics, Finance, Law and Technology, Gatchina, Russia

²Department of Nanostructure Fiber and Composite Materials Named After A. I. Meos, Chemical Faculty, Saint-Petersburg State University of Industrial Technology and Design, Saint-Petersburg, Russia

Email address

frid4141@mail.ru (Fridman L. I.)

Citation

Fridman L. I., Astashkina O. V., Rusova N. V., Lysenko A. A. New Carbon Fibers-Sorbents. *American Journal of Materials Research*. Vol. 2, No. 6, 2015, pp. 57-65.

Abstract

We reviewed the development and production of carbon fibers and carbon fiber adsorbents. Flowcharts of getting CFA by methods of gas phase and solid-phase (chemical) activation are shown. This paper reviews the results of studying processes of solid-phase activation of rayon fiber materials using as activating additives $ZnCl_2$, NH_4Cl , Na_2HPO_4 . It is shown that in this case the yield was 30-38%, 8-10% without impregnation and 20% if impregnated with organosilicon compound. Carbon fiber adsorbents were obtained with pore volume of 0.42-0.62 cm³/g. The mechanism of pore formation in the fibers by chemical activation was proposed. We showed the possibility and efficiency of producing carbon fiber adsorbent by solid-phase (chemical) activation of fiber-precursors of different nature.

1. Forecasts of Production and Consumption of Carbon Fiber in the World up to 2015

Forecasts had predicted the growth of consumption of carbon fibers from 2005 to 2010 by 7-11% annually. Consequently, consumer market of carbon fibers amounted to 45000-50000 tons in 2010, and in 2014 60000-80000 tons per annum [1-3]. According to the data [4] it is seen that the demand for carbon fibers will reach 69000-350000 tons in 2015, while the productive capacity of CF may be over 110000 tons. The forecast expansion of carbon fiber (CF) production and consumption is often connected with the implementation of the USA programs of new planes production by Boeing (in particular Boeing – 777 and airliner 7E7 Dream liner – intended production in 2008), while in Europe it is connected with the increase of consumption of carbon fiber-reinforced plastic by Airbus company [4]. Besides, they predict the expansion of CF consumption resulting from assimilation and expansion of production of wind generator blades, new generation of car fuel tanks, the use of carbon armature in construction, as well as from rapid development of construction unit manufacture for hydrogen energy facilities [5]. Nowadays polyacrylonitrile (PAN) fibers make up the bulk of manufactured carbon fibers. In 2000 productive capacity of CF made of PAN amounted to 27000-28000 tons. Meanwhile productive capacity of CF made of pitch totaled only 1100 tons. From 1992 to 2002 the production of this type of carbon fibers fell almost by half [6, 7].

It is rather difficult to estimate the volumes of manufacture and productive capacity of CF from cellulose hydrate (CH) fibers due to the lack of true and complete information. Moreover, according to the work [8] during the period from 1989 to 1995 a demand for

these fibers ranged from 45 to 450 tons per year. By 1981 commercial production of CF from CH had been cut down overseas, only small production works with the capacity of 100-150 tons per year remained [9]. Nevertheless, the production of CF from CH continues due to the demand of aerospace industry and the development of the production of sorption-active fiber materials [10, 11].

Since the mid-1970s the research and production of CF on phenolic fiber basis have been developing rapidly. Initially produced for protection against flame, they turned out to be excellent precursors for the manufacture of CF, in particular of activated carbon fibers (ACFs) [12-15].

In 1991 carbon nanotubes were discovered, due to their unique qualities they are expected to be widely utilized in many areas of science and technology. Particularly, they are supposed to be used together with carbon nanofibers as effective reinforcing, electrical current and heat conductive fillers in composite materials [16, 17]. In the last 5 years an interest in nanotubes and nanofibers as effective sorbents and accelerant carriers has arisen [18-20].

The great demand for nanotubes and nanofibers nowadays is attested by the fact that in 2004 in England a semi scale production of nanotubes was mastered. In 2006 the company Pyrogruf Products were planning to open a nanotube plant with a capacity of 35 tons per year [21].

2. Concept of Development of Carbon Fiber Adsorbents

The conception of works on activated carbon fiber materials (ACFMs) is a logical development of the conception of diversification of carbon fiber application on the whole; as well as a search for new market outlets and, in particular, is a need to dispose perishable and low modulus products. On the other hand, a priori one could suppose that carbon fiber particles (filaments) with an oriented structure and diameter 5-20 microns after activation would have good sorption-kinetic properties. Moreover, carbon filament formation into various textile fibers would allow us to purify gases (to trap and filter simultaneously) and liquids, to regenerate filters, as well as form these processes in a new constructive way [22].

First western works connected with the production of ACFMs apparently are the USA patents issued in 1966 [23, 24]. In the USSR research on ACF development and study of its properties were carried out by A. S. Fialkov and his co-workers in 1966-67 [25]. The first industrial production of ACFMs in the USSR was performed with the use of cellulose (viscose) fibers in 1970 in a pilot plant Leningrad Research Institute of Synthetic Fiber.

In the early 1970s ACFMS were developed in a laboratory environment and later the industrial production of ACFMS from polyvinylchloride and phenolic precursors, polyacrylonitrile and pitch fibers was mastered. During the period of 1968-74 developments in ACFM were actively

conducted. In the USSR I. N. Ermolenko with his research staff: A. A. Morozova, I. P. Lyubliner and others contributed substantially to the ACFM research development [26]; L. I. Fridman with his research staff: V. A. Perlin, O. A. Portnoy and others [27]; L. I. Fridman contributed to production engineering.

3. Methods of Carbon Fibers Activation

In most cases processes of carbon sorbent preparation are connected with the removal of some part of the substance from the volume of carbon blocks, granula or fibers [28]. In addition, the porosity and surface area increase. The process of removal of carbonaceous substance by means of reagent etching is called activation.

Activation can be done using gases (vapor-phase or physical reactivation), liquids (liquid-phase activation) or reagents introduced into solid carbonaceous source materials (this activation is called solid-phase or chemical).

During the vapor-phase and liquid-phase activations the materials with a preliminary formed, due to the heat treatment (carbonization), carbon skeleton undergo etching. Initial content of carbon in such precursors is 80-90.5%.

During the solid phase activation carbonized materials as well as carbonaceous polymer substances; materials from pitch, peat, lignin and others can act as precursors.

When polymers, pitch, peak or lignin are used, activation processes occur simultaneously with the processes of carbonization and formation of a carbon tridimensional cross-linked porous skeleton.

For production of activated carbon fibers (ACFs) and carbon fiber materials (ACFMs) the processes of vapor phase activation are most often used. Activating agents are carbon dioxide, water vapor, oxygen or nitrogen in noble carrier-gases, ammonia.

Figure 1 shows a circuit diagram of ACFM production using vapor-phase activation, where AA stands for activating additives and FHTT stands for final heat treatment temperature.

The vapor activation and production processes of ACFMs with its use are the most developed and studied almost for all carbon fibers produced from polyacrylonitrile, cellulose, pitch, phenol resins and lignin on an industrial scale [28-35]. Moreover, from the mid 1990s the research on ACF production from precursors such as Kevlar [36], Nomex [37], Oxalon [38] was started.

The key point of ACF production by means of vapor activation is the use of high-temperature processes ($T=600-950^{\circ}\text{C}$) during the stages of carbonization and activation, which expectedly decreases carbon fiber yield and leads to high power consumption. The alternative technologies leading to the reduction in power consumption are the utilization of atmospheric oxygen or ozone (instead of CO_2 and H_2O) as activating agents and the use of different

catalytic additives that enables to decrease the temperature of activation and regulate the porous structure of ACF [39, 40]. However, for a variety of reasons these technologies have not become widely used in production.

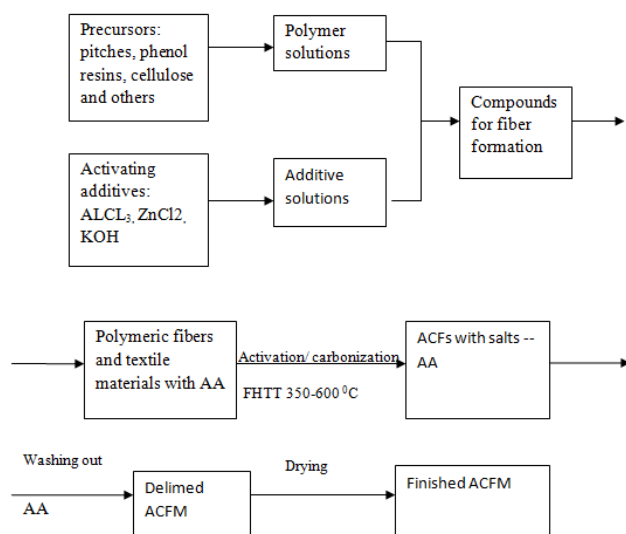


Figure 1. A circuit diagram of ACFM production using vapor-phase activation.

The study of the processes of vapor activation is promising both in practical terms and from the standpoint of the development of theoretic aspects of carbon sorbent production. To be noted is that the method of a solid-phase activation has been known for a long time and applied

industrially for carbon granulated sorbent production [41, 42], though there are rather few works on the production of fibrous sorbents using this method.

A small section on chemical activation of fibers can be found in the book of Ermolenko I. N. [43], where the essence of the method is captured. But specific process parameters and/or characteristics of the produced ACF are not given.

The thread method is based on the fact that series of inorganic compounds can interact with polymeric substances at temperatures of 200-600°C. That, on the one hand, conduces to their transformation into graphitized carbon structures, and on the other hand, formation of volatiles, which leads to gasification and formation of a developed porous structure (activation). ZnCl₂, KOH, NH₄Cl, phosphorus acid and phosphates are most commonly used for solid-phase activation. These compounds can be called activating additives (AA). This technology in the process of granular activated carbon production was developed by Plachenov T. G. and it has been used for a long time [44].

There are several possible variants of introduction of activating additives into fiber structure: by means of impregnation of finished polymeric fibers with solutions of AA and by means of introduction of AA into compounds in order to shape fibers.

Figure 2 shows a possible scheme of chemically activated carbon fiber (CF) production using finished hydrocellulose fiber (CHF) or material (CHFM).

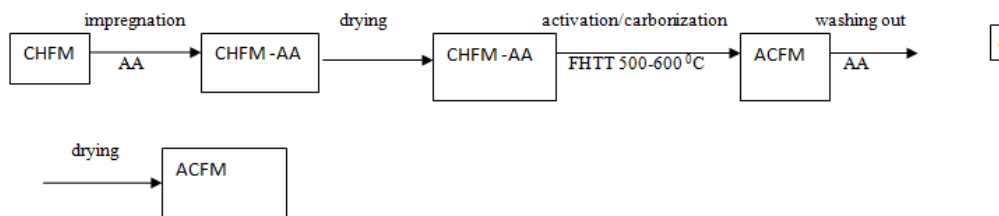


Figure 2. Technological scheme of ACFM production by means of solid-phase (chemical) activation.

Figure 3 shows the scheme of ACFM production using compounds for fiber shaping. In this case solutions of polyimide, phenol resins, lignin, polyacrylonitrile, pitch and others can be used as carbon-containing base (precursors).

The use of solid-phase activation allows us to combine the stages of activation and carbonization and correspondingly to produce ACFM using only one type of equipment – carbonization furnaces. Moreover, as processes of gasification are possible at temperatures of 200-300°C, chemically activated carbon fibrous materials in theory can be produced at the temperature range of 350-550°C when carbonization occurred, which significantly decreases power consumption and time of fiber-precursor modification. Apparently, the lower the temperatures of the beginning of fiber carbonization and formation of carbon three-dimensionally cross-linked structures, at the lower temperatures porous fiber-sorbents can be produced. Obviously, when decreasing the final heat treatment

temperature (FHTT) carbon fiber yield increases, which is cost-efficient as well. (Carbon fiber yield is the amount of carbon fiber (percentage of mass) remained after heat treatment as compared with the mass of the precursor).

Moreover, the use of activating additives in most cases leads to the necessity to wash ACF out from their breakdown product or product of their interacting with ACF-based substances. An incomplete washing out reduces the applicable scope of ACFMs, especially in medicine. Is it possible to produce chemically activated carbon fiber materials omitting washing out from AA? It is logical to presume that this is possible conditioned upon total decomposition of AA at the range of temperatures of carbonization/activation. In addition, the conditions for retention of porous structure, which formed in the volume of filaments, should be observed, i.e. its collapse must not occur.

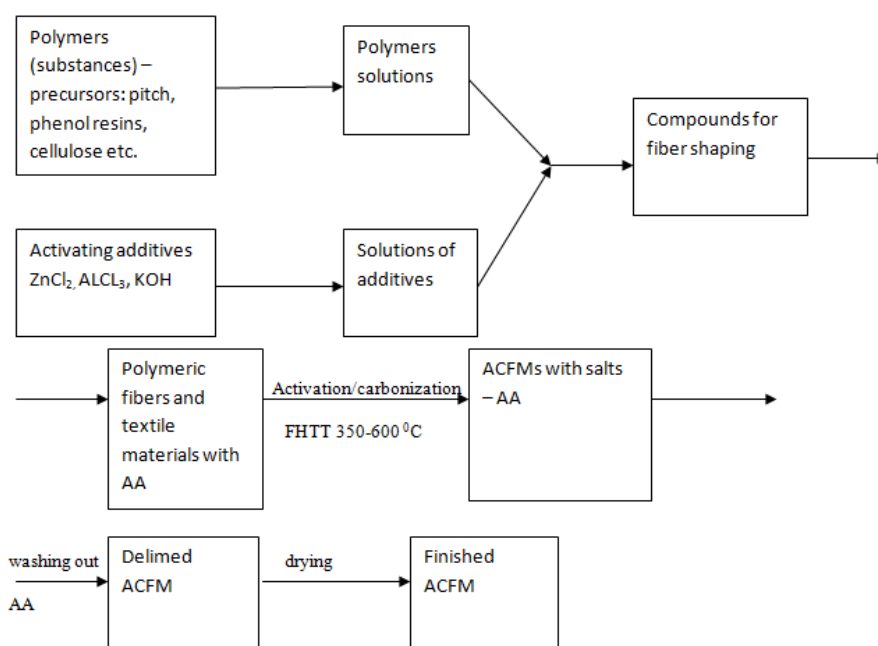


Figure 3. The technological scheme of ACFM production using compounds for fiber shaping.

4. Properties of Activated Carbon Fibers Obtained by Various Technologies

According to the data of the works [44-47] we conducted a comparative study of activation parameters and PAN-based ACF properties, produced by means of vapor, oxygen activation and using KOH. It is shown, that the samples activated by water vapor predominantly have a mesoporous structure; the samples activated by oxygen are predominantly ultra- or supermicroporous. Chemical activation enables to produce microporous fibers with low content of mesopores.

Properties of ACF produced by different means of activation are shown in table 1.

Table 1. Properties of ACF from PAN-fibers activated by different means, at minimum and maximum degrees of activation.

Activating agent	S_{BET} , m ² /g	S_o , m ² /g	$V_{0.95}$, cm ³ /g	V_{mi} , cm ³ /g	D_{av} , nm
H ₂ O	33	7.63	0.02	0.10	0.80
H ₂ O	1241	42000	1.1	0.45	0.73
air	384	13.98	0.17	0.12	0.48
air	527	1986	0.23	0.16	0.49
KOH	1197	3212	0.54	0.42	0.56
KOH	3220	153.90	1.80	1.06	0.62

Note – S_{BET} , m²/g – Brunauer–Emmett–Teller surface area (In case of microporous adsorbents – the value is overstated due to the volume infill of micropores); S_o , m²/g – outer specific surface area; $V_{0.95}$ – total volume of sorption area in terms of nitrogen; V_{mi} – micropore volume; D_{av} , nm – average pore diameter.

This work shows [48] the possibility of high-efficiency

phenolics-based sorbents production by method of solid-phase activation with KOH. The sorbents were produced under heat of the mixture of tar and activating agent in the range of temperatures from 500 to 600°C. The samples had surface area up to 2300 m²/g and volume of sorption area up to 1.21 cm³/g; at high degrees of activation an increase was noted in the number of mesopores in material structure.

The original method of bicomponent chemically activated fiber production was developed by J. Economy and his colleagues [48]. The method was based on impregnation of glass fibrous materials with different polymer solutions containing chemical activators, followed by chemical activation/carbonization of organic part of materials. Polyviol, polyacrylonitrile, cellulose, phenol resins were used as polymers. ZnCl₂ and H₃PO₄ were used as chemical activators.

Table 2. The properties of glass textile material coated with activated carbon.

Primary coating polyme	Activating agent	Max. activation temperature	Yield	Surface area, m ² /g	
				Coating	Composite
PAN	ZnCl ₂	400	90	1000	450
Phenol resin	ZnCl ₂	400	80	1200	600
PVA	H ₃ PO ₄	250	80	1000	400
Cellulose	ZnCl ₂	400	35	2500	1050

The advantages of the developed materials are their durability (owing to fiberglass) and low cost, that, according to the authors, should not exceed 7-12 USD per kilo, which is comparable to the cost of activated carbon – 2-4 USD per kilo. Apparently, one of their disadvantages is their high-density.

According to <http://economy.mse.uiuc.edu/research.htm>, the production of such materials has been started on a semi-industrial scale. Sorption properties of bicomponent ACF are shown in table 2.

The data outlined above show that ACFMs with high sorption characteristics can be produced by means of chemical activation from different polymeric precursors.

In most cases, however, the temperatures of activation/carbonization processes are significantly lower than the temperatures of activation and carbonization of vapor phase processes.

5. Results of the Experiment on the Solid Phase (Chemical) Activation of Rayon Fibers

This paper considers the findings of investigation of solid

phase activation processes of hydrocellulose (viscose) fibrous materials. ZnCl_2 , Na_4PO_4 , NH_4Cl , KOH were used as activating agents (AA). Simultaneously we assessed the impact of AA on the yield of carbon materials in the course of heat treatment. Tapes from hydrocellulose tire yarns, impregnated with AA solutions of various concentrations, underwent a heat treating process. Tapes impregnated with organosilicone additive – CH-2 and tapes without any impregnation acted as comparison objects.

The results of thermogravimetric tests of the additives (Figure 4) showed, that ammonium chloride, zinc chloride and additive CH-2 degrade completely at temperatures 350, 800 and 500°C respectively.

The least thermostable is ammonium chloride, which starts breaking down intensively into NH_3 and HCl at 200°C. As has been shown earlier, mass loss is accompanied by a pronounced endothermic effect.

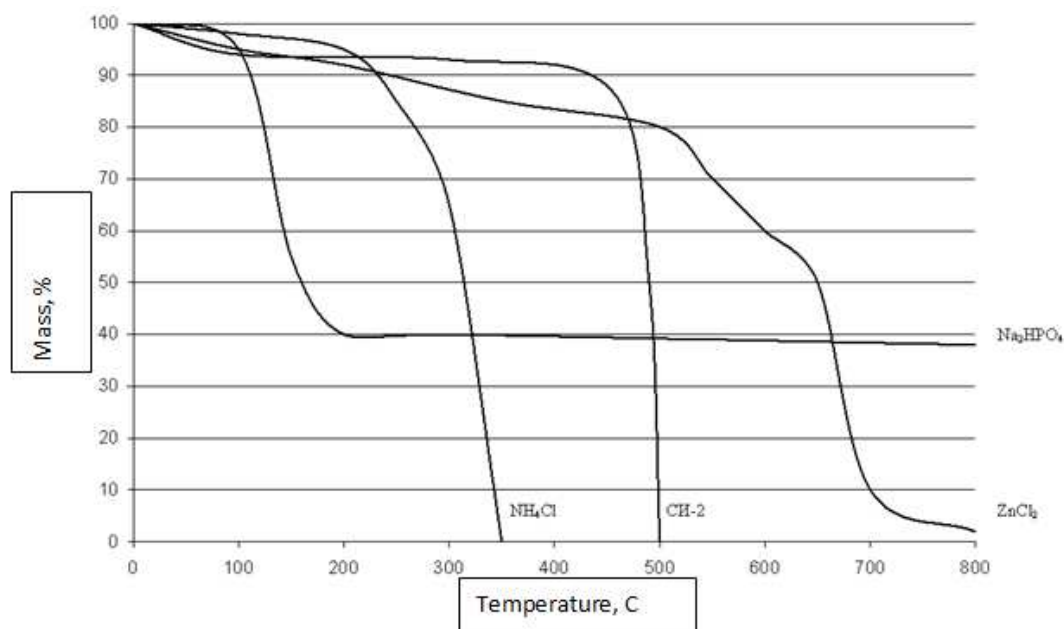


Figure 4. Characteristic curves of thermogravimetric analysis of NH_4Cl , ZnCl_2 , $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, CH-2.

Disodic phosphate crystalhydrate loses mass significantly in the temperature range of 80-180°C, but its residue after pyrolysis at 200°C remains stable even at 800-900°C. The mass loss of sodium phosphate most likely results from dehydration. The thermally-stable residue most probably is trisodium phosphate [49].

The organosilicone additive is thermally-stable up to 450°C. Heating at a higher temperature leads to a sharp mass loss without any noticeable thermal effects.

Zinc chloride in the temperature range of 20-500°C gradually loses up to 20% of its mass; in the temperature range of 500-650°C – additional 30% of its mass. Then after a temperature rise of 50°C it loses 40-45% of its mass. Along with this, there is a well-marked endothermic effect related to salt evaporation.

The research of processes of thermal destruction of viscose fibers, impregnated with different additives, has shown

(Figure 5), that the use of such compounds as NH_4Cl and ZnCl_2 leads to a significant increase of CF yield compared with the CF yield obtained without additives. The amount of CF yield when using NH_4Cl is 38%, and when using ZnCl_2 is 30%. The CF yield obtained by means of carbonization of viscose fibers without additives does not exceed 8-10%.

A slight increase of the yield -- by 10% -- can be observed during carbonization when using the additive Si-2.

Characterizing the CF yield, it should be taken into consideration that at the final heat treatment temperature (FHTT) the additive CH-2, NH_4Cl and ZnCl_2 are fully removed from the structure of carbon fibrous materials.

A different pattern is observed when Na_2HPO_4 is used as an additive. The observed CF yield (Figure 5) at FHTT 800°C (20%) must not be considered as a true one, as CFs can contain up to 50% of residues from the additive thermolysis.

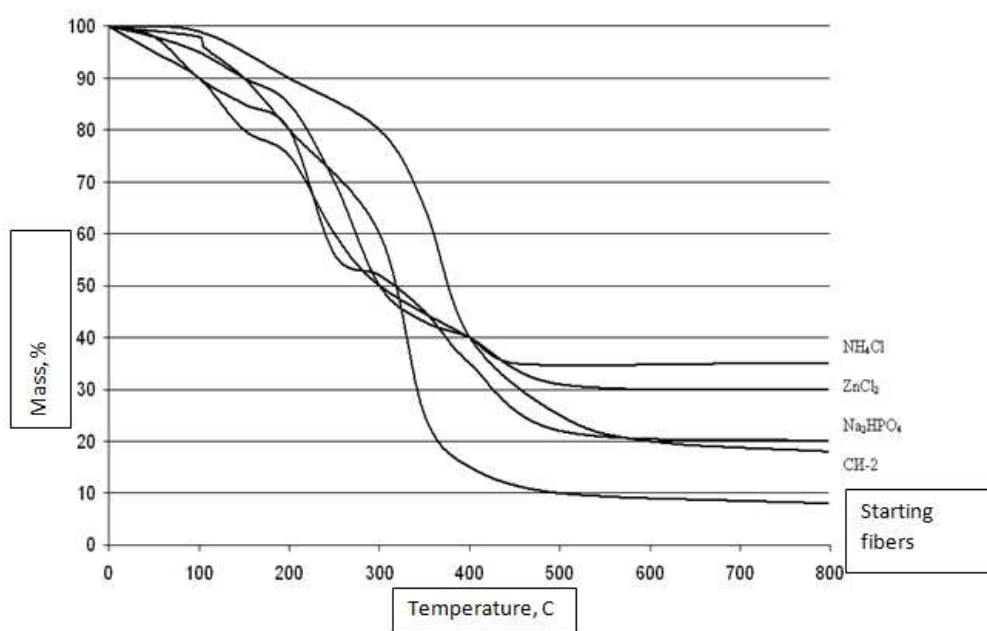


Figure 5. Characteristic curves of thermogravimetric analysis of starting viscose fibers and the fibers impregnated with the additives: NH_4Cl , ZnCl_2 , Na_2HPO_4 , CH-2.

Consequently, if according to the results of the derivatographic research of the carbonization process of hydrocellulose fibers (CHF), impregnated with Na_2HPO_4 , the amount of the CF yield is 20% (apparent yield -- gross yield), the amount of the true yield (net yield) is not more than 10-12%.

The net yield values, calculated according to the

derivatographic research data, were checked through evaluation of the mass-change of carbonized samples after water washing out from residues.

Table 3 shows the results of tests for samples impregnated with additive solutions of various concentrations. It also illustrates the data characterizing tenacity and porosity of CFMs.

Table 3. The dependence of chemically activated carbon fibers properties on the process conditions.

Activating agent	Content on fiber, %	CFM yield, %		Tenacity, cN/tex	Sorption properties		
		before washing out	after washing out		V_t , cm^3/g	SCmb, mg/g	Cl_2 , %
ZnCl_2	5	20.0	19.0	5.0	0.32	120	70
	10	26.5	26.0	4.0	0.35	170	110
	15	30.5	30.0	3.0	0.42	320	110
	20	30.0	30.0	3.0	0.40	220	90
Na_2HPO_4	5	35.0	33.0	4.0	0.22	180	70
	10	27.0	22.5	3.0	0.32	220	110
	15	23.0	16.5	2.2	0.40	380	118
	20	18.0	9.8	2.0	0.62	430	128
NH_4Cl	5	23.0	23.0	3.0	0.10	20	15
	10	35.0	35.0	5.0	0.10	20	20
	15	41.0	40.0	10.0	0.23	75	60
	20	33.0	33.5	8.0	0.32	140	100
CH-2	2	18.0	18.0	16	0.06	40.0	—
	5	18.0	18.0	16	0.07	40.0	—
	10	22.0	21.6	16	0.07	40.0	—
	2	35.0	32.0				
KOH	5	14.0	8.0	Fibers broke up			
	10	—	—				

V_t – total pore volume on benzene, SCmb –static adsorption capacity of methylene blue, Cl_2 –adsorption amount on iodine.

The use of zinc chloride as AA enabled to obtain ACF with high sorption characteristics ($V_t = 0.42 \text{ cm}^3/\text{g}$) and high carbon fiber yield (30%). It appears that 15-18% can be seen

as the desired content of this additive in the structure of starting fibers.

The desired content of NH_4Cl in impregnated CHF is

within 15-20%, which allows us to obtain ACF with total volume of sorption area up to 0.30-0.32 cm²/g and with reasonably good strength properties. When ammonium chloride is used, the carbon fiber yield can reach 40-41%.

The use of sodium phosphate allowed us to obtain ACF with the volume of sorption area up to 0.62 cm³/g. It appears that this additive can be used in practice, though activation/carbonization proceeds with a low ACF yield. However, it should be pointed out that during vapor activation of carbonized fibers, obtained with the use of CH-2, the ACF yield also does not exceed 8-15%. Nevertheless, such ACF remain competitive [50].

The highest strength characteristics of carbon fibers were observed when CH-2 was used as an additive – 16 cN/tex. The yield amounted to 20-22%, however, the volume of sorption area did not exceed 0.19-0.20 cm²/g.

The production of ACF with the use of KOH failed, which can be connected with high hydrolytic activity of alkali toward cellulose macromols.

It was also of great interest to study the influence of heat-treatment temperature on the yield and properties of ACFs. The experiments were conducted with the use of zinc chloride as an additive. The final temperature for heat treatment of impregnated CHF with additive ratio 15-18% was set within 350-550°C. Carbonization/activation proceeded, as in previous experiments, under nitrogen blanket.

The main findings are shown in table 4.

Table 4. The characteristics of ACFs obtained at different heat treatment temperatures.

Temperature, °C	Yield, %		Tenacity, cN/tex	Structural characteristics		
	gross	net		V _t	V _{mi}	V _{mc}
350	48	38	3.0	0.30	0.27	0.02
400	49	38	3.5	0.35	0.33	0.02
450	48	36	4.0	0.37	0.31	0.05
500	38	30	5.0	0.40	0.30	0.10
550	36	30	4.5	0.42	0.30	0.11
350 (without additives)	28	28	2.5	0.20	0.19	0.01

V_t – total pore volume, V_{mi} – micropore volume, V_{mc} – mesopore volume.

Analyzing the findings we can say that heat treatment temperature reduction leads to the increase of ACFM tenacity characteristics and the yield of readymade carbon (including activated) fibers.

Along with FHTT reduction the volume of chemically activated CF sorption area decreases and amounts to 0.40-0.42 cm³/g at temperatures 500-550°C, and at FHTT 350°C – 0.30 cm³/g. In the meantime micropore ratio in sorbents decreases.

Mechanism of Pore-Formation During Chemical Activation.

Concerning the mechanism of pore-formation in fiber volume during chemical activation, one can suppose two main types of physicochemical processes:

1. the formation of microcrystals of AA salts or their

degradation products in the structure of carbonific fibers. Solid nanodispersions can be extracted from fibers after the formation of a carbon skeleton, which forms porous structure. The lower heat treatment temperature, the more thermostable AA and the less reactive degradation products of additives towards supermolecules, the more likely is the formation of CFM porous structure;

2. the formation of ACF porous structure resulting from the chemical action of AA or their products of thermal degradation into fiber-precursor polymers. If low-molecular (resin) volatile products are formed after this interaction, pore-formation occurs due to their subliming at pyrolysis.

Gasification and pore-formation are more pronounced when increasing the amount of the additive admixed into fiber-precursors, and when increasing heat treatment temperature. Moreover, an increase of FHTT often leads to the breakdown of AA, which increases the possibility of chemical interaction both with a polymeric fiber base and a carbon skeleton in carbonific fibers.

6. Conclusion

Producing of carbon fiber adsorbent by solid-phase (chemical) activation of fiber-precursors of different nature is possible and effective. We found out regularities and the mechanism of activation of rayon fibers with various additives: ZnCl₂, NH₄Cl, Na₂HPO₄. We developed CFA using a single-phase process at lower (350-550°C) temperatures with high yield (30-38%), high porosity (0.42-0.62 cm³/g). The designed process is environmentally friendly because of reducing the formation of vapor-gas components during the carbonization-activation.

References

- [1] Carbon fiber market. – Available at: www.e-composites.com/marketcarbon.htm (accessed: 08.06.2015).
- [2] Carbon fiber market. – Available at: www.ecomart.com (accessed: 08.06.2015).
- [3] Carbon fiber market. – Available at: www.e-news.com (accessed: 08.06.2015).
- [4] Pora J. Materials of the 13th Inter. Confer. on Compos. Mater., ICCM-13. - Beijing (China). - 2002. - P. 86-96.
- [5] Keller W. Materials of International Conference, Raleigh, NC (USA). 2002. - P. 21-24.
- [6] Foulds B. Materials of International Conference, Raleigh, NC (USA). 2002. - P. 28-36.
- [7] Sasaki S. S. // Materials of International Conference.-Raleigh, NC (USA). 2002. - P. 15-21.
- [8] Traceski Frank T. Acquisition Review Quarterly – Spring. 1999. - P. 179-194.
- [9] Kazakov M. E. Synthetic fibers. – 1991. - №3 - P. 8–10. (rus).

- [10] Conference information. International Carbon Conference. Oviedo (Spain). - 2003.
- [11] Chun-Xia, Ya., Yan Ya-Ming et. al. // New Carbon Materials. 2002. Vol. 16. № 2. - P. 61-65.
- [12] Hayes J. S. // Encyclopedia of Chemical Technology. 1981. V. 16. -P.125-138.
- [13] Kosaoka S., Sakata Y et. al. International Chemical Engineering. 1989. V. 29. № 1. - P. 101-114.
- [14] Hayes J. S. // Nonwoven Symposium, Geneva. - 2004. - P. 257-263.
- [15] Precursors for carbon fiber production. - Available at: www.kynol.com (accessed: 08.06.2015), (rus).
- [16] Harris P.: Carbon nanotubes and related structures. - Moscow: Tekhnosfera Publ. - p. 338.(rus).
- [17] Salvatat-Delmotte J. P., Rubio A. Carbon. 2002. V. 40. - P. 1729-1734.
- [18] Future Hydrogen Energetics and Platinum Group Metals. Documents and materials of the international symposium. MMoscow, 2004. - P. 135.(rus).
- [19] Effective sorbents and catalyst supports. - Available at: www.nanonewsnet.ru/index.php (accessed: 08.06.2015).(rus).
- [20] Effective sorbents and catalyst supports. - Available at: www.thomas-swan.co.uk (accessed: 08.06.2015).
- [21] Hughes J. - P., Glasgow D. G et. al. JEC-Composites. 2004. № 9. - P. 66-70.
- [22] Fridman L. I. Principy i osnovy napravleniya primeneniya uglevoloknistyh adsorbentov [Fundamentals and the basics of applications of carbon fiber adsorbents]. Himicheskie volokna [Synthetic fibers]. - 2008. - №3. p. 86 - 88 (rus).
- [23] Patent USA RF, no. 3256206, 1966.
- [24] Patent USA RF, no. 3235323, 1966.
- [25] Fialkov A. S., Smirnov B. N., Bayer A. I. et al. *Vysokomolekulyarnye soedineniya* [High molecular weight species] 1969. Vol. 9. № 6. - pp. 464-467.(rus)
- [26] Ermolenko I. N., Morozova A. A., Gavrilov M. Z. *Proceedings of the Conference ASBSSR*, 1974. Vol. 18. № 3. - pp. 234-237 (rus).
- [27] Fridman, L. I., Morozova A. A., Stark I. M. et al. Vesci ASBSSR, 1974. № 2.- pp. 37-41.(rus).
- [28] Elchina V. I., Javorskij I. A., Fridman L. I. et al. *Vnutriporovoe reagirovanie uglerodnyh volokon s kislorodsoderzhashhimi gazami* [Intrapore reacting of carbon fibers with oxygen-containing gases]. *Himija tverdogo topliva* [Solid fuel chemistry]- 1983 - № 1. - pp. 94-99.(rus).
- [29] Fridman L. I., Grebennikov S. F. *Teoreticheskie aspekty polucheniya i primeneniya uglevoloknistyh adsorbentov* [Theoretical aspects of coal-fiber sorbent production and application]. *Himicheskie volokna* [Synthetic fibers]. - 1990. - № 6. - pp. 10-13. (rus).
- [30] Fridman L. I., Morozova A. A., Stark I. M. et al. *Uglerodnye voloknistye adsorbenty na osnove gidratcelluloznyh volokon* [Hydrocellulose -based carbon fibrous adsorbents] Vesci, ASBSSR, Ser. Khim. Nauk, 1974, № 2, pp. 37-41.(rus).
- [31] Abdallah, M. G. Low Cost Carbon Fiber (LCCF) Development Program for Automotive Applications. Carbon Fibers 2002, Materials of International Conference, Raleigh, NC (USA), 21-23 October 2002, pp. 56-59.
- [32] Ryu S. K., Jin H., Condy D., Pusset N. Activation of carbon fibers by steam and carbon dioxide / Carbon. - 1993. 7. pp. 841-842.
- [33] Lin Ry, Economy J. Preparation and properties of activated carbon fibers derived from phenolic precursor. J. Appl. Polym. Symp. 1973. 21. p. 43.
- [34] Fei You Qing, Black Heather. Effect of carbonization temperature on steam activation rate and porosity of activated carbon fibers. Carbon'94. Granada 3-8 July 1994. Extend. Abstr. And Programme. Granada 1994. pp. 446-447.
- [35] Rodriguez-Reinoso F., Pastor A. C., Marsh H. Preparation of activated carbon cloths from viscous rayon. Part II: physical activation processes /Carbon 2000. 38. pp. 379-395.
- [36] A. Cuesta, A. Martinez-Alonso et. al. Chemical Transformations Resulting from Pyrolysis and CO₂ Activation of Kevlar Flocks., Carbon, V. 35, 1997. - pp. 967-976.
- [37] Muhina, O. Ju. // *Poluchenie i issledovanie svojstv aktivirovannyh voloknistyh uglerodnyh materialov s razlichnoj poristoj strukturoj. Diss. kand. teh. nauk.* [Production and study of activated carbon fiber materials properties with various porous structures. Cand. tech. sci. diss.] St.-Petersburg, 2003. p. 163.
- [38] Ismail, I. M. K. Oxidation of Rayon Fabrics in Atomic and Molecular Oxygen / Carbon, 28, 1990. - pp 401-409.
- [39] Ermolenko I. N., Ljumbliker I. P., Gul'ko N. V. // *Jelementosoderzhashhie ugol'nye voloknistye materialy* [Element-containing coal-fiber materials] / Minsk, *Nauka i tehnika* [Science and technology], 1982. - p. 272. (rus).
- [40] Muhi V. M., Tarasov A. V., Klushin V. N. / *Aktivnye ugli Rossii* [Russian active coals] / Moscow: *Metallurgija* [Metallurgy], 2000. -p. 325 (rus).
- [41] Fenelonov V. B. / *Poristyj uglerod* [Porous carbon], Novosibirsk, 1995. - p. 518 (rus).
- [42] Ermolenko I. N., I. P. Lyubliner. Chemically Modified Carbon Fibers and their Applications. VCH, FRG, 1990, p. 295.
- [43] Ryu Z., Zheng J., Wang M. et. al. Nitrogen Adsorption Studies of PAN-based Activated Carbon Fibers Prepared by Different Activation Methods /Fuel Processing Technology, № 77-78, 2002, p. 237-241.
- [44] Ryu S. U., J. W. Shim, K. S. Yang et. al. Activated Carbon Fibers from Chemically Modified Coal Tar Pitches. Carbon Science, VI, № 1, 2000. - pp. 6-11.
- [45] Ismail, I. M. K. On the Reactivity Structure and Porosity of Carbon Fibers and Fabrics. Carbon, 29, 1991. - pp. 777-792.
- [46] Smisek M., Cemy S. Active Carbon. Manufacture, Properties and Applications. N. Y. Elsevier, 1970. -486 p.

- [47] Teng H., S-C. Wang. Preparation of Porous Carbons from Phenol – formaldehyde Resins with Chemical and Physical Activation. *Carbon*, № 38, 2000. – pp 817-824.
- [48] Yue Z., Mangun C. L., Economy J. Preparation of Fibrous Porous Materials by Chemical Activation $ZnCl_2$ Activation of Polymer-coated Fibers. *Carbon*. — 2002. — Vol. 40, № 8. — pp. 1181–1191.
- [49] Piskunova I. A., Lysenko A. A., Astashkina O. V., Basok M. O. *Derivatograficheskie issledovaniya termicheskogo povedeniya nekotoryh solej* [Derivatographic research on thermal behavior of some salts]. *Himicheskie volokna* [Synthetic fibers], 2003. - № 2. pp. 65–68.
- [50] Fridman L. I., Perlin V. A., Tarasova V. V. *Poluchenie, svoystva i primeneniye uglerodnih voloknistykh adsorbentov* [Production, properties and application of carbon fibrous adsorbents]. *Obzor* [Review]. Moscow, NIITEKHIM, 1981, p. 27.