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NANOTECHNOLOGIES
AND NANOMATERIALS

Technology for Manufacture of Pure Fullerenes C_{60}, C_{70} and a Concentrate of Higher Fullerenes

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Abstract—An integrated technology for manufacture of fullerenes was developed. It includes the following stages: synthesis of a fullerene black, extraction of a mixture of fullerenes from the black, preliminary separation of the mixture into concentrates enriched in C_{60} and C_{70} fullerenes, and production of C_{60} and C_{70} fullerenes of purity exceeding 99.5 and 98.0 wt %, respectively, from the concentrates.

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The development of nanotechnologies is a priority of the XXI century and, beginning in 2000, has been attracting considerable investment in all the developed countries of the world. In 2007, the Federal Target Program “Development of the Infrastructure of Nanotechnologies in the Russian Federation in 2007–2010” is brought in force in Russia. According to estimates, no less than 25% of current nanotechnological designs are, and will be, associated with use of fullerenes. However, despite the considerable progress in studies of fullerenes and development of technologies for their production, a number of problems have not been resolved, which hinders wide application of fullerene nanostructures. The major problem is high cost of production, separation, and purification of fullerenes.

Several methods for synthesis of fullerenes are presently known [1–10]. The most preferable of these are the electric-arc technique [9] and method of incomplete combustion of hydrocarbons (benzene, toluene, etc.) [6]. Other methods have been poorly studied and can be only used on a limited scale.

In both methods, the main synthesis product is the so-called fullerene-containing carbon black (FB). In addition to fullerenes, the black contains amorphous carbon and, in the case of incomplete combustion of hydrocarbons, also impurities of polycondensed aromatic hydrocarbons.

A characteristic distinction of fullerenes from other structures composed of pure carbon is their ability to dissolve in organic solvents. This enables recovery of fullerenes from FB by extraction with organic solvents [11–14].

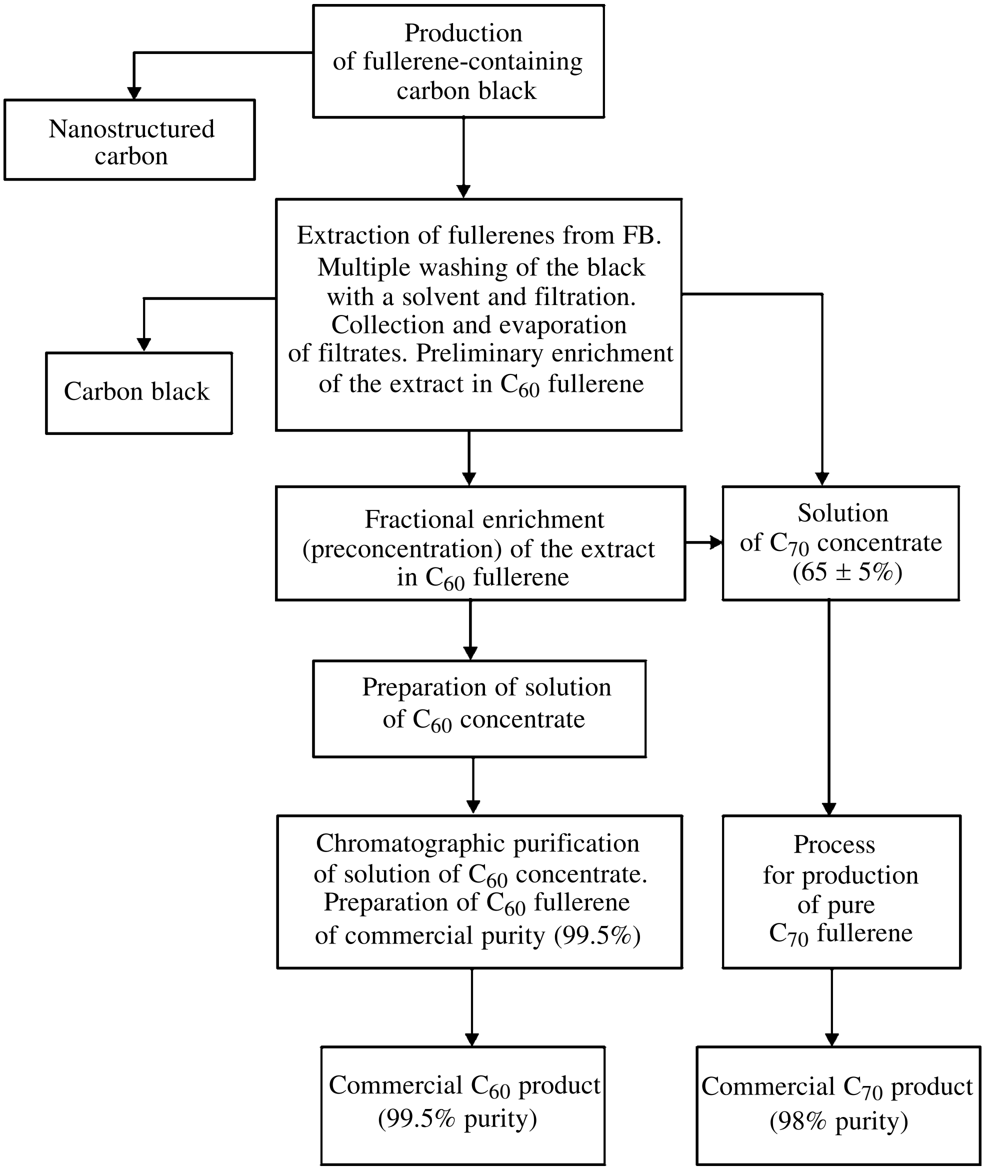
The integrated technology for manufacture of fullerenes, suggested in this paper, includes stages of FB synthesis, extraction of a mixture of fullerenes from the black, and subsequent separation and purification of the fullerenes (see scheme). This technology has been used for more than 10 years at the St. Petersburg Institute of Nuclear Physics for production of kilogram amounts of C_{60} of 99.5% purity (here and hereinafter, the composition of fullerenes is given in weight percents).

Manufacture of FB by electric-arc evaporation of graphite. The fullerene-containing carbon black produced by the electric-arc method, as a rule, contains a mixture of fullerenes with the following content of the main components (wt %): C_{60} 65–88, C_{70} 12–30, and $C_{n>70}$ 1–5. A specific feature of the electric-arc method is that it produces, together with a carbon black containing up to 20 wt % fullerenes, also so-called cathode deposits containing up to 40 wt % multilayer carbon nanotubes, which a valuable material for nanotechnologies.

The designs of electric-arc carbon-black generators (EACBGs), developed by now, provide, under certain conditions, a fullerene yield of up to 43 wt % [5]. However, the increase in the fullerene yield entails a decrease in the evaporation rate of graphite [15]. It has been noted [2] that, as the diameter of the electrodes being evaporated increases, the yield of fullerenes should necessarily decrease. This circumstance serves as a certain limitation in developments of a high-capacity EACBG design [5, 16–19].

Processing of FB with low content of fullerenes is unprofitable because of the increasing expenditure of

Integrated flowsheet for manufacture of fullerenes



electric power, solvents, and labor per gram of the final product. The experience of EACBG exploitation made it possible to find a balance between the content of fullerenes in a black and the output capacity that would be optimal from the profitability standpoint. The optimal output characteristics are provided both by limiting the diameter of a graphite rod being evaporated (as a rule, to 6–15 mm) and by choosing the rate of its evaporation. The generator designs used show the best performance with rods (electrodes) 6–8 mm in diameter. In prolonged operation modes, the average yield of fullerenes varies within 6–10% of the mass of the fullerene-containing carbon black, which, in turn, constitutes 35–50% of the mass of the evaporated graphite (the rest is the cathode deposit). The yield of the carbon black can be raised by reversing the polarity of the electrodes for “back” evaporation of the cathode deposit. However, the evaporation of the cathode deposit is slow because of its high electrical resistivity, which makes the gain in the output capacity insignificant.

The fullerene yield is markedly raised if water-cooled screens, coils, and other devices that shield fullerenes from the detrimental action of hard UV radiation of the arc are present in the evaporation chamber [5, 18]. The yield of fullerenes also depends on the purity of the graphite material. The best results were obtained with domestic raw materials on MPG-6

Table 1. Parameters of an extraction installation for extraction of fullerenes from electric-arc FB

Parameter	Value
Maximum weight of FB charged into extractor, kg	3
Preferable mass of FB charge, kg	1.5–2.0
Extractant/FB ratio, liters of solution/kg of FB	10–12
Number of extraction cycles	3
Duration of agitation (extraction), h:	
first cycle	~1
second cycle	~3
third cycle	~6
Efficiency of extraction process (3 cycles), %	92–95
Residual content of fullerenes in carbon black (3 cycles), %	0.2–0.3
Irrecoverable loss of solvent, %	9.0
Duration of extraction process (3 cycles), h	15–17

spectroscopic graphite rods of ultrapure 7-2 and 7-3 grades [TU (Technical Specifications) 48-4802-14–88].

An EACBG of basic design was used to process 225 kg of graphite rods (6 mm in diameter, 200 mm long). The capacity of the generator in terms of evaporation of graphite rods was, on the average, 100 g per hour. The mean fullerene content of FB was 6–8 wt %.

It was found in a prolonged exploitation of a working prototype of an electric-arc generator that maintaining the fullerene yield at a level not lower than 6 wt % in continuous operation requires that the helium atmosphere in the evaporation chamber should be renewed at regular intervals of time. This is necessary because impurities released from the graphite being evaporated (trace amounts of sorbed moisture, atmospheric oxygen, etc.) accumulate and suppress generation of fullerenes. A promising technical solution concerning the removal of FB from the electric-arc zone with a directed flow of inert gas (helium) and its collection in special containers proved to be poorly efficient for the given case because the system for helium recycling is bulky and complicated in use. A more practically feasible procedure is that with periodic renewal of the helium atmosphere in the evaporation chamber, correlated with maintenance stops.

Thus, the presently used electric-arc FB generators have limited output capacity, mainly determined by the evaporation parameters of the graphite material. The problem of raising the FB yield can be partly resolved by incorporating the electric-arc unit into a computer-controlled multiunit system [10]. This will markedly diminish loss of time for unit recharging.

Extraction of fullerenes from FB. Several methods are known for recovery of fullerenes from FB [11, 12, 14]. Their principal disadvantage consists in long duration of extraction and filtration and low degree of fullerene recovery (≤70 wt %). The solvents used in the process of fullerene recovery from carbon black should satisfy the following requirements: high solubility of fullerenes, as low boiling point as possible, low fire and explosion hazard, low toxicity, and low cost. Published data (e.g., [20, 21]) on the solubility of fullerenes in various solvents can be used to compose a list of solvents best suitable for large-scale extraction: toluene, *o*-xylene, *o*-dichlorobenzene, 1,2,4-trichlorobenzene, and 1,2,4-trimethylbenzene. Of these, *o*-xylene was chosen as satisfying the above requirements to the fullest extent. C_{60} and C_{70} fullerenes have a comparatively high solubility in *o*-xylene at 25°C: 8–10 and 15 $g\,l^{-1}$, respectively. Use of *o*-xylene instead of toluene, which frequently serves as an agent for extraction of fullerenes from carbon black, makes it possible to considerably reduce the volumes of the solutions being processed and thereby to minimize the dimensions of the basic process apparatus. The extraction installation developed in this study includes a mechanical stirrer with a filter, collectors for solutions and solvent, and a vacuum evaporator. The following parameters were found when using this installation: optimal mass of carbon black charged into the extractor, solvent/carbon black ratio, duration and number of repetitions of the extraction procedure, loss of the solvent via its capture by the carbon black, extraction efficiency, and residual content of fullerenes in the carbon black. The values of these parameters are listed in Table 1.

To accelerate the extraction process, the filtration was carried out under a nitrogen pressure of up to 5 $kg\,cm^{-2}$. A suspension of carbon black in the solvent was mechanically agitated at 2–3 revolutions per second. The material remaining on the filter is composed of a solid phase (carbon black, ~40 wt %) and a captured solvent (60 wt %), and, therefore, solvent regeneration requires that an additional operation, vacuum evaporation of the solvent from carbon black, should be performed.

As can be seen from Table 1, the extraction process is long and labor-consuming and involves a considerable irrecoverable loss of the solvent. The previously developed sublimation technique [22, 23] is devoid of the above-mentioned disadvantages. This method consists in the following: A bulk finely dispersed carbon black is mixed in a certain proportion with a noninflammable mixture of solvents and agitated until free-flowing and no-dust-forming grains are formed (compaction). Then the resulting product is charged into a sublimation apparatus and fullerenes are sublimed at a temperature of 500–800°C and residual pressure of 0.1–1.0 Pa and condensed on a water-cooled removable collector. The conditions under which the sublimation occurs with an 88–90 wt % yield in 1–1.5 h were experimentally found. Experiments performed on larger FB samples demonstrated that a large-scale sublimation installation can be, in principle, developed.

A prompt analysis was made using spectrophotometry or microcolumn high-performance liquid chromatography (HPLC) on the C_{18} phase with a 60 : 40 acetonitrile–toluene mixture as eluent. Chromatography on this phase enables reliable observation of C_{60}, C_{70}, and their oxides, but, in this case, the peaks of the higher fullerenes are strongly broadened and their analysis is difficult. For analysis of high-purity fullerenes and higher fullerenes, we used chromatographic columns specially developed by Nacalai Tesque Inc. (Japan) for analysis and separation of fullerenes and metallofullerenes: analytical/semipreparative Cosmosil BuckyPrep 4.6 × 250 column and preparative Cosmosil BuckyPrep 10 × 250 column. The stationary phase of both of these columns is pyrenylpropyl silica gel. Standard analyses and separations use as the mobile phase (eluent) pure toluene. The sample volume and the eluent flow rate were 20 μl and 1 ml min^{-1} for the analytical column, and 4 ml and 4.7 ml min^{-1} in preparative separations. The peaks were recorded by absorption at a wavelength of 330 nm. The ratio of the molar extinctions of C_{70} and C_{60} at this wavelength is 0.76.

A single-stage analysis on the analytical column is sufficient for analysis of C_{60} with a 99.5%+ purity. In analysis of ultrapure (99.9%+) C_{60}, a weighed portion of the substance to be analyzed is preliminarily enriched with impurities on the preparative column. In this case, a fraction that follows C_{60} is taken. This fraction is concentrated to a certain volume and its aliquot is taken for analysis on the analytical column. The main impurities in pure C_{60} are monoxide $C_{60}O$ and C_{70}. On these columns, the retention time of fullerene oxides exceeds that for the corresponding unoxidized fullerenes, in contrast to the case of the C_{18} phase (octadecyl silica gel), on which the oxides are eluted earlier than the corresponding fullerenes with a 60 : 40 acetonitrile–toluene mixture as eluent. Under the above-mentioned analytical conditions, the peaks of C_{60} and C_{70} are well-resolved (the distance between the peaks is 11 times the width of the C_{60} line at half-maximum) and the relative content of impurities can be easily determined.

Enrichment of the extract by fractional concentration. At present, numerous technical solutions that enable production of pure fullerenes C_{60}, C_{70} and $C_{n>70}$ are known [24–26, 28–34]. These solutions are mostly based on the chromatographic method, which produces, in some cases, very pure solutions of C_{60} and C_{70} fullerenes of purity exceeding 99.5 and 98%, respectively. A disadvantage of the chromatographic method is its low output capacity in terms of the target component.

The previously revealed property of the anomalous temperature dependence of the solubility of C_{60} fullerene [20, 21, 24–28] served as a basis for a method of fullerene purification by fractional concentration [28]. The method of fractional crystallization [26, 27] can produce C_{60} fullerene of 99.5% purity; however, the process involves numerous stages and the yield of the target product is very low, only several percents [27]. In [26], a mixed solvent composed of toluene and 1,3-diphenylacetone was used. Three stages of crystallization yielded C_{60} of 99.5% purity, according to HPLC analysis. With this method, the total yield of pure C_{60} fullerene was 69% relative to the mass of the starting extract (at initial C_{60} content of the extract equal to 84%). The main disadvantages of this technique are as follows: large solvent volumes are used because of the low solubility of fullerenes in this solvent, toluene should be completely removed from the solvent after performing the procedure, high temperature (110°C) is necessary, duration of each stage is long, a difficultly available solvent component is used (1,3-diphenylacetone), and the mixed solvent is to be regenerated. Therefore, this technique should also be considered labor-consuming and poorly efficient despite the high yield of pure C_{60}.

The technique we suggest here employs, to obtain pure C_{60}, a kind of liquid chromatography, flash chromatography or flash filtration. This separation method can be used in those cases when the retention time of the components being separated differs by a factor of more than several tens. This method is devoid of the principal disadvantage of the classical chromatography, low output capacity, because it does not require a fixed one-time charging of a limited amount of the starting material. However, the service life of the sorbent in this technique is limited by its capacity for impurities being sorbed. Therefore, in order to make longer the working time of a column

Table 2. Main parameters of the FC process

FC stage	Time, h	Solvent : crystals, ml g^{-1}	Fraction composition, wt %				Mass of deposit, wt % relative to starting extract, for each stage
			deposit		filtrate		
			C_{60}	C_{70}	C_{60}	C_{70}	
First	1.5	10	87.0	13.0	31.4	68.6	79.5
Second	2.0	19	92.0	8.0	75.4	24.6	66.3
Third	3.0	15	96.7	3.3	84.6	15.4	60.8

without replacement of the sorbent, the content of the component being purified in the raw material should be as high as possible.

To obtain a concentrate of this kind, with a C_{60} content of up to 96%, a procedure for enrichment of the starting raw material for flash chromatography, fractional concentration (FC), was developed. The FC process is for the most part performed in three stages, the yield of the enriched product remains high, and the content of C_{60} fullerene in the concentrate is as high as 96 ± 2%. The procedure consists in the following. A fullerene extract with a C_{60} content of 72–85% is dissolved in a certain amount of *o*-xylene heated to 80–85°C until a saturated solution is formed, this solution is filtered on a vacuum filter heated to the same temperature, and the separated crystals are dried under reduced pressure to constant mass. As a result, the crystals are enriched with C_{60} fullerene, and the filtrate, with C_{70} fullerene. The composition and yield of the enriched concentrate of C_{60} depends on the composition of the starting extract of fullerenes and solvent/crystals ratio. A decrease in the enrichment was observed on making longer the time for which the saturated fullerene solution is heated. In the multistage enrichment scheme, the decrease in enrichment becomes noticeable already in the third stage, with no enrichment occurring at a larger number of stages. Presumably, this is due to cross oligomerization of C_{60} and C_{70} under the action of temperature. It was found that the total time of all thermal treatments, including the duration of agitation and hot filtration, should not exceed 7 h. With account of this limitation, a process scheme of FC was developed. This scheme enables effective enrichment of extracts of virtually any composition in C_{60} fullerene, with a considerable yield of the final product. Table 2 lists the results of FC of C_{60} fullerene at the initial C_{60}/C_{70} ratio of 75/25.

It follows from the results presented that three stages of FC give in a 60% yield a concentrate of the following composition (wt %): $C_{60}O$ 2.2, C_{60} 94.9, C_{70} 2.9. This concentrate is a good half-product for production of pure C_{60} by flash-chromatographic purification.

The fractional enrichment procedure enables the following: (1) production of a concentrate with a C_{60} content sufficiently high for practical use in further flash-chromatographic purification; (2) removal of C_{70} from the starting extract in a smaller number of stages; (3) choice of the FC mode in which a first-stage solution with high C_{60} content, suitable for subsequent preparation of this fullerene, is formed; (4) determination of the conditions in which filtrate solutions of second and third stages have a composition close to that of the starting extract and the extract formed in the first stage of FC, respectively, which enables their use in the subsequent cycles of enrichment; (5) reduction of the volume of fractions with a low content of expensive C_{70}.

In continuous processing of fullerene extracts, the yield of the C_{60} concentrate is optimized and the loss of C_{70} is reduced to a minimum.

Production of pure C_{60} fullerene. Several methods for preparation of a pure C_{60} fullerene are known: chromatographic [29–36], fractional crystallization [26, 27], selective extraction [37, 38], and chemical techniques that use complexing agents, such as, e.g., 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) [39] or calixarenes [40], or those based on functionalization of the fullerene molecule (bromination [41] etc.). As already noted, the most efficient method for production of pure C_{60} is flash chromatography. The best, as regards the output capacity, stationary phase in purification of C_{60} fullerene by this method are activated carbons with a large specific surface area, e.g., of Darco (Fluka) or DCL GDC (Waterlink Sutcliffe Carbons) brands [42] or sorbents based on these carbons. Solvents of aliphatic or aromatic nature or mixtures of these, *o*-xylene in the given case, are commonly used as the mobile phase.

The use of a granulated activated carbon as a sorbent enabled application of a simple version of gravitational liquid chromatography. The choice of *o*-xylene for preparing the starting solution is due to the fact that *o*-xylene has been used previously for extraction and fractional concentration. An additional advantage of *o*-xylene over toluene frequently used for this purpose [37] is that, in this case, solutions with high concentration of fullerenes can be prepared; as a result, solutions with considerably smaller working volumes can be used and the duration of the chromatographic process can be made markedly shorter.

A saturated solution of a mixture of fullerenes in *o*-xylene, with a C_{60} content of about 96%, is continuously fed into the column, and the eluate contains C_{60}, in which no C_{70} or higher fullerenes are detected. The process of chromatographic purification is monitored by the concentration of C_{70} fullerene in the eluate. To obtain, e.g., C_{60} of 99.5% purity, the process is terminated when C_{70} appears at the outlet in a concentration exceeding 0.1 %. After C_{70} appears at the outlet, the supply of the feeding solution is terminated and pure solvent is fed into the column. The washing is performed to a C_{60} concentration in the eluate equal to 0.1–0.2 g l^{-1}. Further washing is inadvisable for practical reasons.

The mobile phase is supplied at a velocity of 0.2–0.8 ml min^{-1} cm^{-2} (preferably 0.4–0.5 ml min^{-1} cm^{-2}). If the process is carried out at a lower rate, the purity of the product obtained is improved, but the output capacity of the process decreases. An increased flow rate of the mobile phase not only impairs the quality of C_{60} obtained, but also leads to a decrease in the amount of the pure product obtained in a single cycle of use of the sorbent.

The yield of pure C_{60} is 72–78% relative to the amount of the concentrate charged, with 15–18% being the loss for irreversible sorption and up to 10% representing a material in which the content of C_{70} fullerene exceeds 0.5% (raw material for further recycling). The solvent is removed from the solution collected at the column outlet and crystals of pure C_{60} fullerene. Analysis shows that crystals of C_{60} fullerene, as a rule, contain, in addition to an insignificant impurity of C_{70} fullerene, that of the oxide $C_{60}O$ in an amount of up to 1.5–2.0% in some cases. Activated carbon has low selectivity with respect to this impurity, whose fraction increases in the course of chromatographic purification. This impurity can be removed in several ways. The most efficient way is vacuum treatment of the crystals obtained. This method can reduce the content of the oxide $C_{60}O$ to 0.05–0.1%. An advantage of the technology developed consists in that first portions of the eluate contain high-purity C_{60} fullerene (better than 99.9%). At a flow rate of the liquid phase exceeding 0.2 ml min^{-1} cm^{-2}, the fraction of such a product in the total output can be markedly raised, which improves the profitability of the production process.

With this technology used on a working equipment at St. Petersburg Institute of Nuclear Physics, Russian Academy of Sciences, the average rate of 99.5% C_{60} manufacture with double-shift work was 1–2 g h^{-1} (or 500–600 g per month). The developed flowsheet can be used without any significant change for manufacture of C_{60} fullerene in an amount exceeding 10 kg per month.

Manufacture of pure C_{70} fullerene. Flash chromatography on activated carbon cannot be used to separate C_{70} from C_{60} because C_{70} is sorbed on the carbon considerably more firmly than C_{60}. Therefore, it is advisable to use a combination of several methods for large-scale manufacture of pure C_{70} fullerene [43]. The technology we suggest includes the following sequence of procedures: enrichment of a mixture of C_{60}/C_{70} fullerenes with C_{70} fullerene by fractional concentration to a level of 85–92%; flash chromatographic purification of the concentrate obtained to remove the admixture of higher fullerenes on activated carbon; separation of trace amounts of C_{60} by fractional purification to obtain pure (98%) C_{70} fullerene.

The fractional concentration from *o*-xylene, which is an efficient and high-output-capacity technique for enrichment of C_{60}, has also been successfully used for enrichment of C_{70} fullerene [44].

The stage of fractional concentration in C_{70} fullerene is continuation of the first stage of fractional enrichment with C_{70} fullerene. The concentrate obtained in this stage (20–22% relative to the weight of the starting mixture of fullerenes) is a supersaturated solution (up to 26 g l^{-1}), from which crystals containing 85–92% C_{70} precipitate upon cooling. The yield of the crystals depends on temperature and duration of crystallization, and can be as high as 80% relative to the material contained in the filtrate at –24°C. The mother liquor contains 2–3 g l^{-1} of fullerenes and is enriched in C_{60} fullerene, compared with crystals.

Depending on the composition of the starting extract, the crystals obtained may contain admixtures of higher fullerenes in an amount of up to 4–5%. Such a high content of higher fullerenes makes their recovery feasible. This procedure can be effectively performed with 1,2,4-trichlorobenzene by multistage fractional concentration. It was found experimentally that the content of higher fullerenes in C_{70} crystals can be reduced from 4–5 to 0.7–0.8% at room temperature in three to four stages. In this case, concentrates are obtained in all stages, which contain up to 10% higher fullerenes. The crystalline concentrate of C_{70} fullerene is further dissolved in *o*-xylene and subjected to chromatographic purification on activated carbon. The impurity of higher fullerenes is completely removed in this stage.

The process we suggest allows production of pure C_{70} fullerene in considerable amounts. For example, the concentrate of C_{70} fullerene, obtained in the first stage of fractional concentration from the starting mixture of fullerenes, contains less than 2% higher fullerenes, whereas a single cycle of two-stage crystallization can give C_{70} fullerene with the purity better than 98%. The total yield of pure C_{70} exceeds 100 g in a cycle (48 h) per 1000 g of the starting mixture of fullerenes [composition (%): C_{60}/C_{70} 75/25]. Presence of higher fullerenes in the starting extract in an amount exceeding 2% diminishes nearly twofold the yield of pure fullerene and makes nearly twice longer the purification of the C_{70} concentrate to remove impurities. Therefore, additional one or two stages of crystallization are necessary for obtaining C_{70} fullerene of 98% purity if more than 2% higher fullerenes is contained in the starting C_{70} concentrate.

The scheme suggested can be used to obtain, without any significant modification of the available inexpensive equipment, to produce up to 1 kg of C_{70} of commercial purity in a month. Because this method for production of C_{70} is a part of a unified flowsheet for synthesis of C_{60} and C_{70}, its use makes it possible to improve the output capacity in terms of pure C_{70} and reduce its cost severalfold, compared with the technique suggested in [40].

In 2003, Frontier Carbon Corp. declared that its annual output capacity of fullerenes by incomplete combustion of hydrocarbon raw materials was 40 t [45]. A plant constructed by this company could satisfy the whole world's demand for fullerenes, and their price would decrease severalfold. However, the authors are unaware of any offers by this company on the fullerene market. It would be expected that the raw mixture of fullerenes, produced by this technique, will be contaminated with polycondensed aromatic hydrocarbons. Isolation of pure fullerenes from a raw material of this kind is presently possible only with low-output-capacity and rather expensive chromatographic methods, and, consequently, the production cost of these fullerenes will long exceed that of fullerenes produced by the electric-arc technique.

CONCLUSIONS

(1) A semicommercial technology for manufacture of pure C_{60} and C_{70} fullerenes was developed.

(2) An apparatus for production of up to 1 kg of a fullerene-containing carbon black in 24 h was designed and fabricated.

(3) An apparatus for recovery of a mixture of fullerenes from a fullerene-containing carbon black, with a monthly processing capacity of up to 40 kg of carbon black, was designed and fabricated.

(4) An installation for chromatographic purification of C_{60} (to 99.5 or 99.9%), with a monthly output capacity of up to 500 g of 99.5% C_{60}, was designed and fabricated.

(5) The flowsheet developed can be used to produce up to 100 g of C_{70} (98%) in a month on the already existing equipment, provided that the content of higher fullerenes in the starting C_{70} concentrate is less than 2%. An additional special procedure for removal of higher fullerenes was developed for obtaining C_{70} fullerene of 98% purity from a concentrate with increased content of higher fullerenes.

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