IOP Conf. Series: Earth and Environmental Science **640** (2021) 062010 doi:10.1088/1755-1315/640/6/062010

Fullerene production management system used for creation of hydrated solutions

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Abstract. The use of hydrated solutions of fullerene C_{60} in the food industry is considered. The features of the synthesis of fullerenes C_{60} by the method of plasma evaporation of graphite raw materials are presented. The structure of a complex mathematical model is proposed which allows one to relate the process of the formation of carbon nanostructures (CNS) in a plasma with the synthesis conditions, which allows one to determine the process conducting conditions with the maximum yield of the final product. An automated information management system (AIMS) for the production of fullerenes has been developed, which allows, based by numerical calculations using a complex mathematical model, to determine rational technological parameters for the graphite raw materials used and the synthesis method.The architecture of an automated information system for managingthe synthesis of carbon nanostructures is presented. The description of the interaction modules and subsystems of the control system is given. The scheme of interaction of elements of an automatedinformation management system in the process of collecting and processing information is presented. The developed automated information management system allows you to control the process of synthesis of carbon nanostructures in automatic or manual mode, monitor technological parameters in real time, calculate control actions and stabilize parameters, process the received data and present it to the user in the form of tabular or graphical information.

1. Introduction

The peculiarity of the structure of fullerene molecules of the $C_{32} \div C_{600}$, series, and their unique physicochemical properties, in particular, high electron withdrawal, oxidative activity are of considerable interest for various branches of modern industry[1, 2].

The most stable, studied and promising ones are the fullerenes C_{60} and C_{70}. The framework of the ideal C_{60} fullerene molecule (buckyball) is a form close to the ball (a truncated icosahedron), consisting of 12 pentagons and 20 hexagons, which determines her properties. Fullerenes are poorly soluble in most solvents and practically insoluble in water (their solubility < 10^{-11} g/l). However, free fullerene, when it is specially treated, is capable of forming stable colloidal solutions. In 1995, without the use of solubilizers, a stable composition of fullerene C_{60} and water was obtained, which was called hydrated fullerene $C_{60}(H_2O)_{24}$ [3]. Hydrated fullerene is a stable hydrophilic supramolecular complex in which the C_{60} molecule is enclosed in the first hydration shell consisting of 24 (22) water

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molecules. The first layer of water formed around fullerene is capable of strongly influencing neighboring bulk water and ordering her structure into a specific spherical cluster. Currently, the maximum concentration of C_{60} in a hydrated solution can reach 4 mg/ml.Such solutions are highly stable and can be stored for years without changing their properties.

The hydrated solution of fullerene C_{60} has a wide range of biological action, without showing at the same time signs of toxicity. It can act as an organizer of various reactions and processes that regulate the formation and neutralization of reactive oxygen species, which, for various reasons, proceed without them is not effective enough. This allows its use in nutrient media for growing microorganisms, in media for culturing and storing cell cultures, in creating products with peculiar, highly ordered structural characteristics, etc. [4, 5].

2. Materials and methods

The most common method is transferring fullerenes from solutions in an organic solvent (toluene, benzene, etc.) to the aqueous phase using ultrasonic treatment of the mixture followed by removal of the organic solvent [6].

Currently, various synthesis methods are used to obtain the initial C_{60} fullerenes necessary for creating hydrated solutions. One of the directions that allows obtaining high-quality material in large enough volumes is various variations of the plasma evaporation of graphite raw materials with subsequent deposition of the synthesized product on a cooled surface. The most famous type of such technologies is electric arc synthesis of fullerenes in an inert gas environment [7]. This method is distinguished by a high speed passing of the process, high yield and quality of the final product, the ability to control and manage the synthesis course.

During thermal evaporation, the conditions and stability of maintaining the technological parameters of the synthesis process directly affect the output and quality of the final synthesized fullerenes. Under rational conditions of synthesis using a catalyst, the evaporated carbon raw is deposited on the walls of the reaction chamber in the form of soot, which may contain more than 20% of a mixture of fullerenes. Formed fullerenes can be blown with a stream of buffer gas from the plasma and thus you can make the process be continuous.

In the course of experimental studies with the participation of the authors on a laboratory installation of the electric arc synthesis of carbon nanostructures equipped with an automated parameter control system using graphite electrodes with a diameter of 0.012 m of FDG-4 grade (impurity content <0.02%), as well as maintaining parameters. Force constant current I = 350 A , voltage at the electrodes 25 V, interelectrode distance 0.001 m, pressure in the synthesis chamber 53.3 kPa without using a catalyst, carbon black was obtained containing 15% of a mixture of fullerenes C_{52} – C_{90}. The weight composition of the resulting mixture is presented in table 1. The data are obtained on the basis of mass spectrometric analysis.

Table 1. Weight composition of the resulting mixture of fullerenes.

Fullerene	$C_{50} \div C_{58}$	C_{60}	$C_{62} \div C_{68}$	C_{70}	$C_{72} \div C_{92}$
Weight%	14,69	63,12	5,88	13,25	3,06

The use of special catalysts, as well as other inert buffer media (Ar, Kr, etc.) allows to increase the total yield of fullerenes and directly the proportion of C_{60} in the receiveing graphite carbon black. On the yield and quality of the resulting carbon product are also influenced both the characteristics of the raw materials used, the technological conditions for the synthesis conducting, and directly the stability of the process parameters. Under one conditions of synthesis, up to 90% of the mass of evaporated graphite from the anode can settle on the cathode and form a cathode sediment withthe content up to 60% of different carbon nanotubes. And under

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other up to 100% of evaporated carbon is deposited on the walls of the reaction chamber in the form of soot with a maximum content of fullerenes $C_{60} \div C_{70}$ [8].

To determine the necessary technological conditions for the synthesis of carbon nanostructures (CNS) by plasma evaporation of graphite in order to obtain high-quality nanostructured material with the highest yield, an automated information system of modeling and controlling the process under consideration was developed. This system allows, firstly, searching for rational synthesis conditions on the basis of a mathematical model of the process, and secondly, providing real-time control of the real process by the parameters found.

The use of an automated synthesis control system ensures the maintenance of a given interelectrode space, which makes it possible to achieve high stability of the current arc, the constancy of the temperature parameters in the plasma and to ensure the stability of the technological parameters that determine the process course.

To determine the synthesis conditions necessary for obtaining the largest amount of the required nanostructured product from the carbon raw materials used, a complex mathematical model of processes was developed that allows one to describe collective phenomena in low-temperature plasma and to investigate the formation of stable carbon cluster groups with various types of covalent bonds forming the CNS. In the basis the complex model is based on a set of interconnected mathematical models that describe: heat transfer processes taking into account the mobile boundaries of the original system; kinetics of motion and interaction of various charged particles in a plasma; the formation of carbon cluster groups on the basis of pairwise collisions and the formation of bulk CNS; their deposition on the cooled cathode and on the walls of the working chamber of the synthesis. To construct a model of the motion and interaction of particles in plasma, a molecular kinetic approach was used, based on the use of a system of kinetic Boltzmann equations written for each type of particle, taking into account their paired elastic and inelastic collisions, supplemented by a system of Maxwell equations describing a self-consistent field [9]. This made it possible to connect the process of the formation of CNS in plasma with the synthesis conditions.

3. Discussion of the results

The architecture of the developed automated information management system (AIMS) by CNS synthesis given the technological conditions are obtained on the basis of numerical calculation using the constructed process model is shown in figure 1.

An automated informational control system was performed using the modular principle of building in a modern Python programming environment in an object-oriented style, which allows it to work with individual modules created in other software environments, flexible expansion and work on various operating systems: Windows, Mac Os, Linux. Using a clear, user-friendly interface provides the user with the most convenient interaction with an automated information management system.

A distinctive feature of this program-technical complex is the ability to calculate the necessary parameters of the required CNS synthesis mode based on modern technology of preliminary mathematical modeling of the process in question.

The architecture of an automated information management system (AIMS) is a set of interconnected among themselves subsystems answer for the performance of a certain functional load:

- collection and primary processing of data on the progress of the synthesis process;
- information processing;
- user authorization;
- control and management of technological parameters;
- optimal control calculation;

- calculation based on the model of synthesis parameters of certain CNS;
- database management system (DBMS);
- communication with subsystems;
- user interface provision;
- formation and output of reports to the user.

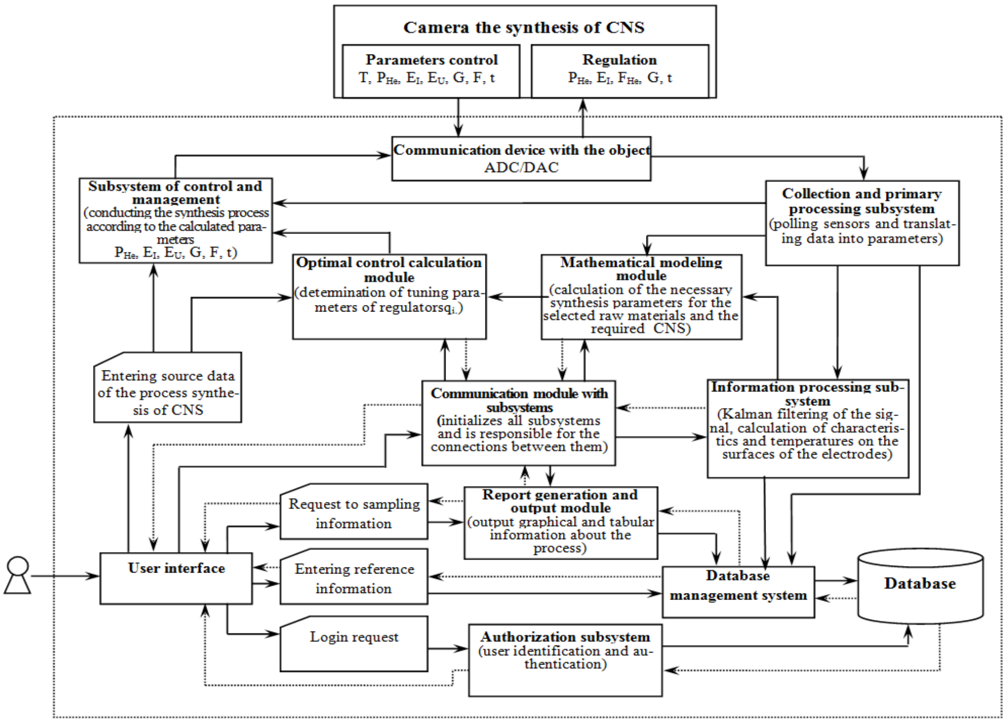

Figure 1. Architecture of an automated information system for managing fullerene synthesis

Using a modular approach as the basis for constructing an automated information system for the synthesis of carbon nanostructures allows not only building separately complex, interconnected software applications, but also provides the ability to make the necessary changes for reworking the software or completely replace it, in purposes to improve the automated information control system or adaptation to new conditions. In the process of constructing the considered automated information management system (AIMS), the tasks related to the formalization of inter-module interaction and the organization of the functioning environment were also solved.Using the principle of "dualism" allowed the organically interconnected among themselves modules of the information system, if necessary, to work autonomously.

The hardware and software of the developed automated information management system (AIMS) allows providing automatic collection, processing and storage of information, as well as the development of control actions necessary to maintain the stability of technological parameters of the synthesis process.

In the automated information management system (AIMS), information about course of the process flow from sensors that control synthesis parameters through a communication device with an object is sent to a personal computer.

The used communication device with the object provides accomplishment of a number of necessary intermediate functions:

1. Normalization of the analog signal, that is, bringing the boundaries of the primary continuous signal scale to the standard input signal range of the analog-to-digital converter.
2. Preliminary low-frequency filtering of the analog signal - limiting the passage band frequencies of the primary continuous signal of the sensors, in purpose to reduce the impact on the measurement result of interference of various origins.
3. Converting the output digital of the control device to a normalized analog form using a digital-to-analog converter.
4. Providing galvanic isolation between signal sources and system channels, to protect the system and the user from possible breakdown of electric current.

In the synthesis process, the developed control system controls the following parameters: closing (opening) the cover of the synthesis working chamber; rarefaction pressure; temperature and pressure of the cooled medium; pressure of the buffer medium in the chamber; voltage at the electrodes; current strength of the interelectrode space; interelectrode distance; synthesis time.

Adjustable parameters that directly determine the stability conducting of the synthesis of carbon nanostructures are: the pressure of the buffer medium in the chamber; current strength with correction for interelectrode distance by moving the anode; the temperature and flow rate of cooling water at the entrance to the synthesis chamber; the time of synthesis.

In the developed system, a data collection and primary processing module (DCPPM) with a given sampling rate polls the sensors (S_1 - S_n), collects the received information from the communication device with the object (CDO) and translates the received code of the analog-to-digital converter (ADC) on the calibration dependence into the final technological parameter in the required units of measurement. A diagram of the interaction ofautomated information management system (AIMS) elements in the process of collecting and processing information is presented in figure 2.

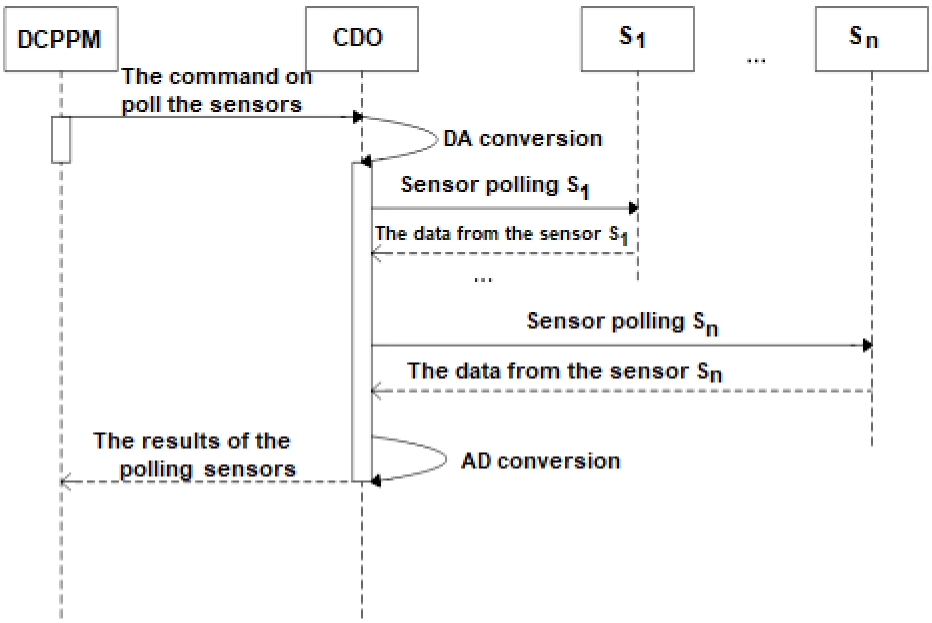

Figure 2. Interaction of elements of an automated information management system (AIMS) in the process of collecting and processing information.

The signals coming from the primary converters of the physical parameters process via shielded connecting wires are subject to the influence of noise interference created by external electromagnetic fields. Therefore, the information processing subsystem eliminates this interference by performing an averaging operation of the obtained data using the Kalman filter and it calculates the mathematical expectation and dispersion of the signal.

The automated information management system (AIMS)of electric arc synthesis of CNS has anintegrated security system capable of protecting the developed information system as much as possible from unauthorized access and operator errors. The developed authorization module ensures data integrity and performs the functions of user identification and authentication.

The optimal control calculation module is responsible for generating the necessary control action based on the control algorithm, which, based on the calculated error, generates the necessary impact on the technological object. The proportional-integral control law is used as a discrete control algorithm.

To store the necessary information about the synthesis process course and perform various operations with her in an automated information system, a compact embedded database SQLitewas used. An application using SQLite sends direct queries to a file that stores data, which provides high speed and performance. Using this database management system allows you to save all the technological indicators of the synthesis process in a file for theirsubsequent statistical processing. The formation and storage of the necessary reference information is provided by the database management system. Background information in addition to the recommended conditions of conducting synthesis contains process constants (coefficients of thermal conductivity, heat transfer , etc.).

Based on a sample of experimental data from the database, formation reports occurs. The system provides the user with access to data obtained at performance the current experiment, as well as to information obtained during previous experiments.

The initial point work of the program is a module for communication with subsystems. It allows one to work with all subsystems and is responsible for the communications between them.

The user interface module is designed for direct user interaction with the subsystems of the automated information system. User interaction with the information system is carried out in a dialogue mode, which allows full control of the process.

4. Conclusion

Thus, the proposed control system for the synthesis of C_{60} fullerenes used to obtain hydrated solutions allows calculating the necessary rational technological parameters of the synthesis process by plasma evaporation for different types of graphical raw materials and conditions providing the maximum yield of a high-quality final product based on numerical calculations using a complex mathematical model.

The developed automated information management system allows you to control the process of synthesis of carbon nanostructures in automatic or manual mode, monitor technological parameters in real time, calculate control actions and stabilize parameters, process the received data and present it to the user in the form of tabular or graphical information.

The developed information support of the control system allows one to perform both physical and numerical experiments on the synthesis of CNS in various operating modes of the system.

References

[1] Belousov V P 1997 Fullerenes: structural, physicochemical, and nonlinear optical properties *Optical journal* **64 (12)** 3-37

IOP Conf. Series: Earth and Environmental Science **640** (2021) 062010 doi:10.1088/1755-1315/640/6/062010

[2] Bychkov A L, Ryabchikova E I, Korolev K G and Bukhtoyarov V A 2019 Synthesis of silver nanoparticles stabilized by the products of mechanically assisted hydrolysis of yeast biopolymers *Proceedings of Voronezh State University of Engineering Technologies* **81(1)** 238-246

[3] Andrievsky G V, Klochkov V K, Karyakina E L and Mchedlov-Petrossyan N O 1999 Studies of aqueous colloidal solutions of fullerene C60 by electron microscopy *Chem. Phys. Lett*. **300** 392-396

[4] Shirinkin S V, Shaposhnikov A A, Volkova T O, Andrievskiy G V and Davidovsky A G 2012 Hydrated fullerene as a tool for understanding the role of special structural properties of the aquatic environment of a living organism for its normal functioning *Scientific Bulletin of the Belgorod state University Series: Natural Sciences* **9(128)**122-129

[5] Meledina T V, Ivanova V A, Razan H, Golovinskaya O V, Novikova I V and Korostelev A V 2018 Influence of the parameters processes of cultivation of yeast Saccharomyces cerevisiae in simple periodic culture on the yield and biosynthesis of some cellular components *Proceedings of Voronezh State University of Engineering Technologies* **80(2)** 175-181

[6] Prylutskyy Y I [et. al.] 2014 On the origin of C60 fullerene solubility in aqueous solution *Langmuir : the ACS journal of surfaces and colloids* **30(14)** 3967–3970

[7] Mikhailenko A V, Smyk S Yu and Kunitsky Yu A 2011 Carbon nanostructures: topology, getting, properties *Surface* **3(18)**50-102

[8] Abramov G V and Gavrilov A N 2016 Automated control system for synthesis of carbon nanostructures in arc discharge plasma *Automation. Modern technology* **3** 10-14

[9] Abramov G V, Gavrilov A N, Kravets O Ja and Varlamov N V 2019 The use of quantum-kinetic models in system design synthesis of carbon nanostructures *IOP Conf. Series: Materials Science and Engineering* **498** 012008