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Synthesis of Carbon Nanotubes Using Azerbaijan's Oil

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Abstract

Distillate fractions of Azerbaijan's oil-gasoline, jet fuel and diesel were tested as a raw material for producing carbon nanotubes. Aerosol CVD technique was employed at atmospheric and low pressures and ferrocene was used as a catalyst. It is shown that at atmospheric pressures carbon nanotubes were formed only from a gasoline fraction. Lower pressure in the reactor during the synthesis process leads to formation of carbon tubular structure from both petroleum fractions-gasoline and jet fuel. Other modifications of carbon were grown at atmospheric pressure in a case used fraction jet fuel and diesel fraction. MWCNTs with diameters of 35 - 65 nm have been grown at lower pressure in the reactor using gasoline fraction. The diameter of the MWNTs grown at atmospheric pressure in the reactor was in the range of 80 - 215 nm and the length reached 6 microns after the purification process.

Keywords

Azerbaijan's Oil, Aerosol-CVD, Gasoline Fraction, Fraction Jet Fuel, Ferrocene, SEM

1. Introduction

Carbon nanotubes are unique structures, which have wide range of application fields, starting from nanoelectronics to heavy industry [1]-[6]. Application fields are choosen depending on physical and chemical properties of carbon nanotubes (structural parameters, the number of walls, empty or filled with any nanoparticles, pure or contaminated with different metal impurities, etc.). For example, for medicine very pure CNTs with small diameters or single wall CNTs are needed, but for heavy industry application of CNTs there are no such

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requirements, only advantages of mechanical and electromagnetic properties are important. Adding a small amount of the CNTs leads to improvement of the properties or eithercreates new properties of matrix materials such as cement, ceramics andpolymers [7]-[14]. In turn, the properties of carbon nanotubes and their cost highly dependoncarbon source and synthesis technology [15].

CNTs can be obtained by different methods; each having its own specificity, advantages and consequences. There are several synthesis methods: the method of arc-discharge [16]-[18]; the method of laser ablation [19] [20]; chemical vapor deposition (CVD) [21]-[26]. Physical methods allow the production of single- or multi-walled CNTs; presenting very few defects, but the selectivity (the presence of amorphous carbon and other substances) and productivity are often low.

Aerosol-assisted CVD method is one of the last generation methods, which gives an opportunity synthesize of cost effective MWCNTs free from different impurities [27]. Moreover Aerosol-assisted CVD (A-CVD) equipment system allows using many types of hydrocarbons and other liquid compounds, excluding high boiling [15].

Until now, many hydrocarbons have been used as carbon source. Although some of them are more suitable for obtaining high quality of end produced CNTs, they are very expensive, and it also directly affects the cost of production, and makes it expensive as well. In fact, in the world market the price of CNTs is $2 - $700 per gram depending on its quality and properties (http://www.sigmaaldrich.com/catalog/product/aldrich/773735?lang=en&region=AZ).

There are only few works in scientific literature dedicated to the production of carbon nanomaterials using petroleum fractions—hydrocarbons as raw materials [28] [29].

In our early studies we have used high pressure hydrothermal method for synthesizing Carbon coated magnetite (Fe_3O_4) nanowires by decomposition of ferrocene ($Fe(C_5H_5)_2$) under solvothermal conditions using Azerbaijan's oil as additional carbon source [30].

For the first time our research group together with Prof. Nakayama's group from Osaka University, Japan have synthesized carbon nanotubes using byproduct of Azerbaijan's oil as carbon source [31].

Present paper will report the first ever synthesis of Carbon nanotubes by new developed by us Aerosol CVD method using different fractions of Azerbaijan's oil to identify the suitability of low cost and large-tonnage raw material in the production of CNTs.

2. Experimental Details

In the experiments on the synthesis of carbon nanotubes (CNT) by aerosol CVD, the following straight-run fractions of Azerbaijan oil were used as a carbon source:

1) Heavy gasoline fraction (C_7-C_{11});
2) Fraction of jet fuel (C_9-C_{16});
3) Diesel fraction (C_{14}-C_{25}).

The synthesis processes were carried out both in atmospheric and lower (10 - 30 kPa) pressures at temperature of 930˚C.

In all experiments ferrocene in concentration of 20 mg/ml of the solvent was used as a catalyst. Raw material with a dissolved catalyst was injected to the reaction zone as an aerosol using an ultrasonic apparatus. The reactor consists of quartz tube of a length of one meter and an internal diameter of 33 mm. For uniform deposition of carbon material the electric furnace (35 cm of length) automatically moved with a velocity of 10 mm/min over the length of quarts reactor during the synthesis process. Deposited carbon materials have been studied using analytical scanning electron microscope (ASEM).

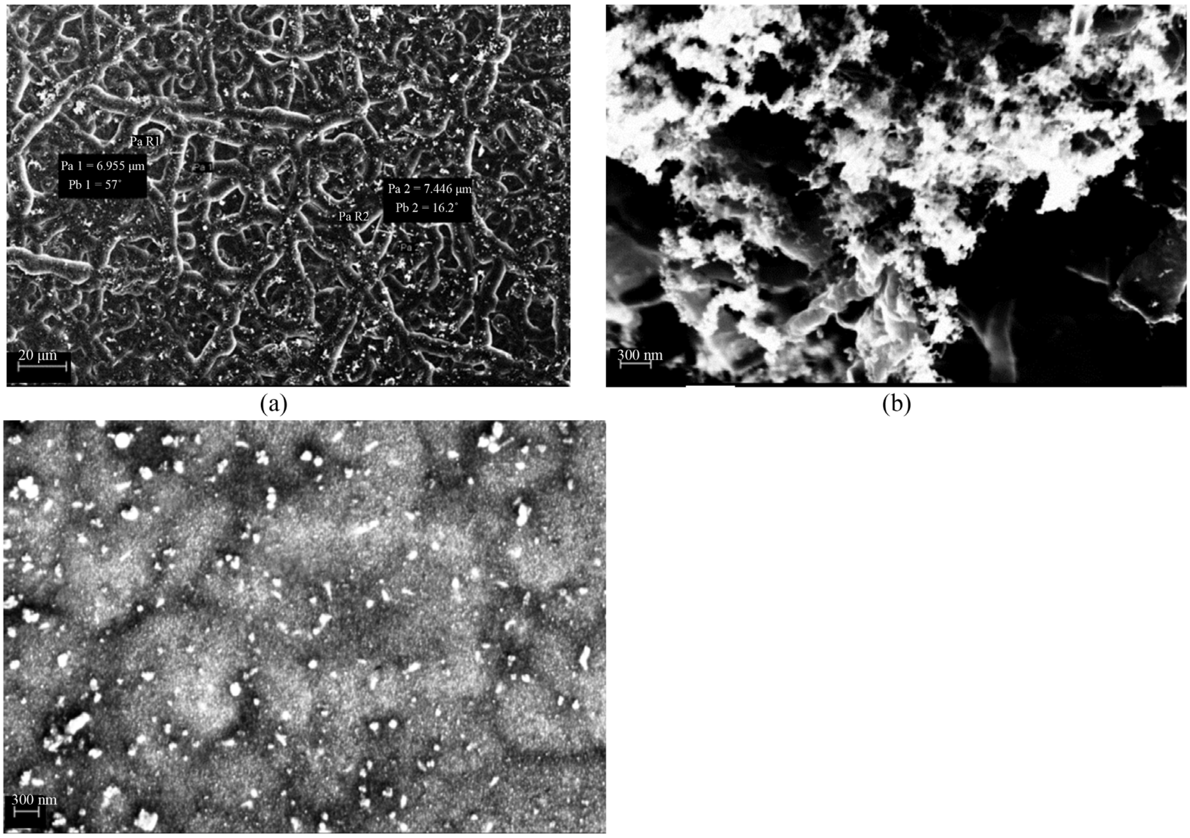
Purification of synthesized carbon nanotubes was carried out by two known successive methods-by washing with solvents (cyclohexane, toluene), with simultaneous action of ultrasound and a half-hour burning at 420˚C in a muffle furnace in air atmosphere.

3. Results

In the case of the gasoline fraction at atmospheric pressure the formation of a tubular carbon structures with a diameter of 6.96 - 7.45 μm were observed in the reaction products (**Figure 1(a)**).

However, it should be noted that under the same conditions, was not deposited any tubular carbon structures from fraction jet fuel and diesel fraction (**Figure 1(b)** and **Figure 1(c)**).

The completely different pictures were observed when the pressure in the reactor is low during the synthesis



(a) (b) (c)

Figure 1. SEM images of Carbon structures obtained at atmospheric pressure in the reactor from: (a) gasoline fraction; (b) fraction jet fuel; (c) diesel fraction.

process comparing with atmospheric pressure therein. Thus, injecting of the gasoline fraction with the catalyst to the reaction furnace led to formation of carbon nanotubes with diameters of 35 - 65 nm (**Figure 2(a)**).

Also, carbon nanotubes obtained from jet fuel fraction, with diameters of 211 - 473 nm were revealed by scanning electron microscopy (**Figure 2(b)**).

The results in the case of the diesel fraction at low pressure in the reactor were similar to those in the atmospheric pressure-tubular carbon structures were not formed (**Figure 2(c)**).

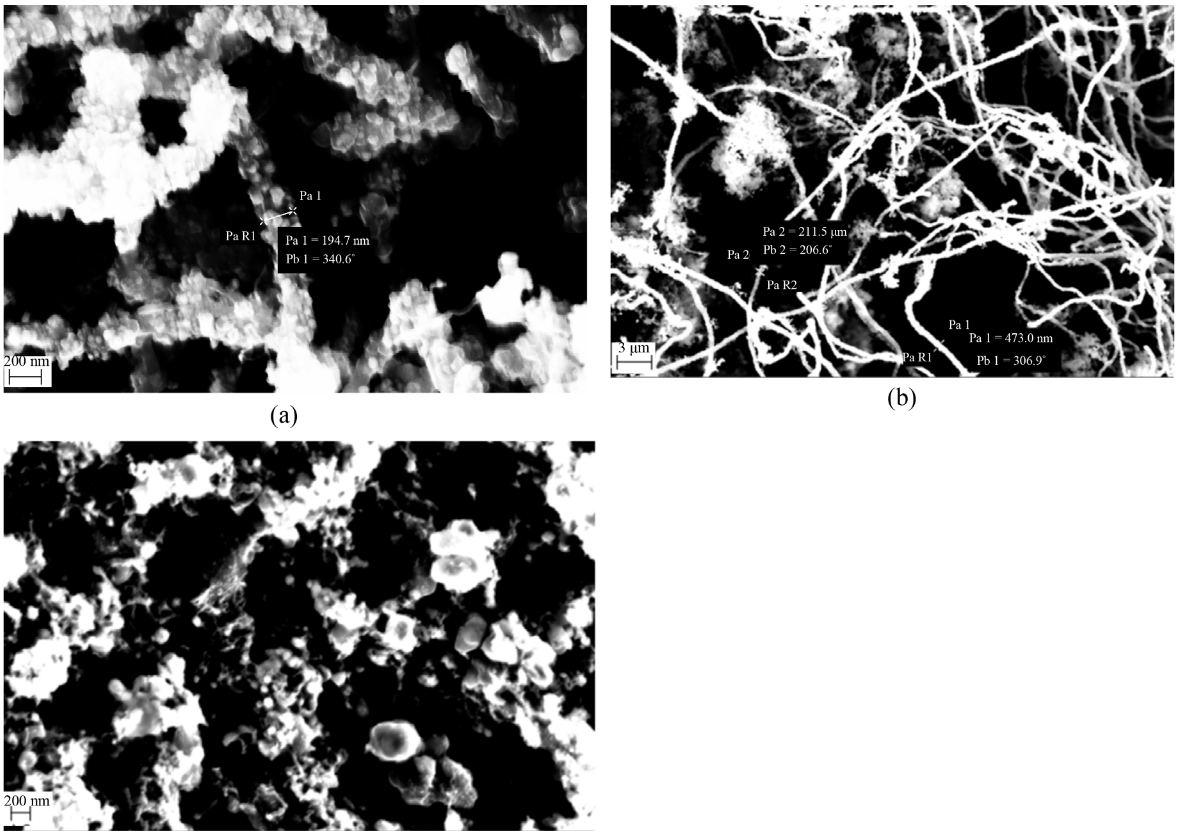
Comparing the results in the case of the gasoline fraction at atmospheric and lower pressures, a large difference in diameter of the synthesized products attracts attention. At atmospheric pressure carbon product was obtained in a form similar to carbon nanotubes, but the tube diameters about hundred times higher than the conventional value of the upper limit (100 nm) for nano-materials, namely 6960 - 7450 nm (**Figure 1(a)**). Moreover, as can be seen from this micrograph, the synthesized carbon nanotubes had outgrowths and branches, which is not typical for pure carbon nanotubes. These facts have raised doubts about the purity of the obtained product and the experiments were conducted to purify the resulting product from possible impurities and stratifications. To do this, two successive methods were applied—purifying by solvents (cyclohexane—**Figure 3(a)** and toluene—**Figure 3(b)**) and burning in open air at 420˚C.

As can be seen from **Figure 3** toluene washes away tar impurities, staining with the reddish-brown color.

Purification of the deposited material obtained from the gasoline fraction at atmospheric pressure (**Figure 4(a)**) and reduced pressure (**Figure 4(b)**) allowed allocating carbon nanotubes with a diameter accordingly 80 - 215 nm and 101 - 141 nm.

4. Discussion

Thus, the results of the investigation showed that when the gasoline fraction was used as raw material at the



(a) (b)

(c)

Figure 2. SEM images of Carbon structures obtained at low pressure in the reactor from: (a) gasoline fraction; (b) fraction jet fuel; (c) diesel fraction.

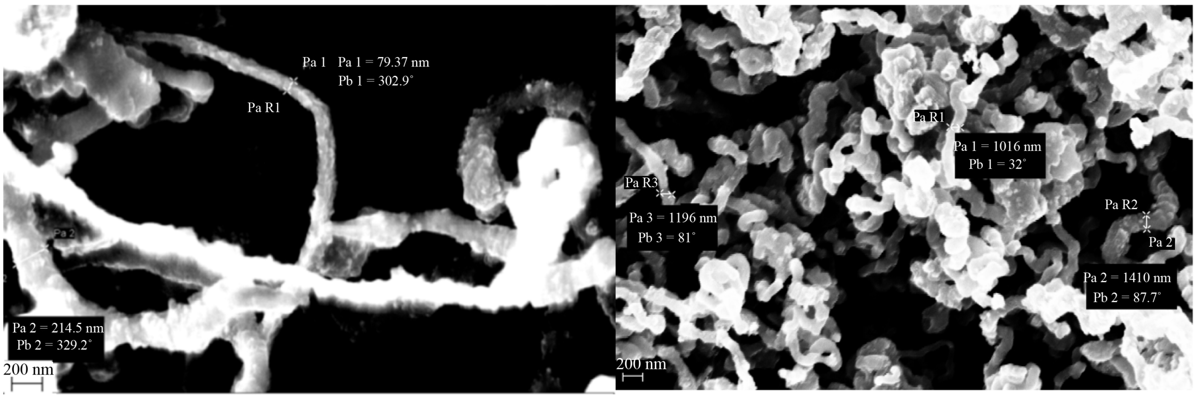
(a) (b)

Figure 3. Washing of CNTs with: (a) cyclohexane; (b) toluene.

temperature of 930˚C the carbon nanotubes formed independently from the pressure in the reactor (10 kPa - 101 kPa).

At the same temperature, but when using oil fractions of jet fuel, CNTs were formed only at low pressure in the reactor. And during the process involving diesel fraction tubular carbon structures were formed neither under atmospheric nor under reduced pressure.

The obtained results demand a scientific explanation. However, given the insufficient development of the



(a) (b)

Figure 4. SEM picture of the deposit obtained from the gasoline fraction at atmospheric pressure (a) and reduced pressure (b) after purification.

theory of these processes and their kinetics and mechanisms, we can try to make just an assumption.

According to the prevailing ideas today the required conditions for the formation of carbon nanotubes by our method of synthesis of "chemical vapor deposition (CVD) method" are the presence of nanosized clusters of metal catalysts (in this case iron), as well as the particles of non tubular carbon (graphite, carbon black, coke, etc.), which can dissolve in molten nanosize clusters of the catalyst, with further separation from it in the form of nanotubes. As a precursor of the catalyst, we used ferrocene, and the carbon precursor was a mixture of different hydrocarbons contained in the fraction of jet fuel.

At temperature of 930˚C regardless of the pressure in the reactor (low vacuum or atmospheric) decomposition of ferrocene with the formation of nanoscale particles of iron catalyst is beyond doubt [32]. Much more difficult is the pyrolysis process of a mixture of hydrocarbons being a part to the fraction of jet fuel, which is carried out in several stages with the formation of multiple intermediates [33] [34].

Simultaneously reversible and irreversible reactions (cyclization, aromatization, polycondensation, circuit break, dehydrogenation, etc.) occur in serial and parallel schemes.

The dehydrogenation reaction for the pyrolysis of hydrocarbons is of particular importance, because on one hand it goes along with the majority of intermediate reactions in the chain of conversions of saturated hydrocarbons into carbon, gradually increasing in molecules the ratio of carbon/hydrogen, and on the other-hand-being reversible for gas reactions in many cases-is subject to the principle of Le Chatelier [35].

For a discussed process this is critical, since the dehydrogenation reaction due to generated hydrogen flows with a substantial increase of the volume of the reaction mixture, and consequently, in accordance with Le Chatelier's principle-reducing the pressure in the system will contribute to the shift of the equilibrium in the direction of increasing of the dehydrogenation product and formation of non tube carbon, which is then structured as carbon nanotube under the influence of the catalyst.

Furthermore, the conduction of this process in vacuum may facilitate the rapid removal of the formed polycondensed resin and the hydrocarbon compounds from the reaction zone, which are not involved in subsequent transformations due to their thermal stability, but can block the nano-clusters of the catalyst, hindering their interaction with carbon. Thus under the influence of vacuum the hydrocarbon substances, which not decomposed to carbon are withdrawn from the reaction zone as vapor, and the heavier solid carbon particles and molten catalyst clusters freely react to form iron filled carbon nanotubes depositing on the reactor walls. In our opinion these circumstances it is possible to explain the beneficial effect of a partial vacuum in the formation of carbon nanotubes from a fraction of jet fuel.

Also, there is a question on another fact detected in this study-why in the case of gasoline fraction, unlike the jet fuel fraction, the carbon nanotubes were formed not only in vacuum but also under atmospheric pressure? This result can be explained by the difference of the hydrocarbon composition of the two oil fractions. Gasoline fraction contains considerably lighter liquid hydrocarbons (C_7-C_{11}) than the jet fuel fraction (C_9-C_{16}) and pyrolysis of the gasoline fraction mostly forms (77% wt.) a mixture of gases (H_2, C_1-C_4) and only about 5% wt. of heavy pyrolysis tar. Pyrolysis of the jet fuel fraction, in addition to reducing the gaseous products gives a sharp—

almost twice the increase in the yield of heavy tar—a thermostable polycyclic compound which, as noted above, may adversely affect the process of synthesis of carbon nanotubes.

Among of the three oil fractions tested us as raw material for production of CNTs, most heavy hydrocarbons (C_{14}-C_{25}) included in the diesel fraction, and they are even more capable to resignification in the pyrolysis process in and blocking of the catalyst than the jet fuel fraction hydrocarbons (C_9-C_{16}). This may explain the absent of carbon nanotubes in the deposited end product involving the diesel fraction at atmospheric pressure or under partial vacuum.

Thus, the formation of nanotubes from the gasoline fraction (in contrast to the jet fuel fraction) at atmospheric pressure lets us assume that this hydrocarbon composition could be more suitable as a raw material providing minimal formation of the heavy pyrolysis tar during synthesis.

5. Conclusion

The first ever multi-walled carbon nanotubes (MWNTs) were synthesized from petroleum distillate fractions of Azerbaijan's oil. It was shown that under atmospheric pressure MWCNT is formed only from the gasoline fractions, while under partial vacuum the synthesis proceeds with the jet fuel fraction as well. At the same time the formation of carbon nanotubes was not observed when diesel fraction was used as a hydrocarbon raw material in the entire range of pressures. An attempt was made to explain the revealed principal differences in the activity of the individual distillate fractions of oil in the CNT synthesis based on the differences in their hydrocarbon composition, and the effect of pressure in the reaction zone on the principle of Le-Chatelier.

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References

[1] Sears, K., Dumée, L., Schütz, J., She, M., Huynh, Ch., Hawkins, S., Duke, M. and Gray, S. (2010) Recent Developments in Carbon Nanotube Membranes for Water Purification and Gas Separation. *Materials*, **3**, 127-149. http://dx.doi.org/10.3390/ma3010127

[2] Marulanda, J.M. (2011) Carbon Nanotubes Applications on Electron Devices. InTech, USA, 556 p.

[3] Schnorr, J.M., van der Zwaag, D., Walish, J.J., Weizmann, Y. and Swager, T.M. (2013) Sensory Arrays of Covalently Functionalized Single-Walled Carbon Nanotubes for Explosive Detection. *Advanced Functional Materials*, **23**, 5285-5291. http://dx.doi.org/10.1002/adfm.201300131

[4] Elhissi, A.M.A., Ahmed, W., UlHassan, I., Dhanak, V.R. and D'Emanuele, A. (2012) Carbon Nanotubes in Cancer Therapy and Drug Delivery. *Journal of Drug Delivery*, **2012**, Article ID: 837327. http://dx.doi.org/10.1155/2012/837327

[5] Balasubramanian, K. and Burghard, M. (2006) Biosensors Based on Carbon Nanotubes. *Analytical and Bioanalytical Chemistry*, **385**, 452-468. http://dx.doi.org/10.1007/s00216-006-0314-8

[6] Makar, J.M. and Beaudoin, J.J. (2003) Carbon Nanotubes and Their Application in the Construction Industry. *Proceedings of* 1st *International Symposium on Nanotechnology in Construction*, Paisley, 23-25 June 2003, 331-341. http://dx.doi.org/10.1039/9781847551528-00331

[7] Xia, Z., Riester, L., Curtin, W.A., Li, H., Sheldon, B.W., Liang, J., Chang, B. and Xu, J.M. (2004) Direct Observation of Toughening Mechanisms in Carbon Nanotube Ceramic Matrix Composites. *Acta Materialia*, **52**, 931-944. http://dx.doi.org/10.1016/j.actamat.2003.10.050

[8] Peigney, A, Laurent, Ch., Flahaut, E. and Rousset, A. (2000) Carbon Nanotubes in Novel Ceramic Matrix Nanocomposites. *Ceramics International*, **26**, 677-683. http://dx.doi.org/10.1016/S0272-8842(00)00004-3

[9] Ferro, G., Tulliani, J.-M. and Musso, S. (2011) Carbon Nanotubes Cement Composites. *Convegno Nazionale IGF XXI*, *Cassino* (*FR*), Italia, 13-15 Giugno 2011, 49-5950.

[10] Yu, X. and Kwon, E. (2009) A Carbon Nanotube/Cement Composite with Piezoresistive Properties. *Smart Materials and Structures* **18**, Article ID: 055010.

[11] Chen, S.J., Collins, F.G., Macleod, A.J.N., Pan, Z., Duan, W.H. and Wang, C.M. (2011) Carbon Nanotube-Cement Composites: A Retrospect. *The IES Journal Part A*: *Civil & Structural Engineering*, **4**, 254-265. http://dx.doi.org/10.1080/19373260.2011.615474

[12] Han, B.G., Yu, X. and Kwon, E. (2009) A Self-Sensing Carbon Nanotube/Cementcomposite for Traffic Monitoring. *Nanotechnology*, **20**, Article ID: 445501.

[13] Nasibulin, A.G, Shandakov, S.D., Nasibulina, L.I., Cwirzen, A., Mudimela, P.R. and Habermehl-Cwirzen, K. (2009) A Novel Cement-Based Hybrid Material. *New Journal of Physics*, **11**, Article ID: 023013.

[14] Chechenin, N.G., Chernykh, P.N., Vorobyeva, E.A. and Timofeev, O.S. (2013) Synthesis and Electroconductivity of Epoxy/Aligned CNTs Composites. *Applied Surface Science*, **275**, 217-221. http://dx.doi.org/10.1016/j.apsusc.2012.12.162

[15] Abdullayeva, S.H., Musayeva, N.N., Frigeri, C., Huseynov, A.B., Jabbarov, R.B., Abdullayev, R.B., Sultanov, Ch.A. and Hasanov, R.F. (2015) Characterization of High Quality Carbon Nanotubes Synthesized via Aerosol-CVD. *Journal Advances in Physics*, No. 4, 3229-3240.

[16] Hutchison, J.L., Kiselev, N.A., Krinichnaya, E.P., Krestinin, A.V., Loutfy, R.O., Morawsky, A.P., Muradyan, V.E., Obraztsova, E.D., Sloan, J., Terekhov, S.V. and Zakharov, D.N. (2001) Double-Walled Carbon Nanotubes Fabricated by a Hydrogen Arc Discharge Method. *Carbon*, **39**, 761-770. http://dx.doi.org/10.1016/S0008-6223(00)00187-1

[17] Shi, Z., Lian, Y., Liao, F.H., Zhou, X., Gu, Z., Zhang, Y., Iijima, S., Li, H., Yue, K.T. and Zhang, S.-L. (2000) Large Scale Synthesis of Single-Wall Carbon Nanotubes by Arc-Discharge Method. *Journal of Physics and Chemistry of Solids*, **61**, 1031-1036. http://dx.doi.org/10.1016/S0022-3697(99)00358-3

[18] Sugai, T., Yoshida, H., Shimada, T., Okazaki, T. and Shinohara, H. (2003) New Synthesis of High-Quality Double-Walled Carbon Nanotubes by High-Temperature Pulsed Arc Discharge. *Nano Letters*, **3**, 769-773. http://dx.doi.org/10.1021/nl034183+

[19] Vander Wal, R.L., Berger, G.M. and Ticich, T.M. (2003) Carbon Nanotube Synthesis in a Flame Using Laser Ablation for *in Situ* Catalyst Generation. *Applied Physics A*, **77**, 885-889. http://dx.doi.org/10.1007/s00339-003-2196-3

[20] Chen, C.X., Chen, W.Z. and Zhang, Y.F. (2005) Synthesis of Carbon Nano-Tubes by Pulsed Laser Ablation at Normal Pressure in Metal Nano-Sol. *Physica E*: *Low-Dimensional Systems and Nanostructures*, **28**, 121-127. http://dx.doi.org/10.1016/j.physe.2005.02.006

[21] Koziol, K., Boskovic, B.O. and Yahya, N. (2010) Synthesis of Carbon Nanostructures by CVD Method. *Carbon and Oxide Nanostructures*, *AdvStruct Mater*, **5**, 23-48.

[22] Meysami, S.S., Dillon, F., Koos, A.A., Aslam, Z. and Grobert, N. (2013) Aerosol-Assisted Chemical Vapour Deposition Synthesis of Multi-Wall Carbon Nanotubes: I. Mapping the Reactor. *Carbon*, **58**, 151-158. http://dx.doi.org/10.1016/j.carbon.2013.02.044

[23] Meysami, S.S., Koos, A.A., Dillon, F. and Grobert, N. (2013) Aerosol-Assisted Chemical Vapour Deposition Synthesis of Multi-Wall Carbon Nanotubes: II. An Analytical Study. *Carbon*, **58**, 159-169. http://dx.doi.org/10.1016/j.carbon.2013.02.041

[24] Meysami, S.S., Koos, A.A., Dillon, F., Dutta, M. and Grobert, N. (2015) Aerosol-Assisted Chemical Vapour Deposition Synthesis of Multi-Wall Carbon Nanotubes: III. Towards Upscaling. *Carbon*, **88**, 148-156. http://dx.doi.org/10.1016/j.carbon.2015.02.045

[25] Nasibulin, A.G., Shandakov, S.D., Timmermans, M.Y., Tolochko, O.V. and Kauppinen, E.I. (2011) Synthesis of Single-Walled Carbon Nanotubes by Aerosol Method. *Inorganic Materials*: *Applied Research*, **2**, 589-595. http://dx.doi.org/10.1134/S2075113311060104

[26] Tian, Y., Nasibulin, A.G., Aitchison, B., Nikitin, T., Pfaler, J., Jiang, H., Zhu, Z., Khriachtchev, L., Brown, D.P. and Kauppinen, E.I. (2011) Controlled Synthesis of Single-Walled Carbon Nanotubes in an Aerosol Reactor. *The Journal of Physical Chemistry C*, **115**, 7309-7318. http://dx.doi.org/10.1021/jp112291f

[27] Krause, B., Ritschel, M., Täschner, Ch., Oswald, S., Gruner, W., Leonhardt, A. and Pötschke, P. (2010) Comparison of Nanotubes Produced by Fixed Bed and Aerosol-CVD Methods and Their Electrical Percolation Behaviour in Melt Mixed Polyamide 6.6 Composites. *Composites Science and Technology*, **70**, 151-160. http://dx.doi.org/10.1016/j.compscitech.2009.09.018

[28] Huo, J., Song, H. and Chen, X. (2004) Preparation of Carbon-Encapsulated Iron Nanoparticles by Co-Carbonization of Aromatic Heavy Oil and Ferrocene. *Carbon*, **42**, 3177-3182. http://dx.doi.org/10.1016/j.carbon.2004.08.007

[29] Huo, J., Song, H., Chen, X. and Lian, W. (2006) Formation and Transformation of Carbon-Encapsulated Iron Carbide/Iron Nanorods. *Carbon*, **44**, 2849-2867. http://dx.doi.org/10.1016/j.carbon.2006.06.016

[30] Abdullayeva, S.H., Musayeva, N.N., Jabbarov, R.B., El-Gendy, A.A. and Leonhardt, A. (2013) Synthesis of Carbon Encapsulated Magnetic Nanostructures by Using Caspian Heavy Oil. *Azerbaijan Journal of Physics*, *FIZIKA*, **XİX**, 20-21.

[31] Abdullayeva, S.H., Musayeva, N.N., Jabbarov, R.B. and Matsuda, T. (2014) Synthesis of Carbon Nanotubes from By-products of Oil Refiner. *World Journal of Condensed Matter Physics*, **4**, 93-100.

[32] Vesselenyi, I., Neiesz, K., Siska, A., *et al*. (2001) Production of Carbon Nanotubes on Different Metal Supported Catalysts. *Reaction Kinetics and Catalysis Letters*, **74**, 329-336. http://dx.doi.org/10.1023/A:1017953514858

[33] Karacan, O. and Kok, M.V. (1997) Pyrolysis Analysis of Crude Oils and Their Fractions. *Energy Fuels*, **11**, 385-391. http://dx.doi.org/10.1021/ef960162+

[34] Savage, P.E. (2000) Mechanisms and Kinetics Models for Hydrocarbon Pyrolysis. *Journal of Analytical and Applied Pyrolysis*, **54**, 109-126.

[35] Le Chatelier, H. and Boudouard, O. (1898) Limits of Flammability of Gaseous Mixtures. *Bulletin de la Société Chimique de France* (*Paris*), **19**, 483-488.