INVESTIGATION OF FUNCTIONALIZED MULTIWALLED CARBON NANOTUBES BY DERIVATOGRAPHY METHOD

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The thermal stability characteristics of multiwalled carbon nanotubes (MWCNTs) functionalized via introduction of oxygen containing groups were investigated by derivatography method. MWCNTs were synthesized for the first time from the light gasoline fraction of the Azerbaijan oil. MWCNTs were chemically functionalized by using sulfuric and nitric acid. IR spectroscopy analysis has confirmed the presence of oxygen containing (COOH, COH, OH) and other functional groups on the surface of the MWCNTs. SEM analysis has displayed that the structure of MWCNTs has curved shapes and surface is covered with layers of non-tubular forms of carbon. According to Termogravitmetric (TGA) and Differential Scannic Calorimetry (DSC) analysis results, f-MWCNTs are thermally stable up to 350^{0}C. At the 350-600^{0}C temperature range was observed the cleavage of carbonyl and carboxyl groups, as well as the oxidation of amorphous carbon with the release of CO, CO2 ,water vapor and MWCNTs combusted at about 600^{0}C in air.

Keywords: Aerosol CVD, MWCNT, oxidative functionalization, thermal stability, TGA, DSC, FTIR, Mass Spectrometry, SEM.
PACS: 61.48.De, 81.65.Mq

1. INTRODUCTION

Carbon nanotubes (CNTs), discovered more than two and a half decades ago by the Japanese scientist Sumio Iijima [1]. Due to their unique structural (tubular structure with an hollow interior) and physicochemical (mechanical, electrical, optical, etc.) properties they are very essential nanomaterials and have a wide range of potential applications in various areas of science and technology [2,3], particularly in medicine, electronics, catalysis, materials science (sensitive elements of different types of sensors, new generation nanocomposites for various purposes, energy (the hydrogen storage, the solar battery elements) and etc [4,5].

Thermal stability of pristine and modified MWCNTs at high temperatures and oxidizing environments is crucial for high - temperature applications of materials based on carbon nanotubes, especially polymer composite materials, catalysts, etc. [6,7] In this regard, a number of research works were devoted to the study of thermal stability and thermodestruction of nanostructured carbon materials at high temperatures, in particular single-walled and multi-walled carbon nanotubes in air or in the inert gas environments (argon and others) [8-19].

In this paper, the thermal stability of the f- MWCNTs with oxygen containing groups has been studied by the derivatography method companied by FT-IR and Mass spectroscopy. TGA / DSC analysis were carried out in the temperature range of 30 - 1000 ^{0}Cin air at a furnace heating rate of 10 deg / min. The obtained results of thermal stability with declared methods showed a good agreement with each other.

2. EXPERIMENTAL

2.1. Synthesis of MWCNTs by ACVD method

The MWCNTs used in this work were synthesized by an Aerosol Chemical Vapor Deposition Technique (ACVD) on the experimental laboratory setup Scientific Instruments Dresden GMBH, SCIDRE, Germany.

The aerosol CVD set - up equipped with a gas flow regulator and flue gases lines consists of the following key modules: carrier gas supply units (Inlet 1-3), ultrasonic aerosol generator (2), high temperature reactor, electric furnace (heating up to 1200^{0}C) (3) and the vacuum system (leak test of the setup).The high - temperature reactor, in turn, consists of a quartz tube (4) placed in a tubular furnace. The tubular furnace is additionally equipped with a mechanism for moving along the quartz tube at a predetermined rate, which allows the thermolysis of the hydrocarbon mixture and the synthesis of carbon nanotubes along the entire length of the tube.

Synthesis process was carried out at a 900^{0}C temperature. A light gasoline fraction of the Azerbaijan oil was used as a raw material and ferrocene (Fc) as a catalyst precursor . A chemical quartz glass with a capacity of 200 ml containing a solution of ferrocene in gasoline with a quantitative ratio of 20 mg / ml was placed in the ultrasonic bath of the aerosol generator of the CVD equipment. A more detailed description of the experimental setup and the standard procedure of the ACVD are presented in the work [20].

The obtained MWCNTs were purified from by-products (impurity inclusions of the iron catalyst, resinous substances) by widely known methods [21].

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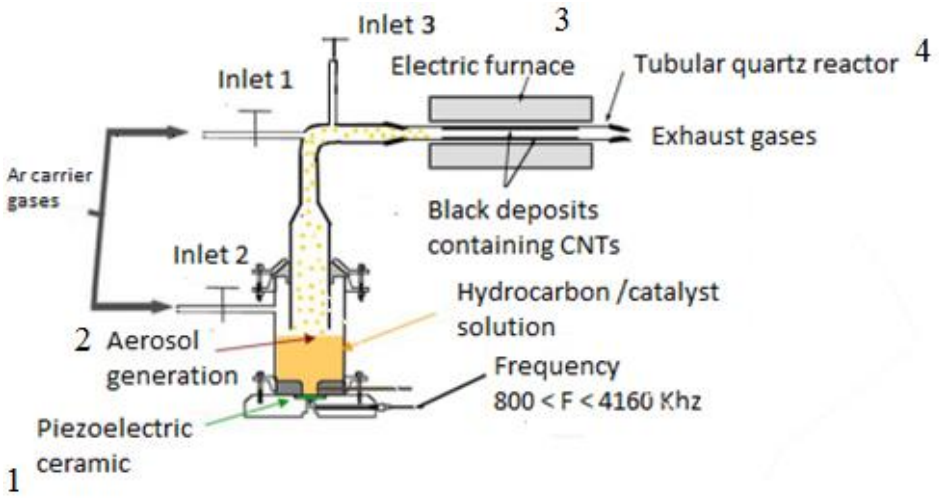

Fig.1. Schematic diagram of ACVD apparatus.

The purification process of MWCNTs from tarry compounds was carried out as a result of extraction using xylene and cyclohexane as solvents in a volume - weight ratio (ml / g) of 30: 1 by heating the nanotubes suspension to T = 80 ^{0}C and continuously mixing.During the heating process, the dispersion of carbon nanotubes acquired a yellowish color, which indicated the presence of tarry impurities. This procedure was repeated several times with small fresh portions of xylene until the solution was completely discolored and completeness removed the resinous products. Subsequently MWCNTs were purified from the catalytic iron (Fe) particles, with dilute nitric acid (28% HNO_3) treatment at a temperature 80 ^{0}C for 2 hours and with constant stirring followed by washing the carbon nanotubes with deionized water to remove the acid and formed nitrogen-containing iron salts.

2.2. Functionalization of the MWCNTs

Surface functionalization of synthesized MWCNTs with oxygen containing groups (COOH, COH, OH) were carried out involving a strong oxidative treatment using the mixture of concentrated sulfuric and nitric acids in a volume ratio (ml / ml) equal to 1: 3 [21].

Purified MWCNTs were placed into a 500 ml glass beaker and 13.5 ml of HNO_3 and 40 ml of H_2SO_4, were alternately poured and this mass was heated on a hot plate for 120 minutes at a 80^{0}C temperature with constant stirring. After treatmen tthe residual acid solution was filtered and repeatedly washed. The oxidized MWCNTs were rinsed with deionized water until stabilization of the filtrate pH. The resulting functionalized product (f-MWCNTs) was dried in an oven at 130 ^{0}C for an hour.

2.3. Scanning electron microscopy (SEM)

The morphology of the functionalized MWCNTs was investigated by scanning electron microscopy using a CarleZeiss device (SigmaVP). The image was obtained at an accelerating voltage of 5.00 kV.

2.4. Fourier Transform Infrared (FTIR) Spectroscopy

Fourier transform infrared (FTIR) studies were carried out in the range 450 - 4000 cm $^{-1}$ to study the attachment of oxygen containing groups on carbon nanotubes surface using Nicolet IS 10 FTIR spectrometr. Resolution - the error of the spectrophotometer according to the scale of wave numbers was - 0.4 cm $^{-1}$.

2.5. Thermal analysis of f-MWCNTs

The thermal decomposition behavior of the f- MWCNTs was studied by TGA/ DSC spectroscopy. Measurements were carried out in derivatograph of the Linseis Corporation company "STA Platinum Series" type - "LINSEIS STA PT1600" coupled with the FTIR Nicolet IS10 spectrometer and the ThermoStar TM GSD 320 T2 mass analyzer .The DTA study, which combines the use of TGA and DSCwas performed in air purging through the derivatograph chamber in the mode of dynamic programmable heating in a temperature range of 30-1000 ^{0}C with a continuous rate of temperature rise in the furnace 10 deg / min. The procedure involved weighing a sample with a mass of 16.6 mg in a cylindrical ceramic crucible, followed by annealing of o - MWCNTs in an oxidizing air atmosphere. The products produced with increasing temperature as a result of thermodestructive transformations of the sample were studied through curves of weight loss (TGA) and thermal effects (DSC), as well as on IR and mass spectra of the resulting compounds, simultaneously – "in situ" entering on appropriate devices.

3. RESULTS AND DISCUSSION

3.1. SEM characterization of f-MWCNTs

The SEM image of f-MWCNTs is presented in Fig. 2. It is determined that the diameter of carbon nanotubes varies within 120 - 288 nm.

SEM micrographs reveal that the tubular structures of nanotubes curved and also contain layers of other carbon phases which explain the excess of the diameter of the f-MWCNTs. The presence of a large number of impurities of non - tubular carbon forms are attributed to the raw material- a mixture of carbon compounds – a light gasoline fraction of Azerbaijan oil.

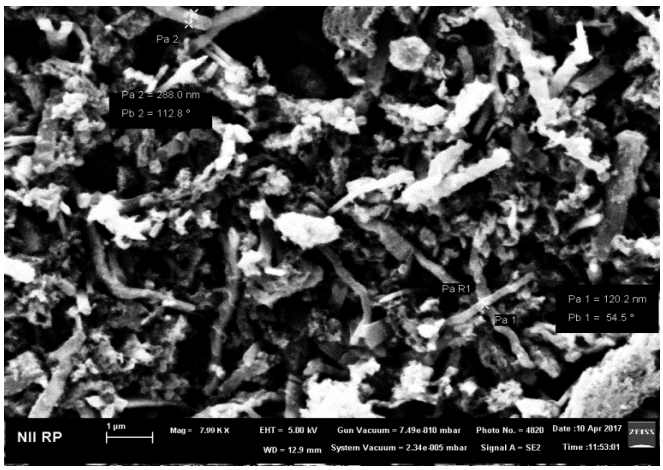

Fig. 2. SEM images of the f-MWCNTs.

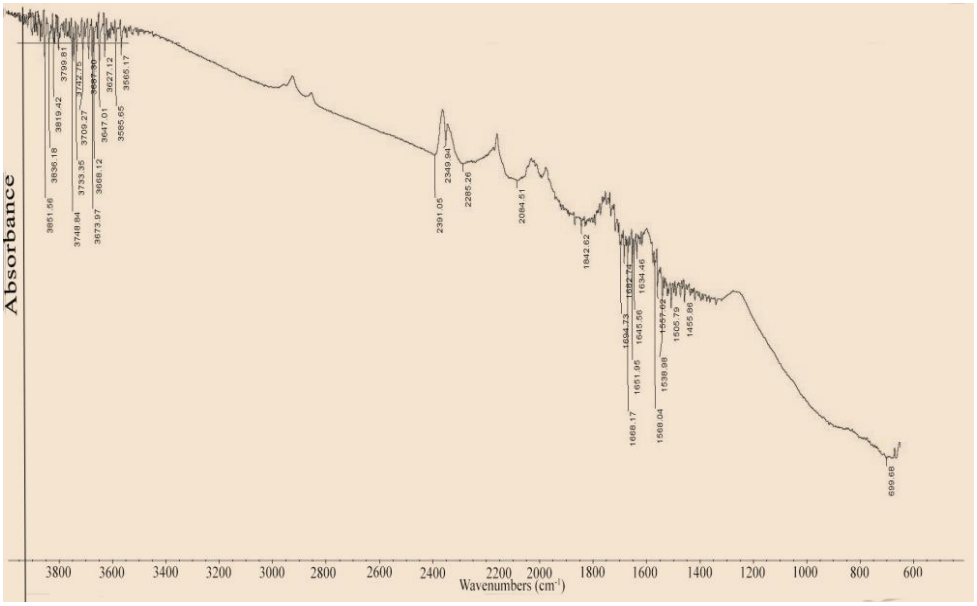

Fig 3. FTIR spectrum of f-MWCNTs

3.2. FTIR analysis of f-MWCNTs.

The FTIR spectra of the f- MWCNTs are shown in Fig.3. FTIR is used to characterize the functional elements absorbed by carbon nanotubes.

FTIR of the f-MWCNTs shows dominant peaks in the region 3946-3585cm^{-1} which can be related to the valence vibrations of the associated hydroxyl (OH) functional groups in carboxyl (O=C-OH).The absorption bands recorded in the 3565.17 - 3460.41 cm^{-1} regions are characterized as the possible presence of adsorbed atmospheric moisture (H_2O) and free (non - hydrogen-bonded) hydroxyl functional groups. The appearance of a narrow peak at a 2391.05 cm^{-1} is due to the stretching vibrations of O – H bonds in the carboxyl group of COOH is strongly bounded by hydrogen bonds, while the peak fixed at 2349.94 cm^{-1} is inherent in the carbon dioxide CO_2 molecule.

The presence of sharp adsorption peaks in the 1634.46 - 1694.73 cm $^{-1}$, range respectively, is explained by the stretching vibration of the C = O bond of the carbonyl group of carboxyl (COOH) or keto group of the quinone type.

In the IR spectrum of the f-MWCNTs also was observed a series of characteristic absorption bands in the frequency range 1455.86-1568.04 cm^{-1}, which correspond to the stretching vibrations of the conjugated C = C bonds of the skeleton of carbon nanotubes.

The FTIR results proved that treatment of MWCNTs with mixture of acid salution caused introduction of different number of oxygenated acidic groups on the carbon surface.

3.3. TGA/DSC analysis of f-MWCNTs.

The thermal decomposition of f – MWCNTs has been studied by TGA/DSC analysis. TG and DSC curves of MWCNTs conducted in air are depicted in Fig. 4.

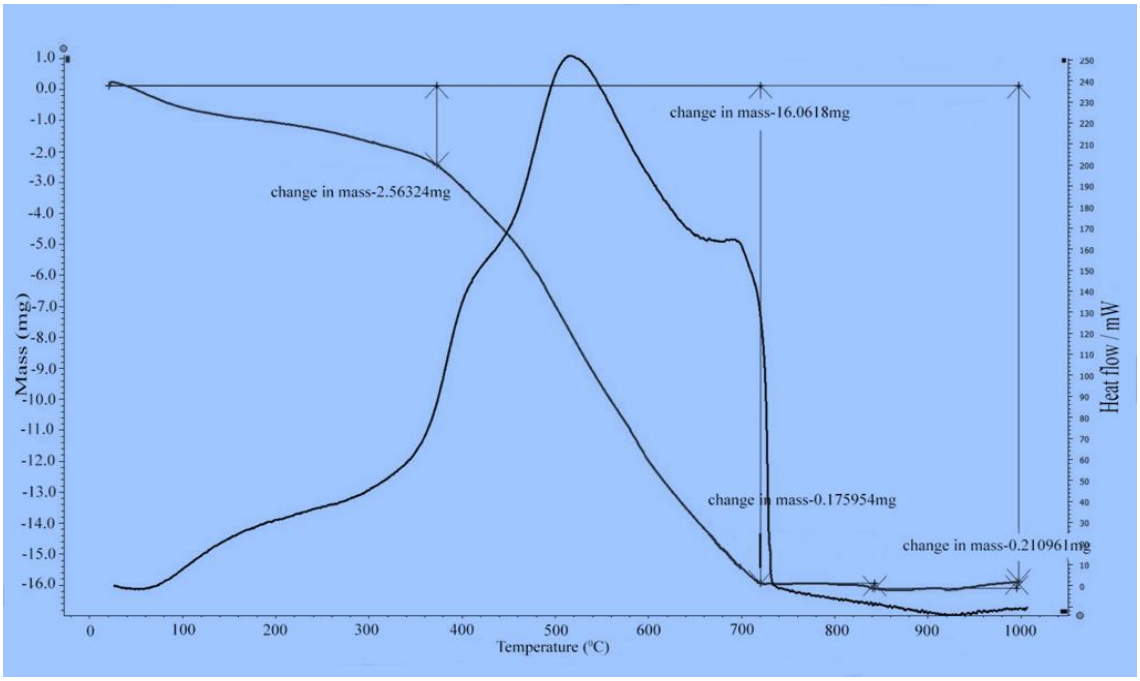

Fig. 4. TGA/DSC analysis of f-MWCNTs

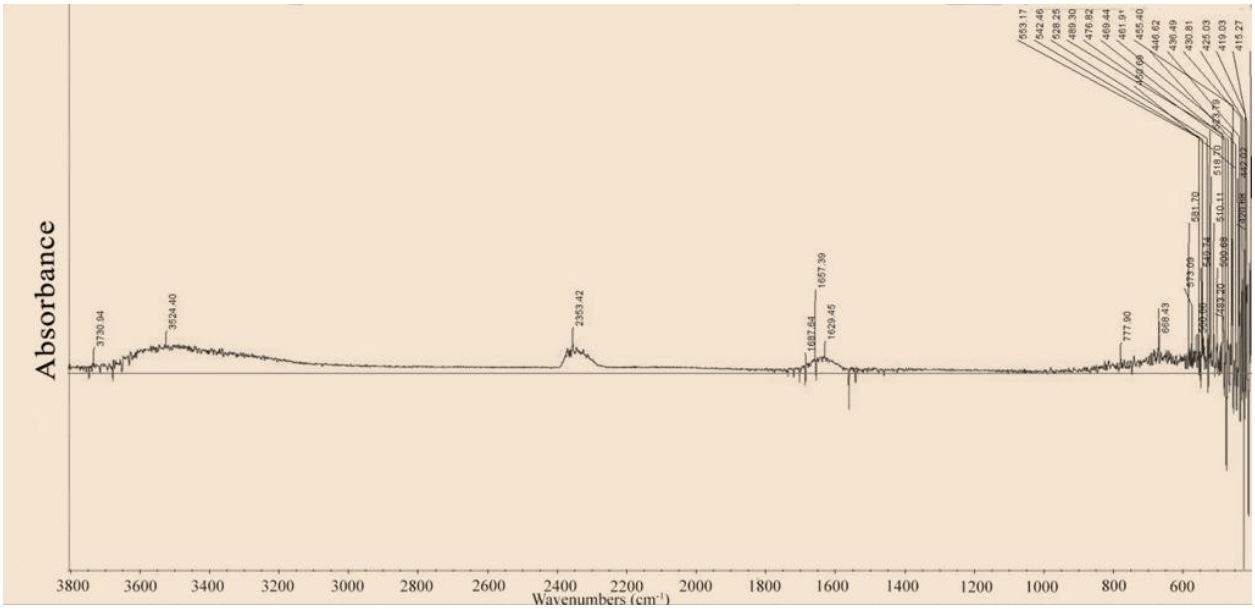

Fig.5. FTIR spectrum of gaseous products of the oxidation-thermal destruction process of f- MWCNTs at 370 ^{0}C.

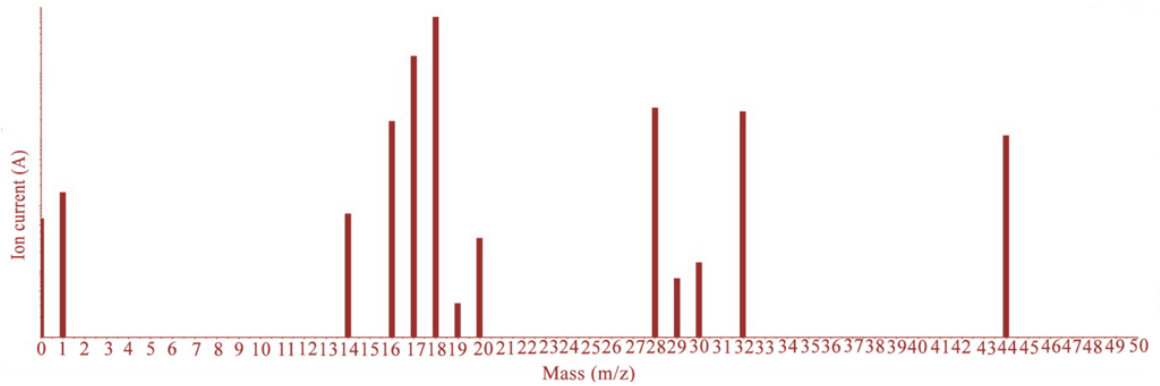

Fig . 6. Mass spectrum of gaseous products of the oxidation-thermal destruction process of the f - MWCNTs sample at 370 ^{0}C.

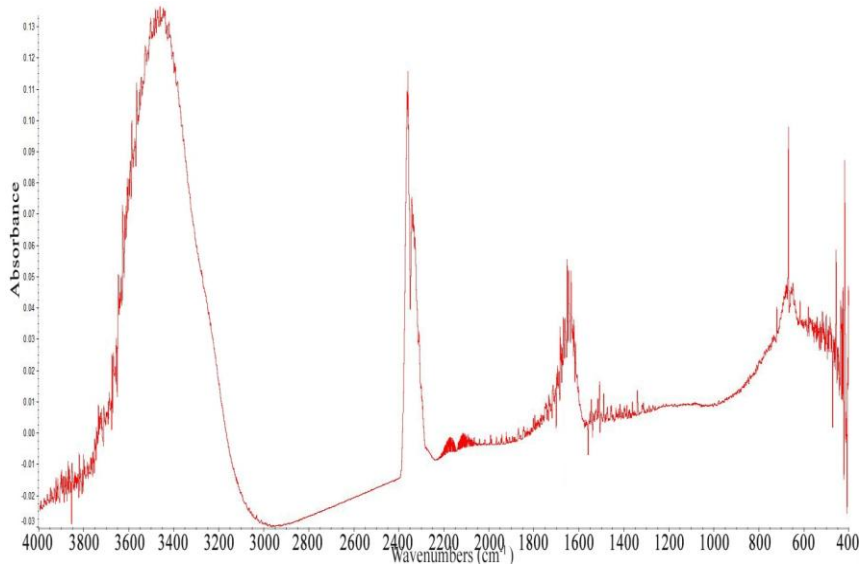

Fig.7. FTIR spectrum of gaseous products of the oxidation-thermal decomposition process of the f– MWCNTs at 500 ^{0}C.

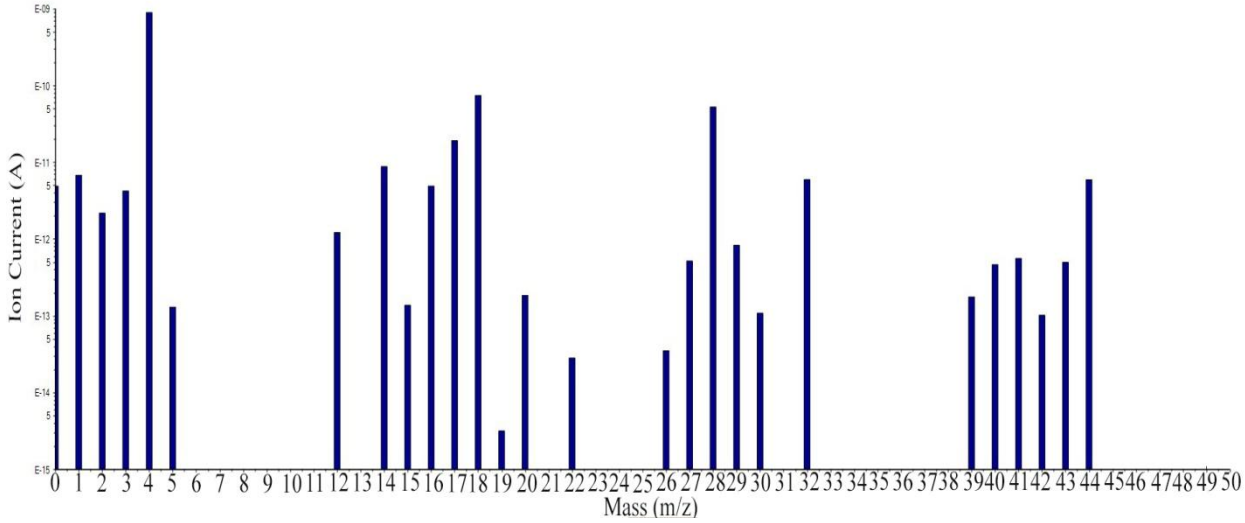

Fig.8. Mass spectrum of gaseous products of the oxidation-thermal decomposition process of the f- MWCNTs at 500 ^{0}C

Reduction in weight in the temperature range 470-600^{0}C is accompanied by a corresponding exothermic effect (T = 400-650^{0}C), which is clearly appeared in the form of a wide pronounced peak on the DSC curve with a maximum at 520^{0}C, indicating that weight loss is due not only by defunctionalization, as well as deep oxidation. At these temperatures both dehydration processes and oxidation of unstructured (amorphous) forms of carbon are taking place. This result is also confirmed by the infrared spectrum of the decay products of the f - MWCNTs at 500 ^{0}C, where very intense peaks at 3500 cm^{-1} and 2200 - 2440 cm^{-1} are distinctly registered, that respond to the existence of water molecules, monoxide and carbon dioxide, accordingly, generated owing to the thermo-oxidative destruction of carbonyl, carboxyl groups and destructive oxidation of carbon. In the mass spectrum, peaks with masses of 16, 28 and 44 amu are also observed, indicating the presence of $^-$OH anions and CO and CO_2 molecules (Fig. 7,8).

Finally, the weight loss in the (600 – 735)^{0}C temperature range and appropriate maximum at 700 ^{0}C in DSC curve can be explained by the oxidation of the more active phase (impurity inclusions of amorphous carbon), also the combustion of pristine carbon nanotubes, which is in good agreement with FTIR and MS analyzes. Thus, in the IR spectrum of the vapors at a temperature of 600^{0}C, adsorption bands were observed with wave numbers of 2250 and 2350 cm^{-1} which corresponds to decomposition of a large number of carbon oxides (CO and CO_2, respectively) and is consistent with the results of the mass spectroscopy. In addition, there is no peak in the IR spectrum responsible for the presence of C=C bonds of the structure of carbon nanotubes, which indicates the degradation of the skeleton of MWCNTs. The weight loss of the sample as a result of the oxidation - thermal reaction was 16.06 mg (Fig. 9, 10).

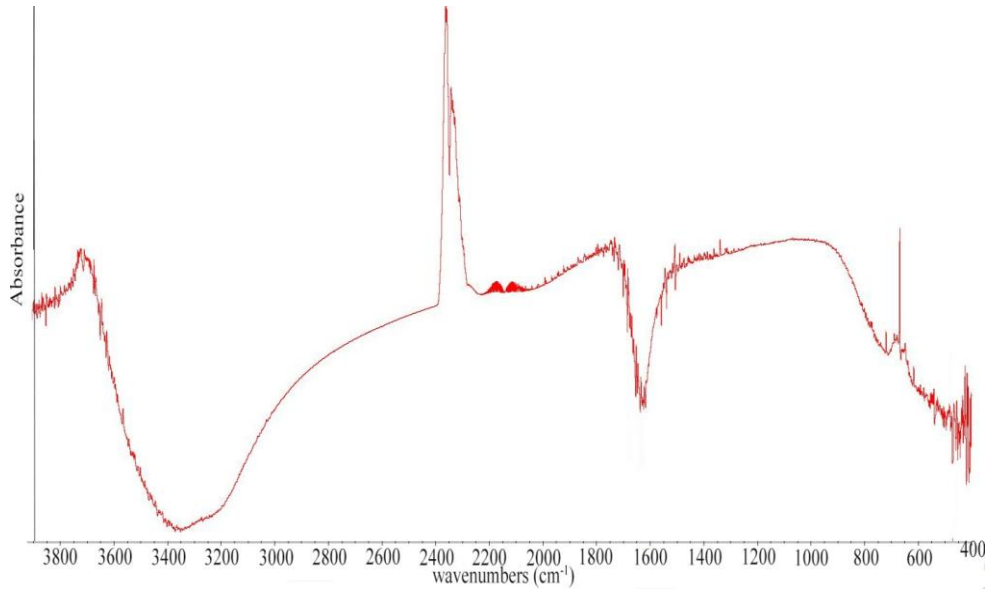

Fig. 9. FTIR spectrum of gaseous products of the oxidation-thermal decomposition process of the f - MWCNTs sample at 600 ^{0}C.

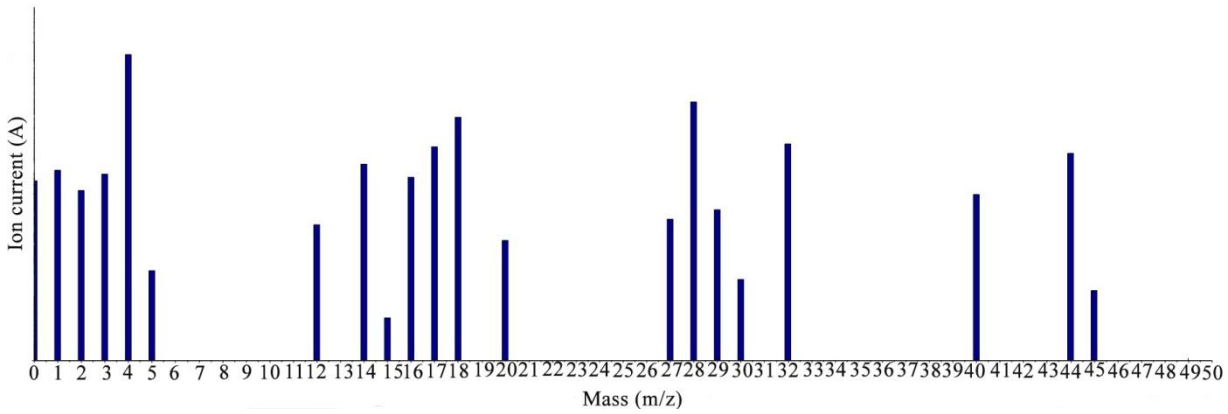

Fig.10. Mass spectrum of gaseous products of the oxidation-thermal decomposition process of the f - MWCNTs sample at 600^{0}C.

CONCLUSIONS

Multiwalled carbon nanotubes (MWCNTs) have been synthesized by ACVD method using for the first time as an inexpensive and affordable raw material – the light gasoline fraction of the Azerbaijan oil. Side-wall functionalization of MWCNTs with oxygen containing groups (COOH, COH, OH) was achieved by oxidative treatment. The IR spectra for the f-MWCNTs identified the characteristic stretching peaks for the successful linkage between MWCNTs and carbonyl, carboxyl and hydroxyl groups. The character of the thermal decomposition of f - MWCNTs in air was studied by derivatography method based on the indices of mass loss of samples and endo/exo effects in the temperature range from 350 to 735^{0}C. It was revealed that in the 350 - 470^{0}C temperature range decarboxylation and in the 470 - 600^{0}C region dehydration and the oxidation of unstructured forms of carbon were observed. FTIR analysis results confirmed that at 600^{0}C combustion of f - MWCNTs occurred as in 1650 - 1500 cm^{-1} region there weren't any peaks observed inherent in the C=C bond of the framework of carbon nanotubes.

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Recevied: 14.06.2017