

Production of Carbon Nanotubes by Iron Catalyst

Ezgi Dündar-Tekkaya and Nilgün Karatepe

Abstract—Carbon nanotubes (CNTs) with their high mechanical, electrical, thermal and chemical properties are regarded as promising materials for many different potential applications. Having unique properties they can be used in a wide range of fields such as electronic devices, electrodes, drug delivery systems, hydrogen storage, textile etc. Catalytic chemical vapor deposition (CCVD) is a common method for CNT production especially for mass production. Catalysts impregnated on a suitable substrate are important for production with chemical vapor deposition (CVD) method. Iron catalyst and MgO substrate is one of most common catalyst-substrate combination used for CNT. In this study, CNTs were produced by CCVD of acetylene (C_2H_2) on magnesium oxide (MgO) powder substrate impregnated by iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) solution. The CNT synthesis conditions were as follows: at synthesis temperatures of 500 and 800°C multiwall and single wall CNTs were produced respectively. Iron (Fe) catalysts were prepared by with Fe:MgO ratio of 1:100, 5:100 and 10:100. The duration of syntheses were 30 and 60 minutes for all temperatures and catalyst percentages. The synthesized materials were characterized by thermal gravimetric analysis (TGA), transmission electron microscopy (TEM) and Raman spectroscopy.

Keywords—Carbon nanotube, catalyst, catalytic chemical vapor deposition, iron

I. INTRODUCTION

IN the last decade due demand of new generation of high technology materials, there is a tremendous interest in nanotechnology [1]. Nanomaterials have unique mechanical, electrical, and optical properties. Therefore, they can be implicated to many fields such as electronics, chemicals, sensors, energy storage, and biotechnology. The identification of the structure of fullerenes in 1985 by Kroto et al. was a breakthrough in nanotechnology [2]. In 1991 Lijima discovered multiwall carbon nanotubes (MWCNT), two years before Lijima and Bethune et al. discovered single wall carbon nanotubes (SWCNT) in separate researches [3,4]. Before the discovery of CNTs there have been studies on syntheses of carbon nanofibers which is very similar to CNT synthesis. In 1960 Bacon produced graphene scrolls in nanoscale and he suggested existence of CNTs before its discovery [5]. Thereafter the highly intensified research into the science of nanotechnology started due to superior mechanical strength, electronic properties, large surface area for adsorption of hydrogen, and high aspect ratio of CNTs [6-9]. They have many applications in different fields such as electronics,

textile, electrodes, drug delivery systems, field emission applications, magnetic field applications, hydrogen adsorption. CVD is an important method for CNT synthesis especially when mass production is concerned. There are different parameters (synthesis method, catalyst, substrate, carbon source, synthesis time) affecting the structure, morphology and the amount of the CNT synthesised. The catalyst plays an important role in growth of CNT. CVD method is deposition of a hydrocarbon gas as carbon source (i.e. acetylene, methane etc.) on a metal catalyst (i.e. Fe, Co, Ni, Pd etc) at temperatures between 500 and 1200°C. Growth of carbon nanotubes generally requires existence of a catalyst placed on high surface area materials of substrates. Practically catalyst particles serve as seeds for CNT growth. CVD has been used for production of nanofibers for long time [10]. This method is preferred for CNT syntheses because of high purity and large scale production [11-13]. CVD which was first reported to produce MWCNTs by Endo et al. can synthesise both SWCNTs and MWCNTs. [14]. The main challenges in CNT production is to maintain mass production and low cost. In this respect, the catalytic method is claimed to be best because of lower reaction temperatures and cost [15]. The amorphous carbon formed as by product during the thermal decomposition of hydrocarbons can be eliminated by purification.

The type of the catalyst is important for the growth and morphology of the CNTs. Cobalt, iron, titanium, nickel, copper, zeolites and combinations of these metals and/or their oxides widely used catalyst materials in literature for multiwall or single wall CNT synthesis [4,16-30]. In a study conducted by Nagaraju et al. [17] catalytic activities of Fe, Co and Fe&Co binary catalyst supported on alumina or silica are compared. The best yield of MWNTs resulted at 700°C on hydrated alumina prepared from aluminium isopropoxide and containing a mixture of Fe and Co. In another study, Seo et al. [18] compared the catalytic activity of Fe, Co, or Ni as the catalyst, and laser treated vanadium plates having high surface area as the catalyst support in the decomposition of acetylene at 720°C under CVD conditions. Best quality CNTs were obtained over the iron catalyst with high density and small diameter of 10–15 nm.

A single metal and mixture of metals supported on oxides, clays or zeolites have a great affect on CNT production by CCVD method [19,20]. Metallic catalyst can be dispersed and stabilised by a number of oxides [21]. The interaction between the catalyst and the substrate material strongly affects the catalytic properties of the catalyst and substrate couple. In a research conducted by Zhu et al. [22] Fe and Co salts are used as catalyst on mesoporous silica. Catalyst/support ratio

E. Dündar-Tekkaya is with Istanbul Technical University Energy Institute, 34469 Maslak, İstanbul, Turkey (e-mail: edundar@itu.edu.tr).

N. Karatepe is with the Istanbul Technical University Energy Institute, 34469 Maslak, İstanbul, Turkey (phone: 0090-212-2853940 e-mail: kmnilgun@itu.edu.tr).

affecting the type of the CNT synthesized was deeply investigated.

In this study, as produced CNTs synthesized by CCVD using $(\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O})$ as catalyst was used to examine the effect of time, temperature and weight ratio of the catalyst to substrate on the carbon efficiency. This was evaluated by TGA, TEM and Raman measurements.

II. EXPERIMENTAL STUDIES

A. Catalyst Preparation

Metal catalyst of Fe was impregnated in MgO substrate. Iron nitrate $(\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O})$ was separately mixed with MgO substrate in ethanol solution by ultrasonic mixer with metal to MgO weight ratios of 1:100, 5:100 and 10:100. The amount of nitrate in the metal nitrate, MgO and ethanol solution was calculated according to the molecule ratios of metals in the compound. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, substrate and ethanol solution was mixed for 30 minutes in "Bandelin Sonoplus" ultrasonic mixer then kept in oven at 80°C for 18 hours. The dried catalyst-substrate mixture was then grinded to avoid any agglomeration that may affect the interaction between acetylene gas and the surface of mixture.

B. Carbon Nanotube Production

CNT production experiments were conducted on a fluidized bed system. The system was composed of a "Protherm" furnace that can operate up to 1100°C and a quartz reactor with a diameter of 2.5 cm and length of 94.5 cm. In the middle of the reactor is a nano porous silica disc allowing gas flow but not the produced CNTs. The furnace is placed vertically and the quartz reactor is placed in it with the nano porous silica disc placed in the middle of hot region of the furnace. CNT production was held on the 5 to 10 cm length region around the quartz disc of the reactor. To fluidize the bed a certain flow rate of gas was necessary for a given substrate catalyst mixture. For this purpose argon was used as carrier and inert gas and acetylene was used as carbon source. The gas was fed to the system through the bottom of the reactor and it left the system from the top. The catalyst and substrate mixture was placed homogeneously on the disc. For MWCNT and SWCNT production while heating the system to 500°C and 800°C respectively 100 ml/min argon was fed to the system to maintain inert atmosphere and/or to make flow of other gases existing in the system. As the temperature reached 500°C for MWCNT and 800°C for SWCNT, acetylene flow started with a rate of 42 ml/min and the argon flow rate was increased to 368 ml/min to make acetylene flow easier. A vacuum pump was used to assist the gas flow during acetylene feeding. The reaction time was chosen 30 and 60 minutes for CNT production. When the furnace was heated to the synthesis temperature, the precursor powder iron oxide clusters were formed due to the thermal decomposition of the iron nitrate at 125°C. The synthesis was started with the introduction acetylene mixed with argon. After synthesis, the CNTs were cooled in inert gas. In this study, the TGA of synthesized CNTs were conducted by the TGA system of TA

Q600 SDT in dry air atmosphere with an increase of 5°C/min between 25 and 800°C. The maximum operating temperature of the existing system is 1500°C. The thermal couple in the system is Pt-Rh alloy. The system is designed to work in various atmospheric conditions. The ultimate gas flow rate is 50 ml/min. It is possible to work under vacuum conditions up to 7 Pa and 0.05 Torr. The range of operating temperature increase is 0.1 to 100°C/min. The maximum amount of material to be analysed is 200 mg and the sensitivity of the system is 0.1 mg.

The Raman spectroscopy measurements of the samples were analyzed by Horiba Jobin YVON HR 800UV and with 632.88 nm of He-Ne laser light. Raman spectra of CNTs are quite interesting because of resonance phenomena and sensitivity to tube structure. That is, there is very strong excitation wavelength dependence of the spectra resulting from the electronic band structure. The features in the Raman spectra are diagnostic of the CNT type. Raman is a reliable diagnosis and a non destructive method to determine structure of CNT and requires a very little amount of sample preparation.

20 kV Tecnai-G2 F-20 model of FEI was used for TEM measurements. The resolution of the device is ranging from 0.14 to 0.18 nm and the maximum thermal current is greater than 100 nA. There is 0.5 nA or larger current in 1 nm probe. The energy distribution is around 0.7 eV. In order to have the TEM image the sample in a solution of 50% ethanol and 50% pure water was mixed with ultrasonic mixer. The formed homogeneous mixture poured on copper grids and dried in oven at 45°C.

III. RESULTS AND DISCUSSION

CNT production generally requires existence of a catalyst. The selection of a proper metallic catalyst may affect the morphology amount of the synthesized product, the quality of the product (i.e. electrical, physical, mechanical etc.). All these parameters in addition to economic factors should be taken into account to improve the efficiency of CNT production by catalyst. In this research the effects of time and weight percent of different catalysts (iron, nickel, cobalt, vanadium) to the substrate (magnesium-oxide) on production of CNTs in decomposition of acetylene were investigated. TGA, Raman, and TEM measurements were used for characterization.

The carbon efficiency of as produced CNTs is calculated according to TGA measurement. In order to eliminate any differences which may be caused due to moisture content of as produced samples, in the calculations the initial temperature is selected as 200°C to have the dry weight percent and the final temperature is taken as 796°C to have the same temperature value for all samples. The formula of carbon efficiency is:

$$\text{Carbonefficiency}(\%) = \frac{\text{Weight}\%(200^\circ\text{C}) - \text{Weight}\%(796^\circ\text{C})}{\text{Weight}\%(200^\circ\text{C})} \times 100 \quad (1)$$

A. Effect of Temperature

The effect of temperature was examined for weight ratios of 1:100, 5:100 and 10:100 for two synthesis times. The selected synthesis temperatures were 500 and 800°C. Temperature is an important parameter in CNT production as with temperature change the type of nanotubes. TEM images of these synthesized materials are given in Fig. 1. It is evident that the structures synthesized by chemical vapor deposition method are CNTs. In Fig. 1, the diameter of the CNTs is nearly 10 nm and their appearance is darker in the picture. The CNTs in Fig. 2 have diameters between 1.5-5 nm and also are transparent. One possible explanation for the dark parts in both two figures is a result of the impurities within the structures. These observations lead to a conclusion such that in the temperature of 500°C MWCNTs were grown and at the temperature of 800°C SWCNTs were synthesized.

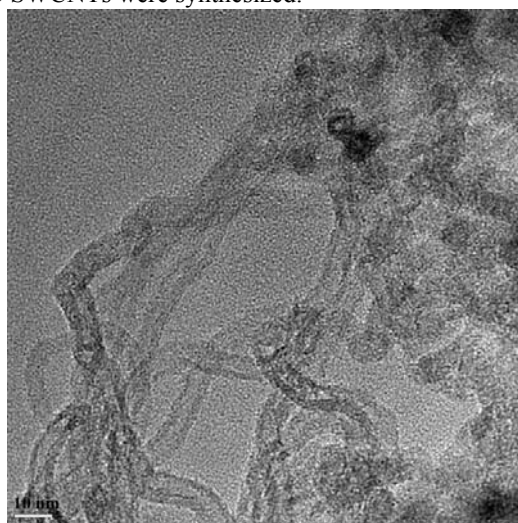


Fig. 1 TEM images of CNTs synthesized at 500°C

The change of the nanotube type as a function of temperature is also clearly seen in the Raman spectra. Raman spectroscopy is a powerful technique for the characterization of the structure of carbon nanotubes. Fig. 3 shows Raman spectrum for carbon deposits excited by 633 nm laser. The spectra of MWCNT and that of SWCNT show a clear difference at the G band (around 1580 cm^{-1}). The intensity of the G band for SWCNT, which is synthesized at 800°C, is considerably higher than MWCNT, which is synthesized at 500°C. Furthermore, at 500°C, the D-band (around 1350 cm^{-1}) is more intense than the G-band. At the temperature of 800°C, the intensity of the G-band becomes higher. The absolute intensities of the bands are increased at 800°C compared to 500°C. The ratio between the D band and the G band and the radial breathing mode (RBM) and its relation with diameter distribution are very important factors in the way that allows us to distinguish between the three variants of nanotubes with one single analysis, which is a probe of the high performance of Raman spectrometer. As seen from Fig. 3, the spectrum in RBM band which is a characteristic of SWCNT is observed in the two samples. The reason of this spectrum which is observed at MWCNTs is that the innermost tube diameter is

below 2 nm and this result is consistent with other studies found in literature [31]. If nanotube diameter is greater than 2 nm, RBM spectrum becomes difficult to be observed.

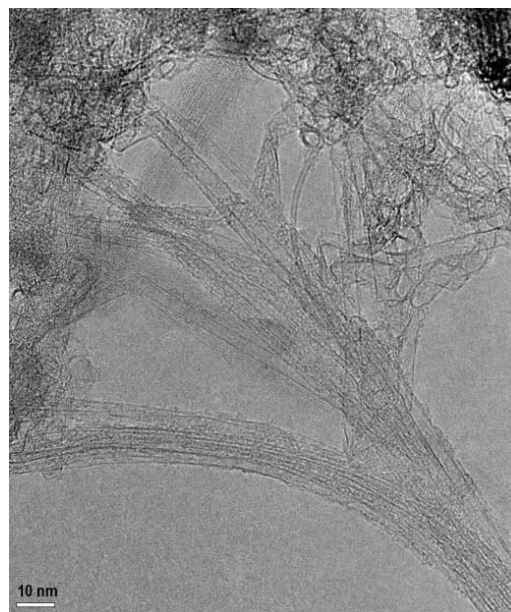


Fig. 2 TEM images of CNTs synthesized at 800°C

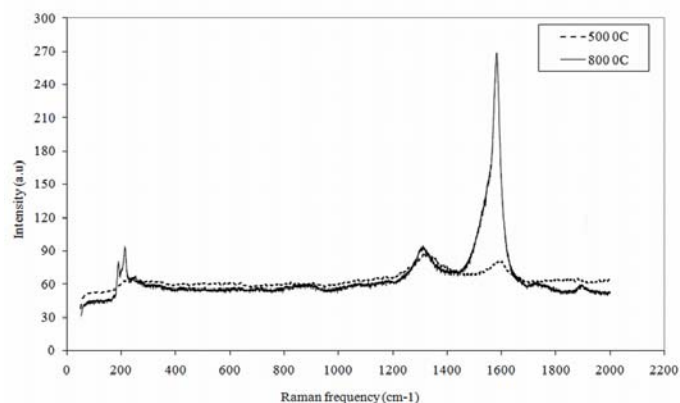


Fig. 3 Raman spectra of CNTs

It is determined that peaks seen on RBM bands have different intensity and appearance of CNTs synthesized at 500 and 800°C. While RBM peak of sample synthesized at 800°C is higher and narrow shape, peak of sample synthesized at 500°C have more wide and scattered shape and it is stated that intensity of this peak is much low. Moreover, it is seen that peak of sample synthesized at 500°C shifted upwards to peak of sample synthesized at 800°C. This shift is explained nearly 5% in the literature [32]. At Raman spectra, the intensity ratio of D and G band (I_D/I_G) express the quality of CNTs. The higher ratio explains the higher amorphous carbon content and defect formation. As seen from Fig. 3, the I_D/I_G ratio of MWCNT is much higher than that of SWCNT and amorphous carbon content and defect formation is much higher. This observation was consistent with that of Mauron, who reported that with existence of 5% Fe catalyst MWCNT production is

observed in a temperature range of 500-650°C and SWCNT production is observed in temperature range of 650-850°C [33]. The effect of temperature on carbon efficiency for production of 30 minutes (for MWCNT and for SWCNT) is shown in Fig. 4. It is seen that there is a tremendous increase in carbon efficiency (from 9.74 to 18.76%) of 1:100 Fe to MgO weight ratio with temperature whereas there exists a decrease in efficiency of 5:100 (from 57.52 to 41.63%) and a drastic decrease in the efficiency of 10:100 (from 54.75 to 19.53%) Fe to MgO weight ratios. With this result it can be said that with the increase in Fe weight ratio there becomes a decrease in the carbon efficiency. In summary the order of the carbon efficiency of given temperature of 500°C for 30 minutes is 5:100≈10:100>1:100, whereas for 800°C it is 5:100>1:100=10:100.

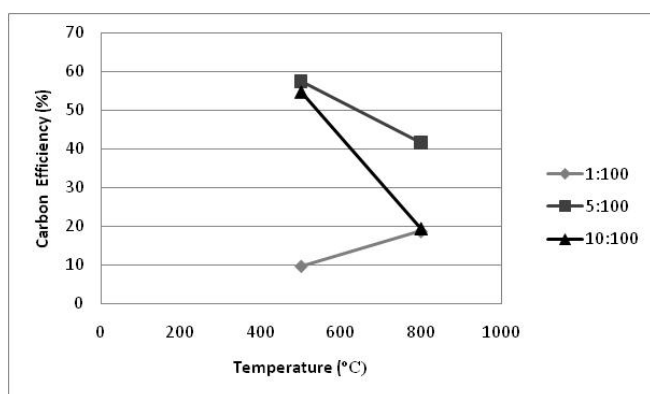


Fig. 4 Temperature vs. carbon efficiency for 30 min

CNT production results for 60 minutes at 500°C and 800°C are given in Fig. 5. It is seen that there is also a tremendous increase (from 9.97 to 51.02%) for 1:100 Fe to MgO ratio for 60 minutes synthesis. There is a slight increase in efficiency (from 53.3 to 54.2%) of 5:100 weight ratio with increasing temperature. 10:100 Fe to MgO weight ratio again shows a drastic decrease in efficiency (from 70.61 to 23.75%) with the increasing temperature which may be related to insufficient contact of acetylene to catalyst due to low fluidization. In summary the order of the carbon efficiency of given temperature of 500°C for 60 minutes is 10:100>5:100>1:100, whereas for 800°C it is 5:100≈1:100>10:100.

B. Effect of Time

The effect of time is analyzed for SWCNT and MWCNT production at 800°C and 500°C respectively. It is observed that for MWCNT production at 500°C in low Fe to MgO ratio (1:100) there is no change in the carbon efficiency (9.74 to 9.79%) with respect to synthesis time (30 and 60 minutes) as shown in Fig. 6. With Fe to MgO ratio of 5:100 there is a

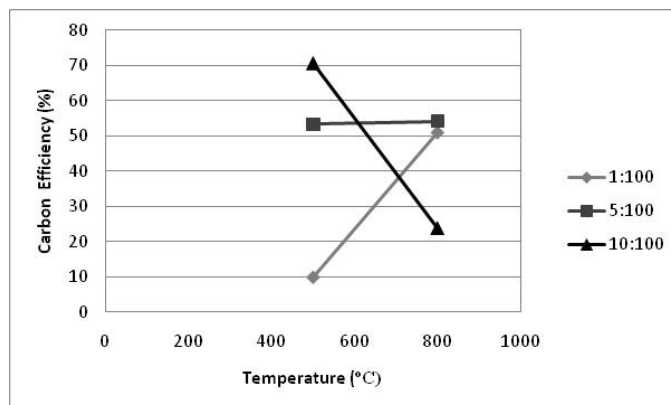


Fig. 5 Temperature vs. carbon efficiency for 60 min

slight decrease in the carbon efficiency (57.52 to 53.3%) as the synthesis time increases whereas, with weight ratio of 10:100 there is a remarkable rise (54.75 to 70.61%) as a result of time increase. In summary the order of the carbon efficiency of given weight ratios for 30 minutes is 5:100≈10:100>1:100, and for 60 minutes is 10:100>5:100>1:100.

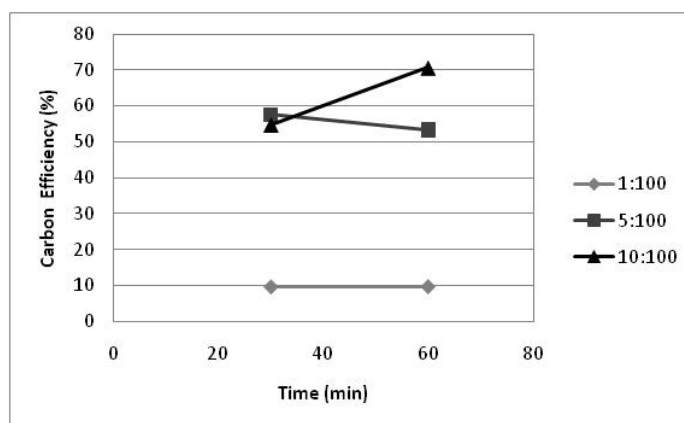


Fig. 6 Time vs. carbon efficiency at 500°C

It is detected for SWCNT production at 800°C for 30 minutes Fe to MgO ratio of 1:100 and 10:100 have the same percentage of carbon efficiency (18.76 and 19.53% respectively) whereas 5:100 weight ratio of Fe has twice as much carbon efficiency (41.63%) than the others. When the production time is increased to 60 minutes it is observed that there is a tremendous rise in the efficiency (51.02%) of 1:100 weight ratio. For 60 minutes production time of 10:100 Fe to MgO ratio has the lowest carbon efficiency (23.75%). In summary the order the carbon efficiency of given weight ratios for 30 minutes is 5:100>1:100=10:100, and for 60 minutes is 5:100≈1:100>10:100. When SWCNT production at 800°C is considered as shown in Fig. 7 it is seen that the carbon efficiency of the catalysts show different behaviour with changing temperature.

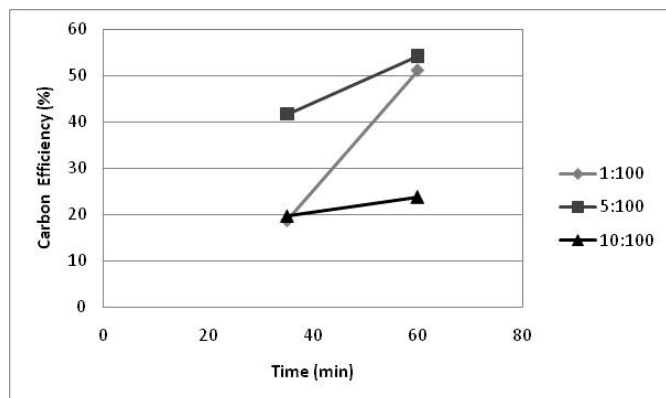


Fig. 7 Time vs. carbon efficiency at 800°C

C. Effect of Weight Ratio of Catalyst to Substrate

The effect of weight ratio is examined for SWCNT and MWCNT production at 800°C and 500°C respectively. As it is shown in Fig. 8 at 500°C for a production time of 30 minutes there is a considerable increase in the carbon efficiency from 1:100 (9.74%) to 5:100 Fe to MgO weight ratio (57.52%) whereas 10:100 has lower carbon efficiency (54.74%) than 5:100 weight ratio. When synthesis time is 60 minutes the carbon efficiency increases with increasing weight ratio (9.79, 53.3 and 70.61% respectively). In summary at 500°C the order of the carbon efficiency of given weight ratios for 30 minutes is 5:100≈10:100>1:100 whereas for 60 minutes it is 10:100>5:100>1:100.

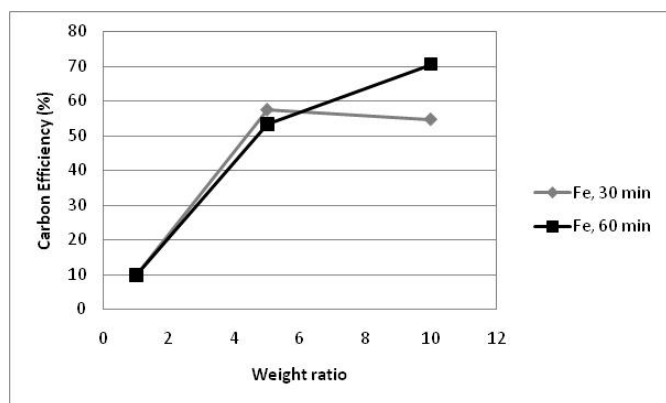


Fig. 8 Weight ratio vs. carbon efficiency at 500 °C

As it is seen in Fig. 9, the effect of weight ratio to carbon efficiency at 800°C shows identical behavior for both 30 minutes and 60 minutes of synthesis times. It can be observed from the graph that for a synthesis time of 30 minutes, the carbon efficiency increases from 1:100 (18.76%) weight ratio to 5:100 (41.63%) and makes a climax at this point. Then it decreases to almost the same efficiency value with 1:100 when the weight ratio is increased to 10:100 (19.53%). Whereas it is seen that for a synthesis time of 60 minutes there is an increase of approximately 10% in the carbon efficiency with an increase of 5:100 weight ratio. However weight ratio reaching 10:100 results with a drastic decrease in the carbon efficiency. In summary at 800°C the order of the carbon

efficiency of given weight ratios for 30 minutes is 5:100>10:100=1:100 whereas for 60 minutes it is 1:100≈5:100>10:100.

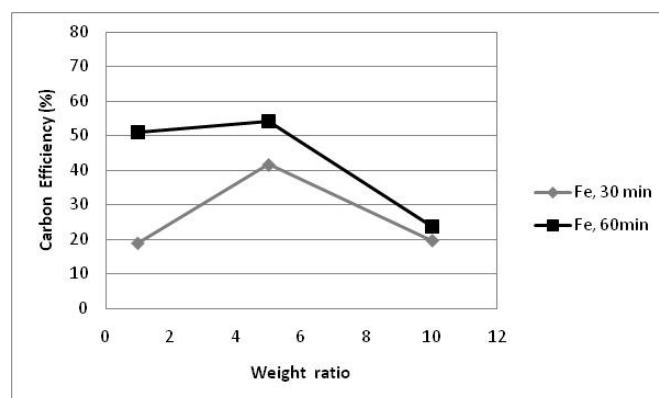


Fig. 9 Weight ratio vs. carbon efficiency at 800 °C

D. Statistical Results

In this study, a statistical design technique was also applied by use of a two level factorial design matrix to interpret the CNTs production with Fe catalyst experimental results. A major advantage of the statistical model over the analytical ones is that they do not use rough approximations and allow for a greater number of factors. In two level factorial design experiments, process variables were selected as synthesis temperature (T) (500 and 800°C), synthesis time (t) (30 and 60 min) and Fe/MgO weight ratio (R) (5 and 10). The number of trials required for this purpose is given by the following equation [34]:

$$N = 2^n \quad (2)$$

where, N and n are the numbers of trials and variables, respectively.

Since the number of variables in the present case are three, the number of experiments required is 8, excluding replicates. If a_k represents the variables, then

$$a_{k,b} = (a_{k,max} + a_{k,min}) / 2 \quad (3)$$

where; $a_{k,b}$ is base level, $a_{k,max}$ is upper level, and $a_{k,min}$ is lower level. It is customary to convert the a_k coordinates to a new dimensionless system of coordinates as follows:

$$X_k = (a_k - a_{k,b}) / \Delta a_k \quad (4)$$

where,

$$\Delta a_k = (a_{k,max} - a_{k,min}) / 2 \quad (5)$$

and x_k stands for coded factors. Thus the upper level of x_k becomes +1 and lower level -1 in the coded form. At the base level, the value of x_k becomes zero. The actual and coded values of the variables of experiments are shown in Table I. The design matrix and results of experiments are listed in Table II. The regression equation developed to predict the carbon efficiency of the synthesized sample and optimize the process conditions using a multi-factor linear model as follows:

$$Y = A_0 + A_1X_1 + A_2X_2 + A_3X_3 + A_4X_1X_2 + A_5X_1X_3 + A_6X_2X_3 + A_7X_1X_2X_3 \quad (6)$$

The variance test of the parameters for the sample showed

that one of the variables is not statistically significant. Therefore, its respective terms can be rejected in the following proposed model:

$$Y=109.41-74.63X_1+57.75X_2-58.95X_3-70.89X_1X_2-61.03X_2X_3+63.14X_1X_3 \quad (7)$$

The correlation coefficient of (7) was determined as 0.89. The relationship between the coded values (X_k) and actual values can be given as follows:

$$X_1 = (T - 650) / 37.5 \quad (8)$$

$$X_2 = (R - 7.5) / 2.5 \quad (9)$$

$$X_3 = (t - 45) / 15 \quad (10)$$

TABLE I
ACTUAL AND CODED VALUES OF THE VARIABLES

Level	Upper Level	Lower Level	Base Level
a_1 (T) Temperature (°C)	500	800	650
X_1	+1	-1	0
a_2 (R) Fe:MgO weight ratio	10	5	7.5
X_2 Coded	+1	-1	0
a_3 (t) Time (min)	30	60	45
X_3 Coded	+1	-1	0

TABLE II
DESIGN MATRIX AND RESULTS OF FE CATALYST EXPERIMENTS

Trial No	X_1	X_2	X_3	Y
1	-1	-1	-1	57.52
2	-1	-1	1	53.30
3	-1	1	-1	54.75
4	-1	1	1	70.61
5	1	-1	-1	54.2
6	1	-1	1	19.53
7	1	1	-1	23.75

The regression equation clearly show that since the coefficient of synthesis temperature is the highest among all the coefficients, the effect of this parameter on the carbon efficiency of the CNT sample is the strongest. Nevertheless, the carbon efficiency of the CNT was affected negatively by this variable. Synthesis time and Fe:MgO weight ratio are also effective parameters on the carbon efficiency. Increasing the Fe:MgO weight ratio effectively enhance the carbon efficiency. However, carbon efficiency decreases with increasing synthesis time. It may also concluded from the regression model that the interactional effects such as (synthesis temperature x Fe:MgO weight ratio) ($X_1.X_2$), (Fe:MgO weight ratio x synthesis time) ($X_2.X_3$) and (synthesis temperature x synthesis time) ($X_1.X_3$) influence the carbon efficiency of the CNTs positively and negatively respectively, at 89 % confidence level. In other words, if one of the

variables is changed with respect to another one, it will have a considerable effect on the carbon efficiency.

IV. CONCLUSIONS

The present study has shown that temperature, time and weight ratio are important parameters for carbon efficiency of CNT production with Fe catalyst. As a result of Raman spectroscopy, TEM, and TGA measurements, the formation of MWCNTs and SWCNTs are observed at 500 and 800°C, respectively. A statistical design technique was applied by use of two-level factorial design matrix to measure the main effects due to the variables in synthesis of CNTs and to optimize the process conditions. Experimental evidence and mathematical analysis showed that the carbon efficiency of as produced CNTs are negatively affected with increase in temperature and time whereas the increase in weight ratio has a positive effect on carbon efficiency.

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