# Improved Arc Discharge Setup for Synthesis of Single and Multi walled Carbon Nanotubes

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## Abstract

Since the advent of the groundbreaking Nanoscience the properties of Carbon Nanotubes (CNTs) had made them potentially useful in numerous applications. Since the properties and purity of CNTs depend on process chosen, various processes have been developed for their synthesis. Some of the most commonly used processes are Arc Discharge, Laser Ablation and Chemical Vapor Deposition. This paper presents the development of a laboratory scale setup for the production of CNTs by arc discharge process in an argon gas environment. The main problem with the existing lab scale production setups is the cleaning of the chamber and this problem is resolved in presented work by placing a circular metal sheet inside the chamber which is removed after the synthesis, thus allowing easy cleaning and recovery of the produced CNTs. The most noteworthy feature of the presented setup is its low cost, hence offering for the first time the synthesis of economical CNTs on small scale. In addition to offering better control over operating conditions and hence the quality of CNTs, another unique feature of the developed setup is its capability to synthesize SWCNTs and MWCNTs with versatile range of diameters. Significant quantity of CNTs using the developed setup were produced and characterized by using Scanning Electron microscope (SEM) and few results are reported.

## Keywords

*Nanotechnology, Carbon Nanotubes, Arc Discharge Process, scanning electron microscopy*

## Introduction

Carbon nanotubes (CNTs) have in recent time’s fascinated great interest as an innovative nanomaterial due to their exceptional mechanical, electrical, and chemical characteristics. In addition, their salient properties, combined with their plain structure and small diameters makes them idyllic one-dimensional test subjects for theories and hypotheses of electrical and thermal conduction at the quantum level. Considerable effort has been expended searching for potential applications of CNTs in a wide range of scientific fields, such as aero science, electronics, biology, medicine, energy and materials engineering [1-4]. The new multifunctional nanomaterials i.e. CNTs represent an attractive research field, which has an important economic potential [5].

Carbon nanotubes (CNTs) are sheets of graphite rolled into tubes and have exceptional properties due to their symmetric structure [1]. The two limiting cases, the armchair and zig-zag nanotubes [5], can be obtained depending on the direction in which the graphite sheet is rolled. CNTs can either be single-walled (SWCNTs) or multi-walled carbon nanotubes (MWCNTs), where MWCNTs are made of concentric SWCNTs [6,7].

To synthesize CNTs, various methods have been developed including arc discharge methods, laser ablation methods and chemical vapor deposition (CVD) methods [8-11]. Besides these, there are ample splices where different methods unite into each other and other ambient conditions are used e.g. submerged arc-discharge [12-15] or where other supporting energy sources prolong e.g. PECVD [16-19]. The Arc-discharge method is widely used as a simple and massive synthesis method [13,20] through which CNTs with a higher crystallinity can be produced as compared to CVD methods. Among several methods for preparing carbon nanotubes, arc-discharge is the most practical one for scientific purposes and yields the most highly graphitized tubes, simply because the process is carried out at a very high temperature (about 4000 K). The high crystalline nature is due to the high reaction temperature; thus, we expect these types of CNTs to have excellent field emission characteristics and to be highly reliable when used at the tip of a field emission display (FED) [21,22].

Historically, the arc-discharge method was the first technique for multi-walled carbon nanotubes (MWNT) [1] and single-walled carbon nanotubes (SWNT) [23,24]. By this method one is able to produce roughly 100 mg/min of SWNT containing soot. However, due to highly fluctuating conditions in the plasma plume of the light arc it is hard to keep a favorable condition for a long time. There are attempts to keep the conditions stable, which is crucial for the fabrication of faultless nanotubes at a high yield. Many studies have been made in order to increase the yield and quality of carbon nanotubes in arc discharge process and growth mechanisms have also been postulated [25].

## Overview of conventional Arc-discharge technology

A DC electric arc discharge is ignited between a pair of graphite electrodes in an inert gas atmosphere. As a consequence, the electrons that are emitted from the cathode forms an electron cloud in the atmosphere while the voltage sill being zero at this instant. In addition, the empty space formed as a result of dissociation of both (anode and cathode), is completely occupied by the emitted electrons and ambient gas. Now the positive charge carriers move to the negative counter pole and hence the electrons are accelerated towards the anode while ionizing the gas molecules on their way by impact ionization. When the concentration of the charge carriers reaches a sufficient value, the arc ignites and at this instant the voltage source has to distribute full voltage. The incoming electrons impart their kinetic energy to the anode which causes the material to sublimate. The discharge vaporizes the surface of one of the carbon electrodes, and forms a small rod-shaped deposit on the other electrode. High yielding production of CNTs depends on the uniformity of the plasma arc and on the temperature of the deposit forming on the carbon electrode. To produce the SWCNTs the graphite rod must contain metal catalyst powder (Co, Ni, Fe). The pressure in the evaporation chamber and the current are the most important parameters of producing high quality SWCNTs. During the process, even though the cathode is cooled by the discharge work of the electrons, a separate cooling mechanism is crucial, thus the electrodes are usually water cooled graphite rods that are separated by few mm. Through out the process, the bias voltage of 15-35V is to be maintained while delivering currents between 50-120A.

The main challenge that offers hindrance in generating a favorable environment for nanotubes growth is the achievement of stable arc discharge plasma, which is complex because the anode is consumed and therefore has to be tracked continuously towards the cathode. In addition the moving nature of the cathode and anode surfaces further limits the stability of the electric arc discharge, which becomes more severe after already a few minutes the resulting uneven consumption of the anode and build-up of the material on the cathode side. A vast amount of studies on the fundamental technical parameters to optimize the arc discharge method has been accomplished and people are still working on it. Apparently, the yield and the properties of the nanotubes are not just reliant on the anode composition, the background gas pressure, the gas composition but also connected to the apparatus size and its geometry, the thermal gradients and other sway of the sublimation system. Due to sometimes total different results (yields) at same parameter sets in different reactors it is hard to work out a general rule for an optimized production [26]. A schematic of a conventional DC arc-discharge chamber is illustrated in Fig-1.

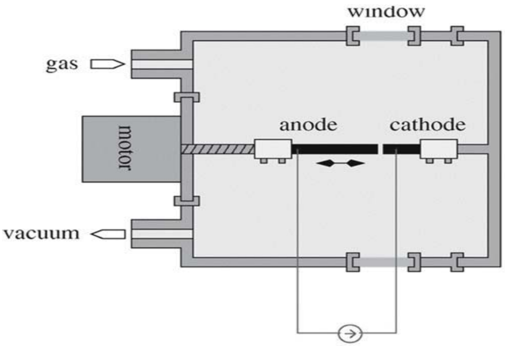

**Fig-1: Schematic of a standard DC arc-discharge Chamber**

However, besides CNTs, arc discharge methods produce many by-products. As a result, the process requires complicated and well controlled purification steps. To overcome this disadvantage and to get high-quality CNTs in a large quantity, various researchers have proposed optimizing the catalyst and process conditions But there are many restrictions on the optimization process with respect to controlling the structure and yield of CNTs because we do not yet fully understand the role of the catalyst and synthesizing mechanisms of CNTs in a dc arc process [27].

In this article, the arc discharge setup for the lab scale economical production of the CNTs is presented, where the design of the chamber and the results obtained during the process are unique in that it offers a better control over the operating conditions thus offering a superior yield and quality since the quantity and quality of the nanotubes obtained depend on various parameters such as the metal concentration, inert gas pressure, kind of gas, the current and system geometry. The developed setup is capable of fabricating single-walled and multi-walled CNTs with a variety of diameters ranging from 35-40 nm to 350-400 nm at startling low cost. This setup also eradicates the problem of cleaning and recovery of the produced material by having a circular metal sheet inside the chamber which is removed after the synthesis, thus allowing easy cleaning and recovery of the produced CNTs.

## Development of New Arc-Discharge Chamber

Since the quantity and quality of the nanotubes obtained depend on various parameters such as the metal concentration, inert gas pressure, kind of gas, the current and system geometry, an Arc-Discharge Chamber was fabricated that could be able to carryout the arc-discharge process for the fabrication of carbon nanotubes in a controlled manner thereby having a high quality and quantity of CNTs at considerably low cost. The apparatus consist of a metal cylinder which is cooled by copper tubing from inside. Pure graphite electrodes were used in an Argon environment where the diameter of anode and cathode are different. The Chamber is provided with a direct current of 50-100A at a low potential of 19-24V. Due to its low cost and ease of machining, Mild steel (MS) was found to be suitable for the construction of the arc-discharge chamber. The chamber is cylindrical in shape with internal diameter of 15.2 cm and length 28 cm and in that way the total volume of the chamber is 5 liters (approximately). One end of the cylinder is closed and on the other end external threads are made so that it can be caped to make it air tight whereby the cape is of the same material having internal threads. Since arc discharge process has to be carried out at a very high temperature therefore cooling of the whole system (i.e. chamber along with the anode and cathode) is decisive so in order to serve the purpose of cooling copper tubing is used as shown in Fig -2.

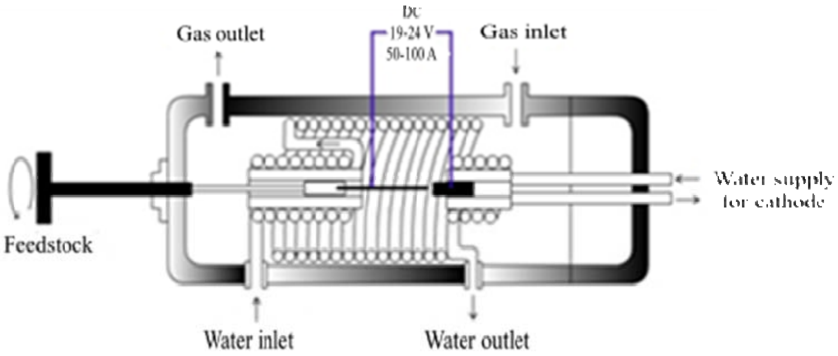

**Fig-2: Cross-sectional View of developed arc-discharge Chamber**

Both, the anode and cathode are made of brass rods with circular copper tubing for the cooling purpose. The brass rod is centered drill in order to place graphite electrode in it. The anode and the chamber wall is cooled by the inter connecting tube while the cathode is cooled separately as demonstrated in Fig-3.

**Fig-3: Anode, Cathode and the copper tubing**

These tubes not only carry chilled water from the chiller but also used as a terminal for the anode and cathode. The cathode is assembled in the cape with Teflon bushes, to make it electrically isolated with the chamber and to collect the deposit easily formed on the cathode just by opening the cape of the chamber. The anode is feed on the cathode by a feed stock, one revolution of feed stock move the anode 1 mm forward, this allows to maintain a constant distance between anode and cathode, which is usually 3 mm and obligatory for the production of CNTs. Now for creating an inert atmosphere two drills were made in the cylinder to serve as the inlet and outlet for the gasses and brass fitting were placed in it with a gas valve.

## Monitoring of the Process

**Pressure:** As the pressure of the gas has a great effect on the quality and quantity of the CNTs produced the outlet is also attached with a pressure gauge as shown in Fig-4, to monitor the pressure inside the chamber which is usually 0.1 to 0.6 bars. A variety of CNTs having different diameters and length can be fabricated by maneuvering the pressure inside the chamber, thus a better control is thus unavoidable to have precise product dimensions.

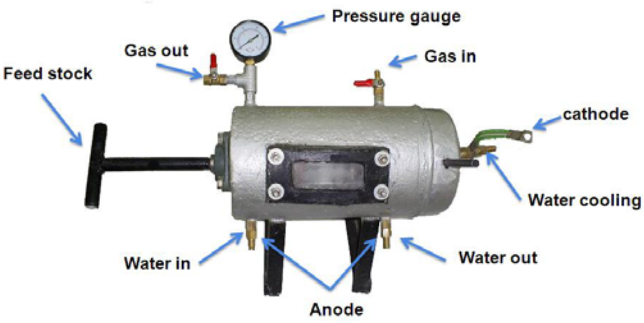

**Fig-4: A labeled illustration of the complete setup**

**Visual:** A glass window of 10 cm by 5 cm is provided in the cylinder and tempered glass is used to cover it, in order to monitor the process and to keep an eye on the distance between the electrodes. Normal window glass is used for this purpose and is tempered by the heat treatment cycle as shown in Fig-5, so that it can bear the high temperature inside chamber.

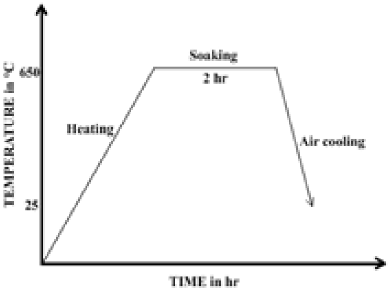

**Fig-5: Glass tempering cycle**

## Experimental work

Large number of experiments was performed using the developed setup to investigate its functionality for effective and efficient fabrication of CNTs. An electric arc was generated using an anode of 6 mm diameter which is capable to be fed at a steady rate ranging from 1 to 3 cm/min and cathode of 12 mm diameter was used and the system was supported by an OTC XD 350 welding supply (Fig-6). A VWR chiller was used to serve for the purpose of effective cooling of the system during operation (Fig-7).

**Fig-6: OTC XD 350 Welding supply**

**Fig-7: VWR Chiller**

Prior to initiating the arc the chamber was first vacuumed and then argon gas was filled inside till the pressure inside the chamber reaches a desired value i.e. within the range of 0.1 to 0.6 bars depending on the desired product. During the discharge the arc current and voltage is monitored and precisely controlled by the welding source and the state of the arc can be visually observed through window by using eye protecting glasses. The arc vaporizes the anode and condenses at cathode as a deposit as shown in Fig-8. Both single walled and multi walled carbon Nanotubes can be produced by this process. Number of experiments has been performed by changing the pressure inside the chamber and a few results are reported to demonstrate the range of variety of CNTs that lie within the capability of the equipment.

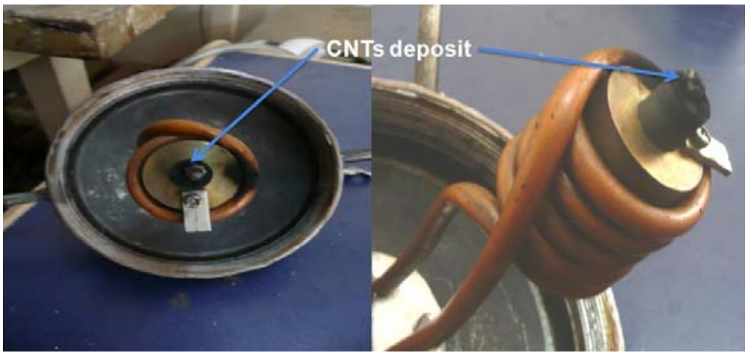

**Fig-8: CNTs Deposit**

## Results

Scanning Electron Microscope with high resolution is powerful instrument for imaging of fine structures of materials and nanoparticles fabricated by the nanotechnology and hence for the observation and morphological analysis of the fabricated CNTs, the Field Emission Scanning Electron Microscope was used. In general, the resolution of secondary electron image (SEI) of the microscope is 1.0 nm (at accelerating voltage 15 kV) or 2.2 nm (at accelerating voltage 1 kV). Accelerating voltage is changing from 0.5 to 2.9 kV in 10 V steps and from 2.9 to 30 kV in 100 V steps. Magnification is from 25 to 19 000 times for low magnification mode and from 100 to 650 000 times for high-resolution mode [28].

During the experiments the cylindrical deposit, which is in the same diameter as anode, grew on the surface of the cathode while the anode was consumed. The deposit is hard grey from outside and soft black from inside. The deposit was collected and sent for characterization by Scanning Electron Microscope (SEM). Before examining the sample it was cut and the black phase was examined in SEM. Some of these results are discussed, which shows MWCNTs of diameter 35-40nm and length 5-10**µ**m. Since SEM only gives the topographical image of the sample, therefore concentric walls inside the tubes are not visible. They can be visualized by using a transmission electron microscope (TEM) but not covered in the domain of this article, since the purpose at this stage is only to demonstrate the effectiveness of the developed arc discharge setup for efficient and economical production of CNTs. The length and diameter of the tube is measured by using the scale represented in the SEM micrograph. SEM observations are shown in Fig-9 at a magnification of 1500 and in Fig-10 at a magnification of 15000.

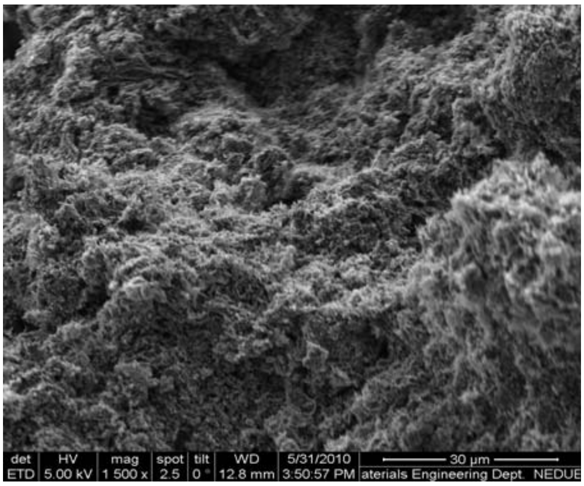

**Fig-9: A sample of CNTs with diameter 35-40 nm and length 5-10 µm (mag=1500x)**

Figure-9 above shows the MWCNT sample at low magnification, and represent highly graphitized and high yield of MWCNTs whereas figure-10 below illustrates the sample at higher magnification where it is evident that most of the graphite is converted into the tube and small amount of impurities are present in the sample.

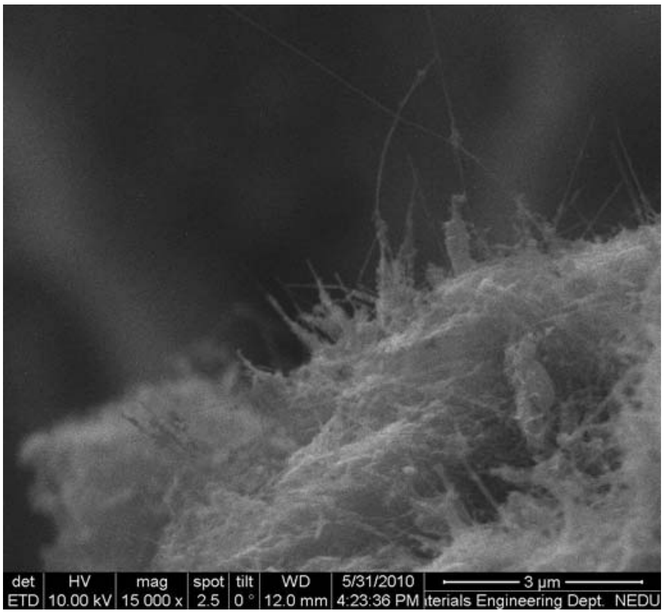

**Fig-10: A sample of CNTs with diameter 35-40 nm and length 5-10 µm (mag=15000x)**

Production of some MWCNTs was also observed during the process and the tubes have a diameter of 350 to 400 nm and length 3 to 4 **µ**m which has not been reported yet by arc discharge process. The SEM results of these MWCNTs are shown below in Fig-11 at a magnification of 15000 and in Fig-12 at a magnification of 60000, where a single carbon nanotube is visible and the diameter of the multi walled carbon nanotubes can be easily measured. A great number of CNTs with outer diameters of 350-400 nm and lengths within the range of 3-4 **µ**m were observed in Figures 9-12. The top of nanotube displayed in the inset of Fig-12 is open, which likes nano-capillary to absorb hydrogen or other gases [29].

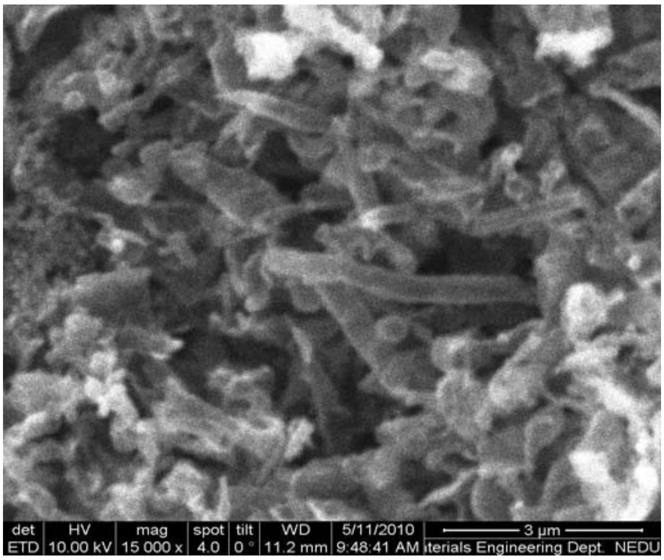

**Fig-11: A sample of CNTs with diameter 350-400 nm and length 3-4 µm (mag=15000x)**

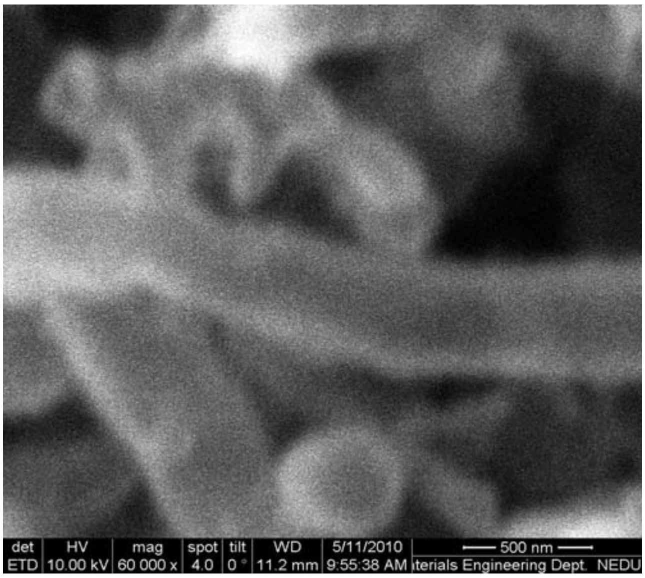

**Fig-12: A sample of CNTs with diameter 350-400 nm and length 3-4 µm (mag=60000x)**

## Cost Effectiveness

A detailed cost calculation was carried out in order to have the cost per gram of the CNTs fabricated by the developed setup along with a detailed survey to investigate the costs of existing setups and the costs of commercially available CNTs by specific vendors. The cost breakup of developed setup includes all equipment costs (Welding supply/VWR chiller), operating cost (electricity/labor/other overheads) and the cost of consumables (electrodes/argon gas) where the cost of equipment was amortized over a period of five years according to the specified service life of the equipment. During the initial period before the amortization period has elasped the net cost of developed CNTs was calculated to be $360/kg which is approximately 40% low as compared to the average cost of commercially available CNTs. After the amortization period is elapsed the cost of fabricated CNTs by developed setup will be further reduced by approximately 50%, thus allowing producing CNTs for as low as $180/kg. Thus the setup proved its cost efficiency and versatility in that, on one hand it allows fabrication of SWCNT and MWCNT having diameters ranging from 35-40 nm to 350-400 nm and on the other hand offers for the first time economical production at small or large scales.

## Conclusion

A new laboratory scale arc discharge setup for the fabrication of carbon nanotubes is presented, which has demonstrated its flexibility in fabricating both single walled carbon nanotubes (SWCNTs) and Multiple walled carbon nanotubes (MWCNTs) in diameters ranging from 35-40 nm to 350-400 nm which shows the superior control of the process on operating parameters thus enabling to produce wide variety of diameters to suit particular applications and of high quality. To the best of our knowledge, CNTs of diameters 350-400 nm have never been fabricated before by using arc-discharge process. The developed setup also eradicates the cleaning problem of the existing setups by having a circular metal sheet inside the chamber which is removed after the synthesis thus allowing easy recovery of the product with less likelihood of having contaminations. In addition to giving superior quality and variety the most noteworthy feature of the process is that it offers for the first time the relieve of having low-priced CNTs with cost less than approximately 40% as compared to the average cost of commercially available CNTs. Various operating conditions were tested in order of have a variety of CNTs which were characterized by Scanning electron microscope (SEM) and few results also reported which confirmed the success of the developed setup**.**

## Future Prospects

The performance of the setup can be improved and production can be enhanced by making the process continuous and computerized which is currently manual and batch type and is currently under development by the authors. In addition to offering a better control over process parameters and hence the quality of the product this automation will allow mass production at a lower cost and with minimized labor and production time A schematic of the proposed plan is shown in Fig-13.

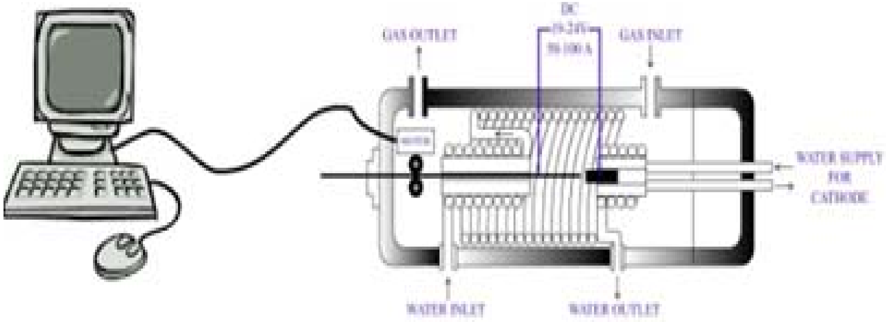

**Fig-13: Automation of the process (future prospects)**

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