# Computationally Numerical Experiment of Carbon Species Densities for Thermal Plasma Dynamic

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*Abstract*— **The present work develops a computationally effective one-dimensional sub grid set in numerical integration for density formulation from thermal plasma. The model incorporates two-body and more collision effects throughout Carbon plasma using continuity equation. The carbon gas inter electrode gap is accelerated by the electric field to produce plasma. In this model the reaction processes of carbon species is identified. The extrapolation of species dominant in arc discharge process is critical issue in significant for predicting carbon nanostructure production. In this paper, we describe chemical kinetic models and their possibilities of carbon ion and neutral species production based on collisions and time dependence. The results show the reaction rate of Carbon ions calculated at 7.85x10$^{28}$ m$^{-3}$ s$^{-1}$ while the temperature increment decreases, the reaction rate is up to 6.25x10$^{27}$ m$^{-3}$ s$^{-1}$. The electron density reduces until 10$^{8}$m$^{-3}$ from initial condition at 1atm. However, the electron density increases 10$^{13}$ m$^{-3}$ from 0.05eV-0.3eV. The ionization of Carbon reaction has been affected by pressure and temperature which gains a quantitative understanding of the density at equilibrium state.**

***Keywords*— *Arc discharge plasma; Carbon ion specie; chemical kinetic model***

## I. INTRODUCTION

Arc plasma process has highly potential for material conversion which can been used to synthesize nanomaterial structure One of the common product developed until nowadays is Carbon Nanotube (CNT) which has fascinated to enhance the highly applicable promising material of the advanced technological application including the development of hologram [1] , the micro- and nano-chip interconnects [2] , and display applications [3]. The carbon is cheap and abundant material with numerous advantage of the physical properties permitting the carbon nanotube an ideal candidate for transparent electrode application e.g. flexible electronics due to their unique properties such as their high intrinsic carrier mobility [4], conductivity, and mechanical flexibility [5].

The arc discharge method for fabricating carbon nanotube has potential for production due to low cost, easier, and production with excellent structural properties where the CNT formed is straight with less topological defects[6]. Large quantities of carbon nanotubes can be produced by arc discharge [7], but this yields a mixture single-walled (SWCNT) and multi-walled carbon nanotubes (MWCNT), along with carbon soot formation. Arc discharge is therefore complementary for fabricating bulky form of nanotubes mixture by added purification process.

The strong electric field (Schottky effect) generated at cathode surface enabling thermionic emission of electron which is accelerated by the voltage drop $V_c$ exist in plasma sheath near with cathode surface. The highly accelerated electrons then collide with neutral and produce intensely ionization in near-cathode plasma. The ions generated at near cathode plasma sheath diffuse toward cathode surface, accelerated by the cathode voltage drop $V_c$. In their way, the carbon ions highly potential to recombine with electron and becomes neutral and form carbon cluster long chain. The recombination of the carbon species within the plasma is dependent on the activation energy, ambient pressure, and the collision rate which alter the formation of neutral carbon. In this model, we investigate carbon ion species to form the neutral carbon at given a nano-time scale and reaction rate densities to form CNT.

## II. CHEMICAL KINETIC MODEL

The function of the ion species distribution can be calculated based on the Saha-Boltzmann distribution function $f_{Saha}(T) = \frac{n_e n_i}{n_n} = \frac{Z_n + Z_e}{Z_n} exp\left(-\frac{W_{ion}}{k_B T}\right)$ when the ion and electron is in thermal equilibrium condition found in Carbon arc discharge used to synthesize CNT where Z is the partition function, $W_{ion}$ is the energy ,$k_B$ is Boltzmann constant and T refer as temperature. The thermodynamic equilibrium state is characterized by the detailed balanced of each process. Here we consider the balance of dissociative electron impact recombination which can be quantified by equilibrium concentration $\frac{[n_{ion}][n_e]}{[n_{neutral}]} = k(T)$. where k is the equilibrium constant function of temperature under the law of mass action. The equilibrium constant is able to find under the constant pressure applied in the reaction $p=nk_BT$ based on partial pressure generated in plasma $\frac{p_i p_e}{p_n} = k_p(T)$ where $p_x=n_xk_BT$, $k_B$ is Boltzmann constant given by $k_B=1.3806488\times10^{-23}$ $m^2$ kg $s^{-2}$ $K^{-1}$ and T is the temperature in K. In plasma the temperature defined is from the electron temperature $T_e$ where the electron is high mobility compared with ions and neutrals. In arc discharge plasma where the Carbon ions and electron is initiated under the pressure equilibrium, the Saha-equilibria can be achieved. The collisions among the species are able to modify the initial density of the ions, electrons and neutrals from the attachment and detachment of the species. The continuity equation solution for density conservation distinctly can estimate the density fluctuation of Carbon ions and neutral species from the arc plasma. In this model, we propose the kinetic model of the continuity equation as follows,

$$\frac{dn}{dt} + n \cdot \nabla \cdot \mathrm{v} = \mathrm{S} \tag{1}$$

where n is the density, v is the velocity, and S describes as the source taking place until it reaches the equilibrium state for the solution of time dependent of rate equation given the initial condition

$$\frac{dn}{dt} = \boldsymbol{R} \cdot \boldsymbol{n} \tag{2}$$

where n is the density and R is the reaction rate.

Fig.1 shows the possible of Carbon ion species in arc plasma discharge. The anode is highly positive charge while the cathode is highly negative charge thus the gap between the electrodes creates highly electrical potential for the electron and ion to accelerate in both directions and induce sensible electron-ion collisions.

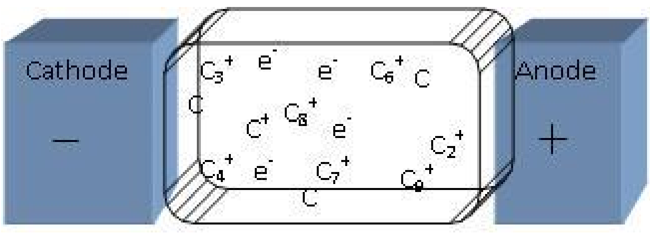


Fig 1. Experimental set up to fabricate fiber coupler

TABLE I
THE REACTION LIST OF THE CARBON ARC PLASMA [8,9]

| | Reaction | α | β | γ |
|---|---|---|---|---|
| 1 | $C_2^+ + e^- \rightarrow C + C$ | 3.00e-7 | -0.5 | 0.00 |
| 2 | $C_3^+ + e^- \rightarrow C_2 + C$ | 3.00e-7 | -0.5 | 0.00 |
| 3 | $C_4^+ + e^- \rightarrow C_3 + C$ | 1.80e-7 | -0.5 | 0.00 |
| 4 | $C_6^+ + e^- \rightarrow C_5 + C$ | 1.00e-6 | -0.3 | 0.00 |
| 5 | $C_7^+ + e^- \rightarrow C_6 + C$ | 1.00e-6 | -0.3 | 0.00 |
| 6 | $C_8^+ + e^- \rightarrow C_7 + C$ | 1.00e-6 | -0.3 | 0.00 |
| 7 | $C_9^+ + e^- \rightarrow C_8 + C$ | 1.00e-6 | -0.3 | 0.00 |

Table 1.describes the list of reaction investigated for the dissociation electron-ion recombination. The parameters used for the Carbon plasma ignition will affect the CNT formation. The substantial temperature is subsequent to activate energy for Carbon cluster growth.

The sufficient activation energy result formed at the surrounded from thermal energy kT will offer the optimize condition for dissociative electron-ion recombination process for Carbon $C_n^+ + e^- \rightarrow C_n^{**} \rightarrow C_{n-1} + C$ where $C^+$ is refers to the Carbon ion ,$e^-$ is the electron, C is the neutral Carbon atom released from the stabilization of the energy from the dissociation of $C_n^{**}$. The chemical reaction process based on the activation energy can be developed from the modified Arrhenius equation

$$k = \alpha \left(\frac{T}{300}\right)^{\beta} e^{-\frac{\gamma}{T}} \tag{3}$$

where k is the reaction rate, α is temperature dependent reaction rate coefficient, T is temperature, β is the fitting parameter of the temperature and γ is the activation energy. The reaction rate for kinetic model is defined as

$$k_{ij} = \langle \sigma v \rangle = n_e \int_0^{\infty} \mathrm{v}\, \sigma_{ij}(\mathrm{v}) f(\mathrm{v}) d\mathrm{v} \tag{4}$$

where σ is the cross section of collision, $v$ is referred as collision frequency, v is the speed of particle and $f(v)$ is the velocity distribution of colliding particles characterized by temperature *T*.

By implying several assumptions from the importance of the pre-collision energy apparent for the collision model of bimolecular reactions; (a) Collision between two reacting molecules ion and electron must occur before they can react. (b) From the total number of collisions in the reaction involved, only those molecules react those have a kinetic energy equal to or greater than or equal to the activation energy, γ along the line of centers at the moment of contact, provided that the ions are oriented for direct head on collision with electron as the effect of attraction Coulomb force.

In this study, the entire reaction process list from Table 1 is simulated by using numerical method Runge-Kutta 4th order model. Density balance equation for each species (electron, ion, and excited atoms) is constructed that takes into account all different production and loss mechanisms from the reaction rate. The Carbon ion species when initiated can be determined from the integration of the Arrhenius equation indicated from (4). The modeling taken into account the initial density for each species tabulated given as $10^{20}$ $m^{-3}$. The integration time is determined starting from $1\times10^{-9}$ s, and the iteration for the density calculation is determined using the tolerance $1\times10^{-2}$.

The influence of the temperature, pressure and density on the formation of neutral Carbon atom is investigated. The relation between the electron density decay within the recombination process with Carbon ion can promote the cluster formation and there exists the optimal electron densities providing the most efficient cluster formation. The list of reaction matrix described the reactions for the formation of the small-sized clusters in the particular activation energy starting from $C_2^+$ until $C_9^+$ used in this model. The reaction of dissociative electron has been chosen in this study in order to study the formation of high number of neutral Carbon from the neutralization of electron-ion recombination begins with the low number of Carbon ion reaction.

The flat one charged caption $C_n^+$ and electron recombine and dissociate into separate C atom and molecule in the process of energy minimization. The reactions are taken place at given equilibrium state of thermal plasma where the density of forward reaction is balanced by the reverse reaction rate. Thus the time to reach equilibrium for each species is dependent on the pressure applied based on the pressure-density relation as given by,

$$\frac{dp}{dt} = nk_B\frac{dT}{dt} + k_BT\frac{dn}{dt} \quad (5)$$

where p is pressure , n is the density, $k_B$ the Boltzmann constant and T is temperature. The time to achieve kinetic equilibrium for Carbon plasma giving electron colliding with singly charged ions we obtain $t=10^{-9}$ s. The pressure change over time will indicate the number of particle moving in a constant volume thus it designates the reaction rate taken place as shown in the relation from (2). The result of modeling Carbon reaction process has shown the self-consistent where the change of electron flux with forward reaction is calculated using the same for reverse reaction used to determine the cooling rate of electron. The density of Carbon ion, electron, and neutral are solved by iterative manner by uncoupling the equations and solving all fifteen densities representatively until the population in equilibrium had converged to estimated limit of time difference.

The Carbon arc plasma is extremely high in density where the pressure at middle of arc discharge exceeds atmospheric pressure by a large factor thus it concedes the arc can exist at various ambient pressure including atmospheric pressure and even higher. Thus in our model, we describe the plasma where it governed by the high pressure relation of each species. The density changes in plasma is result from the macro (expansion) and micro (collision) state.

$$dn = dn_{expansion} + dn_{electron-ion\ recombination} \quad (6)$$

In order to study the density changes by the effect of electron-ion recombination on the arc plasma, the pressure gradient is held constant and neglecting diffusion effect thus we only taken the solution for the time dependent homogeneous thermal plasma at given micro state

$$dn = dn_{electron-ion\ recombination} \quad (7)$$

## III. Result and Discussion

The change of state distribution in plasma is originated by frequent collision in the locality of plasma region. It is also proportional with temperature and collision rate order. If the density and temperature of the plasma decrease, the collision rate between particles intensely decreases. Table 2 shows result of reaction rate for Carbon species at particular pressure and temperature.

The factor of pressure and temperature has played a big role toward the reaction rate in Carbon plasma. The increment of the pressure has brought to the linear regression increasing of the reaction rate as shown in Fig 2. The increment of the reaction rate as a result of the increasing of the temperature can be understood as the highly collision rate at given higher pressure compare with the lower one. On the other hand, the increment of temperature has shown different result in Fig.3. When the temperature increases, the reaction rate has exponentially decreased. The decrement of the reaction rate at higher temperature indicating the decrement of the collisional probability when the mean free path is becoming higher at high temperature given by,

$$P = s/\lambda_{ie} \quad (8)$$

where P is collisional probability, s is the characteristic length, and $\lambda_{ie}$ is the mean free path of ion-electron collision. At higher temperature, the plasma will expand as thermal energy imposed thus increase the distance between the species consequently decrease the collision probability.

TABLE II
THE EQUILIBRIUM FORWARD AND REVERSE REACTION RATES FOR GIVEN TEMPERATURE $T_e = T_i = 0.3eV$ AND $P=10^5$ PA.

| | Reaction rate | | Reaction |
|---|---|---|---|
| 1 | 1.146e+028 | 0.000e+000 | $e + C_2^+ \rightarrow +2\ C$ |
| 2 | 1.146e+028 | 0.000e+000 | $e + C_3^+ \rightarrow C + C_2$ |
| 3 | 1.667e+028 | 0.000e+000 | $e + C_4^+ \rightarrow C + C_3$ |
| 4 | 1.205e+028 | 0.000e+000 | $e + C_6^+ \rightarrow C + C_5$ |
| 5 | 1.205e+028 | 0.000e+000 | $e + C_7^+ \rightarrow C + C_6$ |
| 6 | 1.205e+028 | 0.000e+000 | $e + C_8^+ \rightarrow C + C_7$ |
| 7 | 1.205e+028 | 0.000e+000 | $e + C_9^+ \rightarrow C + C_8$ |

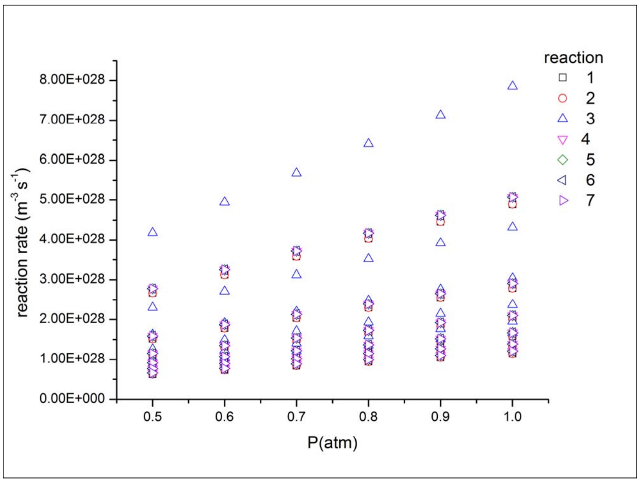


Fig. 2 Reaction rate of Carbon in different pressure.

The capturing of the electron by the ion as regards to the highly collisional thermal plasma and with the support of coulomb collision has brought up to reduce the electron and ion density and increasing of the neutral Carbon. Fig. 4 shows the density fluctuation in the arc plasma at equilibrium state at given particular temperature and pressure applied. The time taken to reach equilibrium state is calculated to establish at $4.4\text{x}10^{-9}$s which is convergent with the time scale of ion impact heating generation [8].

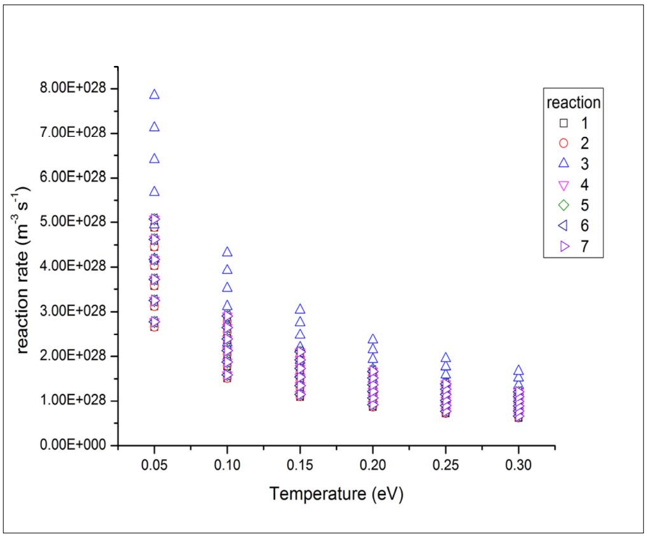


Fig. 3. Reaction rate of Carbon in temperature variant.

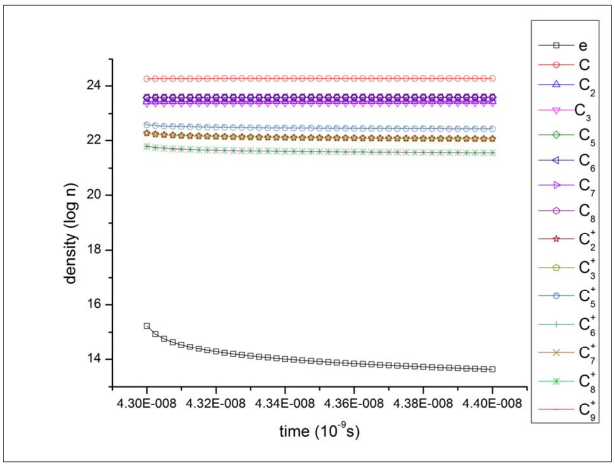


Fig. 4.Density of Carbon neutral, ion and electron in equilibrium state at $p=10^5$ and T=0.3eV.

The high pressure (1atm) applied on the arc discharge plasma has laterally affected the capturing electron by the Carbon ion. At low temperature region (T=0.05eV) the electron density calculated decreases to $10^{12}$ $m^{-3}$ from initial condition. This shows the electron has been decrease as many as $10^8$ $m^{-3}$ from the initial condition given from the reaction. As soon as the equilibrium state of the thermal plasma gets closer to the hotter area, the electron density has been enriched to $10^{13}$ $m^{-3}$, perhaps from the effect of highly collisional activity at higher thermal energy kT at temperature 0.3eV.

Fig.5 shows the density changes over the increment of temperature. The low pressure discharge plasma at 0.5atm tends to reduce the ion density from $10^{22}$ $m^{-3}$ to $10^{21}$ $m^{-3}$ for heavy ion $C_8^+$ and $C_9^+$ whereas the other ions also reduced to one magnitude lower. The low pressure has reduced the tendency of collision among the species as the mean free path being elongated at lower pressure from the relation,

$$\lambda_{ie} = \frac{1}{n_i \sigma_{ie}} = \frac{1}{p \sigma_{ie}} (k_B T) \quad (9)$$

where $\lambda_{ie}$ is the ion-electron mean free path collision, $n_i$- refer to the ion density, $\sigma_{ie}$ is the cross section of collision, $k_B$ is the Boltzmann constant, p is the pressure and T is the temperature.

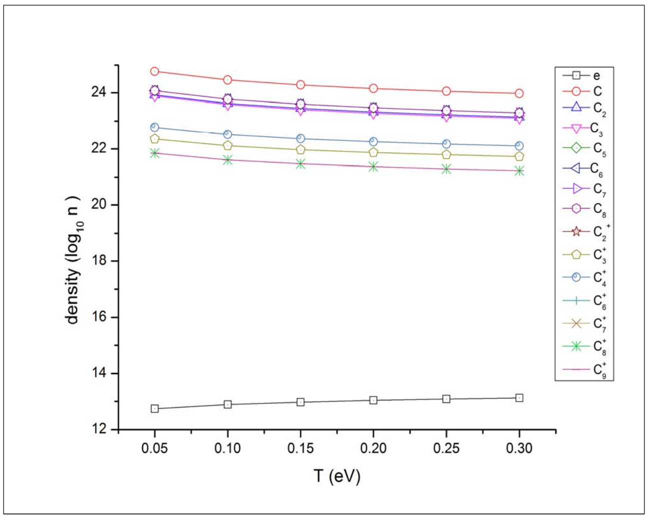


Fig. 5.Carbon density changes in variation of temperature at pressure 0.5atm.

The Carbon reactions have shown the consistent ionization of the species where it takes place at 56% ionization for the reaction 1 at given low pressure (0.5atm) and increase laterally to 60% when the temperature increase to maximum 0.3eV. The reaction at high pressure (1atm) leads to decrease slightly the ionization of the Carbon reaction 1 to only extent to 59% ionization. The high pressure has decreased the ionization for the reaction 1 but inversely increased the ionization of the reaction 7 from 57% ionization (0.05eV) to 61% ionization (0.3eV). The result has shown that pressure, temperature and geometry parameters of the Carbon ions have led to increase the ionization take place in the reactions.

## IV. Conclusion

In conclusion, the high pressure leads to increase the reaction rate of Carbon ions and its maximum calculated at $7.85x10^{28}$ $m^{-3}$ $s^{-1}$ while the temperature increment decreases the reaction rate up to $6.25x10^{27}$ $m^{-3}$ $s^{-1}$. The calculation of the electron density from the reaction has shown the reduction of magnitude to $10^8$ $m^{-3}$ from a given initial condition at high pressure (1atm). However, the electron density calculated increases $10^{13}$ $m^{-3}$ as the temperature increases from 0.05eV to 0.3eV. The ionization of Carbon reaction has been affected by pressure and temperature to form the Carbon in reaction 1 of Table 1. This increment achieves up to 60% ionization at temperature 0.3eV and pressure 1atm as well as 61% ionization for reaction 7 of Table 1.

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