Generation, Characterization and Application of Atmospheric Pressure Plasma Jet
(Penjanaan, Pencirian dan Aplikasi Jet Plasma Bertekanan Atmosfera)

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ABSTRACT
The development of a non-thermal plasma jet with a capillary configuration working at atmospheric pressure is reported in this paper. The plasma jet is powered by a power source with frequency of several kilohertz. The working gas is argon. The plasma obtained has been characterized by optical emission spectroscopic measurements and electrical measurements of the discharge using voltage and current probes. The electron temperature has been estimated by using the modified Boltzmann plot method utilizing the Ar 4p-4s transition. The electron temperatures at various positions along the plasma jet length have been obtained and it is found that the electron temperature decreases at position further from orifice. The electron density has been estimated from current and voltage measurements using the power balance method. The effects of gas flow rate, applied voltage and frequency on the characteristics of the plasma jet have also been investigated. The applications of the atmospheric pressure plasma jet (APPJ) developed to modify the surface properties of Polyethyleneterephthalate (PET) and polycarbonate (PC) have been tested. Our results showed that the atmospheric pressure non-thermal plasma jet can be effectively used to enhance the surface wettability and surface energy of the PET and PC. The plasma jet has also been tested for inactivation of prokaryotic cells (Escherichia coli, Staphylococcus aureus). In the case of E. coli, better than 4 log $_{10}$ reduction can be achieved. The effect of plasma jet on the pH of cell culture medium has suggested that the plasma species, particularly the electrons, are solely responsible for the effect of inactivation of living cells.

Keywords: Electron density; electron temperature; optical emission spectroscopy; plasma jet

INTRODUCTION
Atmospheric pressure non-thermal and low temperature plasma is a subject of great interest in various fields of science. Atmospheric pressure plasma jet attracts great attention because of their potential applications in various fields such as polymer surface treatment for biomedical applications (plasma biology, healthcare and medicine as well as material processing and nanotechnology) and pollution control (Laroussi et al. 2012; Laroussi 2008). Particularly, biomedical applications of plasma jet have become a hot research topic recently. Since plasma jet device generates plasma plumes in open space of atmospheric air environment rather than in confined discharge gap, they can be used for direct treatment and there is no limitation on the size of the object to be treated (Kong et al. 2009 & Zhang et al. 2012). One of the prerequisites for biomedical application is that the jet should be near room temperature and carries a low current under moderate voltage (Kim et al. 2011). To date, applications such as cancer treatment (Joh et al. 2013; Keidar et al. 2013; Nastuta et al. 2013),
sterilization, dental bleaching, blood coagulation and wound healing (Goree et al. 2006; Raheem & Mahmood 2013) have been demonstrated.

Many forms of atmospheric pressure plasma sources with various electrode configurations and a wide range of driving frequencies have been investigated (Weltemann et al. 2008). When operating at higher frequencies, the plasma jet is in the form of a continuous flow. However, when operating at lower frequencies, the plasma jet has been observed to constitute of discrete ionization wave fronts moving at a velocity much higher than the gas velocity (Jiang et al. 2009; Ying et al. 2013). Recently a number of experimental studies have been carried out to understand the dynamic behavior of the plasma jet (Sarani et al. 2010; Schuetze et al. 1998; Yuji et al. 2007).

In order to use these plasmas in industrial, biomedical and environmental applications effectively, it is necessary to know the plasma parameters such as the electron temperature \(T_e\) and electron density \(n_e\). In order to determine the electron temperature and electron density of low pressure plasma, electric or Langmuir probe measurement is widely used (Wu et al. 2013). However, a probe theory for atmospheric pressure plasma having a large electron-neutral collision frequency has not yet been established. The application of probe measurement to atmospheric pressure plasma is difficult due to the small inter-electrode distance and due to the problem regarding large heat load and high frequency noise (Yanguas-Gill et al. 2007). Therefore as an alternative to probe measurement, optical spectroscopy method is widely used to measure the internal plasma parameters \((T_e, n_e)\) under atmospheric pressure environment (Mariotti et al. 2007). Techniques based on optical emission are non-invasive and required only moderate spectroscopic equipments (Hofmann et al. 2011; Xiong et al. 2013).

The electrical performance of the discharge has also been studied by using voltage and current probes. In this work, we present the characteristics of an atmospheric pressure plasma jet source developed for polymer surface modification and biomedical applications.

**EXPERIMENTAL DETAILS**

The plasma jet concerned in this paper is generated using a glass capillary tube with inner diameter of 3.0 mm and an outer diameter of 6.0 mm. High purity argon is used as the working gas and the flow rate is controlled by a volume flow meter. The flow rate of the argon gas is restricted to below 5 L/min so that the flow velocity would not exceed the limit for a laminar argon flow. A sinusoidal voltage at 27 kHz is applied for the excitation of the discharge. The electrodes are made of two strips of 0.5 mm thick aluminium foil wrapped around the capillary tube and the gap between the inner edges of the aluminium strips is 10 cm. The active electrode is 3 mm from the orifice.

Linear array optical spectrometer is used to study the optical emission from the plasma jet. The resistor \(R\) in the circuit shown in Figure 1 is utilized for the measurement of discharge current. The voltage and current waveforms are recorded using digital oscilloscope.

**OPTICAL EMISSION SPECTROSCOPY**

In order to evaluate the performance of plasma, plasma parameters (electron temperature \(T_e\) and electron density \(n_e\)) were estimated from the intensity of atomic emission lines of the plasma jet. The intensity of the spectral line is dependent on electron temperature \(T_e\) and is proportional to the population density of the excited state. So, \(T_e\) can be determined from the spectra using the Boltzmann plot (Shrestha et al. 2015; Tyata et al. 2013):

\[
kT_e = \frac{E_1 - E_2}{\log \left[ \frac{I_1 \lambda_1 \Gamma_1}{I_2 \lambda_2 \Gamma_2} \right]}.
\]

In this equation, indices 1 and 2 refer to the first and second spectral lines, \(I\) is the measured intensity of selected spectral line; \(k\) is the Boltzmann constant; \(E_i\) and \(E_j\) are the excited state energy; \(g\) is the statistical weight; and \(A\) is the transition probability.

The Boltzmann plot method is valid if the plasma under study is in complete local thermodynamic equilibrium (LTE). But in the plasma jet LTE is not valid. Therefore, this method may not be used for the exact determination of \(T_e\) and \(n_e\). It can only provide us estimated values of these plasma parameters under varying working condition of discharge plasma in the APPJ.

The spectrum is recorded by using a linear array spectrometer and the emitted lines were observed in the range of 300 to 850 nm. \(T_e\) is determined from the analysis of selected two Ar-I spectral lines in the observed spectra. The intensities of these spectral lines are obtained from the observed spectra. The values of \(E_i, g\) and \(A\) for the selected lines are taken from the NIST atomic spectra data sheet. Using these values in (1), we can obtain the values of \(T_e\) as a function of applied voltage, inter electrode gap and gas flow rate, respectively. The electron density \(n_e\) can be determined by using the relative intensity of atomic and ionic spectral lines in Boltzmann-Saha equation (Qian et al. 2010):
In this equation, indices 1 and 2 represent the neutral and ionized atomic species; \( T_e \) is the electron temperature; \( E \) is the energy of emission level; \( E_i \) is the ionization energy of neutral atom; \( I_1 \) is the intensity of the Ar-I line; \( I_2 \) is the intensity of Ar-II line; \( \lambda_1, \lambda_2 \) are the respective wavelengths; \( A_1, A_2 \) are the transition probabilities; and \( g_1, g_2 \) are the statistical weights of levels (1-neutral) and (2-ionized), respectively.

MEASUREMENT OF ELECTRON DENSITY BY STARK BROADENING METHOD

One of the most reliable techniques to determine the electron number density is by using the measured Stark broadened line profile of an isolated line of either neutral atom or singly charged ion. Stark broadening is caused by the Coulomb interaction between the radiator (in this case argon atom) and the charged particles present in the plasma.

The Stark broadening due to collision of charged species is the primary mechanism influencing the width of Ar emission line. The Stark broadening function is assumed to have the Lorentz profile. The electron number density is by using the measured Stark broadened line profile of an isolated line of either neutral atom or singly charged ion. Stark broadening is caused by the Coulomb interaction between the radiator (in this case argon atom) and the charged particles present in the plasma.

The Stark broadening is normally very small, it can be neglected as the ion broadening contribution. Since the contribution of the ionic broadening is normally very small, it can be neglected and (3) can be reduced to a simple form:

\[
\Delta \lambda_{\text{ion}} = 2 \omega \frac{\lambda }{10^{10}} \times \frac{5.5}{10^{10}} \times \left[ 1 - \frac{3}{4} \frac{N_e}{N_p} \right] \omega \frac{\lambda }{10^{10}}.
\]

\[
\Delta \lambda_{\text{ion}} = 2 \omega \frac{\lambda }{10^{10}}.
\]

Values of both \( \omega \) and \( \alpha \) for different temperatures are reported in Qian et al. (2010). Hence \( n_e \) can be expressed as:

\[
n_e = \left[ \frac{\Delta \lambda_{\text{ion}}}{2 \times 10^{-11}} \right]^2.
\]

STERILIZATION EXPERIMENT (STRAIN AND MEDIA)

ATCC cultures of *Escherichia coli* were revived on Potato Dextrose Agar (PDA) while *Staphylococcus aureus* on Salmonella Shigella (SS) Agar. Liquid suspension of the aforementioned microbes was prepared in Nutrient Broth (NB) media by incubating overnight at 37°C. The turbidity of overnight culture was compared to standard ½ NTU solutions (McFarland Unit) with optical density (O.D.) of 0.132 at the wavelength of 600 nm. Using these reading of optical density, cell density was estimated to be ~ 1.5 x 10^6 CFU/mL. Optical density was measured by UV-VIS Spectrophotometer.

TEMPERATURE AND PH OF MEDIA

Temperature and pH of distilled water, Phosphate Buffer Solution (PBS) and Nutrient Broth (NB) before and after plasma treatment were measured using IR thermometer and pH meter.

PLASMA TREATMENT

One mL of cell suspension (O.D.~ 0.132) was loaded on 12 well flat bottom tissue culture plates (Corning Inc.). The cells were treated with the atmospheric pressure argon plasma jet (APAPI) for four different time lengths (60, 120, 180 and 240 s). The APAPI was operated at high voltage of 7 kV, high frequency of 27 kHz and argon gas flow rate of 2 L/min. The distance between the APAPI nozzle and the suspension surface was adjusted at 3.5 cm. Movement of the plasma jet was not required as the argon gas flow facilitates the formation of vortex of cell suspension during treatment

RESULTS AND DISCUSSION

Figure 2(a) represents a typical image of the plasma jet obtained at argon flow rate of 1 L/min at fixed discharge voltage of 7.5 kV and discharge frequency 24 kHz. It appears uniform to the human eye and can reach a length of 40 mm from the nozzle. The typical waveforms of the discharge voltage and current at fixed frequency of 24 kHz are shown in Figure 2(b). The sharp positive current pulse and the equally sharp negative current pulse occurring within one cycle of applied voltage is the typical characteristics of atmospheric pressure glow-like discharge.

EFFECT OF GAS FLOW RATE AND APPLIED VOLTAGE

The effect of flow rate on the length of the plasma jet was studied for the flow rate ranging from 1 to 5 L/min for argon gas. The length of the plasma jet is found to be dependent on the gas flow rate and the optimum flow rate for producing long plasma jet is found to be about 1 L/min. The length of the plasma jet decreases dramatically and the end of the plasma jet becomes blunt when the gas flow rate is increased to 5 L/min. It is believed that the flow mode is altered from laminar to turbulent mode when the gas flow rate is increased to 5 L/min.

Figure 3(a) to (d) shows the effect of plasma jet length on the emission spectrum of the atmospheric pressure plasma jet. The intensity of emission spectra decreases as the jet length increases for the same applied voltage.
Figure 4(a) and 4(b) shows the intensities of OH and Ar-I spectral lines at different positions at the downstream of the jet from the nozzle. It was found that intensities of these two species decrease with the increase in distance from the nozzle. Figure 5(a) to 5(c) shows the profiles of spectral lines for determination of full width half maximum (FWHM) by assuming Lorentzian profile. The FWHM of the spectral line decreases at position further from the nozzle for the same applied voltage. The electron density and electron temperature were also found to decrease as shown in Figure 6(a) and 6(b).

Figure 7 shows the effect of applied voltage on the length of plasma jet. It shows that the length of the plasma jet increases with the increase in applied voltage. The length of the plasma jet is varied within a small range of 3 mm when the applied voltage is changed from 2.5 to 10 kV with a fixed flow rate of 1 L/min.

SURFACE MODIFICATION OF PET AND PC

In order to investigate the performance of the plasma jet for surface modification, the contact angles of water and glycerin drop on the surface were measured. Figures 8 and 9 show the contact angles PC and PET after pure argon plasma treatment as function of treatment time at a discharge frequency 27 kHz, respectively and applied voltage of 4 kV.

The decrease of contact angle with increase in treatment time is due to the interaction of plasma species with substrate surface. The contact angle is saturated instead of continuing to decrease with increase in treatment
FIGURE 4. Intensity of OH and Ar-I spectral lines at different position of plasma jet

FIGURE 5. Magnified profiles of spectral lines for the determination of full width at half maxima (FWHM)

FIGURE 6. (a) Electron temperature, $T_e$ and (b) electron density $n_e$ as a function of distance along the jet length
time after 300 s. Figures 10 and 11 show the variation of surface energy with treatment time. The study of contact angle on the surface of PC as a function of discharge frequency has been made and found that the contact angle decreases with increase in discharge frequency for fixed treatment time. The decrease of water contact angle with increase of discharge frequency in pure argon plasma jet is shown in Figure 12. It is possibly attributed to the increase of excited Ar atoms and electrons with the increase of discharge frequency, which collides frequently with contaminants on the treated surface.

**CFU ANALYSIS**

The treated and untreated samples were diluted by 10 to $10^4$ times. 100 μL of diluted sample was spread on Plate Count Agar (PCA) using sterile bent glass rod. Then, the samples were incubated for 24 h at 37°C. After incubation, visible colony of microbes were counted using Quebec colony counter.

Figure 13 shows that there is no significant change in pH of the various media after treatment. Decrease in pH from 7 to about 6.1 is observed for distilled H$_2$O, pH is...
almost constant for PBS and slight acidification is observed for NB medium. The sterilization effect is more pronounced when the exposure time is increased. However, a long exposure time is not possible at short distance because it may cause damage to the sample plate. Therefore, an optimization of distance and exposure time should be determined for effective treatment. Figure 14 shows the sterilization effect of argon plasma jet on S. aureus and E. coli for different exposure time at gas flow rate of 2 L/min, applied voltage of 7 kV, with distance from the sample of 35 mm. The anti-biofilm effect is proportional to the exposure time. We observed a higher than 4 log₁₀ reduction in E. coli and higher than 3 log₁₀ reduction in S. aureus for a treatment time of 240 s.

CONCLUSION

Atmospheric pressure argon plasma jet is generated by the application of high voltage AC source of variable frequency (10-30 kHz). The optical and electrical characterization of the jet has been carried out and the electron density and electron temperature have been determined as functions of applied voltage and downstream distance from the nozzle of the jet. It is observed that the electron density and electron temperature decrease with increase in distance from the nozzle. From electrical measurement of the discharge, it was showed that a stable glow discharge can be obtained by adjusting the gas flow rate. The effect of gas flow rate on the length of the plasma jet has also been confirmed. For glass tube of inner diameter 3 mm and outer diameter 5 mm, the maximum jet length obtained is 6.5 cm at a flow rate of 2 L/min.

The jet generated in our experiment was tested to be capable of improving the hydrophilicity polymers even with a short exposure time. It was believed that the electrons in the plasma are solely responsible for inactivating prokaryotic cells (E. coli and S. aureus) as no significant changes in the temperature and pH of the medium are observed before and after the treatment.

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