OH and O radicals production in atmospheric pressure air/Ar/H₂O gliding arc discharge plasma jet

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Abstract
Atmospheric pressure air/Ar/H₂O gliding arc discharge plasma is produced by a pulsed dc power supply. An optical emission spectroscopic (OES) diagnostic technique is used for the characterization of plasmas and for identifications of OH and O radicals along with other species in the plasmas. The OES diagnostic technique reveals the excitation \( T_e \approx 5550–9000 \text{ K} \), rotational \( T_r \approx 1350–2700 \text{ K} \) and gas \( T_g \approx 850–1600 \text{ K} \) temperatures, and electron density \( n_e \approx (1.1–1.9) \times 10^{14} \text{ cm}^{-3} \) under different experimental conditions. The production and destruction of OH and O radicals are investigated as functions of applied voltage and air flow rate. Relative intensities of OH and O radicals indicate that their production rates are increased with increasing Ar content in the gas mixture and applied voltage. \( n_e \) reveals that the higher densities of OH and O radicals are produced in the discharge due to more effective electron impact dissociation of \( \text{H}_2\text{O} \) and \( \text{O}_2 \) molecules caused by higher kinetic energies as gained by electrons from the enhanced electric field as well as by enhanced \( n_e \). The productions of OH and O are decreasing with increasing air flow rate due to removal of Joule heat from the discharge region but enhanced air flow rate significantly modifies discharge maintenance properties. Besides, \( T_g \) significantly reduces with the enhanced air flow rate. This investigation reveals that Ar plays a significant role in the production of OH and O radicals.

Keywords: reactive oxygen species (ROS), optical emission spectroscopy (OES), gliding arc discharge, plasma kinetics, broadening mechanism

(Some figures may appear in colour only in the online journal)

1. Introduction
Gliding arc discharge is one of the vital sources of nonequilibrium atmospheric pressure plasmas generated between the two electrodes with a high velocity of gas flowing through the electrodes. In recent years, atmospheric pressure gliding arc discharge (APGAD) plasmas are drawing interest for their wide area of applications including materials processing [1–3], energy conversion [4, 5], environmental applications [6, 7], water purifications [8, 9] and decontamination [10, 11]. It gathers more attention from researchers because the energy utilization in APGAD jet is higher than that of dielectric barrier discharge (DBD) plasma jet, amounting to ~80% of the input power used in chemical reactions [12] and produced OH, O, O₂ and NO in air plasma [10]. Many authors reported [9, 13] the applications of OH and O radicals along with their production efficiencies at atmospheric pressure. Du et al [10] applied reactive nitrogen species (RNS) and reactive oxygen species (ROS) for the inactivation of Escherichia coli bacteria. They mentioned that gas–liquid APGAD plasma is effective in killing bacteria. ROS and RNS produced in APGAD plasma have significant effects on seed germination, structural changes of seed surface [14, 15]. Considering the significance of ROS and RNS produced in the APGAD plasmas, it is important to characterize plasmas for understanding the production and destruction mechanisms involved of these radicals. Most of the
previous experimental results on gliding arcs were determined using electrical diagnostic (Voltage-ampere characteristics) [12, 16]. Further, Zhu et al [17] explored the effect of air flow dynamics on the production of APGAD plasmas and noted that the air flow rate significantly modifies discharge maintenance and emission intensity. Zhang et al [18] characterized APGAD plasmas for point to point electrode configuration using nanosecond pulse power supply utilizing voltage–current characteristics along with arc propagation velocity. Potočnáková et al [19] also discussed the propagation of plasma flame using a high-speed camera and the effect of voltage and flow rate on plasma flame. However, in order to understand the production and loss kinetics of the species produced, it is important to identify species and to determine rotational ($T_{\text{r}}$), vibrational ($T_{\text{v}}$), gas ($T_{\text{g}}$) and excitation ($T_{\text{e}}$) temperatures and electron density ($n_{\text{e}}$). Particularly for biological applications of plasma jet the plasma parameters have a significant influence [20] on the sample to be treated and maintain highly stable for efficient chemical reactions to meet the pertaining requirements.

Several research groups [21–23] are working to improve the production efficiency of OH and O radicals under different experimental conditions for the better understanding of physical phenomena and for finding user-friendly applications of these plasma sources. They reported that the densities and temperatures of OH and O radicals are different for different plasma sources, including plasma jet. However, most of the investigations focused on the effect of gas composition and applied voltage on the production optimization of radicals using dielectric barrier discharge (BDB) plasma jets. In our previous experiment [24], the effects of applied voltage, $O_2$ flow rate and electrode spacing of atmospheric pressure $H_2O/O_2$ (constant temperature water steam) gliding arc discharge plasma jet on the production and destruction of $OH$ and $O$ radicals are studied and found that the relative densities of $OH$ and $O$ radicals are increasing with increasing $O_2$ content in the reactor as well as with applied voltage. In this work, air/Ar/H$_2$O APGAD plasma jet is proposed with simple experimental setup and high content of air in the gas mixture for the generation of ROS. Being motivated on the importance of the generation and loss kinetics along with potential applications of the APGAD plasma jets for the $OH$ and $O$ radicals, the present experiment is carried out. Optimum conditions for the species production are achieved by controlling the external parameters namely, applied voltage, flow rate and gas composition.

Experimental setup is presented in section 2, volt-ampere characteristics and species identifications are displayed in sections 3 and 4, respectively, results and discussion are furnished in section 5, and a conclusion is finally drawn in section 6.

2. Experimental setup

Figure 1 shows the schematic of a very simple experimental setup. The jet is made of a pyrex glass tube of 50 mm long and 8 mm inner diameter. Two copper electrodes of 5 mm long and 1.5 mm diameter are placed face to face inside the glass tube. The gap between the electrodes is maintained at 5 mm. The water sprayer is made following the principle of a nebulizer. A small amount of double distilled water is kept in the water sprayer container. The water is sprayed, looking like water fog, and is inserted into the plasma jet chamber. A constant volume of 2% $H_2O$ is mixed with air and air/Ar mixtures within the arc plasma jet discharge tube. The reason of maintaining minimum $H_2O$ concentration in the mixture was explain elsewhere [24]. Two types of gas compositions air/$H_2O$ and air/Ar/$H_2O$ are used in order to investigate the probable production and destruction mechanisms of $OH$ and $O$ radicals and their effects on the addition of Ar gas. The total flow $Q_i$ injected into the jet tube consists of $Q_{\text{air}}$, $Q_{\text{H}_2\text{O}+\text{Ar}}$. A variable voltage 4–7 kV and 250 Hz square wave power source is connected across the electrodes. The waveforms of the discharge voltage and current are recorded with a voltage probe (HVP – 08), and a current probe (CP – 07C), respectively, in combination with a digital oscilloscope (GDS1022). Ar (purity 99.99%) gas is fed to the plasma jet chamber from a gas cylinder with a constant flow rate of 3 lpm. In order to study the effect of air flow rate on plasma discharge and maintenance properties, air flow rate is varied from 3–15 lpm. The flow rates of Ar and air are controlled by an Ar gas flow controller (Yamato) and air flow controller (KIT115P), respectively. The emission spectra of the produced plasmas are fed to the spectrometer (Ocean Optics: USB2000 + XR1) through a 200 cm long optical fiber cable. The head of the optical fiber is placed at the exit end and along the horizontal axis of the discharge tube and the distance between optical fiber head and plasma discharge tube is maintained approximately 5 cm. This spectrometer has an entrance slit of 25 m, grating 500 lines/mm, detector wavelength range 200–1100 nm and
optical resolution 1.7 nm. A computer is associated to acquire spectral data. This spectrometer is used for species identification and measurement of relative intensities of the reactive species produced in the plasmas. Besides, a high-resolution dual channel spectrometer (Avaspc-2048, slit: 10 μm, grating: 2400 lines/mm, optical resolution: 0.07 nm and wavelength range: 300–500 nm) is used in combination with a computer for spectral data acquisition to determine $T_e$, $T_r$, $T_x$ and $n_e$ of the plasmas.

3. Volt-ampere characteristics

Figure 2 shows the voltage and current waveforms of the plasma jet discharge measured at voltage: 5 kV, electrode gap: 5 mm and air flow rate: 9 lpm. It is seen from the figure that the applied voltage is dc pulse type. The duty cycle of the applied pulse is about 10%. The applied electric field accelerates the free electrons, increases the kinetic energy and transfers their energies through different collision processes to the neutral gas particles and the gas particles become excited and ionized. Discharges occur when the applied voltage reaches the breakdown voltage and the conduction current starts to flow. After breakdown the conductivity of the plasma is dramatically increased between two electrodes. The average power deposition in the plasma is proportional to the applied voltage. The consumed power ($W$) of plasma discharge is calculated by integrating the product of the discharge voltage ($V(t)$) and current ($I(t)$) over one period ($T$) using the following equation

$$W = \frac{1}{T} \int_0^T I(t) V(t) \, dt. \quad (1)$$

The amount of power absorbed by the plasma is approximately 5–8 W. The gas flow rate does not play a significant role for the variation of power dissipation in the plasma for the low frequency power supply (250 Hz in our experiment). But, the power dissipation becomes significant [25] for the source frequency in the order of MHz range.

4. Species identification

Optical emission spectroscopy (OES) is an useful tool for species identification as well as atmospheric pressure plasma diagnostics. Figure 3 shows the typical emission spectrum of the gliding arc discharge plasma jet with air/H$_2$O and air/Ar/H$_2$O maintaining the flow rate 9 lpm and 5 kV. It is seen that the emission intensity of O and OH radicals are relatively lower with air/H$_2$O discharges. Due to the addition of a small amount of Ar gas to the discharge tube, a significant amount of O and OH radicals are produced as can be seen from inset of figure 3. This means that the addition of Ar changes the collision mechanisms that will be discussed later. The most dominant molecular transition takes place for air/H$_2$O plasmas from the nitrogen $N_2(C - B)$ second positive system (SPS) with electronic transition
CIII· → BIII· in the wavelength range 280–390 nm. OH(A2Σ_u^+ → X2Π_g) band transition is found in the wavelength range 306–312 nm. While the O radicals are found at wavelengths of 777.4 nm with electronic transitions 4s(1D)4d → 4p(P^o). The spectral lines of Ar atoms including ArI(3p^2(3P^o)^g)4d → 3p^2(3P^o)^g)4p at 695.46 nm, 727.06 nm and 737.37 nm, ArI(3p^2(3P^o)^g)4d → 3p^2(3P^o)^g)4p) at 762.31 nm, ArI(3p^2(3P^o)^g)4p → 3p^2(3P^o)^g)4p) at 750.38 nm, ArI(3p^2(3P^o)^g)4p → 3p^2(3P^o)^g)4p) at 771.48 nm, 800.40 nm, and 810.61 nm, ArII(3p^2(3P^o)^g)3d → 3p^2(3P^o)^g)4p) at 705.67 nm, ArII(3p^2(3P^o)^g)5d → 3p^2(3P^o)^g)4p) and ArII(3p^2(3P^o)^g)3f → 3p^2(3P^o)^g)4p) at 826.95 nm, respectively. For the determination of T_e, Ar lines will be used. Transitions of H_2(3s → 2p) and H_2(4d → 2p) are found at 486.1 nm and 656.3 nm, respectively. The emission intensity of H_2 line is found much stronger than that of H_2 line due to the lower ionization potential of H_2 compared to that of H_2 line and hence more ionization events occur with dissipation of the same amount of energy. Therefore, the density of H_2 can be expected to be higher and this line will be used for the determination of n_e.

5. Results and discussion

5.1. Optical characterization and chemical kinetics

Emission spectra produced from the discharge can be used to characterize plasma. According to the principle of OES, the emission intensity is proportional to the density of the excited states [26]. A spectral line can be represented [27, 28] as functions of intensity (I), wavelength (λ), and species density of upper level (N) of the emitted line as

\[ I_n^{i,j} \propto N_n^{i} A_n^{i,j} h \nu_{n,j} \frac{\nu}{\nu_{n,j}}. \]

where, N, A, h, ν, n, ν and j are the density of the molecules, Einstein’s transition probability, Plank’s constant, frequency of transition, quantum numbers of electronic, vibrational and rotational transitions, respectively. The single and double primes indicate the upper and lower levels of transitions, respectively.

Figure 3 shows the emission spectra of air/H_2O and Ar/air/H_2O discharge plasmas. According to our experimental conditions, for applied voltage 5 kV and electrode gap 5 mm, the reduced electric field E/N ≈ 100 Td before discharge. The relative intensity of the OH(A^2Σ_u^+ → X2Π_g) band in air/H_2O plasma is much less than that of Ar/air/H_2O discharges. There are many reactions that may contribute to the production and loss of ROS in air/H_2O and Ar/air/H_2O discharge plasmas. Out of these only a few will be considered that are the most dominant collision mechanisms for the creation and loss of OH and O radicals. These phenomena can be attributed as follows.

A small amount of OH radicals in air/H_2O plasmas are produced in which the principal role played by direct electron impact dissociation of H_2O through the following
collision process [24]
\[
\text{H}_2\text{O} + e \rightarrow \text{OH}(A) + \text{H} + e,
\]
\[
k_1 \approx (1.68 T_e - 1.237 T_e^2 + 2.19 T_e^3) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}.
\] (R1)

For the typical value of \( T_e = 6 \text{ kK}, \ k_1 \approx 8.06 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}. \) The higher values of \( k_1 \) indicates that the direct electron impact dissociation is the main production channels of \( \text{OH}. \) In atmospheric pressure thermally nonequilibrium plasmas, in most cases the electron does not follow Maxwell–Boltzmann distribution, while the rotational and vibrational population obey Boltzmann distributions. Since, the plasma chemistry is very complex [29] due to using molecular gases as required in many applications, it will be assumed that the mean electron energy follows Maxwell–Boltzmann distribution for the analysis of plasma kinetics. It is seen from figure 4 that O radical production increases with increasing voltage but decreases with increasing air flow rate in \( \text{Ar/air/H}_2\text{O} \) discharges. Thus, the following indirect collision processes also contribute to the formation of \( \text{OH(A-X)} \) radicals [30, 31] through the creation of \( O \) radicals

\[
\text{O}_2 + e \rightarrow O + \text{O}^+(\text{D}) + e,
\]
\[
k_2 \approx 4.2 \times 10^{-11} \exp \left(-\frac{5.6}{T_e}\right) \text{ cm}^3 \text{ s}^{-1}, \] (R2)

\[
\text{H}_2\text{O} + \text{O}^+(\text{D}) \rightarrow \text{OH}(X) + \text{OH}(X),
\]
\[
k_3 \approx 1.62 \times 10^{-10} \exp \left(\frac{64.95}{T_e}\right) \text{ cm}^3 \text{ s}^{-1}, \] (R3)

\[
\text{OH}(X) + e \rightarrow \text{OH}(A) + e,
\]
\[
k_4 \approx 2.7 \times 10^{-10} \exp (-0.55 \ T_e) \frac{5.6}{T_e} \text{ cm}^3 \text{ s}^{-1}. \] (R4)

Considering \( T_e = 5 \text{ kK} \) and \( T_g = 0.8 \text{ kK}, \ k_2 \approx 5.74 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}, \ k_3 \approx 1.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \) and \( k_4 \approx 2.6 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1} \) are obtained. Thus, the reactions R2, R3 and R4 are also contributing to the enhancement of the production of \( \text{OH}(A) \) radicals.

There are many collision processes [31] responsible for the loss of \( \text{OH}(A) \) radicals, but out of these only a few dominant loss processes will be considered below.

\[
\text{OH}(X) + \text{OH}(X) \rightarrow \text{O} + \text{H}_2\text{O},
\]
\[
k_5 \approx 2.5 \times 10^{-15} T_g^{1.14} \exp \left(-\frac{50}{T_g}\right) \text{ cm}^3 \text{ s}^{-1}, \] (R5)

\[
\text{O}^+(\text{D}) + \text{OH}(X) \rightarrow \text{H} + \text{O}_2,
\]
\[
k_6 \approx 2.0 \times 10^{-11} T_g^{-0.186} \exp \left(-\frac{154}{T_g}\right) \text{ cm}^3 \text{ s}^{-1}, \] (R6)

\[
\text{OH}(X) + \text{O} \rightarrow \text{H} + \text{O}_2,
\]
\[
k_7 \approx 2.4 \times 10^{-11} \exp \left(-\frac{109}{T_g}\right) \text{ cm}^3 \text{ s}^{-1}. \] (R7)

The destruction rate coefficients of \( \text{OH}(A) \) radicals through reactions R5 to R7, are \( k_5 \approx 4.79 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}, \)

\[
k_6 \approx 4.76 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}, \text{ and } k_7 \approx 2.09 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}, \]

respectively are obtained for the typical values of \( T_g = 800 \text{ K}. \) These dissociative recombination reaction processes are fractionally responsible for the loss of \( \text{OH}(A) \) radicals. The back diffusion [23] of air in the discharge region plays another important role for the loss of \( \text{OH}(A) \) at higher concentration of \( \text{N}_2 \) and \( \text{O}_2 \).

\[
\text{OH}(A) + \text{N}_2(\text{O}_2) \rightarrow \text{OH}(X) + \text{N}_2^2[\text{O}_2^4],
\]
\[
k_{N_2} = 3.2 \times 10^{-11}, \exp (T_g/300) \text{ cm}^3 \text{ s}^{-1} \ k_{O_2} \approx 7.5 \times 10^{-11} \] (R8)

\[ k_{O_2} \approx 1.08 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \) is obtained for \( T_g = 800 \text{ K}, \) which is much higher than \( k_{N_2}. \) This indicates that \( \text{OH}(A) + \text{O} \rightarrow \text{OH}(X) + \text{O}_2^*, \) as compared to reactions R5 to R7, is dominating as a key player in the reduction of \( \text{OH}(A) \) with increasing air flow rate as well as discharge maintenance of the \( \text{air/H}_2\text{O} \) discharge. Besides, although the concentration of \( \text{H}_2\text{O} \) is only 2% but it plays a significant role in the quenching of \( \text{OH}(A) \) with the relatively high rate coefficient

\[
\text{OH}(A) + \text{H}_2\text{O} \rightarrow \text{OH}(X) + \text{H}_2\text{O},
\]
\[
k_9 \approx 7.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}. \] (R9)

A small amount of \( O \) radicals are produced in the \( \text{air/H}_2\text{O} \) gliding arc discharge plasma through reaction R2 and by the following electron impact dissociative ionization processes [32]

\[
\text{O}_2 + e \rightarrow \text{O}^- + \text{O}, \ k_{O_2} \approx 8.8 \times 10^{-11} \exp \left(-\frac{4.4}{T_e}\right) \text{ cm}^3 \text{ s}^{-1}, \] (R10)

\[
\text{O}_2 + e \rightarrow \text{O}^+ + \text{O} + 2e,
\]
\[
k_{O_2} \approx 5.3 \times 10^{-10} T_e^{-7} \exp \left(-\frac{15.2}{T_e}\right) \text{ cm}^3 \text{ s}^{-1}, \] (R11)

where \( k_{O_2} \approx 1.33 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1} \) and \( k_{O_2} \approx 5.41 \times 10^{-23} \text{ cm}^3 \text{ s}^{-1}. \) Thus, the reaction R10 provides highest contribution among the reactions R2, R10 and R11 in the production of \( O \) radicals. On the other hand, the most probable
quenching of O radicals occur by reactions R3, R6 and R7 and among them reaction R3 plays a significant role in the quenching process. Thus, considering the most significant production and destruction channels, one may conclude that due to the high quenching rate of OH(A) and O radicals by N2 and O2 and H2O along with their products, air/H2O gliding arc discharge plasma produces a little amount of OH(A) and O radicals. In the next section, a significant enhancement of the production of OH(A) and O radicals incorporating Ar gas with air/H2O will be discussed.

A constant flow 3 lpm of Ar is added within the arc jet chamber keeping 2% of H2O for different air flow rate in the range from 3 lpm to 15 lpm. A significant change is observed due to the addition of Ar in the air/H2O composition. Figure 4 shows the effect of Ar addition to the mixture on the production of OH(A) and O radicals, which clearly indicates significant enhancement of the relative intensities of the OH(A) and O radicals with increased Ar content in the gas mixture. Thus, the significant enhancement of the relative intensities of OH(A) and O radicals for the addition of Ar in the gas mixture changes the production channels can be attributed as follows.

The metastable Ar(3P2) atoms are produced through direct electron impact by [33]

\[ \text{Ar} + e \rightarrow \text{Ar}(3P_2) + e, \quad k_{12} = 1.8 \times 10^{-8} \exp\left(\frac{3.1}{T_e}\right) \text{cm}^3\text{s}^{-1}. \]  

\[ \text{(R12)} \]

Many Ar atoms are also excited by \( \text{Ar} + e \rightarrow \text{Ar}^* + e \). The metastable argon atoms are very important in collision processes because they play a major role in ROS generation [34]. For the typical values of \( T_e \approx 0.5 \text{ eV} \), \( k_{13} \approx 3.5 \times 10^{-11}\text{cm}^3\text{s}^{-1} \) is obtained. Since the high density of Ar(3P2) plays a significant role in the production of OH(A) in the Ar/air/H2O plasmas through the following collision process [34]

\[ \text{H}_2\text{O} + \text{Ar}(3P_2) \rightarrow \text{Ar} + \text{OH}(A) + \text{H}, \quad k_{13} \approx 7.8 \times 10^{-10}\text{cm}^3\text{s}^{-1}. \]  

\[ \text{(R13)} \]

Besides, the H2O+ can be generated from H2O molecule by penning ionization with Ar(3P2) metastables since the energy of the Ar(3P2) is high enough (~13.3 eV) to ionize H2O, having a threshold energy for ionization 12.6 eV [23, 35] by

\[ \text{H}_2\text{O}^+ + e \rightarrow \text{OH}(A) + \text{H}, \quad k_{14} \approx 10^{-8} - 10^{-10}\text{cm}^3\text{s}^{-1}. \]  

\[ \text{(R14)} \]

The metastable N2(A) are produced by direct electron impact excitation [36] \( \text{N}_2 + e \rightarrow \text{N}_2(A) + e \) and produce OH(A) radicals through dissociation of H2O molecules [37]

\[ \text{H}_2\text{O} + \text{N}_2(A) \rightarrow \text{OH}(A) + \text{H} + \text{N}_2, \quad k_{15} \approx 4.2 \times 10^{-11}\text{cm}^3\text{s}^{-1}. \]  

\[ \text{(R15)} \]

While, the N atoms are produced through dissociation of N2 molecules and these atomic N dissociates H2O and produces OH(A) radicals [36, 38] by

\[ \text{N}_2 + e \rightarrow 2\text{N} + e, \]

\[ k_{16} = 6.3 \times 10^{-6}T_e^{1.6} \exp\left(-\frac{9.8}{T_e}\right) \text{cm}^3\text{s}^{-1}, \]  

\[ \text{(R16)} \]

\[ \text{H}_2\text{O} + 2\text{N} \rightarrow \text{N}_2 + 2\text{OH}(A) + \text{H}, \]

\[ k_{17} \approx 1.91 \times 10^{-33}\text{cm}^6\text{s}^{-1}, \]  

\[ \text{(R17)} \]

which provides less contribution to the production of OH(A). It should be noted that a huge amount of RNS produced in the discharge due to addition a fraction of Ar with air/H2O composition which is out of the present investigation.

Only a few very significant reactions will be considered for the creation and loss of highly reactive O radicals out of many probable reaction mechanisms [32] involved in the Ar/air/H2O gliding arc discharge plasmas. The O radical production mechanisms are also associated with Ar metastable atoms. Despite the above reactions for O radical production, Ar(3P2) metastable, produced a substantial amount by R12, plays a significant role through the following collision processes [34]

\[ \text{O}_2 + \text{Ar}(3P_2) \rightarrow \text{Ar} + \text{O} + \text{O}, \]

\[ k_{18} \approx 2.10 \times 10^{-10}\text{cm}^3\text{s}^{-1}. \]  

\[ \text{(R18)} \]

The loss of O radicals can occur by the reactions R6, R7, and the presence of N2 molecules also play an important role in the destruction of O radical with the following reactions [39]

\[ \text{O} + \text{N}_2 \rightarrow \text{N} + \text{NO}, \]

\[ k_{19} \approx 3 \times 10^{-10}\exp\left(-\frac{3.837}{T_e}\right) \text{cm}^3\text{s}^{-1}, \]  

\[ \text{(R19)} \]

where \( k_{19} \approx 2.99 \times 10^{-10}\text{cm}^3\text{s}^{-1} \) is obtained for \( T_e \approx 800 \text{ K} \). This indicates a high rate of O radical loss compared to that of reaction R7.

### 5.2. Rotational temperature

It is well known that the lines emitted from the plasma are broadened [40] by natural (\( \lambda_0 \)), Doppler (\( \lambda_D \)), instrumental (\( \lambda_I \)), pressure (\( \lambda_P \)), resonance (\( \lambda_R \)), van der Waals (\( \lambda_{\text{vdW}} \)) and Stark (\( \lambda_S \)) broadenings. Attention has been given for the determination of rotational temperature (\( T_r \)) due to its important role for biological applications of OH and O radicals. The emission intensity of the species produced is dependent on the density of excited species, rotational and vibrational energy distributions, and the volume of the plasma under consideration. In our experiment, OH(A - X) emission spectra are used to determine \( T_r \) in air/Ar/H2O plasma. The emission spectra of OH(A - X) emission are widely used [28] for spectroscopic diagnostics because it facilitates one to determine \( T_r \) by fitting the measured spectra. \( T_r \) is obtained by using LIFBASE simulation software [41] because of its resourceful applications. The emitted spectral line of
Figure 5. Experimental and simulated spectra of OH(X–II (v′ = 0) → A2Σ+ (v″ = 0)) emitted from atmospheric pressure gliding arc air/H2O/Ar discharge plasma measured at air: 9 lpm, Ar: 25%, H2O: 2% and voltage: 5 kV.

equation (2) can be modified to the following form [27]

\[
I_{n_{\nu}^f}^{n_{\nu}^i} = C (\nu_{n_{\nu}^f}^{i}/\nu_{n_{\nu}^f}^{f})^4 n_{\nu} S_{n_{\nu}^f}\frac{\exp\left\{-(he/k)(G_{e}^{i}(v^0)/T_{ij})\right\}}{Q_{ij}^{i}(T_{ij})} \times \frac{\exp\left\{-(he/k)(E_{ij}^{i}(j^i)/T_{ij})\right\}}{Q_{ij}^{f}r_j^i(T_{ij})},
\]

where \( C \) is a constant, \( k \) is the Boltzmann constant, \( c \) is the velocity of light, \( n_{\nu} \) is the density per volume of the molecules in the electronic state of \( n_{\nu}^i \), \( S_{n_{\nu}^f} \) is the band strength, \( S_{n_{\nu}^f} \) is the line strength, \( G_{e}^{i}(v^0) \) is the harmonic oscillator term value, \( F_{ij}^{i}(j^i) \) is the vibrational term value, \( Q_{ij}^{i}(T_{ij}) \) is the vibrational partition function, and \( Q_{ij}^{f}r_j^i(T_{ij}) \) is the rotational partition function. The contribution of the Lorentzian function is taken into account considering the non-Gaussian [27] measured line shape. The best fitted line shape can provide the contributions of Lorentzian and Voigt profiles. Under these conditions, the broadened line intensity profiles can be represented [27] as a function of wavelength (\( \lambda \))

\[
I(\lambda) = I_{n_{\nu}^f}^{n_{\nu}^i} [1 - M \cdot \exp\left\{-(\lambda-\nu_{n_{\nu}^f}^{i}/\nu_{n_{\nu}^f}^{f})/FWHM\right\}^2 \times 4 \ln(2)] + M/4 \times \{(\lambda-\nu_{n_{\nu}^f}^{i}/\nu_{n_{\nu}^f}^{f})/FWHM\}^2 + 1],
\]

where \( M \) is the fraction of the Lorentzian contribution to the Voigt profile of the instrumental function, \( FWHM \) is the full width at half maximum and \( \nu_{n_{\nu}^f}^{i}/\nu_{n_{\nu}^f}^{f} \) is the \( n_{\nu}^f/n_{\nu}^{i} \) transition wavelength.

The OH (A – X) emission spectra in the wavelength 308–311 nm band is used to determine \( T_e \). Both the experimental and simulated spectra are normalized by OH(0–0) band. The simulated spectrum is almost superimposed on the measured spectrum. The best match simulated spectrum can provide \( T_e \), as shown for example in figure 5 for voltage: 5 kV, electrode spacing: 5 mm, air flow rate: 9 lpm, Ar: 25% and \( H_2O: 2\% \) along with the measured spectrum. The Doppler broadening of 0.0015 nm, collisional broadening of 0.036 nm are obtained from the simulated spectrum using LIFBASE software while the instrumental broadening is taken from the spectrometer manufacturer’s datasheet, which is of 0.07 nm. It is noted that the LIFBASE software includes transition moment, rotational, and harmonic oscillator term value with the instrument’s datasheet.

5.3. Gas temperature and electron density

Recently, the \( H_\beta \) line is frequently used for the determination of gas temperature \( T_e \) and electron density \( n_e \) at atmospheric pressure plasmas [40]. Although, the line intensity of \( H_\alpha \) line is much higher than that of \( H_\beta \) line, but it is almost never used to determine \( n_e \) due to its sensitivity to self-absorption and strong broadening by ion dynamics [42]. However, \( T_e \) and \( n_e \) can be determined using the broadening of \( H_\beta \) line using Doppler and Stark broadening respectively. \( \lambda_0 \) is produced due to the thermal motion of excited hydrogen atoms. The instrumental broadening \( \lambda_i \) is related to the resolution of the spectrometer, slit function and lens error of the optical transmission systems. The pressure broadening includes Stark broadening \( \lambda_s \), (due to the interaction of charged particles in plasmas) \( \lambda_e \) and \( \lambda_r \) (due to interaction between neutral atoms or molecules). Natural broadening \( \lambda_n \) (due to consequence of the Heisenberg uncertainty principle applied to the energies of the initial and the final states of the transition) and resonance broadening \( \lambda_r \) (it is caused by the collision between ‘like’ particles) are considered negligible [43] in most atmospheric pressure plasmas because \( \lambda_r \) does not induce shift of spectral line in low density plasmas.

It is important to mention that \( T_e \) and \( n_e \) play a significant role in the broadening of spectral lines. The line broadening can be represented by the Gaussian and Lorentzian line profiles. The \( FWHM \) of the Gaussian profile (\( \Delta \lambda_G \)) is given [44] by

\[
\Delta \lambda_G = \sqrt{\lambda_0^2 + \lambda_i^2},
\]

while the total \( FWHM \) of the Lorentzian broadening (\( \Delta \lambda_L \)) is the sum of the individual broadening, i.e.

\[
\Delta \lambda_L = \lambda_n + \lambda_r + \lambda_s + \lambda_e.
\]

The measured spectrum of the \( H_\beta \) line is fitted by Voigt profile which is the convolution of \( \Delta \lambda_G \) and \( \Delta \lambda_L \). Since the line shapes contain all broadening mechanisms [43], hence all broadening parameters are considered in the fitting equation as noted in the LIFBASE software. The best fitted curve, setting the central value, relative intensity and the base line of the spectrum, provides the broadening parameters. The Voigt fit of \( H_\beta \) line at 486.03 nm, measured at 5 kV with electrode spacing of 5 mm and air flow rate of 9 lpm with 25% Ar, is shown in figure 6.
The Doppler broadening of $H_\beta$ line can be represented [44] by

$$\lambda_D = 7.16 \times 10^{-7} \cdot \lambda_0 \sqrt{\frac{T_e}{M}} \text{ (nm)},$$

(7)

where $\lambda_0$ (nm) is the emission wavelength, $M$ (g $\times$ mol$^{-1}$) is the atomic mass and $T_e$ is in (K). Using equations (5) and (7) one can determine $T_e$.

The FWHM of the Lorentzian profile can be obtained from Voigt fit using equation (6), where $\lambda_0$ and $\lambda_1$ are considered insignificant at atmospheric pressure plasmas. But $\lambda_1$ is usually accounts from 30% to 35% of the total FWHM of Lorentzian profile [44]. Under the experimental conditions considered, the typical value of $\lambda_1 = 0.016$ nm is obtained. Using equation (6) $\lambda_S$ is determined from which $n_e$ can be obtained employing the following relation [40]

$$\lambda_S = 2.0 \times 10^{-11} n_e^{2/3} \text{ cm}^{-3}.$$  

(8)

Figure 7(a) shows the effect of applied voltage on $T_e$ for different air flow rate with constant flow rate 25% of Ar. It is worth mentioning that the concentration of H$_2$O was kept constant 2% in the gas mixture during the entire experiment. This figure represents that $T_e$ is increased with increasing applied voltage. The reason of increasing $T_e$ arises due to the fact that with increasing voltage for fixed electrode spacing, the free electrons are collecting more energy from the enhanced electric field and transfer less energy to molecules through momentum transfer collision process. The results obtained agree well with the results noted by [45]. Besides, the turbulence is become much stronger at higher air flow rate, which increase breakdown voltage of gas mixture. Further, the effect of gas composition on $T_e$ may be caused by several reasons, such as the discharge mode and the nature which governs the gas heating channels and energy transportation.

Figure 7(b) shows the effect of applied voltage on $T_e$ with air flow rate at a constant flow rate 25% of Ar. In atmospheric pressure plasmas $T_e$ may often be considered [28] as $T_g$. But $T_e$ determined from OH(A $\rightarrow$ X) band are found higher than those of $T_g$ obtained from H$_2$ line. Hofmann et al [46] found different $T_e$ determined using different transitions. They pointed out that the results obtained from the H$_2$ line are lower than those obtained with band transition of OH(A $\rightarrow$ X) due to the influence of the stark broadening.

Figure 8 depicts the dependence of $n_e$ on applied voltage and air flow rate. It is seen that $n_e$ is increasing with the increase of applied voltage. The kinetic energy of the electrons are increased due to enhanced electric field, causing more ionization events in the discharge region to occur and consequently increases $n_e$. On the other hand, $n_e$ is decreasing with increasing air flow rate due to short residing time in the...
active discharge region where strong electric field prevails. Because the ionization energy of Ar is (15.76 eV) smaller than the energy (24.34 eV) required for dissociation (9.80 eV) and ionization (14.54 eV) of N₂ molecules. Besides, the content of argon atoms in the gas mixture are increasing with lowering the air flow rate as a result more argon metastable and excited atoms are produced in the discharge region and these metastable atoms may play a significant role in the ionization events in the plasma discharge.

5.4. Excitation temperature

$T_x$ can be determined [47] assuming an equilibrium relation between the electron temperature and density. In atmospheric pressure high density plasmas, $T_x$ is approximately equal to $T_e$ neglecting heavy particle inelastic collisions. Considering the above conditions along with optically thin plasmas, the Boltzmann plot is a simple but widely used method for the determination of $T_x$. In this method, the allowed atomic transitions having large energy difference between the upper level $E_j$ and the ground level $E_i$ are considered. The emission intensity $I_{ji}$ can be expressed [48] assuming the atomic level populations follow Boltzmann distribution as

$$I_{ji} = \frac{hc\gamma_{ji}A_{ji}g_j}{4\pi Z^2\lambda^2_{ji}} \exp\left[-\frac{E_j}{k_BT_x}\right].$$

(9)

where, $\lambda_{ji}$, $A_{ji}$, $g_j$, $k_B$, $h$, $c$, $n_j$, $Z$ are the wavelength of the emitted light, transition probability of the level considered, statistical weight of the upper level, Boltzmann constant, Planck’s constant, speed of light, total population density and partition function, respectively. The Boltzmann plot for $\ln(I_{ji}/\lambda_{ji}^2)$ is drawn as a function of $E_j$ introducing the parameter values required along with the measured intensity $I_{ji}$. The spectral lines of ArI at their emission wavelengths 418.85, 434.42, 705.67, 721.57 and 738.48 nm are selected for the determination of $T_x$. The transition parameters required for the determination of $T_x$ are collected from the NIST database [49]. The Boltzmann plot and a linear fit performed are shown in figure 9 for an example. $T_x$ can be found from the slope of the linear fit. The upper and lower limits of $T_x$ can be estimated in a similar way mentioned earlier.

Figure 10 displays that the $T_x$ is found to increase with increasing applied voltage for a constant electrode gap of 5 mm. It is obvious that when the applied voltage is increased, the electric field intensity also increased between two electrodes and electrons gain more kinetic energy from the field. On the other hand, $T_x$ is significantly decreased with increasing air flow rate. The increased flow rate raises gas density, responsible for the higher collision probability and since, the reduced mean free path of the electrons in the jet nozzle where the electrodes are situated. The electrons can then just acquire a small amount of energy between the two consecutive collision periods, which results in the decrease of $T_x$, leading to reduced dissociation probability by electron impact. $T_x$ has a significant dependency on the

Figure 8. Effect of applied voltage on electron density ($n_e$) with air flow rate in atmospheric pressure gliding arc air/Ar/H₂O discharge plasma.

Figure 9. Boltzmann plot of ArI lines for the determination of excitation temperature ($T_x$) measured at Air: 9 lpm, Ar: 25%, H₂O: 2% and voltage: 5 kV.

Figure 10. Effect of applied voltage on excitation temperature ($T_x$) with air flow rate.
average absorbed power in the discharge region. Another fact of the enhancement of $T_\text{e}$ is that the concentration of Ar atoms in the gas mixture is increased in the discharge region with decreasing air flow rate. Dong et al \cite{50} determined $T_\text{e}$ for air, Ar and He plasmas and they found higher $T_\text{e}$ in Ar plasma than that of air and He plasmas, which indicates that with increasing Ar content in the gas mixture $T_\text{e}$ should be higher.

6. Conclusion

A simple experimental setup is demonstrated for the production of OH and O radicals with nonequilibrium air/Ar/H2O/AAPGAD plasma jet which can produce a large volume of plasma than that of low temperature APPJ. Both optical and electrical methods are employed to characterize the produced plasma with changing the fraction of Ar in the gas mixture and applied voltage. The optical characterization is performed achieving insight on the production and destruction mechanisms of the OH and O radicals through determination of: $T_\text{e} \approx 5550–9000$ K, $T_\text{r} \approx 1350–2700$ K and $n_\text{e} \approx (1.1–1.9) \times 10^{14}$ cm$^{-3}$ under different experimental conditions. It is found that the production of OH and O radicals are increased with increasing Ar concentration in the gas mixture, applied voltage and $n_\text{e}$ because electrons gain higher energies from the enhanced electric fields and hence more effective electron impact molecular dissociation events of H$_2$O and O$_2$ occur in the discharge. On the other hand, the increased air flow significantly modifies discharge maintenance properties and hence the productions of OH and O are decreasing. Besides, $T_\text{e}$ significantly reduces with the enhanced air flow rate due to removal of Joule heat from the discharge region. Finally, it can be concluded that this work offers a competence production of OH and O radicals and can be enhanced by adding a fraction of Ar and its properties can be modified with high flow rate of air. The plasma jet is producing significant amount of ROS, which promises its potentiality in the wide range of applications including environmental, surface modification and seed treatment also.

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