Generation Process and Sterilization Effect of OH Radical in a Steam Plasma Flow at Atmospheric Pressure for a Plasma Autoclave

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ABSTRACT: The reactive flow field and the mechanism of sterilization by steam plasma flow at atmospheric pressure were clarified to develop a new sterilization system by experimental and computational methods. The emission lines of OH, whose intensity increased with increased applied voltage and frequency, were observed in the discharge region. The OH radical finally changed to H₂O₂ in the condensed water. The OH radical was capable of sterilizing spores of *Geobacillus stearothermophilus*, although the condensed water did not have such effect. The discharge process was clarified with an axisymmetric, non-Maxwellian model. The OH radical was generated by a wire electrode toward the ground electrode, and the concentration of H₂O₂ increased after streamer propagation.

KEY WORDS: dielectric barrier discharges (DBD), sterilization, computational analysis

I. INTRODUCTION

Infectious diseases caused by pathogenic microorganisms pose a widespread problem. To prevent such infection, a safe and low-cost sterilization system needs to be developed. The autoclave has been the main method for sterilizing medical instruments because of its simple configuration and low-cost operation. However, this method is not suitable for low-heat-resistant materials such as polymers, which are increasingly employed in modern medical instruments. Therefore, it is necessary to establish an advanced sterilization method that can be operated at lower temperature.

To decrease the operating temperature, sterilization methods using low-temperature plasma flow at atmospheric pressure have been developed.^{1–4} There are several methods to produce such plasma, including direct current discharge, radio-frequency discharge, dielectric barrier discharge (DBD) and pulsed corona discharge. For example, Shimizu et al.⁵ have applied a microwave argon plasma flow, which generates toxic by-products at a safe level, to treat dermatoses. Sladek and Stoffels⁶ have developed a plasma needle, which has been reported in many papers, using helium gas for plasma treatment; and Weltmann et al.⁷ have also developed atmospheric pressure plasma jets (APPJs) for antimicrobial treatment. Deng et al.⁸ have sterilized bacteria using atmospheric pressure glow discharges with helium gas. Furthermore, Moisan et al.⁹ have also clarified

the effectiveness of chemically active species for sterilization. Laroussi and Leipold¹⁰ have reported the effects of UV light, heat, and reactive species on the inactivation of bacteria; and Kim et al.¹¹ have applied species generated with atmospheric air plasma to kill cancer cells. Sato et al.^{12,13} have reported the sterilization mechanism of *Escherichia coli* by chemical species.

We have previously reported the sterilization efficacy and mechanism of a tube using DBD.^{14,15} This system consisted of an insulated wire electrode set in the tube and a flat grounded electrode set below the tube. It was possible to sterilize spores of *Geobacillus stearothermophilus* by such treatment for 5 minutes around 70°C. The main sterilization factors were transport and concentration of chemical species such as nitrogen oxide and reactive oxygen species by a twin vortex induced by plasma.

In our previous studies, this plasma sterilization system was applied to a pure steam flow operated at 100°C and atmospheric pressure to develop an innovative autoclave. The plasma source consisted of a stainless steel wire installed in a quartz tube with diameter of 8 mm and a grounded electrode located at the outer wall of the tube. The flow rate of the steam at atmospheric pressure in the tube is 8.1 L/min, which is equal to a velocity of 2.7 m/s. When the applied voltage was 13 kV peak-to-peak and its frequency was 3 kHz, the highest efficacy of sterilization against *G. stearothermophilus* spores was obtained in the voltage range from 11 to 14 kV peak-to-peak and the frequency range from 1 to 5 kHz. Complete sterilization required 50 min, and partial sterilization required 30 min.¹⁶ However, the sterilization mechanism in the pure steam plasma flow is not yet fully understood.

The objective of the present study was to clarify experimentally and computationally the reactive flow field and the mechanism of sterilization by a steam plasma flow at atmospheric pressure in order to develop a new sterilization system.

II. EXPERIMENTAL PART

A. Methods

Figure 1 shows a schematic of the experimental apparatus (a) and details of the discharge reactor for a straight type (b) and a branch type (c). Pure steam is generated by boiling purified water in a flask with a 250-W electric heater. The average volume flow rate of generated steam was 8.1 L/min, which equals a velocity of 2.7 m/s in a quartz tube with an inner diameter of 8 mm, an outer diameter of 10 mm, and a length of 155 mm. A stainless steel wire electrode (SUS304), 0.28 mm in diameter, was set in the quartz tube, and a grounded aluminum electrode 2 mm in width and 100 mm in length was set on the outer wall of the quartz tube. The configuration of the grounded electrode changed from the previously reported configuration¹⁶ to enable direct analysis of the region. This change resulted in a sterilization effect different from that previously reported.¹⁶ A high peak-to-peak voltage of 16 kV with a frequency of 3 kHz by a high voltage amplifier (HVA4321, NF Corp., Japan) generated the plasma flow. Water condensed by the steam plasma flow using a cooling system was collected. When OH increased, air from a gas

FIG. 1: Schematic of experimental apparatus (a) and details of the straight-type (b) and branch-type (c) tubes.

cylinder was bubbled through the purified water and fed into the steam.

The discharge current I_d and the applied voltage V_d were measured by a digital oscilloscope (Wave Runner 62Xi, LeCroy, France). A current probe (AP015, LeCroy, France) was used for measuring the current of the cable that supplied the wire electrode. The average discharge power P_d was obtained by the equation.¹⁷

Side view photographs were taken with a digital camera (Nikon, D50). Spectrum photographs of the discharge region in the cross section were taken with a highly sensitive UV camera (C9299-02, Hamamatsu Photonics, Japan) using a bandpass filter with a center wavelength of 310 nm and a full width at half maximum (FWHM) of 10 nm (Andover, USA). The spectrum from 200 to 860 nm was measured by a high sensitivity optical multichannel analyzer (PMA-12, Hamamatsu Photonics, Japan), because the emission intensity from the discharge region was weak.¹⁸

The concentration of H_2O_2 in the condensed water was measured with a digital water quality meter (DPM-MT, Kyoritsu Chemical-Check Lab., Japan) and a reagent (WAK- H_2O_2 /- H_2O_2 (C), Kyoritsu Chemical-Check Lab., Japan). The pH and oxidation reduction potential (ORP) as measured by a digital pH/ORP meter (PC6500, Eutech Instruments, USA) have resolutions of 0.001 pH and 0.1 mV, respectively.¹⁹

The sterilization test was performed using a biological indicator (Attest Auto Reader 290, 3M), which evaluates spores of *G. stearothermophilus* (ATCC 7953) as reference bacteria. The bacteria were not sterilized at 100°C for 180 minutes. As shown in Figure 1, three bacteria test sample papers, 25 mm long and 5 mm wide, were set along the wall circumferentially for each sterilization condition. A negative sign (–) means that spores of *G. stearothermophilus* were sterilized by at least a log reduction number of 5 (10^{-5}). A positive sign (+) means that the log reduction number was less than 5.²⁰

To clarify the effect of gas velocity on sterilization, we reduced the gas velocity by setting the tube normal to the main flow tube, as shown in Figure 1 (c). The quartz tube was surrounded by a heat insulator. The effect of the condensed water on sterilization was tested by immersing the test samples in the condensed water.

B. Experimental Results and Discussion

Figure 2 (a) shows waveforms of the discharge current and the applied peak-to-peak voltage of 16 kV with a frequency of 4 kHz. When the applied peak-to-peak voltage was greater than 12 kV, pulse currents were observed. When the pulse currents appeared, radiation was also observed, as shown in Figure 2 (b). The radiation region was distributed along the wire electrode and extended towards the grounded electrode from the wire electrode. The radiation intensity rose with the increase of the applied voltage and the frequency as shown in Figure 3 (a) and (b), respectively. These results of the optical emission spectroscopy imply the generation of OH with wavelengths of 282.9 nm, 289.3 nm, and 308.9 nm in the steam plasma flow.²¹ There is a small peak of H α with a wavelength of 656.2 nm,²² although background noise increased with increasing wavelength.

The two-dimensional profiles of emission intensity are shown in Figure 4, for case (a) without filter, and case (b) with a bandpass filter of 310 nm corresponding to OH

FIG. 2: (a) Waveforms of discharge current and applied peak-to-peak voltage of 16 kV with a frequency of 4 kHz. (b) Side view photograph of the discharge region at $V_{pp} = 16$ kV.

FIG. 3: Optical emission spectroscopy for (a) different applied voltages at $f = 4$ kHz and (b) different frequencies at $V_{pp} = 16$ kV.

FIG. 4: Two-dimensional profiles of emission intensity. (a) Without filter. (b) Through the band-pass filter of 310 nm.

emission. The bright region between the wire and the ground electrodes is large because the discharge occurs in this region. Although the greater intensity of OH emission is distributed near the wire electrode, which is different from the result obtained when a filter is absent.

Figure 5 (a) shows the H_2O_2 concentration against the applied voltage for different frequencies. The concentration increased to greater than 30 mg/L at a peak-to-peak voltage of 18 kV with a frequency of 4 kHz and then increasing voltage or frequency.

FIG. 5: (a) H₂O₂ concentration against the applied voltage for different frequencies. (b) Relationship between the intensity of OH and H₂O₂ concentration.

FIG. 6: (a) pH value and (b) ORP against the applied voltage.

The H₂O₂ concentration was proportional to the 308.9-nm intensity of OH, as shown in Figure 5 (b). This result means that the generated OH finally changes to H₂O₂. However, the characteristics of the pH value and ORP against the applied voltage were slightly decreased, as shown in Figures 6 (a) and (b), respectively, but their tendencies were not congruent with H₂O₂ concentration. Therefore, most of the generated H, which was generated in the process of OH generation, was possibly changed to a stable compound such as H₂ gas, because those values are affected by the H concentration in water.

Table 1 shows the sterilization efficacy (a) with a gas flow of 2.7 m/s using a straight-type tube, and (b) under the low-gas flow velocity using the branch-type tube, as shown in Figure 1 (b) and (c), respectively. For the straight-type tube, one test sample was sterilized under the condition of $V_{pp} = 16$ kV, $f = 3$ kHz, and sterilization time $t = 40$ min. When the applied voltage was increased to $V_{pp} = 18$ kV, two test samples were sterilized. This result implies that the OH is an important sterilization factor,^{3,4} because the intensity of the OH emission line and the concentration of H₂O₂ increased correspondingly. For the branch-type tube, two test samples were also sterilized under the condition of $V_{pp} = 16$ kV, $f = 3$ kHz, and sterilization time $t = 40$ min. Thus, three test samples were not sterilized within 40 min in both types of tubes. To increase OH generation, air was mixed with the steam flow, results of its optical emission spectroscopy are shown in

TABLE 1: Sterilization efficacy (a) under the gas flow of 2.7 m/s using straight-type tube, and (b) under the low-gas flow velocity using branch-type tube.

(a) Straight-type tube			
Applied voltage V (kV)	Frequency f (kHz)	Sterilization time t_s (min)	Sterilization result
16	3	30	+ + –
16	3	40	+ + –
18	3	40	+ – –
(b) Branch-type tube			
Applied voltage V (kV)	Frequency f (kHz)	Sterilization time t_s (min)	Sterilization result
16	3	10	+ + +
16	3	20	+ + +
16	3	30	+ + –
16	3	40	+ – –

Figure 7. The emission intensity of the OH line increased with increasing air flow rate. The intensities of the N_2 second positive system also increased. The sterilization efficacy under the air mixing condition at $V_{pp} = 16$ kV and $f = 3$ kHz is shown in Table 2. Three test samples were sterilized for 30 minutes under air flow rates of 1 and 4 L/min, although sample sterilization was not achieved under a rate of 8 L/min.

III. COMPUTATIONAL PART

A. Computational Model

Figure 8 shows the computational domain. It was a two-dimensional axisymmetric model since the streamer is considered to be a filament rather than a plane configuration. The quartz tube had an inner diameter of 8 mm and an outer diameter of 10 mm. The wire electrode with a diameter of 0.28 mm was set at the center of the tube. Computational analysis was performed with the commercial software program CFD-ACE+ (ESI-Group).

B. Assumptions

We determined that the OH was generated in the plasma from water vapor and later changed to H_2O_2 . Computational analysis was performed assuming the following conditions: (1) two-dimensional axisymmetry; (2) three fluids (electrons, ions, and neutral particles) and two temperatures (electrons and heavy particles); (3) non-Maxwellian distribution for electron energy; (4) unsteady, laminar flow and perfect gas; (4) dissociation, ionization, recombination, and electron attachment; (5) presence of surface

FIG. 7: Optical emission spectroscopy in the case of mixing of air in the steam flow.

TABLE 2: Sterilization efficacy under the air mixing condition at $V_{pp} = 16$ kV, $f = 3$ kHz.

Flow rate Q_{air} (L/min)	Sterilization time t (min)	Sterilization result
0.1	15	+ + +
1	15	+ + -
4	15	+ - -
8	15	+ + -
0.1	30	+ + +
1	30	- - -
4	30	- - -
8	30	+ + +

charge on the inner wall; and (6) absence of radiation loss, photoionization, gravity and condensation of water vapor.

C. Governing Equations

The governing equations included conversation of mass, momentum, energy, and chemical species; state of equation, and Poisson’s equation. The flow, heat, chemical, plasma, and electromagnetic modules of CFD-ACE+³⁵ were used for solving the governing equations. The electron distribution was derived by the Fokker-Planck equation in the plasma module.

The following 23 chemical species were adopted in this model: H^+ , H^- , H_2^+ , H_2O^+ , H_3^+ , HO_2^+ , O^+ , O^- , O_2^+ , O_2^- , O_3^- , OH^+ , OH^- , H , H_2 , H_2O , H_2O_2 , HO_2 , O , O_2 , O_3 , OH , and

FIG. 8: Computational domain.

electrons. Sixteen electron collision reactions by using electron collision cross section data and 86 chemical reaction equations were considered, as shown in Table 3.

D. Initial and Boundary Conditions

All species were assumed to have velocity $u = 0$ m/s, temperature of heavy particles $T_h = 373$ K, electron temperature $T_e = 0.04$ eV, and potential $\phi = 0$ kV. Mass fractions of chemical species were $Y_H = Y_{H_2} = Y_{H_2O_2} = Y_{HO_2} = Y_O = Y_{O_2} = Y_{O_3} = Y_{OH} = 10^{-8}$ for neutral particles; $Y_{H^-} = Y_{O^-} = Y_{O_2^-} = Y_{O_3^-} = Y_{OH^-} = 10^{-12}$ for negative particles; and $Y_{H_3^+} = Y_{H_2O^+} = Y_{HO_2^+} = Y_{O^+} = Y_{O_2^+} = Y_{OH^+} = 10^{-11}$ for positive particles. Electron number density was derived from $n_e = \sum_{i=ion} q_i n_i$. Total mass fraction of all species Y_0 except H_2O was derived from $Y_{H_2O} = 1 - Y_0$.

Figure 9 shows the boundary conditions. The surface temperature of the wire electrode was constant at 100°C. The outer wall of the quartz tube was adiabatic.

E. Computational Results and Discussion

Figure 10 shows the time and spatial evolutions of (a) number density of OH and (b) number density of H_2O_2 . The cross section of the tube wall is dark gray. When the positive applied voltage increased to $t = 0.8$ μ s, the strength of the electric field and the electron temperature increased around the central axis. Correspondingly, the electrons gathered here.

At $t = 0.8$ μ s, the OH is generated around the wire electrode, then a high-density region of OH started to propagate toward the ground electrode. At $t = 0.82$ μ s, the OH reached and spread widely along the upper wall surface. At $t = 0.90$ μ s, the density

TABLE 3: Electron collision reactions by using electron collision cross section data and chemical reaction equations.

No.	Chemical reaction	Rate constants (m ³ -kmol ⁻¹ -s ⁻¹)	Ref.
1	e + H ₂ O → e + H ₂ O	collision cross section data	23
2	e + H ₂ O → 2e + H ₂ O ⁺	collision cross section data	23
3	e + H ₂ O → 2e + OH ⁺ + H	collision cross section data	23
4	e + H ₂ O → 2e + O ⁺ + H ₂	collision cross section data	23
5	e + H ₂ O → 2e + H ₂ ⁺ + O	collision cross section data	23
6	e + H ₂ O → 2e + H ⁺ + OH	collision cross section data	23
7	e + H ₂ O → H ⁻ + OH	collision cross section data	23
8	e + H ₂ O → O ⁻ + H ₂	collision cross section data	23
9	e + H ₂ O → OH ⁻ + H	collision cross section data	23
10	e + H ₂ O → e + OH + H	collision cross section data	23
11	e + H → 2e + H ⁺	collision cross section data	24
12	e + H → 2e + H	collision cross section data	24
13	e + H → 3e + H ⁺	collision cross section data	24
14	e + O → 2e + O ⁺	collision cross section data	24
15	e + O → 2e + O	collision cross section data	24
16	e + O → 3e + O ⁺	collision cross section data	24
17	e + O ₃ → O ⁻ + O ₂	3.0 × 10 ⁻¹⁵	
18	e + O ₃ → O ₂ ⁻ + O	1.3 × 10 ⁻³³	
19	e + H ₂ O ⁺ → OH + H	6.6 × 10 ⁻⁹ T _e ^{-0.5}	33
20	e + H ₂ O ⁺ → O + 2H	2.88 × 10 ⁻⁹ T _e ^{-0.5}	33
21	e + H ₂ O ⁺ → O + H ₂	2.52 × 10 ⁻⁹ T _e ^{-0.5}	33
22	e + H ₂ ⁺ → H ₂	2.0 × 10 ⁻¹⁰ T _e ^{-0.5}	
23	O + O ₃ → 2O ₂	8.0 × 10 ⁻¹⁵ exp(-2060/T)	
24	O + OH → O ₂ + H	2.4 × 10 ⁻¹⁴ exp(110/T)	25
25	O + HO ₂ → OH + O ₂	2.7 × 10 ⁻¹⁴ exp(224/T)	25
26	O + H ₂ O ₂ → OH + HO ₂	1.4 × 10 ⁻¹⁵ exp(-2000/T)	25
27	OH + H ₂ → H ₂ O + H	7.7 × 10 ⁻¹⁵ exp(-2100/T)	25
28	OH + HO ₂ → H ₂ O + O ₂	4.8 × 10 ⁻¹⁴ exp(250/T)	25
29	OH + H ₂ O ₂ → H ₂ O + HO ₂	2.9 × 10 ⁻¹⁵ exp(-160/T)	25
30	OH + O ₃ → HO ₂ + O ₂	1.7×10 ⁻¹⁵ exp(-940/T)	25
31	2HO ₂ → H ₂ O ₂ + O ₂	2.2 × 10 ⁻¹⁶ exp(600/T)	25
32	2H + H → H ₂ + H	8.8 × 10 ⁻³⁹	26
33	2H + H ₂ → H ₂ + H ₂	2.8 × 10 ⁻³⁷ T ^{-0.6}	26
34	2H + H ₂ O → H ₂ + H ₂ O	2.8 × 10 ⁻³⁵ T ^{-1.0}	26

TABLE 3: (continued)

No.	Chemical reaction	Rate constants ($\text{m}^3\text{-kmol}^{-1}\text{-s}^{-1}$)	Ref.
35	$\text{H} + \text{HO}_2 \rightarrow \text{H}_2 + \text{O}_2$	$4.2 \times 10^{-14} \exp(-350/T)$	27
36	$\text{H} + \text{HO}_2 \rightarrow 2\text{OH}$	$4.2 \times 10^{-13} \exp(-950/T)$	27
37	$\text{H} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}$	$8.3 \times 10^{-14} \exp(-500/T)$	27
38	$\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2$	$1.4 \times 10^{-17} \exp(-600/T)$	27
39	$\text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2$	$1.2 \times 10^{-13} \exp(-560/T)$	27
40	$\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$	$1.6 \times 10^{-14} \exp(-4570/T)$	28
41	$\text{H} + \text{O}_2 + \text{O}_2 \rightarrow \text{HO}_2 + \text{O}_2$	$1.77 \times 10^{-35} T^{-1.0}$	28
42	$2\text{OH} + \text{O}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$3.5 \times 10^{-35} T^{-0.7}$	28
43	$\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$	$3.3 \times 10^{-13} \exp(-8460/T)$	29
44	$\text{H} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}_2$	$7.5 \times 10^{-19} \exp(-9270/T)$	29
45	$\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2 + \text{HO}_2$	$2.8 \times 10^{-15} \exp(-1890/T)$	29
46	$\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{H}_2\text{O}$	$1.7 \times 10^{-14} \exp(-1800/T)$	29
47	$\text{H} + \text{O}_2 + \text{H}_2 \rightarrow \text{HO}_2 + \text{H}_2$	$5.8 \times 10^{-36} T^{-0.8}$	29
48	$\text{H} + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{HO}_2 + \text{H}_2\text{O}$	$4.3 \times 10^{-36} T^{-0.8}$	29
49	$\text{H} + \text{OH} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{H}_2\text{O}$	$3.9 \times 10^{-31} T^{-2.0}$	29
50	$2\text{OH} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{H}_2\text{O}$	4.0×10^{-36}	29
51	$2\text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$	$2.9 \times 10^{-23} T^{2.6} \exp(945/T)$	30
52	$\text{H}^+ + \text{O} \rightarrow \text{O}^+ + \text{H}$	3.75×10^{-13}	31
53	$\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{H}$	8.2×10^{-12}	31
54	$\text{H}^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{H}$	1.17×10^{-12}	31
55	$\text{H}_2^+ + \text{H} \rightarrow \text{H}^+ + \text{H}_2$	6.4×10^{-13}	31
56	$\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$	2.0×10^{-12}	31
57	$\text{H}_2^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{H}_2$	2.7×10^{-12}	31
58	$\text{H}_2^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{H}_2$	7.3×10^{-12}	31
59	$\text{H}_3^+ + \text{O} \rightarrow \text{OH}^+ + \text{H}_2$	8.0×10^{-13}	31
60	$\text{H}_3^+ + \text{O}_2 \rightarrow \text{HO}_2^+ + \text{H}_2$	6.7×10^{-13}	31
61	$\text{O}^+ + \text{H} \rightarrow \text{H}^+ + \text{O}$	6.4×10^{-13}	31
62	$\text{O}^+ + \text{H}_2 \rightarrow \text{OH}^+ + \text{H}$	1.62×10^{-12}	31
63	$\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{O}$	2.6×10^{-12}	31
64	$\text{O}^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{O}$	2.1×10^{-14}	31
65	$\text{OH}^+ + \text{H}_2 \rightarrow \text{H}_2\text{O}^+ + \text{H}$	9.7×10^{-13}	31
66	$\text{OH}^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{OH}$	2.89×10^{-12}	31
67	$\text{OH}^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{OH}$	3.8×10^{-13}	31
68	$\text{H}_2\text{O}^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{H}_2\text{O}$	3.3×10^{-13}	31
69	$\text{HO}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{O}_2$	3.3×10^{-13}	31

TABLE 3: (continued)

No.	Chemical reaction	Rate constants (m ³ ·kmol ⁻¹ ·s ⁻¹)	Ref.
70	O ₃ + O ₃ → O ₂ + O + O ₃	1.65 × 10 ⁻¹² exp(-11435/T)	32
71	O ₃ + O ₂ → O + O ₂ + O ₂	7.26 × 10 ⁻¹³ exp(-11435/T)	32
72	O ⁻ + O ₂ → e + O ₃	5.0 × 10 ⁻¹⁸	32
73	O ⁻ + O ₂ + O ₂ → O ₃ ⁻ + O ₂	1.0 × 10 ⁻³⁵	32
74	O ₂ ⁻ + O → e + O ₃	3.0 × 10 ⁻¹³	32
75	O ₃ ⁻ + O ⁺ → O ₃ + O	1.7 × 10 ⁻⁹ T ^{-0.5}	32
76	O ₃ ⁻ + O ₂ ⁺ → O ₃ + O ₂	3.5 × 10 ⁻⁹ T ^{-0.5}	32
77	O ₃ ⁻ + O → O ₂ ⁻ + O ₂	1.1 × 10 ⁻¹⁴	32
78	O ⁻ + O ₃ → O ₃ ⁻ + O	5.5 × 10 ⁻¹³	32
79	O ⁻ + O ₃ → O ₂ ⁻ + O ₂	1.0 × 10 ⁻¹²	32
80	O ⁻ + O ₃ → e + 2O ₂	3.0 × 10 ⁻¹³	32
81	O ₂ ⁻ + O ₃ → O ₃ ⁻ + O ₂	4.0 × 10 ⁻¹³	32
82	OH ⁻ + O ₃ → e + O ₂ + HO ₂	1.0 × 10 ⁻¹⁵	32
83	OH ⁻ + O ₃ → O ₃ ⁻ + OH	5.0 × 10 ⁻¹³	32
84	OH ⁻ + O ₃ → O ₂ ⁻ + HO ₂	1.0 × 10 ⁻¹²	32
85	2OH + O ₂ → H ₂ O ₂ + O ₂	6.615 × 10 ⁻³⁵ T ^{-0.8}	34
86	H ₂ O ⁺ + O ₂ → H ₂ O + O ₂	3.464 × 10 ⁻⁸ T ^{-0.5}	34
87	O ₂ ⁺ + O ₂ ⁻ → 2O ₂	3.464 × 10 ⁻⁸ T ^{-0.5}	34
88	O ⁺ + O ₂ ⁻ → O + O ₂	3.464 × 10 ⁻⁸ T ^{-0.5}	34
89	H + H ₂ O ₂ → H ₂ O + OH	4.0 × 10 ⁻¹⁴ exp(-2000/T)	34
90	H + H ₂ O ₂ → HO ₂ + H ₂	8.0 × 10 ⁻¹⁴ exp(-4000/T)	34
91	H ₂ + O ₂ → H + HO ₂	2.4 × 10 ⁻¹³ exp(-28500/T)	34
92	H + O ₂ → OH + O	2.8 × 10 ⁻¹⁰ T ^{-0.9} exp(-8750/T)	34
93	OH + O ₂ → O + HO ₂	3.7 × 10 ⁻¹⁴ exp(-26500/T)	34
94	OH + H → O + H ₂	1.14 × 10 ⁻¹⁵ T ^{0.67} exp(-518/T)	34
95	HO ₂ + H ₂ → H ₂ O ₂ + H	5.0 × 10 ⁻¹⁴ exp(-13100/T)	34
96	H ₂ O + O → 2OH	7.6 × 10 ⁻¹⁸ T ^{1.3} exp(-8605/T)	34
97	O ⁻ + H ₂ ⁺ → O + H ₂	5.196 × 10 ⁻⁸ T ^{-0.5}	34
98	O ₂ ⁻ + H ₂ ⁺ → O ₂ + H ₂	5.196 × 10 ⁻⁸ T ^{-0.5}	34
99	H ⁻ + H ₂ ⁺ → H + H ₂	5.196 × 10 ⁻⁸ T ^{-0.5}	34
100	H ⁻ + H ₂ O ⁺ → H + H ₂ O	5.196 × 10 ⁻⁸ T ^{-0.5}	34
101	O ⁻ + H ₂ O ⁺ → O + H ₂ O	5.196 × 10 ⁻⁸ T ^{-0.5}	34
102	O ⁻ + O ₂ ⁺ → O + O ₂	5.196 × 10 ⁻⁸ T ^{-0.5}	34

FIG. 9: Boundary conditions.

of OH between the wire electrode and the wall surface started to decrease, then OH remained in the vicinity of the wall surface and the wire electrode. The OH is mainly generated by the electron impact on H_2O as in equation No. 10 in Table 3, and by the electron-attachment dissociation to H_2O^+ , shown in equation No. 19 in Table 3. The density of H_2O_2 increased gradually in the vicinity of the wire electrode and the wall surface as it possibly decomposed, and it did not decrease because H_2O_2 is more stable.

IV. CONCLUSION

The reactive flow field and the mechanism of sterilization by a steam plasma flow at atmospheric pressure was clarified by experimental and computational methods to develop an innovative autoclave. The results obtained in this study are summarized as follows.

When the applied peak-to-peak voltage was 18 kV with a frequency of 3 kHz, sterilization was attained in 40 min for two test samples, although sterilization was observed for only one sample at a peak-to-peak voltage of 16 kV. When the air was mixed with the steam flow at a rate of 1 or 4 L/min, sterilization was attained in 30 minutes for all three test samples, because the OH generation was increased. The radiation intensity of OH observed in the discharge region increased with the increase of applied voltage, frequency, and mixing gas flow rate of the air. The OH radical was converted to H_2O_2 in the condensed water. However, the condensed water did not sterilize the spores of *G. stearothermophilus*. Computational analysis was performed with the axisymmetric, non-Maxwellian model, which clarified that the OH radicals were generated from the wire electrode toward the ground electrode and that the concentration of H_2O_2 increased.

FIG. 10: Time and spatial evolutions of (a) number density of OH and (b) number density of H₂O₂.

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