Calculation of Ozone and NOx Production under AC Corona Discharge in Dry Air Used for Faults Diagnostic

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Abstract. Air is one of the most widely used insulation medium in power systems. However, up to now there is no any existing quantitative gas analysis method used for fault diagnostic based on air by-products detection and analysis. In this paper, a new discharge diagnostic method — gas analysis method based on air by-products (ozone and NO_x) is proposed. The feasibility of this method is studied in this paper. Firstly, the chemical reaction of air under discharge is analyzed; then a typical partial discharge — protrusion defect discharge is simulated based on electron induced chemical reaction and chemical kinetics. The reaction models are built using differential equation and solved using Runge-Kutta method. The density of O_3 and NO_x is obtained near needle tip under different discharge and air condition. The results show there are detectable O_3 and NO_x generated even when discharge capacity is only 5 pC. Meanwhile, when discharge capacity is less than 100 pC the production of O_3 and NO_x are in the same order. When discharge capacity increases, the production of O_3 becomes the main by-product. NO_x is less than 1% of O_3 when discharge capacity is about 10000 pC. The density of O_3 increases linearly with discharge strength and density. Both gas temperature T and pressure P have little impact on the density of O_3 and NO_x in calculated ranges. However the [NO]/[NO_2] does decrease as P and T increases. These properties imply gas analysis method is a potential method to detect discharge faults.

Introduction

Chemical detect method also called decomposition gas analysis method is widely used in power system to monitor the discharge faults in electrical equipment, having the advantages to be not invasive, not affected by unwanted electrical disturbances. For example, when discharge or overheat happening, the transformer oil will decomposes to small molecules such as H_2, CH_4, C2H4, and C_2H_6. And a fault diagnostic method which is called dissolved gas analysis (DGA) is based on detection of these molecules [1]. DGA is one of the most effective method to diagnostic the faults in oil insulated apparatus, especially transformers. Based on this method, one can know the operating condition of the equipment and which kind of faults is happening. For SF_6 insulted apparatus, a similar method is also exist [2]. Air is the most widely used insulation material; however there is few study on fault diagnostic method based on the air derivatives such as ozone(O_3), NO_x. One knows that there is O_3 and other chemical molecules generated under discharge, but few do more research on this. L.Lepine and D.N.Nguyen from Canada measured the ozone distribution inside stator core of an air-cooled hydro-generator and shows ozone measurement can be used to locate partial discharge qualitatively [3][4]. But no intensive study is done both at home and abroad. Besides, a lot of work has been done on O_3 generation by gas discharge [5-9]. And many researchers study the O_3 production under different kinds of discharge. However, as we know no one has focus on faults diagnostic of electrical equipment.

In this paper, a typical corona discharge pattern—protrusion defect discharge is simulated based on the electron induced chemical reaction and chemical kinetics. By solving differential equations describing the process step by step the total O_3 and NO_x production are obtained. Meanwhile, the influence of discharge strength and density, air temperature and pressure are studied. The results imply gas analysis method in air similarly with gas analysis in SF_6 is a potential method to detect corona discharge of electrical apparatus happening in air.

Generation of Ozone and NOx under Corona Discharge

A lot of research has been done on how to effectively generate ozone which is used in ozone generator. In these studies, the mechanism of ozone generation in silent discharge of oxygen-fed and air-fed ozonisers are studied [5][6]. As the main process is show as in table 1. Here we need to note that this is just one of many mechanisms which include only the main reactions.

Tab.1 Chemical model of by-product generation during corona discharge

Serial No.	Chemical Reaction	Reaction rate constant	Serial No.	Chemical Reaction	Reaction rate constant
R1	$e+O_2 \rightarrow O+O+e$	k_{1e}	R8	$O+NO_2 \rightarrow NO+O_2$	$k_8=1.7*10^{-11}e^{(-300/T)}$
R2	$O+O_2+M \rightarrow O_3+M$	$k_2=1.06*10^{-35}e^{(510/T)}$	R9	$NO+O_3 \rightarrow NO_2+O_2$	$k_9=1.5*10^{-12}e^{(-1300/T)}$
R3	$O+O_3 \rightarrow O_2+O_2$	$k_3=1.9*10^{-11}e^{(-2300/T)}$	R10	$NO_2+O_3 \rightarrow NO_3O_2$	$k_{10}=1.2*10^{-13}e^{(-2450/T)}$
R4	$e+O_3 \rightarrow O_2+O$	k_{4e}	R11	$NO+NO_3 \rightarrow 2NO_2$	$k_{11}=8.7*10^{-12}$
R5	$e+N_2 \rightarrow N+N+e$	k_{5e}	R12	$NO_2+NO_3 \rightarrow N_2O_5$	$k_{12}=3.8*10^{-12}$
R6	$N+O_2 \rightarrow NO+O$	$k_6=1.1*10^{-14}Te^{(-3150/T)}$	R13	$N_2O_5 \rightarrow NO_2+NO_3$	$k_{13}=5.7*10^{14}e^{(-10600/T)}$
R7	$N+O_3 \rightarrow NO+O_2$	$k_7=5.7*10^{-13}$	R14	$O+N_2O_5 \rightarrow 2NO_2+O_2$	$k_{14}=1.5*10^{-13}$

As said in literature [5][6] the R1and R5 is the initial step involved in the formation of O_3 and NO_x. It means the electron density which stands for PD capacity is a key role that influences the production of ozone and NO_x. At the same time, considering the band energy of O_2 and N_2 the kinetic energy of electrons which stand for discharge intensity will also infect the production or production rate of ozone and NO_x. There are some relations between the concentrations of ozone and NO_x and discharge parameters. It means the conditions of air by-product may be used to diagnostic the discharge faults of electrical apparatus in air. However, we can also see from table 1 that the O_3 and NO_x will interact with each other and the O_3 will decompose naturally. Meanwhile, in practical application the gap, temperature, pressure and humanity will affect the gas concentration too. So it will be hard to build the relation between by-products concentration and discharge pattern. And a good knowledge of the physical chemistry reaction would be useful for the building of diagnostic criterion. However, it is hard to study the chemistry reaction by experiment. Simulations are used to determine the changing process.

Simulation Model

1) Description of Corona Discharge by Needle-Plane Electrodes

Fig.1 illustrates the typical corona discharge between needle-plane electrodes. The needle electrode is connected to the high voltage. The plane electrode is earthed. Free electrons formed naturally in the inter-electrode space are accelerated toward the wire. In the region very near the needle, where the electric field strength is greater than 3 kV/mm, inelastic collisions of electrons and neutral gas molecules produce electron-positive ion pairs. The dissociation rate coefficient of O_2, N_2 and O_3 by electron impact depends on the energy distribution of electrons in the silent discharge. In the paper these coefficients are treated as functions of the electric field strength per unit gas density. Thus the average rate of O atom formation by (R1) is

$$\left.\frac{d[O]}{dt}\right|_{R1} = 2\frac{\chi(O_2)}{N}v_{de}[e][O_2] \tag{1}$$

Where $\chi(O_2)/N_2$ corresponding to k_{1e} in table 1, is the dissociation rate coefficient of O_2 normalized by the number density N of air, v_{de} is the drift velocity of electrons, and [e] and $[O_2]$ are the average electron number density and the average O_2 number density.

[e], the average electron density reflects the discharge density. It can be calculated using conservation equation of charge electrons, positive ions and negative ions and Boltzmann equation. It is complex, inaccurate and unnecessary. In this paper we use the discharge quantity to indicate the electron density. For ac corona discharge the discharge is not stable, it only happens when $|U|$ is

higher than initial voltage *Uc*. The time *Td* with discharge indicate the discharge intensity. it makes no sense to get average value of [e] in the all period. Meanwhile, we assume there are no electrons generated during this time. However, for each discharge pulse the period *Tp* is about 50-200us depending on the discharge intensity as measured by PD measurement device, and it is ok to get average value of [e] during discharge period. Then the average electron density [e] expressed in terms of the discharge quantity is:

$$\begin{cases} [e] = \dfrac{P_c \cdot T_p}{q_e \cdot v_{de} \cdot T_p \cdot S}, U_c \le U \\ [e] = 0, U < U_c \end{cases} \tag{2}$$

Where *Pc* is the discharge quantities of each discharge pulse, q_e the charge of electron, *U* is the average electric potential in the electrode, *Uc* is the corona discharge initial voltage; *S* is the discharge area of electrode.

From equations (2) and (3), when discharge happen the rate of O atom formation by (R1) is:

$$\left.\frac{d[O]}{dt}\right|_{R1} = 2\frac{\chi(O_2)}{N}\frac{P_c}{q_e \cdot S}[O_2] \tag{3}$$

Similarly, when discharge happen the rate of N atom formation by (R5) and O atom, O_2 formation by (R4) are:

$$\left.\frac{d[N]}{dt}\right|_{R5} = 2\frac{\chi(N_2)}{N}\frac{P_c}{q_e \cdot S}[N_2]$$

$$\left.\frac{d[O]}{dt}\right|_{R4} = \frac{\chi(O_3)}{N}\frac{P_c}{q_e \cdot S}[O_3] \tag{4}$$

$$\left.\frac{d[O_2]}{dt}\right|_{R4} = \frac{\chi(O_3)}{N}\frac{P_c}{q_e \cdot S}[O_3]$$

The transportation of molecular is not considered in the above model. The densities of O and N atoms produced by the electron collision processes are inhomogeneous. But, as all of the reactions included in the proposed mechanism are of first order with regard to these atoms, the above inhomogeneities are not important in so far as one considers the macroscopic processes of gas production on a time-scale close to the residence time of the gas under the needle electrode. The residence time is defined as an average time of the gas stain under the needle as gas flow through the needle-plane electrodes gap in flow rate Q (L/min). So we assume that the electrons induced reactions occur in a small closed region near the needle are homogeneous. The calculated results are only used in small area near the needle with stable discharge. For the gases away from discharge point the electron-impact reaction will not exist. Only chemical reactions are calculated.

2) Description of Chemical Reactions

All the chemistry reactions and corresponding Arrhenius rate coefficients included in the calculation are listed in table 1. As we can see only gas-phase reactions of neutral species are chose. They include 9 neutral species and 11 reactions. Based on reaction kinetics, the rate of O3 formation by (R2) is:

$$\left.\frac{d[O3]}{dt}\right|_{R2} = k_2[O][O_2][M] \tag{5}$$

The rate of O consumption by (R2) is:

$$\left.\frac{d[O]}{dt}\right|_{R2} = -k_2[O][O_2][M]$$

The formation and consumption of other species can obtain similarly.

Where M is the third body of three-body reaction, in dry air it is O_2 or N_2.

3) Initial Conditions

Normally, in dry air as we studied there are some O_3 and NO_x exist. For O_3, the concentration is

about 8ppbv and for NO_x, NO_2 in main is about 20ppbv. The initial concentration of O_2 and N_2 are 0.21 and 0.78 separately. The yields of other species are set to be 0. The dissociation rate coefficient of O_2, O_3, and N_2 is obtained from reference [6]. They are varied a little under different temperature [9]. We assume it is constant from 273 K to 313 K(0~40℃). The values are list in table 2. The calculation method is verified by comparing the results with the earlier literature [6]. The results show in figure 1.

Tab.2 Dissociation rate coefficient of O2, O_3, and N_2

Dissociation rate coefficient	$k_{1e}(O_2)$	$k_{4e}(N_2)$	$k_{5e}(O_3)$
Value (cm^2)	$3.03*10^{-16}$	$8.48*10^{-19}$	$5.15*10^{-15}$

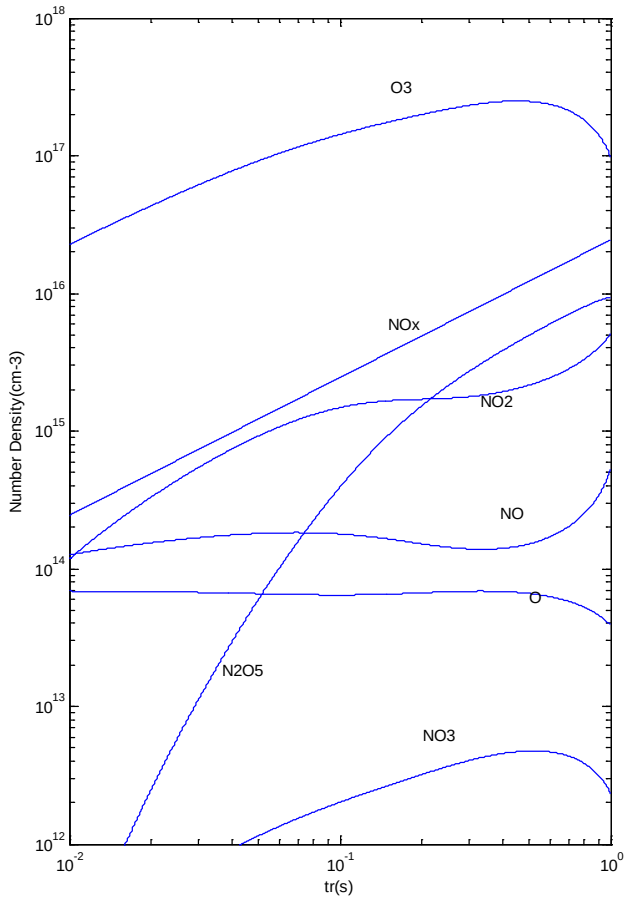

Figure 1. Generation of O_3 and NO_x from dry air under streamer discharge

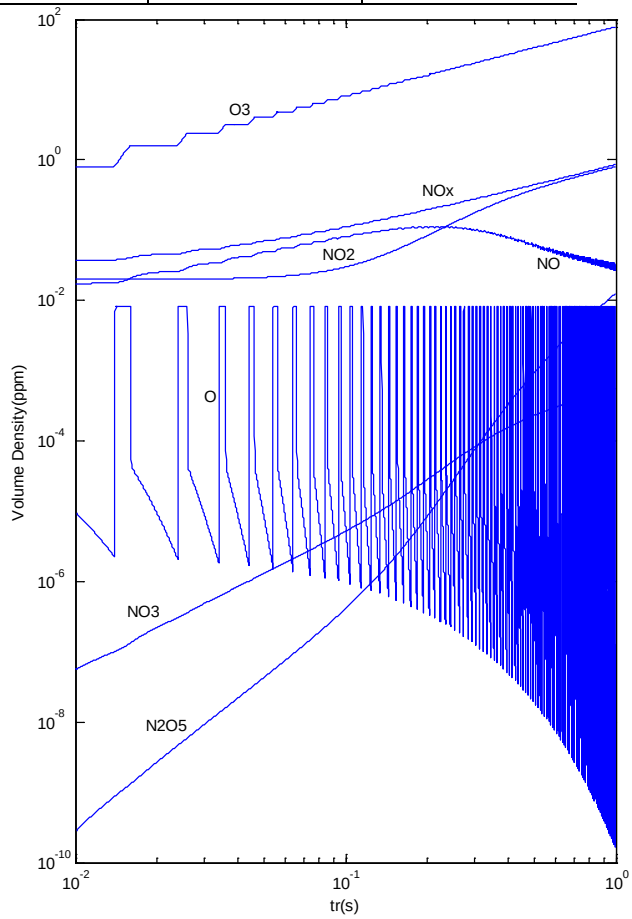

Figure 2. Generation of O_3 and NO_x from dry air under corona discharge

Results and Discussion

1) Generation of O_3 and NO_x in Dry Air

The results of calculations of the Volume density of each species are presented as solid curves in figure 2. The discharge parameters assumed in the calculation are listed in table 3.The abscissa of Figure 2 is the residence time *tr* of the gas in the discharge zone, in here it means the needle tip area, and the ordinate is the species density expressed in volume density ppm.

Tab.3 Discharge parameters of corona discharge

Parameter	P	T	Pc	Td	S
Value	1 atm	293 K	10000 pC	4 ms	2 mm^2

As we can see from Figure 2 as residence time *tr* increases the density of most species increase except O and NO. It indicates that the flow speed of gas near the needle tip is a main character that effects the concentration of species. Meanwhile, the O_3 is the main by-product. NOx is little compare to O_3 and is less than 1% of O_3. The density of NO is bigger than NO_2 when residence

time is small. When *tr* is bigger than about 0.2s, NO_2 becomes bigger. That is because as chemical reaction continues the NO transfer to NO_2. The square wave indicate the density of O, it clearly reflects the periodicity of PD under AC voltage. When there is PD happens, the density of O increases; when PD stops, the O is consumed by R2, R3 etc. The density of O decreases. The top value of O is nearly stable. This shows the generation of O is faster than its consumption in the calculated *tr*. The main product of NOx is NO and NO_2. The production of NO_3 and N_2O_5 are very small compare to NOx especially when residence time is little and are not listed in the following table. The calculation results also show that productions of NOx tell more messages about the reactions.

2) Influence of Discharge strength and density

In this part, the impact of discharge strength and density are studied. The discharge strength Pc is assumed to be 5 pC, 100 pC, 500 pC and 1000 pC. And the discharge time Td which in here indicates density in each power frequency circle is assumed to be 2 ms, 4 ms and 6 ms. Gas pressure P and temperature T are assumed to be 1atm and 293 K. The calculated results for residence time *tr* equal to 1s are list in table 4.

Tab.4 Influence of Discharge strength and density to O_3 and NOx production

Serial No.	Pc (pC)	Td(ms)	cO_3 (ppmv)	cNO_x (ppmv)	cNO (ppmv)	cNO_2 (ppmv)	cNO/cNO_2
1	5	2	0.0160	0.0191	0.0101	0.0090	1.12
2	100	2	0.207	0.0211	0.0115	0.0095	1.21
3	500	2	1.01	0.0293	0.0169	0.0124	1.36
4	1000	2	2.01	0.0397	0.0220	0.0177	1.24
5	500	4	2.00	0.0396	0.0219	0.0177	1.24
6	500	6	2.99	0.0499	0.0255	0.0245	1.04

As we can see in tab.4 there are about 16 ppbv of O_3 generated when discharge capacity is only 5 pC. The density of O_3 is nearly proportion to both discharge strength and density. And the density of NOx including NO and NO_2 only becomes twice as discharge strength increases to 10 times. The density of NOx is nonlinear to discharge density. It shows that NOx is insensitive to discharge strength and density. The ratio of [NO] and [NO] decreases with discharge density. However it does not change too much as discharge strength increases.

3) Influence of Gas Temperature

In this part, the impact of gas temperature is studied. The discharge strength Pc, the discharge time Td, Gas pressure P and discharge area S are assumed to be 500 pC, 2 ms, 1 atm and 2 mm^2. The gas temperature T is assumed to be 273, 293 and 313 K. The calculated results for residence time *tr* equal to 1s are list in table 5. As can see from table the density of O_3 and NOx show no variation as T changes. However $[NO]/[NO_2]$ does decrease as T increases.

Tab.5 Influence of Gas Temperature to O_3 and NOx production

Serial No.	T (K)	cO_3 (ppmv)	cNO_x (ppmv)	cNO (ppmv)	cNO_2 (ppmv)	cNO/cNO_2
1	273	1.01	0.0293	0.0176	0.0117	1.5
2	293	1.01	0.0293	0.0169	0.0124	1.36
3	313	1.01	0.0293	0.0162	0.0131	1.24

4) Influence of Gas Pressure

In this part, the impact of gas pressure is studied. The discharge strength Pc, the discharge time Td, gas temperature T and discharge area S are assumed to be 500 pC, 2 ms, 293 K and 2 mm^2. The Gas pressure P is assumed to be 0.9, 0.95 and 1atm. The calculated results for residence time *tr* equal to 1s are list in table 6. As can see from table the density of O_3 and NOx show no variation as P changes. However $[NO]/[NO_2]$ does decrease as P increases.

Tab.6 Influence of Gas Pressure to O_3 and NOx production

Serial No.	P (atm)	cO_3 (ppmv)	cNO_x (ppmv)	cNO (ppmv)	cNO_2 (ppmv)	cNO/cNO_2
1	0.9	1.01	0.0293	0.0172	0.0121	1.42
2	0.95	1.01	0.0293	0.0171	0.0122	1.4
3	1	1.01	0.0293	0.0169	0.0124	1.36

Conclusion

In this paper, a new discharge diagnostic method—decomposition gas analysis method based on air by-products, ozone and NO_x, is proposed. The density of O_3 and NO_x near the discharge area is calculated based on reaction kinetics theory. Some results are obtained based on the calculations.

1) When discharge capacity is less than about 100 pC the production of O_3 and NO_x is in the same order. When discharge capacity increases, O_3 becomes the main by-product under discharge. NO_x is less than 1% of O_3 when discharge capacity is about 10000 pC. Among NO_x which includes NO, NO_2, NO_3 and N_2O_5, NO and NO_2 are much more than NO_3 and N_2O_5.

2) There are 16ppbv of O_3 generated when discharge is only about 5 pC. The density of O_3 increases linearly with discharge strength and density. The density of NO_x increases nonlinearly.

3) Both gas temperature T and pressure P have little impact on the density of O_3 and NO_x. However the $[NO]/[NO_2]$ does decrease as P and T increases.

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