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Research on active particle distribution in the crop stalk plasma reaction under the condition of streaming and discharging micro electric current

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Abstract. In order to further study sugar-production mechanism in the crop stalk plasma reaction under the condition of streaming and discharging micro electric current with N_2 and H_2O as the electro-discharging gases, the active particles distribution is researched and analyzed. Through the study of methods and theories of statistical mechanics and statistical thermodynamics, the ionization process of the mixed discharging gas and the distribution features of the active particles changing with temperature in the plasma reactor are discussed. The constant pressure form of Saha equation that applies to this experiment is deduced. And the active particles generated in the dense ionization discharging process and the crop stalk conversion processes are also analyzed. The experimental results show that N_2 and H_2 can ionize synchronously. And it is found that during the crop stalk conversion process, while one gas is ionised, the other gas will not take the energy away, which will not affect the conversion. Among the discharging gases consisting of water vapour and nitrogen, the main components are ions of H_2O^+ , H^+ , N_2^+ and molecules of N_2 , H_2O , which are all beneficial to a high sugar yield.

1. Introduction

Presently, development and application of the crop stalk biomass in the chemical industry has become a hotspot and a leading-edge research subject in the field of biomass resources study [1]. In the preliminary stage of this experiment, sugar is produced in the plasma conversion process of crop stalks. [2]. It is found that the active particles generated during the discharging process and the energy distribution is often related to atmospheric gas, which will directly affected the sugar yield in crop stalks. To study the distribution features of the active particles, this paper analyzes the discharging process of dense ionization in the plasma reactor and the active particles generated during the stalk conversion process, which has a significant meaning for improving the sugar yield in the crop stalk plasma reaction.

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2. The Experiment

2.1. The Experimental Materials

The crop stalks, the main experimental material used in this experiment were produced in the countryside of Heilongjiang province in 2010, which were naturally preserved before being used and not moldy. For the experiment, the stalks were cut into segments of an inch or so and then were crushed and grounded into particles of an average size of less than 0.2 mm.

2.2. The Experimental Operation

The devices and equipments in this experiment was described in detailed previously [2]. The N_2/H_2O mixture is prepared in the range: $N_2/H_2O > 5$.

3. The experimental result

3.1. The Particle Types in the Crop Stalk Plasma Reactor

To analyze the complex physical and chemical processes occurred in the plasmas, the reactants, intermediates and products in the excited state must be taken into account [3]. Under the condition of N_2/H_2O mixture, the following types of active particles may exist: N_2^+ atoms, N atoms or ionized atoms, ie, N atoms in the ground state, N atoms in the excitation state, N ions and H_2O^* , H_2O^+ , H_3O^+ in the stimulated state, etc.. The reacting processes in the plasma reactor all obeyed the fundamental laws of energy conservation and mass conservation. In the stalk plasma reactor, on the basis of the above two conservation laws, the thermodynamics laws and characteristics of this system can be explored through theoretically analyzing.

3.2. Analyzing the Ionization Degree of the Particles by Statistical Thermodynamics Method

When the system is in or approaches the equilibrium stage, the chemical, thermal and ionization equilibriums will reach, at least in one tiny element volume [4, 5]. When the stable plasma reaches ionization equilibrium, it obeys the Saha equation. But generally, the Saha equation is introduced in the constant-volume process. The stalk plasma reactor used in this study operated under the constant voltage condition, thus it is necessary to derive the Saha equation in the form of constant voltage.

It can be assumed that the plasma is generated by A , that is, the following reaction occurred: $A = A^+ + e$. In this formula, A^+ and e denote to positive ion and electron, respectively. The above reaction reaches equilibrium at a certain temperature. It should be assumed that in the state of equilibrium, with the total pressure of P , molecule A will be ionized, which is caused by the external electric field's effect or the electron collision. The ionization degree is α . Thus, when ionization equilibrium is reached, the partial pressures of all the gases will show the following relationship:

$$\frac{P_{A^+} P_e}{P_A P^0} = K^0(T) \quad (1)$$

In formula (1), P_{A^+} , P_e and P_A represent the partial pressures of each component, respectively. P^0 is the standard pressure with the value of 101325 Pa. And $K^0(T)$ is the thermodynamic equilibrium constant of the system. When the total pressure reaches P , in accordance with the Dalton law, the partial pressures of each component are as follows:

$$P_{A^+} = P_e = \frac{\alpha}{1 + \alpha} \quad (2)$$

$$P_A = \frac{1 - \alpha}{1 + \alpha} \quad (3)$$

If we substitute formula (1) and (2) into (3), the following expression can be obtained:

$$\frac{P\alpha^2}{1-\alpha^2} = K(T) \quad (4)$$

In accordance with the basic thermodynamic equation, the following formula can be obtained:

$$\ln K(T) = -\frac{\Delta_r G^0}{RT} = \frac{\Delta_r S^0}{R} - \frac{\Delta_r H^0}{RT} \quad (5)$$

In the above formula, $\Delta_r G^0$, $\Delta_r H^0$ and $\Delta_r S^0$ denote to the standard Gibbs free energy variable, the standard enthalpy (heat) variable and the standard entropy variable of the reaction system, respectively. Under the condition of gas ionization, the standard enthalpy (heat) variable $\Delta_r H^0$ can be represented by I_1 , which stands for the first ionic energy of the gases. See the material I_1 in the following table [6]:

Table 1. The first ionic energy of some gases I_1 .

Units	N ₂	H ₂	H ₂ O	Ar
eV	15.59	15.42	12.6	15.75
kJ mol ⁻¹	1504.1	1489.5	1215.1	1519.9

From this table, we can see that I_1 changes little with temperature. Then we can decide that it is independent on temperature. The relationship between the standard entropy variable $\Delta_r S^0$ and temperature can be calculated as following when the temperature of the ideal gases change merely:

$$\Delta_r S^0 = \int \frac{\Delta_r C_p^0}{T} dT = \int \frac{\lambda kR}{T} dT = \lambda kR \ln T \quad (6)$$

In formula (6), $\Delta_r C_p^0$ stands for the reaction's thermal capacity variation in constant voltage and can be calculate as follows:

$$\Delta_r C_p^0 = \sum_i \nu_i C_p^0(i) \quad (7)$$

For ionization, when regarding any matter in it as the ideal gas, C_p of A and A⁺ is equivalent. And for linear molecule it will always be 7/2R. Electron e can be regarded as monatomic molecule, whose heat capacity in constant voltage is 5/2R. The above relationship can be expressed as following:

$$\ln K(T) = \frac{5\lambda \ln T}{2} - \frac{I_1}{RT} \quad (8)$$

$$K(T) = \kappa(T)^{\frac{5}{2}} \exp\left(-\frac{I_1}{RT}\right) \quad (9)$$

If we substitute the expressions of ionization constant and degree of ionization α into the above formula, the Saha equation in constant voltage can be obtained:

$$\frac{P\alpha^2}{1-\alpha^2} = \kappa(T)^{\frac{5}{2}} \exp\left(-\frac{I_1}{RT}\right) \quad (10)$$

In the above expression, m_e , h and k represent electron mass, Plank constant and Boltzmann constant respectively.

For the molecule system, the chemical bonds will crack and become dissociations, which form molecules in high temperature. We can take the reacting gas N_2 in plasma reactor as the sample. It can be assumed that the molecules and atoms of N_2 have reached equilibrium as follows:

$$N_2(g) = 2N(g) \quad (11)$$

The dissociation degree x can be expressed as follows:

$$x = \frac{n}{n_0} \quad (12)$$

In expression (12), n and n_0 stand for the dissociated molecules and the mol number of the total molecules, respectively.

The molecule dissociation degree x , the total pressure P and temperature T all obey the following equation which is similar to Saha equation:

$$\frac{Px^2}{1-x^2} = \exp \left(\int_{T_1}^T \frac{[\Delta H^0(T_1) + \int_{T_1}^T \Delta C_p dT]}{RT^2} dT + I \right) \quad (13)$$

In expression (13), $\Delta H^0(T_1)$ is the enthalpy variable of the dissociation process in temperature T_1 , and ΔC_p is the heat capacity variable in constant voltage, which can be expressed by relevant temperature polynomial. Here the linear part of the temperature is: $\Delta C_p \approx \alpha + \omega T$. I stands for the determined integral constant.

The dissociation process demands large number of energy consumption. In the general form (13), $\Delta H^0(T_1)$ in the exponential molecules is much larger than the latter. But in the case of the less accurate, $\Delta H^0(T_1)$ can be replaced by molecule dissociation energy E_{A-A} (or bond energy D_{A-A}). Then (14) can be:

$$\frac{Px^2}{1-x^2} = T^\omega \exp\left(-\frac{D_{A-A}}{RT}\right) \quad (14)$$

In expression (14), ω stands for an empirical parameter whose approximation is 2.

3.3. Ionization of the Mixed Discharging Gas

In this experiment, the plasma reaction is a process of dielectric barrier discharge under 80 kPa. In the high frequency alternating electric field, N_2 partially discharges, generating a small number of electrons and positive ions, which results in the ionization and dissociation of N_2 and H_2O , ionization equilibrium is reached subsequently. Thus, the ionization degree of the reacting gas at different temperatures α can be obtained by the Saha equation as following:

$$\alpha = \left(\frac{\kappa(T)^{\frac{5}{2}} \exp\left(-\frac{I_1}{RT}\right)}{p + \kappa(T)^{\frac{5}{2}} \exp\left(-\frac{I_1}{RT}\right)} \right)^{\frac{1}{2}} \quad (15)$$

The obtained relationship between the temperature and the ionization degrees of the gases is shown in figure 1. From experimental results, the ionization degrees of all the gases with temperature show the same trend with two transition temperatures. The first situation appears in a certain low temperature range, when the temperature exceeds this range, ionization degree can be significantly

increased. The second situation appears in a high temperature range. Under the operating pressure condition of the calculation for N_2 and H_2O , these two group values are: 2800 K, 2500 K and 3200 K, 2800 K. The ionization energy of N_2 , H_2 , Ar are all reached to 250 kJ mol^{-1} , which is significantly higher than H_2O . This result indicates that N_2 , H_2 and Ar can be ionized synchronously, which can be confirmed by Saha equation.

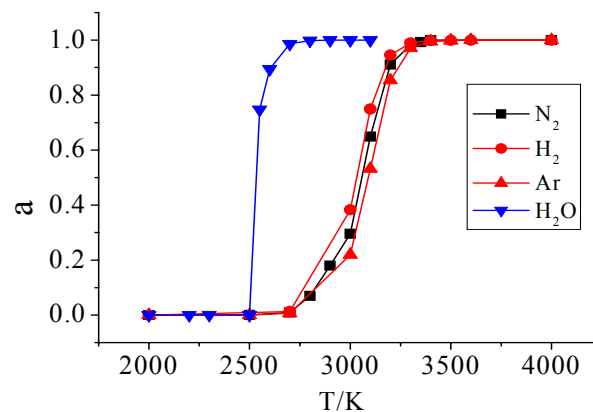


Figure 1. The relationship between the ionization degrees of the gases and the temperature under the plasma hydrolyzation condition.

It is assumed that when there is a less current conveyance through the system, namely, the ionization degree α_i a small value can meet the demand of $1+\alpha_i^2 \approx 1$. Under this situation the ratio between α_i/α_j , the two ionization degrees, can be expressed by the following equation:

$$\frac{\alpha_i}{\alpha_j} = \exp\left(\frac{I_{1j} - I_{1i}}{2RT}\right) \quad (16)$$

The ionization ratio between the two different gases at a certain temperature can be calculated by the formula (16). In the discharging gas mixed by nitrogen and water vapour, the current rate of N_2 is five times larger than H_2O in the same temperature and pressure. So we can conclude that N_2 is the main discharge gas. The ionization of H_2O is 289 kJ mol^{-1} , which is lesser than that of N_2 . So when H_2O is ionized, the main discharge gas is ionized too.

The mixed discharging gas composed of nitrogen, hydrogen and water vapour. The first ionization energy of N_2 and H_2 are $1504.1 \text{ kJ mol}^{-1}$ and $1489.5 \text{ kJ mol}^{-1}$. The difference between them is 14.6 kJ mol^{-1} . So at a certain temperature, such as 4000 K, the ionization degree ratio between N_2 and H_2 can be expressed as following:

$$\frac{\alpha_{H_2}}{\alpha_{N_2}} = \exp\left(\frac{14600}{2 \times 8.314 \times 4000}\right) = 0.2195 \quad (17)$$

This number increases with increasing temperature, so when H_2 ionizes N_2 also ionizes. In the discharging process, N_2 and H_2 are the main gases, the summed current rate of them are five times larger than that of H_2O under the same conditions. Even when very small part of water vapour ionizes, H_2 and N_2 will also be ionized.

4. Conclusion

In this paper, through the studying methods and theories of statistical mechanics and thermodynamic, the molecules, atoms, ions and mixture of N_2/H_2O and $N_2/H_2/H_2O$ in plasma reactor were analyzed.

The experimental results show that, when H_2O was ionized, N_2 will be ionized too. And N_2 and H_2 can ionize synchronously. What's more, it is found that the mixed gases are very favourable for producing H^+ sheath layer, which can enhance the acidity and the sugar yield in the crop stalk.

Because of the large ionization energy difference between these two gases, when a gas ionizes the other one can not follow. Under this condition, a large number of heat energy will be released. The gas combination in this experiment can avoid the loss of the heat energy and increase the stalk conversion rate in a large extent.

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