DECOMPOSITION OF ETHELENE IN LOW TEMPERATURE PLASMA OF BARRIERLESS DISCHARGE

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The experimental setup for investigation of conversion the ethylene impurity in the air on the basis of automated container systems, which using for storing and transporting vegetables and fruits, was developed and tested. The high efficiency of using a barrierless gas discharge to conversion the ethylene impurity in the air experimentally confirmed.

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INTRODUCTION

Research and development of atmospheric pressure gas discharge has shown significant progress in the past decade [1 - 5]. But the widespread industrial application has so far received only ozone generators [6] and systems for cleaning of combustion gases.

In the food industry, in addition to the tasks of decontamination and disinfection, there are still a number of prospective applications for gas discharge of atmospheric pressure, among them, the ethylene (C_2H_4) decomposition for sealed volumes.

Back in the 1930's, it was discovered that low concentrations of ethylene admixture in the storage atmosphere resulted in a rapid deterioration of products [7]. Later, it was found that ethylene is produced by many fruits and vegetables in the process of maturation and its increased concentration leads to accelerated maturation of products and loss of consumer properties. Some fruits, such as apples, produce a very high level of ethylene and can significantly accelerate maturation and spoil other fruits and vegetables in storage facilities. The ethylene concentration of 1 ppm can spoil the entire lot within one day. Even if, as a result of such impact the loss of stored produces is of 3…5%, the scale of overall losses is a very high.

The temperature also has a strong influence on maturation, but the production of ethylene with the "breathing" of the collected vegetables and fruits does not stop there. Control over the level of ethylene in the air can extend the shelf life of vegetables and fruits from days to weeks. Today, to prevent an ethylene production the special catalysts and sorbents are used. The strong influence of humidity on the efficiency of sorbents and their sorption capacity creates significant logistic issues for application, maintenance and disposal of these materials. Therefore, the study of plasma-chemical methods of decomposition of ethylene impurities in air at atmospheric pressure is of actual real-life problem.

As shown in works [8 - 10], the barrierless gas discharge can be used to degrade minor impurities of hydrocarbons in the air.

EXPERIMENTAL SETUP AND EQUIPMENTS

Experimental studies were carried out in a standard container-refrigerator with volume of 65 m^3.

The schematic of the experimental setup on the study of dynamics of the ethylene decomposition is shown on Fig. 1. The 100% concentration of ethylene from a 40-liter cylinder was injected in container by using of a pressure regulator. The control of amount of C_2H_4 was carried out by using of the Alicat Scientific MC-200SCCM-D/5M C2H4 electronic flow meter. The flow rate of ethylene was 4, 8 and 16 cm^3/minute.

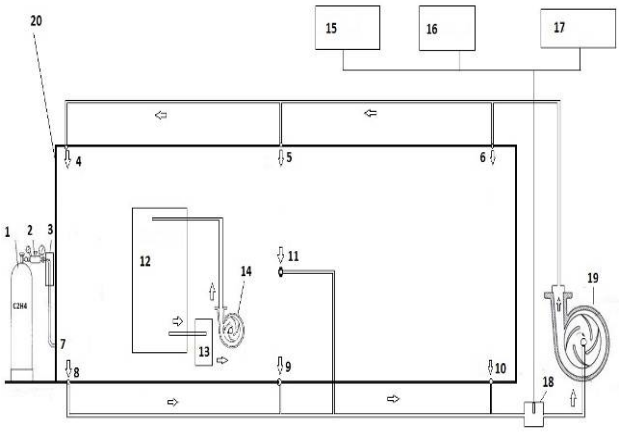

Fig.1. The schematic of experimental setup. 1 – ethylene cylinder; 2 – pressure regulator; 3 – C2H4 flow meter; 4 - 11 – ports for circulation of air and injection of ethylene; 12 – plasmochemical system; 13 – carolithic filter for ozone decomposition; 14 – blower; 15 – ozone monitor; 16 – ethylene monitor; 17 – humidity meter; 18 – gas sampler; 19 – circulating air compressor; 20 – container

The air in the container is forcibly circulated by an external air pump at the rate of 2000 m^3/hour and cooled down to 5°C.

The concentrations of ethylene and ozone, as well as air temperature and humidity were measured by sensors introduced into the circulation line and at different points in the container. The ethylene concentration was measured by the ItaCA56 meter and monitored by sampling from the circulation line air probes, which analyzed by the HP Series II gas chromatograph with a flame-ionization detector. Samples were taken from different control sites of the circulation line (in the middle of the container, near the door and at the end, at different heights) with a syringe of 1 ml. The chromatograph was pre-calibrated with a standard gas mixtures 10 and 100 ppm of ethylene. The Fig. 2 shows the chromatographic peak of the gas mixture with an ethylene concentration of 10 ppm.

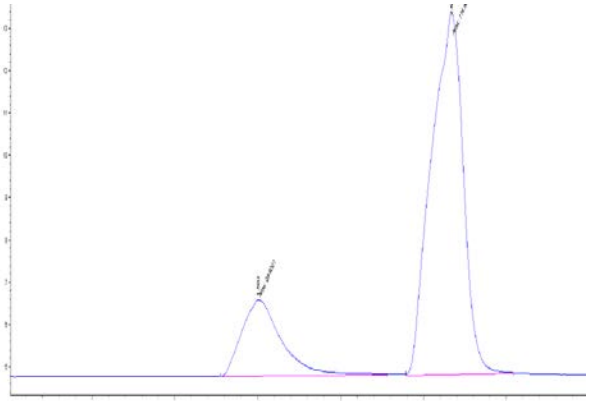

Fig. 2. The chromatogram of a standard gas mixture with an ethylene concentration of 10 ppm

The Fig. 3 is shown the chromatogram of the standard gas mixture with an ethylene concentration of 100 ppm.

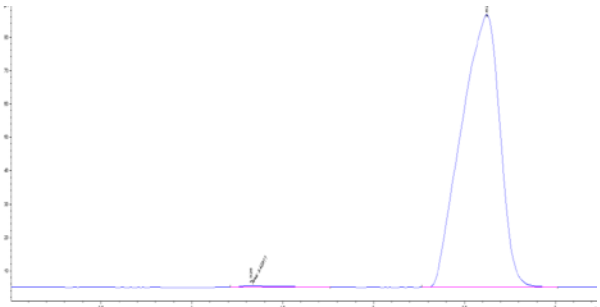

Fig. 3. The chromatogram of a standard gas mixture with an ethylene concentration of 100 ppm

The chromatographic peak of ethylene was observed at 2.5 min. The concentration of ethylene in samples is calculated on the area of the chromatographic peak. The obtained data for samples from different sites have been averaged.

In the middle of the container plasma-chemical system based on three pulsed power supplies with a maximum operation power of 320 W was installed. The air flows are circulated in parallel-connected plasma-chemical reactors (PCRs) with a total flow rate of 160…180 m^3/h. Since the increasing of ozone concentration in air above 1 ppm is unacceptable for fruit storage technology, air after PCRs is fed to a carulite filter [11]. Thus, the ozone concentration in container doesn't exceed of 0.2…0.4 ppm in the entire range of power applied to reactors.

RESULTS

Experimental studies of the influence of low-temperature plasma of barrierless gas discharge on the content of ethylene in the air circulating in a container have been carried out.

The Fig. 4 is shown a typical dynamic for the filling of container with ethylene and next dropping of ethylene concentration after the turn of the plasma-chemical system. The rate of ethylene injection is of 4 cm^3/min.

As can be seen from Fig. 4, after the turn ON the plasma-chemical system, there is a fairly rapid decrease in the concentration of ethylene in the air.

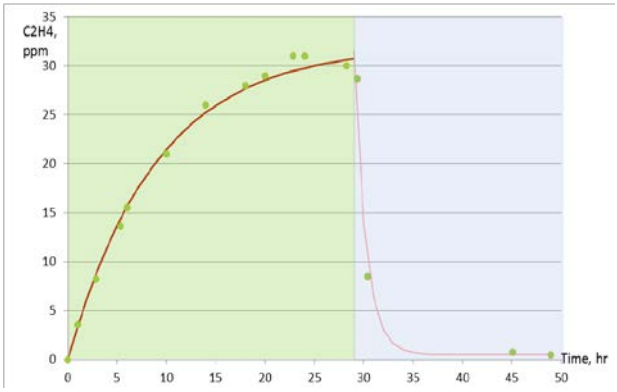

Fig. 4. The dependence of the ethylene concentration for OFF and ON mode of the plasma-chemical system

The Fig. 5 is shown dependence of ethylene concentration after the plasmachemical system was ON. The ethylene flow rate is of 4, 8 and 16 cm^3/minute.

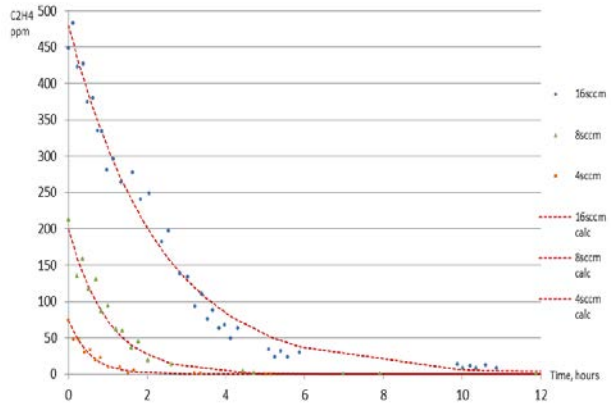

Fig. 5. The dependence of the ethylene concentration in the container after the plasma-chemical system was ON. The ethylene flow rate is of 4, 8 and 16 cm^3/minute

It is seen that the character of the dependence is similar, and when the plasma-chemical system with a power supply of 320 W is turned on, the concentration of ethylene is reduced-to less than 1 ppm.

If the destruction of ethylene in the PCR is due to collisions with electrons that result is either a direct collapse of a molecule or transfer it into an excited state, followed by reaction with the constituents of ozone-air-ethylene mixture (a) or slow ozonolysis accumulated ozone (b) then the rate of disintegration of ethylene in the discharge occurs in proportion to its concentration. The speed of its development is determined by the products of decomposition of ethylene in PCR, that is, doesn't depend explicitly on its concentration. Therefore, the kinetics of the decomposition of ethylene in the discharge will be described, in the simplest case, by the equation

$$\frac{dC(t)}{dt} = k_o - k_1 C(t), \qquad (1)$$

If $C(t=0) = C_o$, then decision (1) has the form:

$$C(t) = \frac{k_o}{k_1} + \left(C_o - \frac{k_o}{k_1} \right) \cdot \exp\left(-k_1 t\right), \qquad (2)$$

where k_o – rate constant of ethylene production, a k_1 – the rate constant of ethylene destruction in PCR. At

$t \to \infty$, get stationary concentration $C^{SS} = k_o / k_1$. The solution (2) is shown in Fig. 6.

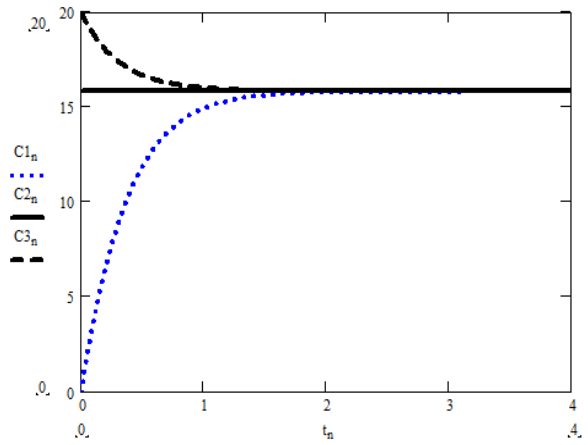

Fig. 6. Dependence $C(t)$ *on time at different initial concentrations –* $C_o < C^{SS}$, $C_o = C^{SS}$ *and* $C_o > C^{SS}$

We can assume that the equation for the rate of destruction of ethylene contains not only a member proportional to the first degree of concentration, but also a member proportional to the second degree. In this case, equation (1) becomes more complicated. But as before, it can be integrated, and its solution has the form shown on Fig. 6.

Since the injection of air-ethylene mixture layer into the PCR at the initial stage of its passage, in this mixture practically no products of disintegration of ethylene, then ethylene can't be synthesized, that is, k_o= 0, which means that C^{SS} = 0. Thus, at a single passage of a air-ethylene mixture layer through PCR it's impossible to get into the area below C^{SS} (see Fig. 6), where the synthesis would start, and not the destruction of ethylene. The area $C_o < C^{SS}$ – it's reactor working area. For PCR, which should break down ethylene, the working area should be an area $C > C^{SS}$. As the layer of air-ethylene mixture passes through PCR, there are products of ethylene decomposition, which leads to the possibility of its synthesis. That is, k_o becomes more than zero, which leads to $C^{SS} > 0$. Thus, along the length of the PCR C^{SS} increases from zero to some extent, which is determined by the rate of ethylene destruction in the discharge. It is important that the output of PCR $C^{SS} > 0$, that is, to obtain a zero concentration of ethylene at the outlet of PCR is impossible. The character of the received experimental graphs completely coincides with the region $C_o < C^{SS}$ theoretical calculation.

Thus, it has been demonstrated that using a gas barrierless discharge can significantly reduce the equilibrium concentration of ethylene in air of a closed hermetic volume.

CONCLUSIONS

The high efficiency of the use the barrierless gas discharge plasma-chemical reactor for decomposition of the ethylene in the air has been theoretically and experimentally demonstrated.

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РАЗЛОЖЕНИЕ ЭТИЛЕНА В НИЗКОТЕМПЕРАТУРНОЙ ПЛАЗМЕ БЕЗБАРЬЕРНОГО ГАЗОВОГО РАЗРЯДА

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Разработано и протестировано экспериментальный стенд для исследования разложения примеси этилена в воздухе на базе систем автоматизированного контейнера, который используется для хранения и транспортировки фруктов и овощей. Экспериментально подтверждена высокая эффективность использования безбарьерного газового разряда для окисления примеси этилена в воздухе.

РОЗКЛАДАННЯ ЕТИЛЕНУ В НИЗЬКОТЕМПЕРАТУРНІЙ ПЛАЗМІ БЕЗБАР'ЄРНОГО ГАЗОВОГО РОЗРЯДУ

В.І. Голота, Д.В. Кудін, О.В. Мануйленко, Г.В. Таран, Л.М. Завада, М.О. Єгоров, В.Ф. Хмелівська

Розроблено та протестовано експериментальний стенд для дослідження розкладання домішки етилену в повітрі на базі систем автоматизованого контейнера, що використовується для зберігання та транспортування овочів та фруктів. Експериментально підтверджено високу ефективність використання безбар'єрного газового розряду для окиснення домішки етилену в повітрі.