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Photocatalytic oxidation of gaseous acetone and ethanol mixtures over titanium dioxide powders

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A gas-plate reactor coated with a commercial titanium dioxide (TiO_2) was used to investigate the performance of ultraviolet photocatalytic oxidation (UV-PCO) of ethanol and acetone contained in air. The device was challenged with organic compound mixtures: ethanol and acetone. The influence of the interaction, temperature, air flow rate on the conversion rate has been studied for the compounds. The result shows that the presence of ethanol reduces the initial degradation rate of acetone, the inhibition increases with increasing of ethanol in the system. This could not be interpreted by classic Langmuir-Hinshelwood (L-H) model. Acetone also inhibits the degradation of ethanol but it still can be described by L-H model. Acetaldehyde in the system comes from the degradation of ethanol, the behaviour of production and consumption of which is affected by the amount of ethanol and acetone in the mixture. Temperature significantly affects the degradation of organic compounds. Increasing the temperature accelerates the degradation of ethanol and acetone as well as the degradation of acetaldehyde, an intermediate produced in the system. Conversion efficiency generally diminished with increased airflow rate. The surface reaction mainly controls the oxidation rate while the gas-phase mass transfer effect is negligible.

Key words**:** photocatalytic degradation; VOCs; ethanol; acetone

INTRODUCTION

Indoor air quality (IAQ) can significantly impact human health, comfort, satisfaction, and productivity. Volatile organic compounds (VOCs) are an important group of air pollutants widely present in indoor enviroment [17]. Since VOCs emitted from buildings materials can attack human organs for a long period of time, thus causing various diseases, numerous attempts have been made to remove them form the atmosphere using several methods such as adsorption on activated carbon, thermal treatment, catalytic oxidation technologies, and so on [6, 8].

Ultraviolet photocatalytic oxidation (UV-PCO), as a convenient innovative and promising advanced oxidation technology, has been suggested as an alternative and energy efficient method to improve IAQ through the photocatalytic degradation of volatile organic compounds [3,16,21,25]. In the past decades, numerous studies have been carried out by researchers from all over the world on the application of PCO process to decompose and mineralize many VOC_S. For example, formaldehyde [4,13,19], benzene [3,17,25], ethanol [7,14], acetone [14,18], toluene [9,11,15,17,20], trichloroethylene [10], dichloromethane were successfully degraded using UV-PCO technique. The previous study on the PCO process mainly focuses on the purification of a single type of pollutants, but little attention is paid to the interaction between organic compounds during photocatalytic decomposition [5].

In this work, the photocatalytic oxidation of acetone, ethanol and the interaction between them during photocatalysis process have been investigated using a Fourier-transform infrared spectroscopy (FTIR). Ethanol is a typical organic compound indoors, and acetone is a popular indoor air pollutant. Indoor air, the presence of acetone and ethanol are due to the use of domestic materials and products as paints and cleaning products. Thus, in this present paper, ethanol and acetone were chosen as target pollutant species. This paper presents the experimental results and discusses the influent of the interaction between acetone and ethanol on photocatalytic activity of TiO_2.

MATERIALS AND METHODS

2.1 Catalyst preparation

Titanium dioxide (TiO_2) exhibits high activity and stability, was selected as the most active metal oxide semiconductor among heterogeneous photocatlysts and now it plays an important role in many industrial and technological processes, environmental and biomedical application (Tang and Yang, 2012). A commercial TiO_2 powder catalyst, without pretreatment, was supplied by Degussa (P-25, composed of 75% anatase and 25% rutile). The mean size and specific surface area of the catalyst particle was 21 nm and 50m^2/g, respectively, measured by Micromeritics ASAP 2020 (Micromeritics, USA) nitrogen adsorption and desorption equipment.

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TiO_2 powders were dispersedly deposited on a glass tube using the dip-coating method. TiO_2 powder was put into distilled water and dispersed fully in a magnetic stirring apparatus to get 2.5wt% TiO_2 slurry in advance. The glass tube was loaded with TiO_2 slurry, impregnated for 30 min and then dried at 373 K for 2 h in a loft drier heated by electricity. It was soaked and dried again and again until 2.05g TiO_2 was coated, i.e., the loaded TiO_2 on the tube was 3.24×10^{-3}g/cm^2. The total mass of TiO_2 loaded was determined by the weight difference before and after the coating procedure. By the way, when the density of TiO_2 on the side of the tube is over 3.2×10^{-3}g/cm^2 no light could permeate it.

Experimental apparatus

To develop a methodology for evaluating the performance of UV-PCO, an innovative system was built up, and the schematic diagram of the test apparatus employed a recycling loop is shown in Fig.1. It consists of a stainless steel UV-PCO reactor and an air stream circulation system. The reactor includes a 20-W lamp with 98% of the UV lamp radiation emitted at 254 nm and a glass tube (6.6 cm i.d. × 62 cm long) that coated with TiO_2 powder in advance. They are located concentrically with 5 mm radial clearance. The ports on the left are used to put in the air containing reactants before each experimental run. The fan in the system is used to control the flux of the air. Fig.1 presents the system to generate the air containing the ethanol, acetone or the mixture of them. Compressed synthetic air (mixture of nitrogen and oxygen with volume ratio 79:21) was supplied by a gas cylinder. The compressed air was divided into three streams. Two of the ways are used to produce the air containing pollutants and one is used for cleaning the set-up before experiment. The bottles in the ways were filled with ethanol and acetone solutions respectively. The mass percentage of the solution of ethanol is 99.7% and that of acetone is 99.5%. Ethanol and acetone sol were mixed with the compressed air and then was supplied through different mass flow controllers to the PCO reactor.

Procedure

The PCO experiments were carried out following a standard procedure. Before experiment the set-up is washed for 10 min by fresh air at the rate of 500 ml/min and then the air with pollutants is pressed in the set-up. After valves No.1 is turned off the No. 2 is turned on. The fan in the system starts to work and No. 3 and No. 5 on the sample ports are open. After the system is stable the UV-lamp is turned on and the photocatalytic degradation of organic compounds is enabled.

During experiment the valve No.1 is closed and the valve No.2 is open. Sampling ports are on the right. They are connected with a FTIR (Perkin Elmer, UK) spectroscopy apparatus which is used to monitor the reactants and products. The valve No. 4 is closed while No. 3 and No. 5 are open for air to go into FTIR monitoring system during experiment. The data is recorded by a FTIR per 10 min, which has been quantified in advance by a gas chromatographic analysis (SP2100, made in Beijing, China). Temperature in the reactor is regulated through the water temperature in the water bath. The flux of air in the system is adjusted through the fan

RESULTS AND DISCUSSION

Developing an effective PCO reactor for IAQ purpose requires the ability to predict the performance of the device over the range of variability of the appropriate atmospheric variables

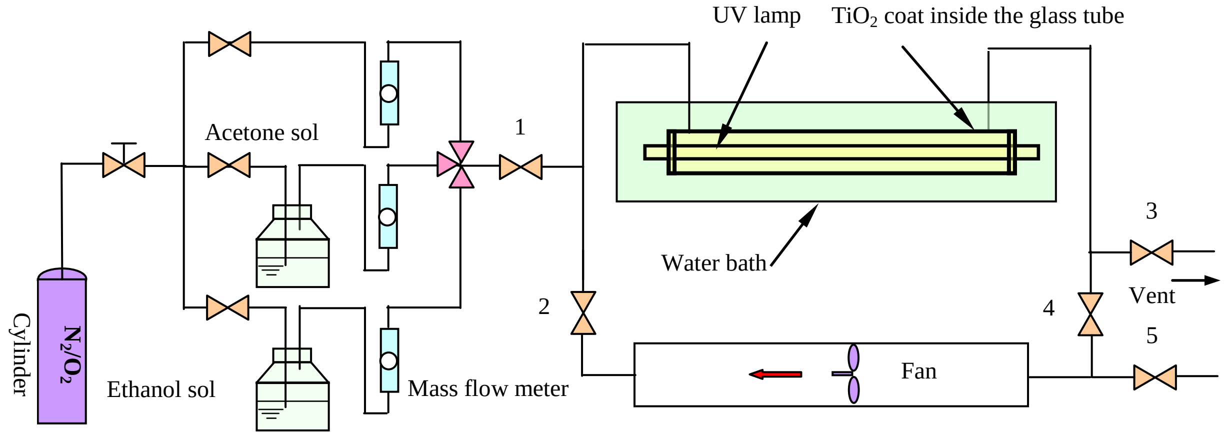

Fig.1. Schematic diagram of the experimental set-up.

(e.g. temperature, relative humidity, and initial concentration) and design variables (e.g. flow rate, UV-light intensity, and catalyst surface area) (Zero *et al.*, 2010).

Degradation of acetone in the presence of ethanol

Fig.2 demonstrates the degradation of acetone in the presence or absence of ethanol. The experiments were carried out at the average temperature of 14°C and the flow rate of 500 ml/min. The slope of the short dash lines drawn in Fig.3 denotes the mean reaction rate of acetone, the values of which are given in Table 1.

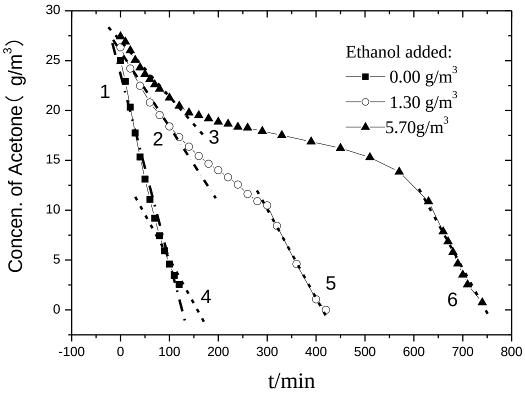

Fig. 2. Degradation of acetone in the presence and the absence of ethanol.

Table 1. Mean slope rate of the lines in Fig.2.

No.	1	2	3	4	5	6
Values	0.210	0.080	0.064	0.100	0.100	0.100
			Error ±0.005			

It is clear that during the degradation of single acetone the reaction rate can be described approximately by the rate of slope of dash line 1, while it can characterized by the slope coefficient of line 4 when the concentration of acetone in the system is less than 8g/m^3. The rate of slope of line 1 is the steepest among lines 1, 2 and 3 indicating that the initial degradation rate of acetone in single case is the fastest. The presence of ethanol reduces the initial degradation rate of acetone and the inhibition of ethanol increases with increasing the amount of ethanol in the system.

With the development of the photocatalytic degradation, acetone concentration decreases against time gradually. Before it reaches 8g/m^3 the inhibitory action of ethanol has existed. It can be seen from Fig. 2 that the higher the concentration of ethanol the lower the degradation rate of acetone. After the concentration of acetone falls to 8g/m^3, the degradation rate can be expressed by the slope coefficient of parallel lines 4, 5 and 6, which is less that of line 1. This result indicates the effect of ethanol disappear hereafter. In a word, compared with the degradation of acetone alone, it cannot be explained by Langmuir-Hinshelwood (L-H) model in presence of ethanol. The presence of ethanol reduces the initial degradation rate of acetone and the inhibition is increased with the increase of ethanol in the system.

Degradation of ethanol in the presence of acetone

Fig. 3 presents the concentration of the ethanol against time with and without acetone. The average initial concentration of ethanol is 6.14 g/m^3. The initial concentration of acetone is 0, 12.54 g/m^3 and 27.42 g/m^3 respectively, the temperature is 4°C, and the flow rate is 500 ml/min.

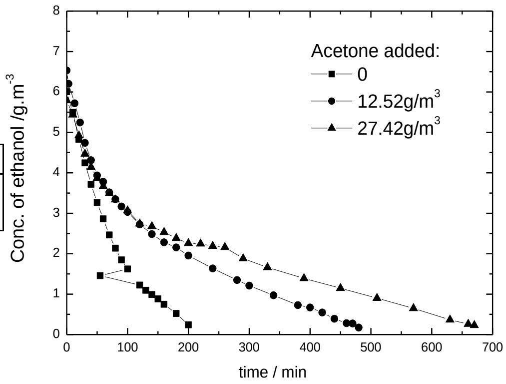

Fig. 3. Ethanol concentration against time in the presence and the absence of acetone.

As shown in Fig. 3, the concentration of the ethanol decreases gradually against time. The presence of acetone inhibits the degradation of ethanol. The higher the initial concentration of acetone is, the stronger the inhibition is. Nevertheless, the degradation of ethanol still can be described by L-H model. The existence of acetone makes the time for degradation of ethanol longer.

Production of acetaldehyde

Fig.4 shows the acetaldehyde concentration produced during the degradation of ethanol, acetone and the mixture of them. It can be observed that only two acetaldehyde curves appear. There is no acetaldehyde produced during the photo-catalytic degradation of acetone. It is concluded that the acetaldehyde comes from the degradation of ethanol, which was in accordance with the conclusion reported by Ding *et al.* [2].

The behaviour of production and consumption of acetaldehyde is affected by the amount of ethanol in the mixture. With the increase of the initial concentration of ethanol the peak concentration of acetaldehyde increases and the time for acetaldehyde to be exhausted is prolonged.

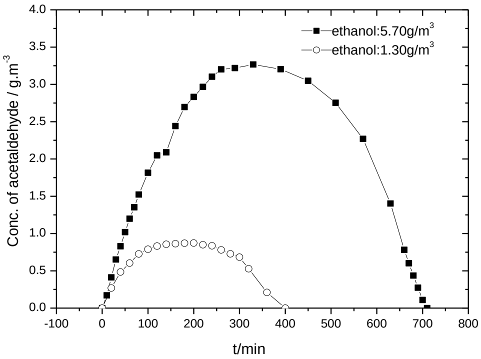

Fig. 4. Acetaldehyde produced during the degradation of ethanol in presence of acetone of 26g/m^3

The behavior of production and consumption of acetaldehyde is affected by the amount of ethanol in the mixture. With the increase of the initial concentration of ethanol the peak concentration of acetaldehyde increases and the time for acetaldehyde to be exhausted is prolonged.

Acetone affects the production and consumption of acetaldehyde (See Fig. 5). The amount of acetone in the system also affects the behavior of production and consumption of acetaldehyde. Increasing the initial concentration of acetone in the system can raise the peak concentration of acetaldehyde and extend the subsistence time of acetaldehyde. It can be understood since the acetaldehyde concentration in the reaction system results from the balance of the two reactions: one is the reaction that ethanol is oxidized to acetaldehyde and the other one is that acetaldehyde is photo-catalytically degraded. The results above indicate that the presence of acetone inhibits the degradation of acetaldehyde, resulting that the increase of peak concentration acetaldehyde and the prolongation of the subsistence time.

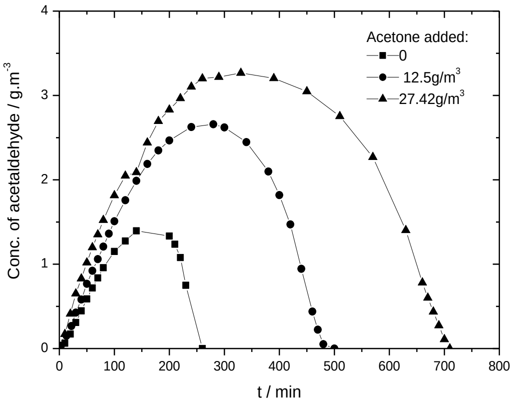

Fig. 5. Effect of the acetone in presence of ethanol of 6g/m^3.

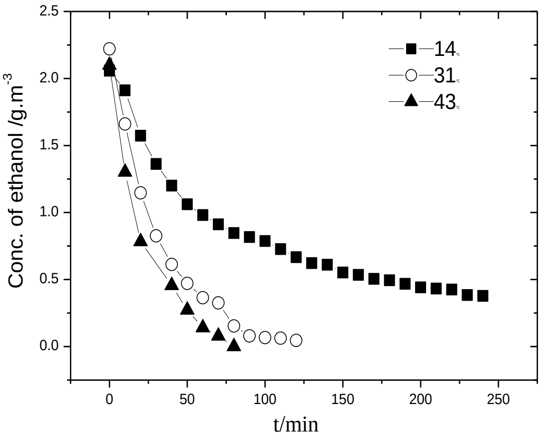

Fig. 6. Effect of temperature on the ethanol degradation.

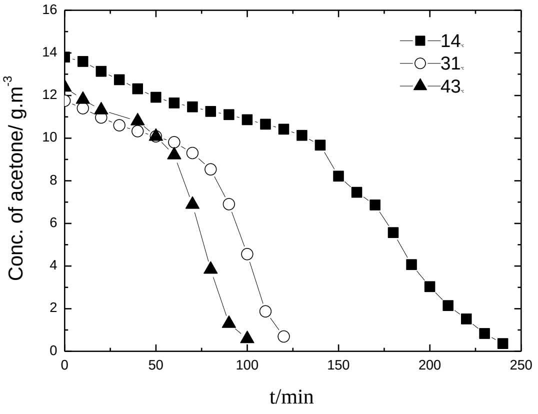

Fig.7. The effect of temperature on acetone degradation.

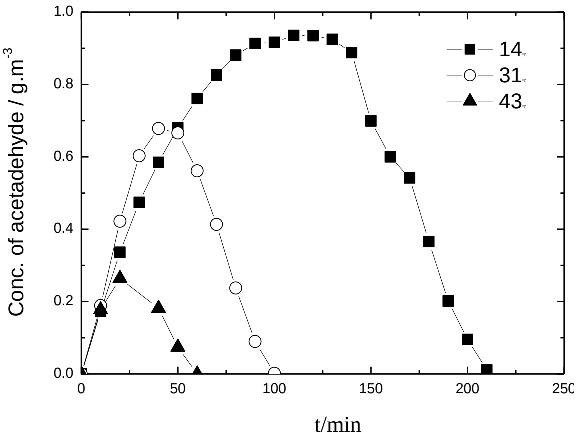

Fig.8. The effect of temperature on acetaldehyde produced.

Effect of temperature

Temperature is usually considered a key factor that influence of UV-PCO process based on the widely accepted mechanism [4]. Fig. 6, 7 and 8 illustrate the ethanol, acetone and acetaldehyde concentrations against time at the temperature of 14, 31 and 43°C respectively. The flow rate is 500 ml/min.

Fig.6 shows the higher the temperature is, more quickly the ethanol concentration decreases. It is demonstrated that temperature significantly influences the degradation rate. In Fig.7, the degradation rate of acetone in the system is also found to increase with increasing temperature. With the increasing of temperature the peak concentration and the time for acetaldehyde to be exhausted are reduced (See Fig. 8). The results indicate that temperature affects greatly the degradation of organic compounds. It can also be noted that the optimal temperature may be varied with different compound. It is applicable in this work, raising the temperature of the reaction system can accelerate the degradation of ethanol, acetone as well as the degradation of acetaldehyde, an intermediates produced in the system.

Effect of flow rate

Changes in flow rate will affect the PCO reaction rate by changing the convective mass transfer and the adsorption of ethanol and acetone molecules onto the photocatalyst surface. To verify the effect of flow rate on the PCO of ethanol and acetone, two different flow rates were evaluated with degradation. Fig.9, 10 and 11 present the concentration of ethanol, acetone and acetaldehyde against time in the reaction system at the flow rate of 0.5 and 0.25 L/min. Temperature is 14 °C.

As can be seen from Fig.9, 10 and 11, the curves between the two flow rates are overlapped and trends almost in the same way. The degradation efficiency decreased consistently when increasing flow rate from 0.25 L/min to 0.5 L/min and became stable when flow rate increased further. The results indicate that the degradation rates of ethanol, acetone and acetaldehyde at the different flow rates are proximal or the oxidation rate does not change significantly with a higher flow rate. It can be easily understood that although increasing the flow rate in the batch reactor means the increase of the circling times of the gas, it decreases the contact time of gas with TiO_2 film at every circling.

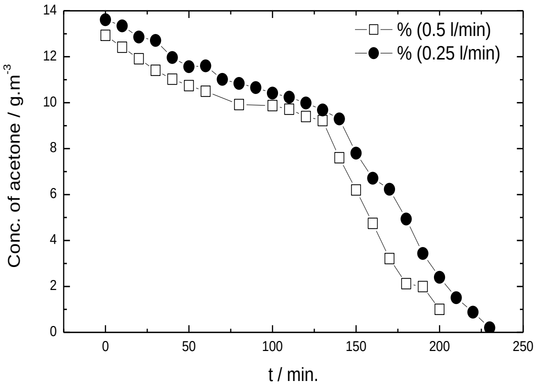

Fig. 9. Effect of flow rate on the degradation of acetone.

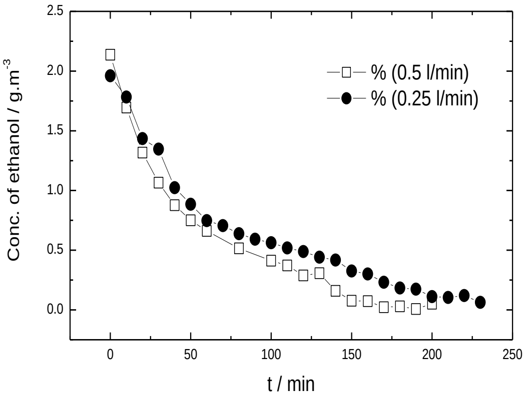

Fig.10. Effect of flow rate on the degradation of ethanol.

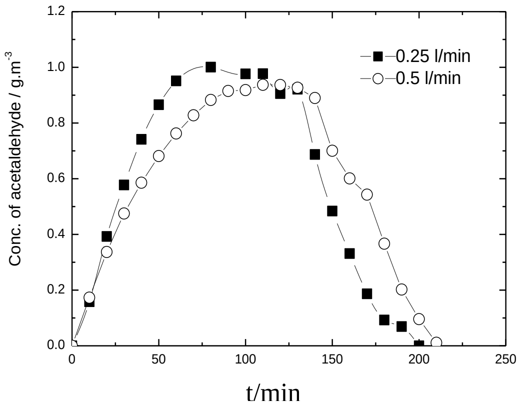

Fig. 11. Effect of flow rate on the degradation of acetaldehyde.

This is in line with the result of Yu *et al.* (2007) where they found that too high a flow rate resulted in shorter residence time and reduced the amount of formaldehyde degraded. Similar finding was also reported by Yu and Brouwers (2009) where they found that the lower the flow rate was, the faster the conversion increase speed was obtained. This indicates the surface reaction mainly control the oxidation rate under this condition while the gas-phase mass transfer effect is negligible.

CONCLUSIONS

- An UV-PCO experimental set-up for VOCs removal was designed and constructed. The photocatalytic oxidation of acetone, ethanol and the interaction between them during photocatalysis process were investigated using a FTIR. The following conclusions can be drawn based on the results obtained in this study.
- Compared with the degradation of acetone alone, it cannot be described by L-H model in presence of ethanol. The presence of ethanol reduces the initial degradation rate of acetone and the inhibition increases with increasing the amount of ethanol in the system. Acetone also inhibits the degradation of ethanol while it still can be described by L-H model.
- Acetaldehyde in the system comes from the degradation of ethanol, the behavior of production and consumption of which is affected by the amount of ethanol and acetone in the mixture.
- Temperature is a key factor of UV-PCO process and affects greatly the degradation of organic compounds. Raising temperature accelerates the degradation of ethanol, acetone as well as the degradation of acetaldehyde, an intermediate produced in the system.
- Conversion efficiency generally diminished with increased airflow rate. The surface reaction mainly controls the oxidation rate while the gas-phase mass transfer effect is negligible.

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ФОТОКАТАЛИТИЧНО ОКИСЛЕНИЕ НА ГАЗООБРАЗНИ СМЕСИ ОТ АЦЕТОН И ЕТАНОЛ ВЪРХУ ПРАХОВЕ ОТ ТИТАНОВ ДИОКСИД

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(Резюме)

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Изследвано е фотокаталитичното окисление на газообразни смеси от ацетон и етанол в двуфазен реактор с титанов диоксид (TiO_2) при ултравиолетово лъчение (UV-PCO). Изследвани са влиянието на концентрациите, температурата, дебита на газовете върху скоростта на реакциите. Резултатите показват, че наличието на етанол понижава началната скорост на разлагането на ацетона, като инхибирането се усилва с повишаване концентрацията на етанола. Това не може да се обясни с класическия модел на Лангмюир-Хиншелвуд (L-H). Ацетонът също инхибира окислението на етанола, н този ефект се интерпретира с (L-H) модела. В системата се натрупва и разлага ацеталдехид като продукт на окислението на етанола, като ходът на този процес зависи от количествата ацетон и етанол в сместа. Температурата влияе значително върху разлагането на тези органични съединения-повишаването й води ускоряване на разлагането на ацетона, етанола и ацеталдехида и другите междинни съединения. Степента на превръщане намалява с повишаване дебита на газовата смес. Скоростта на реакциите се контролира т скоростта на повърхностната реакция, докато масопренасянето в газовата фаза не оказва забележимо влияние.