Synergistic low-temperature plasma (DBD) treatment of n-hexane gas

Kai Liu, Sai Li*, Jinjin Han, Qi Li, Guangning Liao, Zeyi Xin
School of Chemistry and Chemical Engineering, Xi’an University of Science and Technology, Xi’an 710054, PR China

Abstract: The experiment is based on a single dielectric barrier discharge (DBD) plasma generator, using micro-discharge to produce non-equilibrium plasma synergizing with two different catalysts (TiO2, 4A molecular sieve) to decompose n-hexane gas. In the n-hexane degradation experiment, the study investigates the influence of factors such as the type of catalyst, discharge voltage, and flow rate on the degradation rate of n-hexane. The experiments revealed that in all synergistic experiments with catalysts, the degradation rate of n-hexane increased with the decrease in flow rate and with the increase in voltage. Among the four catalysts selected, the 4A molecular sieve catalyst showed the best removal effect for n-hexane gas, reaching 73.2%.

1 Introduction

Since the beginning of the Industrial Revolution, human civilization has entered a stage of rapid development. However, during this process, the problem of environmental pollution has increasingly attracted people's attention. With the development of the chemical industry, volatile organic compounds (VOCs) have become a prominent source of pollution in the environment. VOCs are organic compounds involved in atmospheric photochemical reactions, including alkanes, alkenes, alkynes, and aromatic hydrocarbons, which are important precursors to the formation of fine particulate matter (PM2.5) and ozone (O3) pollution. According to the classification of carcinogens by the European Classification and the International Agency for Research on Cancer (IARC), n-hexane is recognized as a substance with carcinogenic, mutagenic, and retoxic properties, posing a huge threat to human health. Therefore, the purification of volatile organic compounds is particularly important. The working principle of DBD plasma is that high-energy electrons can be generated by an electric field at room temperature and atmospheric pressure, and these high-energy electrons can effectively degrade VOC gas molecules through collision.

Although DBD is widely used for the degradation of VOC gases, it still faces many issues. For instance, Santos et al. conducted a study on the removal of n-hexane. They found that increasing the efficiency of n-hexane removal led to a decrease in energy yield. As a result, research on the synergistic treatment of VOC gases and catalysts has become a globally significant issue.

2 Experiment Preparation

The schematic diagram of the experimental setup is shown in Figure 1, consisting of an AC power supply (50-150v), DBD reactor, and gas chromatograph (GC9790II). Nitrogen is used as the carrier gas, and the vapor of n-hexane (30°C) is passed through a water bath into a buffer bottle, where it is thoroughly mixed. n-Hexane enters the DBD reactor through a buffer bottle (filled with catalyst in the emission area). The products are tested using a gas chromatograph and eventually absorbed by the absorption bottle. The flow rate of the flow meter is between 40-80ml/min, with a concentration of n-hexane at 100,000ppm. The material of the DBD reactor is composed of quartz, and the total length of the entire device is 30cm (inner diameter 15mm, outer diameter 18mm). The outer electrode is wrapped with 12cm steel wire mesh, and the inner electrode is composed of a metal rod (15.3cm long, 1.3cm in diameter).

The experiment evaluates the removal efficiency (RE) of n-heptane, specific input energy (SIE), energy efficiency, LHC selectivity and H2 selectivity to assess the removal performance of the DBD device. The formulas are as follows:
3 Results and discussion

3.1 Voltage test

The Specific Input Energy (SIE) is a crucial factor influencing the degradation of volatile organic compounds (VOCs) in dielectric barrier discharge (DBD) reactors. The higher the reactor voltage, the higher the efficiency in treating VOC gases. However, excessive voltage can lead to increased costs and energy consumption. Therefore, it is necessary to experiment with different voltage ranges to adjust the treatment of different VOC gases and the required catalyst. This study investigated the effects of five voltage parameters (50-150V) on the degradation of n-hexane under constant conditions of 40 ml/min, as shown in Figure 2.

From Figure 2(a), it is evident that the removal efficiency of n-hexane gas increases with the increase of SIE, reaching a maximum of 36.5% at 56.8 kJ/L. This is because when the voltage increases, the electric field strength and density inside the low-temperature plasma reactor increase. The more high-energy electrons produced, the more n-hexane decomposes in the same period of time. From Figure 2(b), it can be observed that during the process of n-hexane gas residence time increasing from 1.4s to 2.8s, the removal efficiency of n-hexane gas shows an increasing trend, reaching the highest removal efficiency of 21.6% at 2.8s. This is because the slower the flow rate, the longer the residence time of the n-hexane gas in the plasma reactor, and the longer the time for the n-hexane gas to be treated. Therefore, the degradation efficiency of VOCs gases. Control of the residence time of the reaction gases. While a longer effective length of the reactor discharge zone is better, excessively long lengths can increase costs. Therefore, it is important to select a suitable reaction length based on practical considerations in order to conduct more effective research on the degradation of VOCs gases. The effect of residence time on the removal efficiency of n-hexane is shown in Figure 3.

Based on Figure 3, it can be observed that during the process of n-hexane gas residence time increasing from 1.4s to 2.8s, the removal efficiency of n-hexane gas shows an increasing trend, reaching the highest removal efficiency of 21.6% at 2.8s. This is because the slower the flow rate, the longer the residence time of the n-hexane gas in the plasma reactor, and the longer the time for the n-hexane gas to be treated. Therefore, the degradation efficiency also increases accordingly.

3.2 Velocity test

By changing the gas flow rate, the residence time of the gas in low-temperature plasma equipment can be controlled. The residence time can be obtained by dividing the volume inside the tube by the flow rate. Research has shown that extending the residence time of gases in the reactor can increase the collision frequency between VOCs gases and active substances such as high-energy electrons and reactive particles, thereby facilitating the degradation of VOCs gases. Control of the residence time of the reaction gases. The effect of residence time on the removal efficiency of n-hexane is shown in Figure 3.

Energy efficiency (g/kWh) = $\frac{\text{RE} \times [\text{C}_6\text{H}_{14}]_{\text{in}} \times M_{\text{H}_2}}{\text{SIE} \times V_{\text{in}}}$

Where $[\text{C}_6\text{H}_{14}]_{\text{in}}$ is the concentration of n-hexane inlet, $[\text{C}_6\text{H}_{14}]_{\text{out}}$ is the concentration of n-hexane outlet, and Q is the gas flow rate.
the only source of hydrogen production is the decomposition of n-hexane. Therefore, as the residence time increases, the higher the degradation efficiency of n-hexane, the more hydrogen is produced. From Figure 3 (d), it is evident that as the residence time of n-hexane gas increases, the selectivity of lower chain hydrocarbons also increases. It can be seen that in the degradation process of n-hexane, the longer the residence time, the less energy consumed and the more thorough the decomposition. This is because n-hexane gas has a greater chance of collision with high-energy electrons and active particles, which is more conducive to the degradation of n-hexane gas.

Figure. 3 (a) Effect of gas flow rate during reaction. (b) Variation of energy efficiency with gas residence time. (c) Hydrogen selectivity as a function of gas residence time. (d) Variation of low-chain hydrocarbon selectivity with gas residence time

3.3 Catalyst type test

Under the same experimental conditions, four catalysts were selected (each weighing 0.5g). The experiment was conducted in a constant temperature water bath with a gas flow rate of 40ml/min, and the voltage parameters ranged from 50V to 150V. Under the same conditions, the effect of low-temperature plasma synergistic catalyst on the degradation of n-hexane was tested, as shown in Figure 4.

In Figure 4, it can be observed that the degradation rate of n-hexane increases with the rise of SIE for the four catalysts. The highest removal efficiencies of the four catalysts are as follows: pure nitrogen (36.5%), Al2O3 (49.7%), TiO2 (53.5%), activated carbon (68%), molecular sieve (73.2%). It can be seen that molecular sieve (4A type) has the best degradation effect on n-hexane, possibly due to the large volume of the molecular sieve reducing the space of the discharge gap, resulting in a smaller space for the activity of high-energy electrons and n-hexane molecules, increasing the probability of collision between electrons and n-hexane molecules. In addition, the molecular sieve itself has the characteristics of high specific surface area, high porosity, and high thermal stability. The high specific surface area can fully expose its surface, enhancing adsorption and degradation ability; thermal stability avoids the impact of high heat generated by micro-discharge in the DBD reactor on the molecular sieve catalyst; and the high porosity (approximately 24%) allows small molecules to pass freely, making it very suitable for gas separation.

The properties of the same activated carbon, such as high specific surface area, high adsorption capacity, and ultra-high chemical stability, increase the efficiency of n-hexane removal.

The Al2O3 catalyst, as a bifunctional catalyst, has a certain catalytic effect on n-hexane. During the experiment, the high-energy electrons generated by DBD and the catalyst jointly act on n-hexane molecules. In Figure 4, it can be observed that although the catalytic effect of the Al2O3 catalyst is stronger than that without the catalyst, its degradation efficiency of n-hexane is lower compared to other catalysts.

Figure. 4 Treatment of n-hexane gas by different catalysts

3.4 Impact of catalyst placement

As shown in Figure 5, experiment was conducted to compare the effects of different catalyst placement methods on the degradation of n-hexane gas. Keeping the gas flow rate and gas residence time constant, as well as maintaining a low-temperature plasma environment, TiO2 was used as the catalyst, with varying voltages used in the experiment. Within this experimental group, voltage ranges of 140V, 150V, 160V, 170V, 180V, and 190V were selected for two sets of parallel experiments. Depending on the different ways the catalyst and reaction apparatus are connected, there are two forms of catalytic synergistic treatment of n-hexane gas. One involves parallel placement with the plasma device (PPC), where the TiO2 catalyst is placed at the rear end of the plasma reaction area, where the n-hexane gas first passes through the plasma reaction discharge area for the initial treatment, followed by the cracked small molecules reacting with the TiO2 catalyst. The other involves series placement with the plasma device (IPC), where the TiO2 catalyst is placed in the plasma reaction discharge area, where the plasma acts on the catalyst, and both work together to degrade the n-hexane gas. A comparison in Figure 5 clearly shows that the IPC placement method is more effective for treating n-hexane gas compared to the PPC method. In the figure, it can be observed that in the PPC mode, the degradation efficiency of n-hexane only reaches a maximum of 51%, lower than the IPC mode (with a maximum degradation rate of 83.2%). This could be due to the energy released by high-energy electrons during low-temperature plasma
treatment dispersing the TiO₂ catalyst powder more evenly within the DBD reactor, where the powder mixes more uniformly with the n-hexane gas. Additionally, the low-temperature plasma emits ultraviolet light when high-energy electrons are released, potentially exciting the photocatalytic properties of TiO₂ for the degradation of n-hexane. In the PPC mode, since the catalyst is deposited at the bottom of the DBD reactor, the contact area between n-hexane gas molecules and the catalyst is small, and the photocatalytic effect of the TiO₂ catalyst is not activated, resulting in n-hexane mostly being decomposed by high-energy electrons with minimal catalytic synergy.

4 Conclusion

This article utilises DBD technology to treat VOCs, using n-hexane as a model. By analysing the influencing factors of n-hexane gas treatment, the optimal degradation conditions were determined. Finally, experiments were conducted to synergistically treat n-hexane gas using various catalysts and low-temperature plasma technology. From these experiments, the following conclusions can be drawn:

Under pure nitrogen gas, the products of n-hexane decomposition mainly consist of low-chain hydrocarbons ranging from C₁ to C₄ and hydrogen. With lower gas flow rates, n-hexane spends more time in the plasma discharge zone, leading to a more thorough conversion of n-hexane. As the voltage increases, the high-energy electrons in the plasma discharge zone increase, enhancing collisions between active groups and the plasma, thereby improving the efficiency of treating volatile organic compound gases. Parallel experiments on four catalysts revealed that molecular sieve catalysts exhibit the highest efficiency in treating volatile organic compound gases, reaching up to 73.2%.

Acknowledgments

This work was financially supported by the Natural Science Foundation of China (NSFC, No. 22109126) and Shaanxi Province Key Point Research and Development Project (2022GY-378) and Key Laboratory of Coal Resources Exploration and Comprehensive Utilization, Ministry of Land Resources (KF2021-12).

Reference