

Detection and treatment of VOCs in the food industry

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ABSTRACT

Volatile organic compounds (VOCs) are common pollutants in the atmosphere, which will do some harm to the environment and the human body. At present, the detection and treatment of VOCs are mainly concentrated in chemical, petroleum, pharmaceutical, household and other industries, but few scholars have studied the management of VOCs emitted by food industry. According to the characteristics of VOCs emitted from food industry, this article summarizes the research progress of relevant detection methods (gas chromatography, gas chromatography-mass spectrometry, gas chromatography-ion mobility spectrometry, electronic nose technology) for VOCs emitted from food industry in recent years, focusing on the research progress, advantages, and disadvantages of destruction technology (combustion method, low temperature plasma technology, biological method), treatment and recovery technology (adsorption method, absorption method, condensation method, membrane separation method) and combination technology for VOCs emitted from food industry. Based on the understanding of various governance technologies and the relevant policy requirements of VOCs governance, the future research trends in this field are prospected.

KEYWORDS

Food industry; Volatile organic compounds; Detection technology; Treatment technology

1. INTRODUCTION

VOCs are the abbreviation for volatile organic compounds, which is an important gaseous pollutant. There are many definitions of VOCs. The World Health Organization (WHO) defines VOCs as organic compounds with boiling point between 50 and 260 °C and saturated vapor pressure greater than 133.32 Pa in the air at normal temperature and pressure, or any organic solid or liquid that can volatilize at normal temperature and pressure [1]. VOCs are a kind of important gaseous pollutants, which will do harm to the environment and human health. In terms of environment, VOCs are the main precursors of ozone formation and the main components of photochemical smog, and will react with free radicals in the atmosphere to form secondary aerosols. In terms of human health, VOCs in the air will enter the human body through breathing, skin absorption and other ways, causing damage to human respiratory tract and digestive tract, endangering human health, and most VOCs have strong toxicity, teratogenicity and carcinogenicity [2] [3].

VOCs come from a wide range of sources, and the emission characteristics, emission substances and treatment and detection methods of VOCs in different industries are different. Food manufacturing industry is one of the important sources of VOCs, and its VOCs components are quite different from those produced in chemical and pharmaceutical industries. Typical odor substances in food enterprises mainly include aldehydes, ketones, alcohols, acids, esters, etc [4], which are not exactly the same as volatile organic compounds (VOCs) such as benzene series, halogenated hydrocarbons, chlorobenzene, etc. monitored in the current environmental standard method [5]. Volatile organic

compounds in food manufacturing are mainly produced by fermentation and cooking or heat treatment. In the fermentation process, including the production of dairy products, alcoholic beverages and baked goods, VOCs are produced by microorganisms through enzymes and chemical reactions, mainly from amino acids. VOCs produced during heat treatment are produced by Maillard reaction caramelization of sugars degradation of amino acids and oxidation and degradation of lipids. Volatile organic compounds in food production have three main characteristics. First, the components are more complex, and the main components of VOCs produced by different food processing enterprises are different. Odor substances mainly include aldehydes, ketones, alcohols, acids, esters, etc., which include not only odor emissions and organic by-products of fermentation, but also a large number of recyclable aroma substances, as well as impurities such as oils and dust. Second, the temperature of waste gas produced by food industry is generally high, which can be as high as 420°C. Even after waste heat recovery, the temperature is still as high as 90 C. High temperature limits many treatment methods, such as the temperature required by activated carbon adsorption is not higher than 45°C, and the temperature required by biological method is not higher than 40°C. Third, its water vapor content is relatively large, which limits some treatment methods. For example, the adsorption method is adopted, and supersaturated water vapor is enriched on the surface of activated carbon and porous catalyst, which hinders the contact between waste gas components and activated carbon, resulting in the decrease of adsorption efficiency of activated carbon [6] [7] [8].

The main components of VOCs produced by different food processing enterprises are different, so their treatment methods will be different. It is necessary to choose the appropriate treatment methods according to the main components and contents of VOCs emitted by them. Therefore, before treating VOCs emitted from food production, it is necessary to detect the components and contents contained in them. This paper mainly introduces the main detection technology and treatment technology of VOCs in food industry at present.

2. VOCS DETECTION TECHNOLOGY IN FOOD INDUSTRY

2.1. Gas Chromatography

Gas Chromatography (GC) is an effective gas-gas separation technology based on liquid-liquid separation chromatography, which is widely used in the qualitative and quantitative analysis of multi-component mixed volatile organic compounds. The principle of gas chromatography is: gas is used as mobile phase, that is, carrier gas, sample vapor passes through chromatographic columns filled with different fillers along with the carrier gas, and each component in the sample flows out of the chromatographic column at different characteristic times due to different flow rates in the chromatographic column, then enters the detector, and generates corresponding signals through physical or chemical processes [9]. Gas chromatography has many advantages, such as high sensitivity, high efficiency, high selectivity, fast analysis speed and fast application range, but it can not separate substances with similar or close components in complex component samples well.

Method 8131 of EPA uses gas chromatography to analyze aniline and its derivatives, which is suitable for the determination of 19 aniline compounds in environmental samples [10]. Jian et al [11]. Sampled by silica gel adsorption tube, and determined six aniline compounds in ambient air by capillary column gas chromatography. The recovery rate was 98.8%~104%, and the relative standard deviation of the determination results was 1.3%~1.8%(n=6).

2.2. Gas Chromatography-Mass Spectrometry

Gas chromatography-mass spectrometry, also known as gas chromatography-mass spectrometry, is an analysis and detection technology combining gas chromatography and mass spectrometry, in which gas chromatography plays the role of sample injection and separation, while mass spectrometry plays the role of detector [12].The combination of gas chromatography and mass spectrometry can

not only give full play to their respective advantages, but also make up for their respective shortcomings. It has both the efficient separation function of color spectrum and the sensitive identification function of mass spectrometry. Therefore, GC-MS technology has the advantages of high sensitivity, high accuracy, high selectivity, high efficiency and wide application range [13]. GC-MS is the most important analytical technology in VOCs detection in food processing industry because of its long development time and mature technology.

2.3. Gas Chromatography-Ion Mobility Spectrometry Technique

Gas-Ion Mobility Spectrometry (GC-IMS) is a new detection technology in recent years, which has the advantages of high separation efficiency of GC and fast response speed of IMS [14] [15]. Gas phase-ion mobility spectrometry has the advantages of high sensitivity and fast response speed, and effectively improves the detection sensitivity of volatile organic compounds. Compared with GC-MS, gas phase-ion mobility spectrometry has the advantages of simple and portable device and no complicated pretreatment of samples. Therefore, gas phase-ion mobility spectrometry technology has been widely used in the analysis and detection of atmospheric VOCs pollutants, environmental monitoring, food odor determination and other fields [16]. Hu et al [17] Used GC-IMS to measure the changes of volatile components during the processing of ready-to-eat dried shrimp. The results showed that the volatile components of dried shrimp were quite different in different processing stages, and the volatile substances in fresh shrimp were less; After boiling, the types and contents of volatile compounds increased obviously. With the drying, the contents of volatile components in dried shrimp increased obviously, including 2-butanone, ethyl propionate and pyrazines.

2.4. Electronic Nose Technology

Electronic nose is an electronic system that can obtain response images through gas sensors, so as to identify gas components [18]. Electronic nose technology has the advantages of good sample detection, fast analysis speed, short detection time, wide detection range, less sample consumption, no pretreatment, etc. It can detect various gases with good repeatability and can be used for field detection, so it is widely used in many fields and plays an important role in the detection of VOCs and their composite gases. In the food industry, electronic nose is widely used [19], such as freshness detection, storage time prediction and judgment, food flavor evaluation and so on. Huang et al [20] Used electronic nose technology to study the components and contents of volatile organic compounds in cooking fume. The results showed that the concentrations of aromatic hydrocarbons, aldehydes and ketones with pungent odor, oil fume and odor in cooking fume were low.

3. CURRENT SITUATION OF VOCs TREATMENT IN FOOD INDUSTRY

At present, the treatment methods of VOCs emitted by food industry can be divided into two categories: destruction technology and recovery technology. Destruction technology is to convert VOCs into non-toxic and harmless small molecular substances such as CO₂ and H₂O by chemical or biochemical actions, including biological oxidation, biological oxidation, low-temperature plasma treatment, high-temperature plasma incineration and other technologies; The recovery technology uses physical methods to enrich and separate VOCs, and realize its resource recycling, including absorption, adsorption, condensation technology and membrane separation technology.

3.1. Destruction Technology

3.1.1. Combustion method

At present, the food industry uses combustion method to treat VOCs with complex components and high concentration. Combustion method uses the flammable characteristics of most VOCs and

decomposes VOCs into inorganic small molecules such as CO₂ and H₂O at high temperature. Combustion methods include direct combustion, regenerative combustion and catalytic combustion.

Direct combustion method is to use waste VOCs as fuel for direct combustion, which is suitable for the treatment of VOCs with high concentration and no recovery value [21]. The direct combustion method is simple to operate, and there is no requirement for the components of VOCs to be treated. However, the direct combustion method has great potential safety hazards and high energy consumption, so it is rarely used in the food industry.

3.1.2. Catalytic combustion

Catalytic combustion technology uses the action of catalyst to reduce the reaction temperature and increase the reaction rate, so that VOCs can burn flameless at the low temperature of 200~400°C, and oxidize and decompose into small inorganic molecules such as CO₂ and H₂O. The key of catalytic combustion technology lies in the selection of catalysts. At present, noble metal catalysts have the best catalytic oxidation effect, such as Pt, Pd and Au, which have the advantages of low light-off temperature, high heat resistance temperature, high activity, high selectivity and high catalytic efficiency [22]. They are one of the most widely used catalysts in food industry when treating VOCs by catalytic combustion. However, precious metals are expensive, which greatly limits their wide application in industry. Therefore, in order to reduce the cost of catalyst, looking for its substitutes has become a research hotspot at present. It has been found that composite metal oxide catalysts and perovskite oxide composites have the advantages of many kinds, high catalytic activity and low price, and have good catalytic activity for VOCs catalytic combustion. Yang et al [23] found that using new kaolin sodium zeolite crystal (KL-NY) as carrier and adding CeO₂ to modify manganese oxidant can contribute to the catalytic combustion of VOCs, and can completely oxidize benzene with low concentration at 260°C. Deng et al [24] Found that coating modification of NiMnO₃/cordierite perovskite catalyst with Ce_{0.75}Zr_{0.25}O₂ can contribute to the catalytic combustion of VOCs, and the benzene conversion rate can reach 95.7% at 275°C.

3.1.3. Cryogenic plasma technology

Low temperature plasma technology uses corona discharge, dielectric barrier discharge and frequency emission discharge to convert gas into plasma. Plasma is an active particle such as atoms, ions, electrons and free radicals, which interacts with VOCs molecules to cause VOCs to undergo physical and chemical reactions such as ionization, dissociation, excitation, redox, and then be decomposed into CO₂ and H₂O, thus realizing the purpose of complete degradation of VOCs. Low-temperature plasma technology can effectively remove ammonia, hydrogen sulfide, methyl sulfide, trimethylamine, styrene carbon disulfide and other substances in VOCs, and can quickly decompose toxic substances such as alcohols, phenols, amines, and fatty acids [25]. Low-temperature plasma technology has become a common treatment method for VOCs in food industry because it can produce high-activity low-temperature plasma and high treatment efficiency. However, it has high energy consumption and harsh conditions for uniform low-temperature plasma generation, so low-temperature plasma technology is mainly suitable for treating low-concentration VOCs.

At present, scholars at home and abroad mostly based on corona discharge and dielectric barrier discharge, combined with adsorption method or catalyst to explore the influence of discharge mode, initial concentration of VOCs, exhaust gas flow rate and other factors on VOCs waste gas treatment effect. For example, Sun et al [26] used dielectric barrier discharge combined with MOF material adsorption to treat benzene-containing waste gas. When benzene concentration is lower than 500 mg/m³, the removal rate is over 98%, and the removal rate is positively correlated with discharge frequency and residence time.

3.1.4. Biological treatment technology

Biological treatment technologies are mainly divided into biological filtration, biological trickling filtration and biological washing, and the general situation is shown in Table 4. This method is mostly

used for the treatment of low concentration VOCs waste gas and malodor, and the treatment process will be affected by bacteria, VOCs waste gas composition, reactor process conditions and fillers used. Fu et al [27] found that the purification rate of total volatile organic compounds (TVOC) containing dichloromethane reached over 90% when the biofilter pressure was reduced to 0.45 kPa/m. Su et al [28] found that adding surfactant rhamnolipid into the biological trickling filter tower can enrich the dominant bacteria, and the removal rate of ethylbenzene reaches 92%. However, it is difficult for the cultured strains to degrade volatile organic compounds with complex and strong chemical stability at present, so it is necessary to cultivate and screen out highly adaptable strains with high decomposition ability and short culture period.

3.2. Recovery Technology

3.2.1. Adsorption

Adsorption technology is to use a variety of porous solid adsorbents to treat VOCs. This kind of adsorbent has a large specific surface area, which can adsorb VOCs gas molecules and retain them in a porous structure, and then desorb the adsorbate, so as to achieve the purpose of recovering VOCs. In addition to the type, concentration, operating temperature and pressure of VOCs, the adsorption effect mainly depends on the type of adsorbent [29]. Adsorbents for VOCs adsorption need to have stable chemical properties, easy regeneration, fast adsorption rate, and high adsorption capacity. Common adsorbents include carbon-based adsorbents (such as activated carbon, graphene), oxygen-containing adsorbents (silica gel, zeolite, metal oxide), polymer-based adsorbents (polymer adsorption resin). Among them, activated carbon is the most commonly used adsorption material. Activated carbon has a relatively rich microporous structure and a large specific surface area. It has a good adsorption effect on VOCs of different molecular sizes. It has absorption effects on aliphatic hydrocarbons, aromatic hydrocarbons, halogenated hydrocarbons, aldehydes, alcohols, ketones, esters, etc, and has high adsorption efficiency and fast desorption rate [30]. However, activated carbon has poor adsorption for polar substances such as water; When it is used for the adsorption of high concentration VOCs, it is difficult to regenerate and easy to deactivate, and the failed adsorbent will also cause a certain degree of environmental pollution [31].

3.2.2 Absorption

Absorption method is mainly based on the principle of similar dissolution of organic compounds, using organic solvents with high boiling point, low vapor pressure, low volatilization or non-volatilization as absorbents, making use of the different solubility of VOCs in absorbents to transfer VOCs from gas phase to liquid phase, and then desorbing the absorption liquid to recover VOCs and regenerate the solvent. The most common absorption devices are falling film, bubble column, stirred tank, static mixer, plate column, packed column and spray column [32]. For VOCs absorption, packed column and spray column are mainly used. Absorption technology has the advantages of high removal efficiency, wide detection concentration, treatment of VOCs waste gas with large flow rate, relatively simple equipment requirements and low operation cost. However, due to the low concentration of VOCs in the airflow, they may have high operating costs and require a large amount of absorption liquid. In addition, the removal efficiency of the absorbent mainly depends on the selected absorption liquid [33].

The absorption liquid not only needs good absorption rate and capacity, but also must be generally considered safe and can be used in food. The common absorbents in the absorption and recovery of VOCs mainly include oil-based absorbents, water composite absorbents, high boiling point organic solvents, etc. The application range of different absorbents will be different. Therefore, it is usually necessary to investigate each kind of waste gas to be treated before selecting the best absorption liquid. Zhang et al [34] compounded water and ionic liquid as absorbents according to a certain proportion to absorb toluene and acetone. It is found that under certain intake air concentration and absorption

conditions, the initial absorption rates of 100 g compound absorbents with 10% ionic liquid mass fraction for toluene and acetone reach 94% and 95%, respectively.

3.2.3. Condensation

Condensation recovery technology is a method to recover VOCs by changing the temperature or pressure of the system to transform gaseous volatile organic compounds into droplets and then separate them. Condensation recovery technology is more suitable for VOCs with high boiling point, high concentration and need to be recovered [35], and can usually be used as an auxiliary means such as adsorption technology or catalytic combustion technology.

The traditional condensation process mostly adopts cascade refrigeration technology, and there are some unsatisfactory places. First of all, a large amount of additional electric energy is needed. Secondly, the refrigerant in the closed-circuit cycle is insufficient in terms of safety, while the refrigerant supply in the open-circuit cycle and the reuse of vaporized gas are limited. Moreover, the treated gas still contains a certain amount of VOCs when discharged into the atmosphere [36]. In order to solve the limiting factors of traditional condensation technology and realize the effective recovery of VOCs, some scholars have begun to study new condensation technology.

The use of liquid nitrogen (-196°C) or liquefied natural gas (-163°C) is another way to achieve lower temperatures, and the condensation target can be achieved economically by using liquid nitrogen. The mixed organic components in waste gas can be deeply condensed, and the recovery rate is as high as 99.8%. Xu et al [37]. analyzed and studied the process and device of a VOCs recovery system with three-stage liquid nitrogen condensation, and proposed to use helium as refrigerant in a multi-stage helium expansion refrigeration system to obtain high-purity liquid hydrogen. Therefore, considering the condensation performance of LPG and the cost of medium, the turbo-expansion refrigeration cycle with nitrogen as refrigeration medium has good performance, which can make up for the shortcomings of cascade refrigeration cycle such as insufficient refrigeration temperature and complex structure.

3.2.4. Membrane technology

Membrane separation technology makes use of the different ability of different gas molecules to permeate the membrane, so that different gas components can be enriched and separated on both sides of the membrane. In the separation process, compounds that are more conducive to permeation of the membrane can be separated from the gas mixture, and the specific migration gradient of each compound on both sides of the dense membrane also ensures the separation [38]. Membrane separation method is generally used for the treatment of VOCs with medium and high concentration, low flow rate and low temperature. Membrane separation and recovery technology has rapidly developed into an effective measure for VOCs recovery in petrochemical, pharmaceutical, food processing and other industries due to its high efficiency, no secondary pollution and high recovery efficiency.

Membrane separation processes commonly used in the treatment of organic waste gas include: vapor permeation (VP), gas/vapor membrane separation (GMS/VMP) and membrane contactor [39]. Li et al [40] discussed the research progress of vapor permeation, gas membrane separation and membrane-based absorption for the removal and recovery of volatile organic compounds in waste gas. The results show that the relative diffusion coefficient and relative solubility of the compound in the membrane material determine the separation efficiency of the membrane. Since most VOCs encountered in the food industry have a wide range of molecular sizes and various chemical categories, it is a very meaningful problem to select the appropriate membrane technology to recover VOCs.

3.3. Combination Technology

Because the components of VOCs in food industry are complex, and the types, concentrations and properties of VOCs in different food industries are different, and the single treatment technology has

certain limitations [41], in order to improve the purification efficiency and recovery rate of VOCs, two or more treatment methods are often combined to make full use of the advantages of different treatment technologies, so as to achieve effective treatment of various waste gases, meet the treatment requirements of VOCs emission or achieve economic benefits.

To select the corresponding combined treatment technology according to the actual emission of VOCs in enterprises, it is necessary to comprehensively consider VOCs concentration, exhaust gas emission flow, operating cost, etc., and flexibly select according to process characteristics, so as to meet the treatment requirements and minimize the treatment cost. For example, for high-concentration VOCs, absorption or condensation are generally used to recover them first, and then plasma technology or catalytic combustion technology is used to remove low-concentration VOCs. At present, there are many research process combinations: condensation+adsorption recovery process, catalytic combustion + absorption treatment technology, plasma synergistic catalysis technology and so on.

4. CONCLUSION

The composition of cooking fumes is complex, and there are many influencing factors, and the toxic and carcinogenic substances seriously endanger the health and safety of the human body. On the detection of VOCs in the catering industry, gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS), high performance liquid chromatography (HPLC), and electronic nose technology have been applied. Among them, gas chromatography-mass spectrometry (GC-MS) has the most practical application and the most mature technology. At the same time, in order to meet the needs of rapid determination of VOCs on site, more and more portable VOCs rapid analysis instruments have begun to appear. These on-site rapid detection methods for VOCs determination can not only enrich the detection of volatile organic compounds in the environment, but also provide important significance for the prevention and control of VOCs.

With the development of food industry, the types of VOCs emitted by food industry are becoming more and more complex and diverse, and their chemical properties are quite different. Facing the increasingly strict emission requirements, the subsequent advanced treatment is particularly important. At present, all kinds of treatment methods have been applied, but due to the complexity of VOCs components emitted by food industry, two or three treatment processes are generally needed to achieve ideal treatment effect. For the waste gas with high VOCs concentration, condensation method and adsorption method are generally used to treat it first, and then the combined removal process is used for advanced treatment to reduce the emission concentration. In the actual process of VOCs organic waste gas treatment, related enterprises need to apply more scientific and reasonable treatment technology from the actual situation, and improve the economy and practicability of waste gas treatment on the basis of ensuring the waste gas treatment effect. Because the composition of VOCs has strong complexity, repeated and single application of the same treatment technology often fails to achieve the expected treatment effect, and will also consume more economic costs. In view of this situation, it is necessary to make accurate judgment, carry out in-depth analysis and research, and strengthen the comprehensive application of treatment technology, so as to further improve the level of VOCs organic waste gas treatment.

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