Evaluation of Decomposition Performance of Asphalt Odor Components by Direct Combustion and Catalytic Combustion

AUTHOR

Hideto HORAI*1

ABSTRACT

In road pavement construction, recycled asphalt mixtures account for approximately 70% of all asphalt mixtures used. These recycled mixtures are produced by manufacturing reclaimed aggregates from asphalt concrete waste generated during the rehabilitation of aged pavements and incorporating them at a specified proportion into new asphalt mixtures. During the drying and heating process of reclaimed aggregates, volatile organic compounds (VOCs) derived from asphalt are generated, causing offensive odors. These VOCs consist mainly of a wide variety of hydrocarbons, and it is impractical to identify all the components responsible for the odors and implement individual countermeasures for each of them. Therefore, combustion-based deodorization methods, which can reliably decompose these odor-causing components into odorless products, are effective for asphalt plants. Combustion deodorization methods currently in practical use are mainly classified into direct thermal oxidation and catalytic oxidation. These systems achieve deodorization efficiencies exceeding 95% by decomposing odor-causing components into carbon dioxide and water in a high-temperature oxygen-rich atmosphere.

This study examines the operating conditions, including temperature and residence time, required to economically and efficiently oxidize and decompose asphalt-derived VOCs, which are the primary odor-causing components, into odorless products using direct thermal oxidation and catalytic oxidation methods. The results indicate that, in order to achieve an outlet odor concentration of 1,000 or less and a deodorization efficiency of 95% or higher, a temperature of at least 800°C is required for the direct thermal oxidation method. For the catalytic oxidation method, the required temperatures are 250°C at a space velocity (SV) of 10,000, 300°C at SV = 20,000, and 350°C at SV = 30,000.

Keywords: asphalt plant; recycling; blue smoke; VOCs; offensive odor; deodorization

1. Introduction

An asphalt plant (hereinafter referred to as "AP") is construction equipment used to produce asphalt mixtures for road pavement materials (hereinafter referred to as "asphalt mixtures"). From the AP, volatile organic compounds (VOCs), which are asphalt-derived odor-causing substances, are generated in the form of blue smoke and sticky mist, and these emissions constitute a major source of offensive odors1).

Asphalt concrete waste generated during the replacement of deteriorated road pavements (hereinafter referred to as "asphalt concrete debris") is designated as a specified construction material under the Construction Recycling Act (Act on the Recycling of Construction Materials), which aims to promote the effective use of resources and reduce waste generation. Asphalt concrete debris produced from demolition work that meets certain scale requirements is legally required to undergo appropriate treatment and active recycling. In current practice, asphalt concrete debris is crushed and graded to produce reclaimed aggregates (hereinafter referred to as "R aggregates"). These reclaimed aggregates are dried and heated and then incorporated at a specified proportion into asphalt mixtures for reuse. Asphalt mixtures produced using reclaimed aggregates are referred to as recycled asphalt mixtures (hereinafter referred to as "R mixtures"), and they currently account for approximately 70% of the asphalt mixtures produced for road pavement.

In particular, during the drying and heating process in which R aggregates are heated to approximately 160°C, asphalt-derived VOCs are generated in the form of blue smoke and sticky mist from the recycling dryer (hereinafter referred to as the "R dryer") responsible for this process, thereby becoming a source of offensive odors. The R aggregates contain approximately 5% asphalt by mass and are coated with an asphalt film on their surfaces. When the R aggregates are heated through contact with hot air in the R dryer, the vapor pressure of the asphalt increases, which is considered to promote the generation of VOCs. These VOCs are discharged from the stack together with the exhaust gas from the R dryer. As the exhaust gas disperses into the atmosphere and its temperature decreases, the VOCs tend to descend toward ground level. Consequently, depending on seasonal variations, wind direction, and the siting conditions of the asphalt plant, complaints regarding offensive odors may be raised by nearby residents.

Appropriate countermeasures against such odor complaints are required in accordance with the provisions of the Offensive Odor Control Act2)3). Under this Act, regulatory limits for odors are established for each area designated by local governments4)5). As an initial measure against the offensive odors from asphalt plants, increasing the stack height to promote the dispersion of exhaust gases is an effective approach for reducing ground-level odor concentrations. In addition, lowering the heating temperature of R aggregates, within a range that does not adversely affect mixture quality or workability, is also an effective means for reducing the generation of VOCs. If the situation does not improve even after implementing these odor control measures, it becomes necessary to consider the introduction of a full-scale deodorization system6).

Effective deodorization technologies currently used in practice7) include adsorption methods8), in which odor-causing components are removed by adsorption using activated carbon or similar materials; chemical scrubbing methods9), in which odor-causing components are removed and decomposed using chemical solutions; and combustion methods10), in which odor-causing components are heated and oxidatively decomposed at high temperatures. Regardless of the deodorization method adopted, it is important to identify the odor-causing components and their characteristics and to examine a system capable of achieving deodorization in the most efficient and cost-effective manner.

As previously mentioned, the odor-causing components emitted from asphalt plants consist of a wide variety of asphalt-derived volatile organic compounds (VOCs). Under high-temperature, oxygen-rich conditions, oxidation reactions proceed rapidly, resulting in the formation and increase of organic compounds bearing odor-causing functional groups such as carboxyl (–COOH), aldehyde (–CHO), and ketone (–C(=O)–) groups. Consequently, it is impractical to identify all the odor-causing components contained in the exhaust gas. Focusing on the fact that these compounds are primarily composed of hydrogen, oxygen, and carbon, high-temperature oxidation can decompose them into odorless products, namely water and carbon dioxide, which may provide a rational approach to deodorization.

These considerations provide the basis for the increasing number of applications of combustion-based deodorization methods to APs, as such methods can reliably oxidize and decompose odor-causing components into odorless products.

Combustion-based deodorization methods currently in practical use include direct thermal oxidation and catalytic oxidation11). In these methods, odor-causing components are completely oxidized in an oxygen-rich atmosphere, thereby decomposing them into odorless products and achieving deodorization efficiencies (odor removal rates) exceeding 95%. The catalytic oxidation method10) enables deodorization at lower temperatures than direct thermal oxidation by utilizing catalysts such as platinum. Regenerative thermal oxidation systems recover heat using heat-storage media and are generally classified as a form of direct thermal oxidation.

In this study, given that it is impractical to identify all of the numerous VOCs generated from the asphalt film on heated R aggregates, the focus is placed on direct thermal oxidation and catalytic oxidation. The operating conditions required to oxidatively decompose VOCs into odorless products in an efficient and cost-effective manner are investigated. Furthermore, based on a review of previous studies, the generation mechanisms of VOCs (odor-causing components) released from heated asphalt are summarized, and the deodorization mechanisms are examined together with new findings.

---

*1 Ph.D. (Engineering), Executive Officer, Technical Headquarters, NIKKO Co., Ltd.

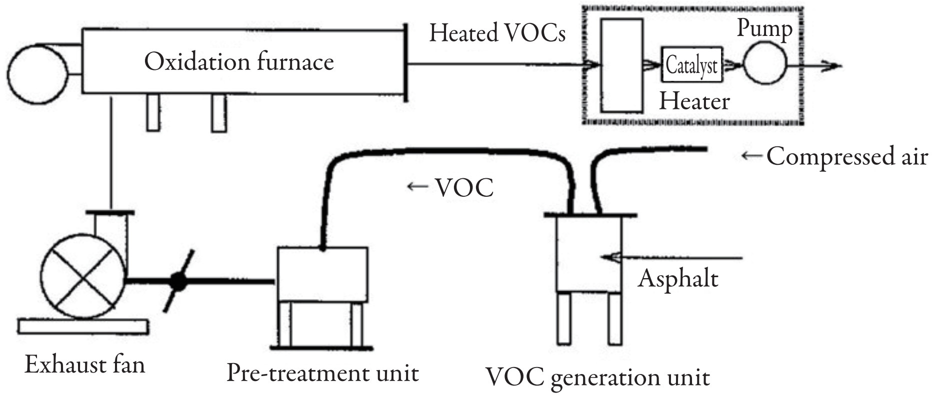

Figure 1: Overall flow diagram of the VOC deodorization experimental system

2. Experimental Methods

Asphalt plants (hereinafter referred to as "AP") are frequently operated in an intermittent manner. In such AP operations, operating conditions change continuously over time. As a result, exhaust gas flow rate, temperature, oxygen concentration, and water vapor content fluctuate, which is considered to have a significant influence on odor concentration and odor-causing components. In the present study, rather than using emissions from an actual AP, which include numerous external disturbance factors, simulated asphalt-derived VOCs (odor-causing components) were continuously and stably generated in order to eliminate these disturbances and to evaluate the intrinsic deodorization performance. Using these simulated VOCs, operating conditions for deodorization by direct thermal oxidation and catalytic oxidation were investigated.

In the following sections, an overview of the experimental apparatus is first presented, followed by a detailed description of the experimental procedures.

2.1 Experimental Apparatus

The experimental apparatus shown in **Figure 1** and **Photo 1** was used to investigate the operating conditions required for deodorization by direct thermal oxidation and catalytic oxidation. As shown in the figure and photograph, the cylindrical vessel installed at the front right side of the photograph serves as the generation unit of VOCs (odor-causing components). The generated VOCs are first passed through a pretreatment unit installed at the front left side of the photograph, where sticky mist components are removed. The VOCs are then drawn by an exhaust fan installed at the rear left side of the photograph and subsequently introduced into the oxidation furnace located at the rear right side. For direct thermal oxidation, gas samples corresponding to each deodorization condition were collected at the outlet of the oxidation furnace. For catalytic oxidation, the VOC stream whose temperature was preliminarily adjusted in the oxidation furnace was further heated to the target temperature using an electric heater, as shown in the figure, and then introduced into the catalyst.

Photo 1: Overall view of the VOC deodorization experimental apparatus

The following sections describe in detail the characteristics and specifications of the equipment used in the present study.

2.1.1 VOC (Odor-Causing Component) Generation Unit

The VOC (odor-causing component) generation unit shown in **Photo 2** was designed to continuously and stably generate asphalt-derived VOCs. Inside the R dryer of an AP, VOCs are considered to volatilize from the asphalt film as R aggregates are heated through contact with hot air. However, if the R aggregates are heated batchwise in this experiment, it can readily be assumed that the composition of VOCs generated from the asphalt film, accounting for less than about 5% by mass, would vary significantly over time. Therefore, in order to generate stable VOCs from asphalt, compressed air was directly injected into a sufficient quantity of straight asphalt heated to 300°C, thereby generating VOCs[12]. Furthermore, by varying the flow rate of the injected air, the concentration of the generated VOCs was freely controlled.

The main specifications of the VOC generation unit are listed below.

- Asphalt filling capacity: 36 L
- Asphalt type: 80–100 penetration grade straight asphalt
- Heating method: electricity and propane gas
- Operating temperature: 250–300°C
- Air injection rate: 1–5 L/min

The VOC generation unit is heated in a batch manner. Accordingly, it can be expected that the residual asphalt components and the generated VOCs may gradually polymerize over time. However, the amount of VOCs generated is extremely small compared with the sufficient quantity of asphalt charged in the unit, and the generation of VOCs is predominantly governed by the oxidative decomposition of asphalt caused by the injected air. Therefore, the influence on the VOC composition is considered to be limited during short-term operation. In particular, in order to maintain the stability of the generated VOC composition, it was assumed that the asphalt used in the experiment would be periodically replaced according to the duration of VOC generation.

2.1.2 Direct Thermal Oxidation furnace

The direct thermal oxidation furnace shown in **Photo 3** is a horizontally oriented cylindrical furnace whose inner wall is lined with 100-mm-thick refractory ceramic fiber. The furnace is equipped with a kerosene-fired burner and is designed such that the gas to be treated is introduced from the outer periphery of the flame.

The main specifications of the oxidation furnace are listed below.

- Manufacturer: Sunray Reinetsu Co., Ltd.
- Overall length × inner diameter: 3,000 mm × 600 mm
- Internal volume: 0.85 m^3
- Firing rate: low firing, 11 L/h; high firing, 27 L/h
- Temperature control range: 200–1,000°C
- Fuel: kerosene

Because the burner firing rate can be switched between two stages (low and high firing), the furnace temperature is controlled by adjusting the flow rate of the gas to be treated.

Photo 2: VOCs (odor-causing components) generation apparatus

Photo 3: Direct thermal oxidation furnace

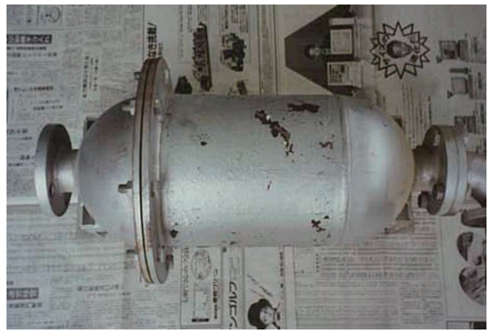

Photo 4: Platinum catalyst reactor

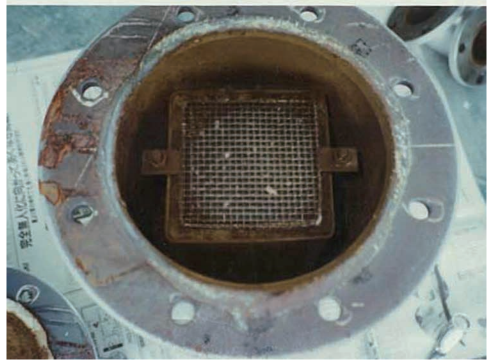

Photo 5: Platinum catalyst support in the reactor

Photo 6: From left: NOx concentration analyzer, recorder, oxygen concentration analyzer, and other instruments

Photo 7: Continuous total hydrocarbon analyzer (FID)

Table 1: Temperature levels for the blank test and VOCs (odor-causing components) deodorization test

Treatment temperature (℃)	800	700	600	500	400

Table 2: Temperature levels for heating the VOC source gas

Heating temperature (℃)	50	300	400	500	600

Table 3: SV values and presence/absence of sampling at each temperature

Temperature / SV value	33,000	30,000	20,000	10,000
400℃	×	◎	×	×
350℃	◎	◎	◎	◎
300℃	×	◎	◎	◎
250℃	×	◎	◎	◎

※ ◎ : With sampling 、× : Without sampling

2.1.3 Catalytic Reactor

The external appearance of the catalytic reactor is shown in **Photo 4**, and the honeycomb structure of the catalyst support is shown in **Photo 5**. The main specifications of the catalytic reactor are listed below.

- Manufacturer: Nippon Shokubai Co., Ltd.
- Model: CH-702 (honeycomb structure)
- Catalyst type: platinum
- Catalyst volume: 188 cm^3
- Operating temperature range:
  250–400°C (sheath heater)
- Space velocity (SV) range:
  10,000–33,500

2.1.4 Other Measurement Instruments

Photo 6 shows the NO$_x$ analyzer, oxygen analyzer, and other related instruments, while **Photo 7** shows the continuous total hydrocarbon analyzer equipped with a flame ionization detector (FID).

With respect to hydrocarbons, quantitative analyses were conducted for both non-methane hydrocarbons containing odor-related functional groups, such as carboxyl groups (–COOH) and ketone groups (–C(=O)–), and methane, which is odorless. Odor concentration analysis, which is sensory evaluation using the triangular odor bag method[13)14)], requires considerable time, labor, and trained panelists. Therefore, deodorization performance was evaluated based on total hydrocarbon concentrations, and sensory tests were conducted within 24 hours for verification.

2.2 Detailed Experimental Procedures

2.2.1 Direct Thermal Oxidation

(a) Blank Test

When the gas to be treated is supplied to the direct thermal oxidation furnace, there is a possibility that the combustion state of the kerosene-fired burner may be affected, potentially resulting in the generation of odor components due to unburned fuel. Therefore, at each treatment temperature level, only clean air was supplied to the furnace, and the odor concentration at the furnace outlet was measured. The temperature levels used in the blank tests are summarized in **Table 1**.

(b) Deodorization of VOCs (odor-causing components)

VOCs at a constant concentration were supplied to the oxidation furnace, and the temperature and residence time were varied. Sensory evaluation was used to determine the relationships between temperature and deodorization efficiency and between residence time and deodorization efficiency based on the inlet and outlet odor concentrations. The temperature levels used for VOC deodorization were the same as those employed in the blank tests, as shown in **Table 1**.

(c) Heating of VOCs (odor-causing components)

The temperature of the VOCs supplied from the VOC generation unit was approximately 50°C. The VOCs were heated to the temperature levels shown in **Table 2** to examine how the odor concentration changes with temperature. In an oxygen atmosphere, it is expected that, as the temperature increases, odor-related functional groups such as carboxyl groups (–COOH) and ketone groups (–C(=O)–) increase in the VOCs, resulting in an increase in odor concentration.

2.2.2 Catalytic Oxidation

(a) Deodorization of VOCs (odor-causing components)

VOCs at a constant concentration were supplied to the catalyst, and the reaction temperature was varied using a preheater. The odor concentrations at the catalyst inlet and outlet were measured. The relationships between temperature and deodorization efficiency and between space velocity (SV) and deodorization efficiency were then examined.

The temperature levels and SV values employed in the catalytic deodorization tests are summarized in **Table 3**. The space velocity (SV) is defined as follows:

SV = gas flow rate (m^3/h) / catalyst volume (m^3).

(b) Evaluation of Deodorization Performance Based on Hydrocarbon Concentration

In parallel with the VOC deodorization tests, total hydrocarbon (THC) concentrations at the catalyst inlet and outlet were quantified by gas chromatography. The relationships between temperature and removal rate and between SV and removal rate were then examined. In addition, THC concentrations were evaluated using a flame ionization detector (FID).

3. Experimental Results and Discussion

3.1 Mechanism of Asphalt-Derived VOC Generation

This section discusses the mechanisms of VOC (odor-causing component) generation occurring during the drying and heating process of R aggregates in the R dryer of an AP, as well as the mechanisms of VOC generation when air is injected into asphalt using the VOC generation unit developed in the present study.

Asphalt is the residue remaining after crude oil is refined and distilled to extract petroleum products such as gasoline, kerosene, and heavy oil[15)16)]. It is a mixture of high-molecular-weight hydrocarbons and is broadly classified into asphaltenes, which are insoluble in the solvent n-pentane, and maltenes, which are soluble. The molecular weight of asphaltenes ranges from approximately 500 to 5,000, whereas that of maltenes is relatively lower, typically in the range of 200 to 1,500. Maltenes are further classified into oils and resins. These oils and resins are composed mainly of aliphatic and aromatic hydrocarbons with carbon numbers of approximately C_5–C_{20} and are responsible for the fluidity of asphalt. From these characteristics, asphalt is considered to exhibit a micellar structure in which asphaltenes are dispersed within maltenes. The black color of asphalt is attributed to the absorption of visible light by the high-molecular-weight aromatic structures present in asphaltenes.

VOCs are considered to be generated primarily from maltene components with relatively low molecular weights. As the temperature increases and the vapor pressure of low-molecular-weight hydrocarbons rises, the injection of air into asphalt causes these components to move into air bubbles. Subsequently, hydroxyl radicals (·OH), generated through the catalytic action of trace metals present in asphalt and the effects of elevated temperature, abstract hydrogen atoms from hydrocarbons to form organic radicals (R·). These radicals are considered to react with oxygen in the injected air, leading to chain reactions that produce oxygen-containing functional groups such as carboxyl (–COOH) and aldehyde (–CHO) groups.

Based on these considerations, the mechanism of asphalt-derived odor generation can be summarized as follows:

$$\mathrm{R\cdot + O_2 \rightarrow ROO\cdot} \qquad (1)$$

$$\mathrm{ROO\cdot + RH \rightarrow ROOH + R\cdot} \qquad (2)$$

$$\mathrm{ROOH \rightarrow RO\cdot + \cdot OH} \qquad (3)$$

Equations (1) and (2) indicate that peroxy radicals (ROO·) react with VOCs to form organic hydroperoxides (ROOH) and new radicals, thereby allowing the reaction to proceed as a chain reaction. The ROOH formed subsequently decomposes, as shown in Equation (3), under the influence of heat or metal catalysts to produce alkoxy radicals (RO·) while regenerating ·OH radicals.

The alkoxy radicals (RO·) undergo β-scission[17] to generate low-molecular-weight carbonyl compounds as shown in Equation (4):

$$\mathrm{R{-}CH{-}CH{-}OOH \rightarrow R{-}CHO\ (aldehyde) + R'{-}CO\cdot\ (acyl\ radical)} \qquad (4)$$

Representative compounds associated with aldehyde and ketone formation and odor intensification include formaldehyde (HCHO), acetaldehyde (CH_3CHO), and acetone (CH_3COCH_3). These carbonyl compounds are known to have extremely low odor thresholds (minimum concentrations perceptible by humans) and to produce strong irritating odors even at trace concentrations. In general, chemical reaction rates are known to increase exponentially with increasing temperature. Therefore, the reaction rates within the R dryer are presumed to be significant because the materials are exposed to high-temperature air in the vicinity of the burner flame.

In addition to temperature, oxygen concentration is another factor affecting the reaction. Auto-oxidation reactions are known to proceed readily in atmospheres with oxygen concentrations exceeding approximately 3%. Furthermore, radical initiation reactions are promoted by photoexcitation due to ultraviolet (UV) radiation, and UV radiation emitted from the burner flame may further accelerate these reactions. In addition, the presence of water vapor can act as a source of ·OH radicals, thereby promoting the oxidation reactions.

Through these radical chain reactions, the oxidation process progresses, resulting in the formation of compounds containing highly odorous functional groups such as aldehydes and ketones, which increase the odor intensity of the exhaust gas.

In the following sections, the deodorization performance of direct thermal oxidation and catalytic oxidation methods is examined and discussed.

3.2 Direct Thermal Oxidation

3.2.1 Blank Test

In the direct thermal oxidation process, the oxidation furnace uses kerosene as fuel. Since there is a concern that odor-causing components may be generated during the combustion of the kerosene itself, blank tests were conducted in which only clean air was supplied to the oxidation furnace without introducing VOCs (odor-causing components). The odor concentrations measured at the outlet of the oxidation furnace at each operating temperature are summarized in **Table 4**. At a treatment temperature of 800 °C, the combustion was stable and almost no odor was perceptible at the furnace outlet; therefore, sensory evaluation was omitted under this condition. The combustion characteristics of kerosene depend strongly on the design of the burner and the structure of the oxidation furnace. Nevertheless, the results of the blank tests are considered meaningful for the relative comparison of operating conditions affecting deodorization performance in this experiment.

As shown in the table, the odor concentration resulting from the combustion of kerosene alone remained below 500 across all temperature ranges. In this experiment, the residual odor detected in the exhaust gas was mainly attributed to nitrogen oxides generated during the combustion of kerosene. Since kerosene contains little sulfur, nitrogen oxides are considered to account for the majority of the residual odor in the exhaust gas under complete combustion conditions. Nitrogen oxides include nitric oxide (NO), nitrogen dioxide (NO_2), and nitrous oxide (N_2O), among which nitrogen dioxide is mainly responsible for the irritating odor. These nitrogen oxides, referred to as thermal NOx, are formed by the reaction of nitrogen and oxygen in the combustion air under high-temperature conditions. Because their formation strongly depends on combustion temperature, burners and combustion furnaces must be designed to avoid localized high-temperature regions. Furthermore, exhaust gas recirculation (EGR) is an effective technology for reducing NOx emissions.

Table 4: Blank test (combustion of kerosene)

Processing temperature (℃)	830	610	300	200
Odor concentration (—)	—	230	410	98

Table 5: Oxidation temperature and deodorization efficiency

Oxidation temperature (℃)	800	700	600	500	400
Deodorization efficiency (%)	96.8	—	82.2	—	25.0

Table 6: Heating temperature and odor concentration of VOCs (odor-causing components)

Heating temperature (℃)	170	300	400	500	600
Odor concentration (—)	13,000	17,400	15,600	13,030	9,770

3.2.2 Deodorization of VOCs (odor-causing components)

The direct thermal oxidation furnace used in this experiment employs a fixed two-stage firing system with low- and high-stage firing. Therefore, the temperature was controlled by varying the flow rate of the gas supplied to the oxidation furnace. Accordingly, although a constant amount of VOCs was supplied from the VOC generation unit, the VOCs were diluted with air in order to control the treatment temperature. As a result, the odor concentration at the inlet of the oxidation furnace varied; therefore, deodorization efficiency was evaluated by comparing the odor concentrations at the inlet and outlet of the oxidation furnace.

Table 5 and **Figure 2** show the relationship between oxidation temperature and deodorization efficiency for the direct thermal oxidation furnace used in this experiment. As shown in the figure, deodorization efficiency increased sharply from 25.0% to 82.2% as the oxidation temperature increased from 400°C to 600°C. When the temperature was further increased from 600°C to 800°C, deodorization efficiency gradually increased from 82.2% to 96.8%.

These experimental results indicate that a temperature close to 800°C is required to achieve a deodorization efficiency of 95% or higher for asphalt-derived VOCs.

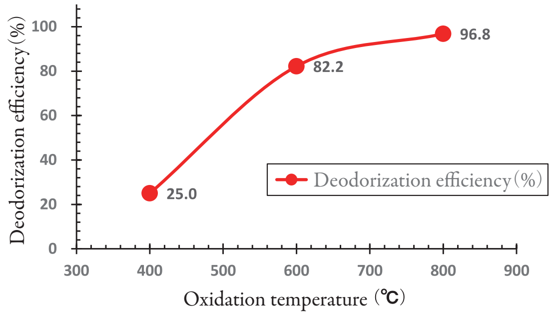

Figure 2: Relationship between oxidation temperature and deodorization efficiency of VOCs (odor-causing components)

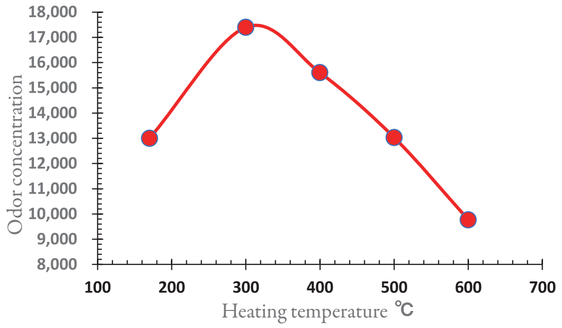

Figure 3: Relationship between heating temperature of VOCs (Odor-causing components) and Odor Concentration

3.2.3 Heating of VOCs (odor-causing components)

While supplying a constant amount of VOCs, the VOCs were heated in the oxidation furnace to examine the relationship between temperature and odor concentration. As described earlier, the burner operates with a fixed two-stage firing system. Accordingly, it was not possible to raise the temperature to each target level while continuously supplying a constant amount of VOCs. Therefore, the furnace temperature was first increased to 800°C, after which the burner was turned off, and test samples were collected as the temperature gradually decreased. The experimental results are shown in **Table 6** and **Figure 3**.

As shown in the table and figure, odor concentration increased sharply with increasing temperature, reached a peak at approximately 300°C, and then gradually decreased as the temperature continued to rise. This behavior supports the VOC generation mechanism discussed earlier, in which oxidation reactions proceed and odor-related functional groups, such as aldehyde groups (–CHO) and carboxyl groups (–COOH), which have extremely low odor thresholds, are formed and increase in concentration. It is assumed that, at higher

Table 7: Results of comparative experiments using direct thermal oxidation

Conditions	Temperature (℃)	O_2 concentration (%)	Air ratio (−)	Dry gas Nm³/min	Wet gas Nm³/min	Residence time (S)	Inlet odor concentration	Outlet odor concentration	Deodorization efficiency (%)
Low firing	200	19.75	16.8	28.5	28.8	1.45	3,090	1,740	43.7
	400	17.50	6.00	10.1	10.3	4.08	4,120	3,090	25.0
High firing	600	14.40	3.18	12.6	13.2	3.27	9,800	1,740	82.2
	800	9.10	1.76	6.9	7.4	5.97	13,000	410	96.8
Blank	200	20.0	21.0	35.7	35.9	1.15	-	98	-
	300	18.75	9.33	37.6	38.2	1.10	-	410	-
	610	14.75	3.36	13.4	13.9	3.09	-	230	-
	830	8.40	1.67	6.5	7.1	6.34	-	-	-
Heating up	600	21.0	∞	2.6	-	16.1	9,770	-	-
	500	↑	↑	↑	-	↑	13,030	-	-
	400	↑	↑	↑	-	↑	7,330	-	-
	300	↑	↑	↑	-	↑	17,400	-	-

temperatures, oxidative decomposition of these compounds becomes dominant, resulting in a decrease in odor concentration. Conversely, these results suggest that VOC oxidation in the temperature range around 300°C leads to the greatest increase in odor-causing components.

3.2.4 Oxidation temperature

As described above, the present experiment indicates that a temperature of at least 800℃ is required to reduce the odor concentration of VOCs to 1,000 or less and to achieve a deodorization efficiency of 95% or higher. According to the literature[18)], most hydrocarbons are decomposed into odorless components at temperatures in the range of 600–800℃. Accordingly, it is considered that, for asphalt-derived VOCs, the formation of odor-causing components through oxidation and their decomposition into odorless products through oxidative decomposition proceed simultaneously. In temperature ranges below approximately 300℃, the formation of odor-causing components is dominant, whereas at temperatures exceeding 300℃, decomposition becomes the dominant process.

VOCs are generated by batch processing in the VOC generation unit. Therefore, it is considered that, with increasing operation time, the volatile components shift from low-boiling to higher-boiling fractions, making oxidative decomposition more difficult. The VOCs generated in actual R dryers include components originating from asphalt exposed to hot air at temperatures of approximately 600℃, and therefore the deodorization conditions are expected to be even more severe.

Furthermore, when the oxidation temperature is reduced below 800℃, the formation of intermediate oxidation products, such as aldehydes (–CHO) and ketones (–C(=O)–), becomes dominant, which may conversely lead to an increase in odor concentration. Therefore, it is inferred that a temperature of at least 800℃ is required to achieve complete deodorization of VOCs.

3.2.5 Residence Time

Table 7 summarizes the measured oxygen concentration, excess air ratio, exhaust gas flow rate, and residence time obtained in the direct thermal oxidation tests. In this experiment, the combustion rate of the oxidation furnace was operated by a fixed two-stage switching system, and the temperature was controlled by adjusting the dilution air flow rate of the VOCs. Therefore, it was not possible to examine the relationship between residence time and deodorization efficiency. However, according to **Table 7**, at a oxidation temperature of 600℃ and a residence time of 3.3s, the odor concentration was 1,750 and the deodorization efficiency was 82%. From this result, it can be inferred that even when a residence time of 3.3s is provided at a temperature of 600℃, it is not possible to reduce the odor concentration to 1,000 or less by deodorization treatment. Therefore, it is suggested that, in the direct combustion method, the deodorization efficiency is governed more strongly by temperature than by residence time.

Table 8: Deodorization Efficiency at each temperature and each SV value

Temperature (℃) / SV value	33,500	30,000	20,000	10,000
400	—	99.3% (98)	—	—
350	94.8% (730)	93.0% (980)	96.1% (550)	96.1% (550)
300	—	83.5% (2,320)	90.7% (1,300)	94.8% (730)
250	—	47.8% (7,330)	70.7% (4,120)	90.7% (1,300)

※ ( ) Values in parentheses indicate the odor concentration at the catalyst outlet.

3.2.6 Decomposition Reactions of VOCs (odor-causing components)

In this section, the decomposition reactions of VOCs are discussed. A direct thermal oxidation furnace is a thermochemical process in which VOCs are thermally decomposed and oxidized by high-temperature flames and ultimately converted into odorless carbon dioxide (CO_2) and water (H_2O). The primary reactions proceed through rapid radical chain oxidation, which is known to follow a staged sequence consisting of initiation reactions, chain propagation, and termination reactions.

[Thermal Initiation]

At high temperatures, molecules undergo thermal dissociation to generate radicals, or radicals are produced by reactive species such as $\cdot OH$ and $\cdot O$ present in the combustion flame. The reaction rate in the initiation stage accelerates with increasing system temperature.

[Chain Propagation]

The generated radicals react with O_2 to form peroxyl radicals ($ROO\cdot$) and hydroperoxyl radicals ($HO_2\cdot$). These radicals subsequently attack hydrocarbon molecules to generate new radicals, thereby sustaining the chain reaction. Representative reaction pathways include reactions such as $R\cdot + O_2 \rightarrow ROO\cdot$ and $ROO\cdot + RH \rightarrow ROOH + R\cdot$.

[Formation of Partial Oxidation Intermediates]

During the chain propagation process, partial oxidation products such as alcohols (R–OH), ethers (R–O–R), aldehydes (R–CHO), ketones (R–CO–R), and carbon monoxide (CO) are generated. These compounds may cause irritating odors; therefore, the temperature and residence time to allow the reactions to ultimately proceed to complete oxidation are important.

[Termination and Complete Oxidation]

Through radical recombination and rapid oxidation at high temperatures, the reactions proceed toward complete oxidation, i.e., $CO \rightarrow CO_2$, carbon residues → CO_2, and hydrogen residues → H_2O. With sufficient temperature, oxygen, and residence time, effective odor reduction is achieved.

Through the above chain reactions, the decomposition of hydrocarbon-based odor components in a direct thermal oxidation furnace can be regarded as the overall outcome of high-temperature radical chain oxidation. The final deodorization performance is governed by four key factors: temperature, oxygen supply, residence time, and mixing. Reduction of partial oxidation intermediates and promotion of complete oxidation are considered to be most important for effective odor reduction.

3.3 Catalytic Oxidation

3.3.1 Deodorization of VOCs (odor-causing components)

In this section, deodorization efficiency was examined by varying operating conditions such as reaction temperature and space velocity (SV) in the catalytic deodorization system. The odor concentration at the catalyst inlet used as the reference for deodorization efficiency was set to 14,000, corresponding to the odor concentration obtained when VOCs were heated to 200℃, based on the results shown in **Figure 3** in Section 3.2.3, "Heating of VOCs (odor-causing components)." **Table 8** summarizes the deodorization efficiencies under each operating condition. **Figure 4** shows the relationship between catalytic reaction temperature and deodorization efficiency at each SV value, and **Figure 5** shows the relationship between SV and deodorization efficiency at each temperature.

These tables and figures indicate that, in order to achieve a deodorization efficiency of 95% and an odor concentration of 1,000 or less, temperatures of at least 250℃ at SV = 10,000, 300°C at SV = 20,000, and 350℃ at SV = 30,000 are required. In addition, the results suggest that temperature dependence is dominant and that deodorization below 250℃ is difficult even when the SV value is reduced (i.e., the residence time is increased).

Catalytic deodorization has the advantage that the reaction temperature required for oxidative decomposition can be reduced to less than half that required for direct thermal oxidation, thereby reducing operating costs, particularly fuel consumption. Conversely, a disadvantage is that the heat resistance temperature of the ceramic catalyst support used in this experiment is approximately 500 °C. If this temperature is exceeded, the support may melt and block its porous structure. As a result, the specific surface area may decrease and catalytic activity may be inhibited, and therefore careful attention is required. In particular, this issue does not become problematic when the hydrocarbon (odor) concentration in the gas to be treated is low; however, when the concentration exceeds approximately 500 ppm, heat generation may raise the temperature above 500 °C, leading to catalyst degradation. In addition, consideration must be given to the effects of catalyst poisons such as sulfur, arsenic, dust, and mist. To prevent a decrease in catalytic activity, pretreatment of the gas to be treated is therefore essential.

Reducing the SV value (i.e., increasing the residence time) improves deodorization efficiency within a given temperature range; however, excessively lowering the SV value directly leads to an increase in initial capital cost. An economically optimal SV value therefore exists, depending on factors such as initial cost, operating cost, and annual operating time. Specifically, when fuel costs increase, it becomes economically advantageous to reduce operating costs by setting a lower SV (longer residence time) and lowering the oxidation temperature. Conversely, when the operating time is short, it is more advantageous to reduce initial cost by setting a higher SV (shorter residence time) and increasing the oxidation temperature. When a honeycomb-structured catalyst is used, an SV value of approximately 30,000 is generally considered typical.

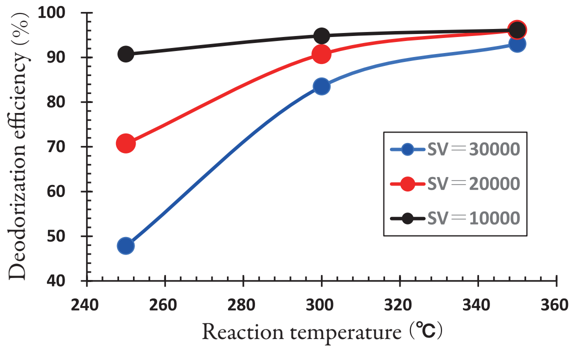

Figure 4: Relationship between catalytic reaction temperature and deodorization efficiency at each SV value

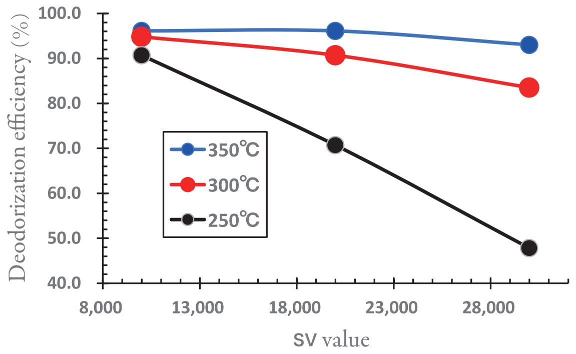

Figure 5: Relationship between SV value and deodorization efficiency at each catalytic reaction temperature

3.3.2 Deodorization Evaluation Based on Hydrocarbon Concentration

Asphalt-derived VOCs consist of a complex mixture of hydrocarbons, including aliphatic and polycyclic aromatic compounds. For instrumental evaluation of their concentrations, total hydrocarbon concentration (THC) is commonly used. All hydrocarbons are composed solely of hydrogen (H) and carbon (C). Accordingly, their concentrations are expressed on a methane-equivalent basis, with methane (CH_4) being the smallest hydrocarbon unit. Straight-chain hydrocarbons in the methane series (aliphatic hydrocarbons) are generally odorless, whereas polycyclic aromatic hydrocarbons and hydrocarbons bearing functional groups such as carboxyl (–COOH) and ketone (–C(=O)–) groups possess odors. Therefore, deodorization performance can be evaluated by distinguishing between odorless methane-series hydrocarbons and non-methane hydrocarbons. Moreover, non-methane hydrocarbons generally exhibit lower oxidative decomposition temperatures than methane. Therefore, it is not necessary to decompose methane itself; evaluation based on non-methane hydrocarbon concentrations is effective for assessing deodorization performance.

Table 9: THC removal rate and non-methane removal rate at each temperature and each SV value

Temperature (℃)	Parameter / SV value	30,000	20,000	10,000
350	THC removal rate	73.0%	79.0%	82.0%
	Non-methane hydrocarbon removal rate	97.9%	98.4%	—
300	THC removal rate	64.0%	70.0%	81.0%
	Non-methane hydrocarbon removal rate	90.0%	94.4%	99.0%
250	THC removal rate	45.0%	53.0%	70.0%
	Non-methane hydrocarbon removal rate	70.0%	—	—

In the following, total hydrocarbon (THC) concentrations were measured together with sensory evaluation using the triangular odor bag method, and THC removal rate was determined. **Table 9** summarizes the measured THC removal rate and non-methane hydrocarbon removal rate at each SV value and reaction temperature. **Figure 6** shows the relationship between reaction temperature and THC removal rate at each SV value, and **Figure 7** shows the relationship between SV and THC removal rate at each temperature. In addition, **Figure 8** shows the relationship between reaction temperature and non-methane hydrocarbon removal rate at SV = 30,000, and **Figure 9** shows the relationship between SV and non-methane hydrocarbon removal rate at a reaction temperature of 300°C.

Comparison between the results evaluated by sensory testing (**Figure 4**) and those evaluated by FID measurements (**Figure 6**), as well as between **Figure 5** (sensory testing) and **Figure 7** (FID), clearly shows that there is a correlation between the two methods. These results suggest that the use of FID for evaluating the deodorization performance of asphalt-derived VOCs has little influence on relative evaluation. Although the triangular odor bag method is more realistic because it relies on human olfactory perception, FID measurement is effective in terms of efficiency and speed.

3.3.3 Reaction Mechanism of Catalytic Deodorization

A catalyst is defined as a substance that is not consumed during a chemical reaction and remains unchanged before and after the reaction, while lowering the activation energy and facilitating the reaction. In contrast, substances that retard reactions are referred to as inhibitors.

According to the present experimental results, in direct

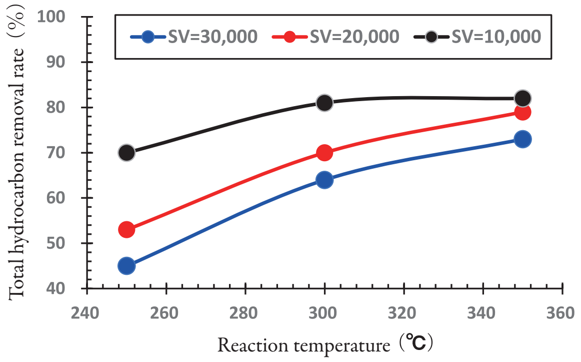

Figure 6: Relationship between temperature and total hydrocarbon removal rate at each SV value

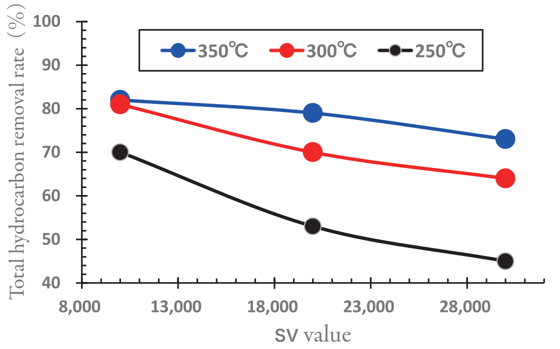

Figure 7: Relationship between SV value and total hydrocarbon removal rate at each temperature

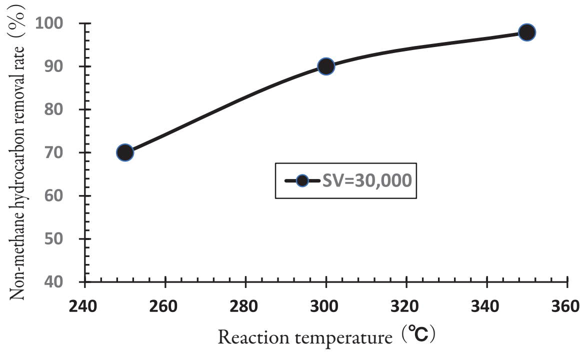

Figure 8: Relationship between reaction temperature and non-methane hydrocarbon removal rate

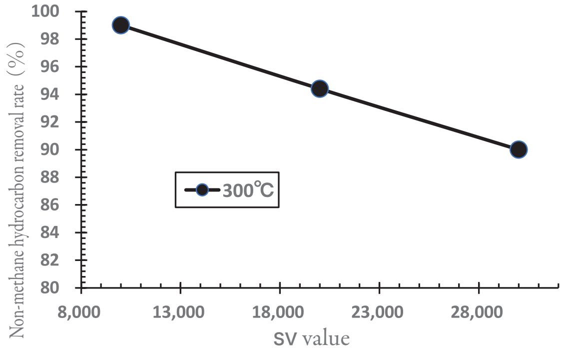

Figure 9: Relationship between SV value and non-methane hydrocarbon removal rate

thermal oxidation, VOCs consisting of numerous hydrocarbon species must be heated to approximately 800°C in order to be oxidatively decomposed into odorless components such as water and carbon dioxide. In contrast, when a catalyst is used, most hydrocarbon-based odor-causing components can be decomposed into odorless products at temperatures as low as 350°C, which is less than half the temperature required for direct thermal oxidation. Platinum (Pt), a noble metal, is commonly used as a deodorization catalyst; however, its high cost and susceptibility to catalyst poisoning and thermal degradation require careful consideration.

This catalytic deodorization experiment employed a honeycomb-structured platinum catalyst manufactured by Nippon Shokubai Co., Ltd. When catalytic deodorization is applied, it is necessary to investigate in advance whether the gas to be treated contains components that may act as catalyst poisons, as mentioned above. Known catalyst poisons include silica, sulfur, and arsenic. In addition, sticky mist and dust may indirectly clog the porous structure of the catalyst support, reducing its specific surface area and causing a decrease in catalytic activity.

Specifically, in the catalytic reaction mechanism, hydrocarbon oxidation over platinum catalysts proceeds as a surface catalytic reaction involving sequential steps of adsorption and activation on the catalyst surface, reactions on the surface, and desorption from the surface. Deodorization efficiency in the low-temperature range is strongly influenced by factors such as activation of molecular oxygen, reactivity of adsorbed species, and contributions from the catalyst support and structure.

Three representative reaction mechanisms are commonly recognized. The first is the Langmuir–Hinshelwood (L–H) mechanism, in which both hydrocarbons and oxygen are adsorbed on the catalyst surface and react on the surface to form products. The second is the Eley–Rideal (E–R) mechanism, in which gas-phase oxygen or oxidizing species directly react with adsorbed hydrocarbons. The third is the Mars–van Krevelen (MvK) mechanism, in which lattice oxygen of the catalyst oxidizes the substrate and is subsequently replenished by gaseous oxygen.

These mechanisms do not operate independently; rather, they coexist and transition depending on operating conditions such as temperature, oxygen partial pressure, catalyst particle size, and catalyst support properties. Consequently, in practical operation it is necessary to design the reaction behavior in an integrated manner.

In the following, the mechanism of catalytic deodorization is discussed in greater detail.

(a) Activation at Low Temperatures (200–400℃)

With regard to oxygen activation ($O_2 \rightarrow O^*$), oxygen molecules (O_2) adsorbed on the platinum (Pt) surface dissociate after molecular adsorption to generate highly reactive atomic oxygen (O^*). This reaction is difficult in the low-temperature region because the barrier for dissociation is temperature dependent. However, interactions with catalyst supports such as titanium oxide (TiO_2), as well as the formation of single-atom or nanostructured platinum (Pt), can promote the activation of oxygen (O_2) and improve oxidation performance at low temperatures. In addition, when existing oxygen species on the catalyst surface (such as surface oxygen or lattice oxygen) assist the reaction, the system exhibits behavior closer to the Mars–van Krevelen (MvK) mechanism.

With regard to the adsorption and initial activation of hydrocarbons (C–H bond cleavage), hydrocarbons are first molecularly adsorbed on platinum (Pt) surfaces and are partially dehydrogenated ($R\text{–}H \rightarrow R^* \rightarrow R\text{–}H_n$), forming alkyl species, alkoxy species, or surface carbonyl precursors. These species act as reaction intermediates and subsequently react with surface oxygen, leading to further oxidation to products such as aldehydes, ketones, CO, and CO_2. In particular, dehydrogenation requires relatively high activation energy and is sensitive to the reaction temperature and the electronic state of the catalyst surface.

With regard to the formation of intermediate products and irritating odors, partial oxidation (i.e., oxidation that does not proceed to complete combustion) produces intermediate compounds such as aldehydes and ketones, which have strong irritating odors. Therefore, in catalytic reactions, it is important for deodorization that these intermediates be rapidly further oxidized (e.g., aldehydes → acids → CO_2).

With regard to the roles of catalyst supports, structure, and promoters, the particle size of platinum (Pt) strongly influences catalytic performance. Extremely small nanoparticles or single-atom Pt exhibit a high specific surface area and improve activity at low temperatures, although their durability and selectivity may also change. Catalyst supports (oxides), such as cerium oxide (CeO_2) and titanium oxide (TiO_2), assist the activation of oxygen (O_2) through their oxygen storage and supply capability (oxygen storage capacity, OSC) and electron-donating properties, thereby promoting oxidation reactions at low temperatures. Elements known to enhance the performance of Pt catalysts include palladium (Pd), gold (Au), and lanthanoids (elements with atomic numbers 57–71). In addition, it is known that control of defects in oxide supports improves the adsorption and dissociation of oxygen (O_2) and enhances the activation of hydrocarbons.

(b) Catalyst Poisons and Deactivation Factors

Sulfur compounds (SO_x), silica, and arsenic can act as catalyst poisons when they strongly adsorb on the surface of platinum (Pt), thereby covering or deactivating active sites. In addition, oil mist and dust can physically cover the catalyst surface, leading to a reduction in surface area and clogging of flow channels; therefore, it is essential to remove these substances through pretreatment. Furthermore, particle coarsening (sintering) under high-temperature cycles can lead to a decrease in catalytic activity, and thus appropriate thermal management and optimization of catalyst–support interactions are required.

(c) Reaction Kinetics Perspective and Operating Parameters

The dominant factors governing catalytic deodorization include the surface oxygen supply rate, the rate of C–H bond cleavage, and the oxidation rate of intermediate species. In the low-temperature range, oxygen dissociation and C–H activation tend to be rate-limiting factors. With respect to the relationship between space velocity (SV) and temperature, reducing SV (i.e., increasing contact time) enables a similar removal rate to be achieved at lower temperatures, while increasing the catalyst volume and equipment size. Conversely, increasing temperature allows higher SV operation, but adversely affects catalyst lifetime and cost. Furthermore, accumulation of partial oxidation products with low odor thresholds (e.g., aldehydes) may result in decreased deodorization efficiency. Therefore, catalyst design must ensure sufficient oxidation capability to further oxidize intermediate species.

From a practical design standpoint, the foll points need to be considered.

As a pretreatment of the gas to be treated, sticky mist removal using air scrubbers, cyclones, or filters should be implemented to reduce the risk of catalyst fouling. In selecting deodorization catalysts, platinum (Pt)-based catalysts with high oxygen activation activity at low temperatures should be prioritized, particularly those whose supports possess oxygen supply capability, and the particle size and dispersion of platinum should be optimized. Regarding operating conditions of the catalytic deodorization system, temperature and SV must be optimized according to the target deodorization efficiency in order to balance catalyst lifetime and deodorization performance. In many industrial applications, combinations such as SV = 20,000–30,000 and temperatures of 300–350 °C are often effective. To mitigate catalyst poisoning, pretreatment and protective measures to reduce sulfur-containing components are required. For monitoring, continuous monitoring of outlet total hydrocarbons (THC), non-methane hydrocarbons, and sensory evaluation is necessary to detect signs of partial oxidation product accumulation.

4. Conclusions

In this experiment, for deodorization treatment of VOCs (odor-causing components) emitted from the R dryer of an AP, simulated VOCs were generated by directly blowing air into heated asphalt. Using these VOCs as source gases, operating conditions for both direct thermal oxidation and catalytic oxidation were investigated.

The findings obtained from the above experiments are summarized as follows:

1. For direct thermal oxidation deodorization, it was found that a temperature of at least 800°C is required to reduce the odor concentration of asphalt-derived VOCs (odor-causing components) to 1,000 or less.
2. For catalytic oxidation deodorization, it was found that reducing the odor concentration of asphalt-derived VOCs (odor-causing components) to 1,000 or less requires temperatures of at least 350°C at SV = 30,000, 300°C at SV = 20,000, and 250°C at SV = 10,000.
3. Asphalt-derived VOCs (odor-causing components) are composed of aliphatic and aromatic hydrocarbons and can therefore be oxidatively decomposed into

odorless water (H_2O) and carbon dioxide (CO_2), indicating that combustion-based deodorization methods are effective.

4. By focusing on non-methane hydrocarbons bearing odor-related functional groups, such as aldehyde (–CHO), carboxyl (–COOH), and ketone (–C(=O)–) groups, deodorization performance can be evaluated. This approach enables results equivalent to those obtained by sensory evaluation using the triangular odor bag method.
5. Exhaust gas from the R dryer containing VOCs (odor-causing components) also includes catalyst poisons such as sulfur, dust, and sticky mists. For this reason, direct thermal oxidation is suggested to be operationally more advantageous than catalytic oxidation.
6. After deodorization treatment by both direct thermal oxidation and catalytic oxidation, residual odors remain; however, they are predominantly governed by nitrogen oxides, which cannot be removed by oxidative decomposition.

In general, when considering a deodorization system, it is necessary first to identify odor-causing components, investigate exhaust gas flow rate and the frequency of odor generation, and then select the most economical and efficient deodorization system. However, the composition of the numerous odor-causing components emitted from an AP varies depending on the heating temperature of recycled aggregates. Therefore, it can be concluded that the application of combustion-based deodorization methods—either direct thermal oxidation or catalytic oxidation—is rational. In particular, AP exhaust gas contains catalyst poisons such as sulfur (S), as well as sticky mists and dust. Accordingly, direct thermal oxidation is considered effective, as it can oxidatively decompose these substances together with odor-causing components without requiring pretreatment equipment such as dust collectors.

If direct thermal oxidation deodorization can be achieved at lower temperatures and shorter residence times, fuel consumption can be reduced and the deodorization system can be designed in a more compact form, thereby lowering both the operating and initial costs. Furthermore, from the standpoint of effective waste heat utilization, the use of a heat exchanger is essential; however, a trade-off exists between the size of the heat exchanger, which affects initial cost, and fuel consumption. The optimal heat exchanger size is therefore determined by fuel price and the operating time of the AP. In addition, for the R dryer of an AP, minimizing exhaust gas flow rate is an important factor in reducing both initial and operating costs.

REFERENCES

1) Horai, H. (2022). Evolution and prospects of carbon dioxide emission reduction technologies in asphalt plants. NIKKO Technical Report, 3(1), 7–32.

2) Moroi, S. (2012). Background of offensive odor control law amendment of odor index regulation for the introduction. Journal of Japan Association on Odor Environment, 43(6), 388–394.

3) Fujikura, M. (2012). Policy on Offensive Odor Control and the background to the Olfactory Measurement Method. Journal of Japan Association on Odor Environment, 43(6), 408–414.

4) Miyagi, S. (2021). Examples of Policies on Odor Countermeasures by Local Governments; Prior Guidance for the Installation of Malodor Emission Facilities. Journal of Environmental Conservation Engineering, 50(6), 302–307.

5) Kotare, S. (2021). Current Status of Odor Measurement Technology; Addition of Official Method and Measures against COVID-19. Journal of Environmental Conservation Engineering, 50(6), 308–313.

6) Nakatsuyama, K. (2014). Overview of deodorizing equipment and deodorizer technology. Journal of Japan Association on Odor Environment, 45(6), 396–401.

7) Higuchi, T. (2021). Malodor Measures and Deodorization Techniques. Journal of Environmental Conservation Engineering, 50(6), 314–319.

8) Nakatsuyama, K., & Naota, S. (2014). Deodorization, deodorant technology (active carbon adsorption and deodorization, deodorant). Journal of Japan Association on Odor Environment, 45(6), 416–422.

9) Misaki, T. (2014). The washing deodorization system and biological deodorization system (In the waste treatment facilities). Journal of Japan Association on Odor Environment, 45(6), 408–415.

10) Iijima, S. (2014). Introduction of Deodorization Treatment using Regenerative Thermal Oxidizer. Journal of Japan Association on Odor Environment, 45(6), 402–407.

11) Tanaka, T., & Muroi, T. (1983). Purification of industrial exhaust gases using catalysts. Fuel and Combustion, 50(2), 1–14.

12) Murayama, K. (1964). Studies on Asphalt (IV): Manufacture of Blown Asphalt. Journal of the Fuel Society of Japan, 43(443), 191–199.

13) Iwasaki, Y. (2012). Background of development of Triangle Odor Bag Method. Journal of Japan Association on Odor Environment, 43(6), 395–400.

14) Kunieda, S. (2014). The current state and future prospects of sensory evaluation. Journal of Japan Association on Odor Environment, 45(5), 332–343.

15) Iijima, H. (1978). Fractional Composition and Their Chemical Structure of Petroleum Heavy Residue. Journal of the Fuel Society of Japan, 57(610), 75–86.

16) Murayama, K. (1963). Studies on Asphalt (I): Fluidity of Asphalt. Journal of the Fuel Society of Japan, 42(434), 480–485.

17) Kamigaito, M., & Sato, K. (2009). Radical Polymerization. Network Polymer, 30(5), 234–249.

18) Ibuki, E. (1949). Thermal decomposition of pure hydrocarbons (Part 1): Thermal decomposition of aliphatic hydrocarbons. Journal of the Chemical Society of Japan, 70(11), 431–435.

AUTHOR

Hideto HORAI

Joined in 1986

Ph.D. (Engineering),
Technical Headquarters