



Characterization of Odorous Gaseous Emissions from a Rendering Plant by GC-MS and Evaluate the Performance of Existing Refiners

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Abstract

Background: Among the industrial activities that may cause odor nuisance problems, baking waste one is of the sources of bad odor, and therefore individuals complain from the industry. The aim of this study was to evaluation of pollutants released from poultry rendering plant and also performance of existing refiners in removing these pollutants.

Methods: In this study, 66 air samples were collected from air pollution sources, environmental and worker's breathing zone using absorbent activated carbon and silica gel at two slaughterhouses in North and West of Iran. The samples were analyzed by GC-MS, and then efficiency of the three refiners condenser, thermal oxidation and water tank had been determined.

Results: Overall, 56 chemical pollutants in the slaughterhouse A and 41 chemical pollutants in the slaughterhouse B had been identified. These compounds were included hydrocarbons, aldehydes, ketones, alcohols, ethers, halogenated compounds, sulfur compounds, nitrogen compounds, acids and hormones. Condenser efficiency was 38 to 100%. Thermal oxidation efficiency was 15.41 to 100% and the efficiency of the water tank was 8.93 to 100%.

Conclusions: Occupational exposure to pyridine and carbon disulfide, in the slaughterhouse A, and carbon disulfide in the slaughterhouse B, was excessive. The concentrations of toluene, carbon disulfide and pyridine in the slaughterhouse A and concentrations of toluene, carbon disulfide and acetone in a slaughterhouse B was much more than the threshold of smell. Results showed that the combination of condenser and thermal oxidation, could remove large volumes of gases emitted.

Keywords: Rendering plant, GC-MS, Condenser, Thermal oxidation, Water tank.

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Introduction

One of the main characteristics of the rendering plant is one of the main characteristics of the rendering plant is the diffusion of volatile organic compounds that causes an unpleasant odor, which may be a nuisance to workers and residents residing near this industry.¹ In a rendering plant, poultry slaughterhouse organic waste, which consists of offal, dead poultry, poultry products, and others, can be converted into valuable products, such as animal feed and fertilizer. In this unit, feathers can be hydrolyzed, usually at a temperature of 140°C-150°C and at a pressure of 276-345 kPa for 20-45 min, to break down the creatinine, which can then be combined

with offal and water vapor at a temperature of 121°C-135°C under a pressure of 172-517 kPa for cooking. In both these steps, volatile organic compounds (VOCs) are produced, some of which have an unpleasant odor.^{2,3}

The investigation showed that the organic waste processing of slaughter not only emits an unpleasant odor but also causes the spread of contaminants that are very dangerous. In order to avoid the scatter of these contaminants in the surrounding atmosphere and to make a suitable environment, the development of treatment technology is required.⁴ Refiners that are used for this process can refer to the carbon filtration for low gas concentrations and thermal oxidation and catalytic reactions for medium and relatively high gas concentrations, and chemical scrubbers and bio filters for high concentrations.⁵

Odorous compounds that have been identified in gaseous emissions from rendering plants include hydrogen sulfide, ammonia, organic sulfides, disulfides, mercaptans, aldehydes (especially C-4-C-7 aldehydes), amines, quinoline, dimethyl pyrazine, other pyrazines, indole, skatole, and C-3-C-6 organic acids. In addition, lesser amounts of C-4-C-7 alcohols, ketones, aliphatic hydrocarbons, and aromatic compounds are potentially emitted.^{1,2,5}

Dincer et al. (2006) reported the diffused contaminants of animal rendering plants in 49 volatile organic compounds, including alkanes, alkenes, carbonyls, arenes, chlorinated and other halogenated compounds, organic chlorides, and volatile fatty acids.⁶ Kastner and Das (2002 and 2005), however, reported that the efficiency of wet scrubbers and biofilters in the removal of VOC diffusions of animal rendering plants was 23%-64% and 40%-100%. System analysis in this study was GC-MS.^{2,3} Anet et al. (2013) also reported that the pollutant removal by biofilter according to the types of packing materials for biofiltration was 75%-93%.⁷

The poultry rendering plant that exists in Iran has odor problems and health effects due to the diffused contaminants of this industry for workers and residents. Moreover, in Iran and other countries, there are many differences in the method of the poultry rendering plant, such as nutrition, using hormones to grow poultry, use of different drugs to control disease, and so on, which impact the pollutants generated by the poultry of contaminants processing. The assessment of pollution in this industry is very limited and is shown by the lack of studies in this field (in Iran) that have been published formally. This study, therefore, aimed to study the pollutants released from the

poultry rendering plant and evaluate the performance of existing refiners in removing these pollutants.

Materials and Methods

Studies on poultry slaughterhouses are based on two cities in the North and West of Iran. The capacity of each slaughterhouse is 28,000 pieces/day. This collection includes the slaughter, packaging, refrigeration, sewage treatment, and the rendering plant. The capacity of the rendering plant is 10 tons/day, and in North, it is called rendering plant A, whereas in the West, it is called rendering plant B. The rendering plant is the main source of odor emission in this collection.

Sampling of rendering plant A was completed in June 2013 at a temperature of 24°C and humidity of 67%. In this unit, the pollutant emissions from the cooker entered the cyclone by the channel to remove particles from the air stream. Overhead vapors from the feather hydrolyzer and driers are passed through condensers to remove some VOCs. The non-condensable gases typically are passed through thermal oxidation units to remove the VOC fraction not removed in the condensers. Flow condenser inlet was 4400 m³/hr. Condenser size was 2.3 m³ and the inlet water flow was 6 L/min with a temperature of 35°C. Outlet water temperatures reached 75°C. Thermal oxidation chamber volumes were 1.5 m³ and the chamber temperature was 200°C without a catalyst. To check and set the pollutant emissions from the cooker and determining the efficiency of the condenser and thermal oxidation, sampling of before the condenser (A1), after the condenser and before the thermal oxidation (A2) and after thermal oxidation (A3) had to be completed. Assessment of environmental and personal exposure environmental (A4) and personal sampling (A5) was also performed.

Sampling from rendering plant B was performed in July 2013. The temperature was 22°C and humidity was approximately 66%. In this unit the pollutant emissions from the cooker enter the refiner by the channel. The refiner is a water tank that enters the air from the bottom of the tank, where some of the gases are dissolved in water and the rest of the water comes to the surface to be removed. The volume of this tank was 3.5 m³ with 3,000 m³/hr air flow. The water of this tank was changed every day and the initial water temperature was around 15°C. To check and set the pollutant emissions from the cooker and determine the efficiency of this refiner, sampling before the refiner (B1) and after refiner (B2) had been done. To assess environmental and personal exposure, environmental sampling (B3) and personal sampling (B4) was also performed.

The air samples were collected by a personal sampling pump (SKC Inc., PA, USA) which absorbed activated carbon (SKC Inc., PA, USA) and silica gel (SKC Inc., PA, USA), in accordance with the National Institute for Occupational Safety and Health (NIOSH) method 15018, 13009, 160010, and 2002.11 The number of sampling was three for every sorbent in each place. Personal samples, however, due to the importance of personal exposure, the number of samples was raised to six for every sorbent in each place. Sampling time, according to the pre-test previously completed for breakthrough controls, was considered to be 40-90 min. Flow sampling was adjusted

using a digital flow meter at 0.2 L/min. After sampling, input and output sorbents was sealed by a plastic cap. The samples have been placed in a cool box and within <24 h were transferred to the laboratory for analysis.

Two blank samples in each rendering plant were taken in order to assess the possible secondary pollution during sampling, transport, and analysis of samples. Pollutant concentrations in the control samples should be <0.1 µg/m³. In this study the pollutant concentration in the control samples was <0.1 µg/m³.

Carbon disulfide (99.5%) (Merck Inc., Germany) and toluene (99.5%) (Merck Inc., Germany) was used for the sample preparation of activated carbon, and methanol (99%) (Merck Inc., Germany) was used for sample preparation of silica gel. Of every three charcoal samples that were sampled at the site, two samples were prepared with a solution of carbon disulfide and a sample with a solution of toluene. Toluene solvent was used to evaluate contaminants in samples of carbon disulfide.

After sample preparation, measurements had been completed by using the GC-MS (model CP-3800 gas chromatograph and Saturn 2200 mass spectrometer, Varian Technologies Japan Inc., Japan) focusing on the VOCOL capillary column with a length of 60 m and an inner diameter of 0.25 mm. Film thickness was 1.5 µm and the helium carrier gas flow was 1 ml/min. GC-MS was programmed at 35°C for 5 min and then ramped at 5°C/min to 180°C/min, further being held for 1 min. Injection temperature was 200°C. Determination of the area under the chromatographic peak measurements were performed using Varian workstation software. In order to identify and determine the quality of compounds, we used the data of the library of mass spectra interpretation software version 98 from the national institute of standards and technology (NIST). More importantly, the toxicological effects of pollutants, air pollution, and assessment of the feasibility of quantification were quantified.

Results

A total of 56 chemical pollutants in rendering plant A and 41 chemical pollutants in rendering plant B were detected. These compounds included hydrocarbons, aldehydes, ketones, alcohols, ethers, halogenated compounds, sulfur compounds, nitrogen compounds, acids, and hormones. The results of qualitative detection of pollutants are shown in Tables 1 and 2. Five compounds, acetone, benzene, pyridine, toluene, and carbon disulfide were quantified for various reasons, such as to study their carcinogenic and toxic nature, low odor threshold, and unpleasant odors. Quantification of these pollutants has been shown in Tables 3 and 4.

The refiner's efficiency was calculated according to the pollutant concentrations before and after the refiners. Figures 3, 4, and 5, show the efficiency of the condenser, thermal oxidation of rendering plant A, and the experimental refiner of rendering plant B. The condenser efficiency for various contaminants was 38%-100%, thermal oxidation efficiency was 15.41%-100%, and the efficiency of water tank was 8.93-100%.

Table 1. Organic volatiles identified in the cooker exhaust air from rendering plant A

Hydrocarbons	Alcohols	N-compounds
Benzene	Ethyl hexanol	Propyl amine
Toluene	3-methyl-3-pentanol	Benzyl amine
Ethyl benzene	1-tetradecanol	Pyridine
1-ethyl-2-methyl benzene	2-methyl-1-propanol	3-methyl pyridine
1,2,3-trimethyl benzene		Acetonitrile
2-butane	Halogenated compounds	Benzonitrile
Pentane	Trichloro ethylene	2-amino-1-methyl benzene
2-decane	Tetrachloro ethylene	2-chloro-2-nitro propane
Undecane	Hydrogen bromide	Isobutyl amine
Tridecane	P-chloro aniline	Amino anthrax Quinone
2-nonane	Isobutyl chloride	
Naphthalene	2-chloro phenol	Esters
		Methyl acetate
		Hydrocortisone acetate
Aldehydes	S-compounds	Acids
Nonanal	Carbon disulfide	
Octanal	Dimethyl disulfide	
2-methyl pentanal	Dimethyl tetrasulfide	Mercapto acetic acid
2-ethyl butanal	Methyl methane sulfonate	Carbamic acid
	Methyl sulfinylmethylthio methane	Ricinoleic acid
Ketones	Ethanethiol	
Acetone	Methanethiol	Hormones
2-decanone	Propanthiol	Cortisone
2-tridecanone		Aldosterone
2-dodecanone		Prednisone

Table 2. Organic volatiles identified in the cooker exhaust air from rendering plant B

Hydrocarbons	Ketones	S-compounds
Benzene	Acetone	Carbon disulfide
Toluene	2,4-dimethyl hexanone	Dimethyl disulfide
Ethyl benzene	2-decanone	Dimethyl tetrasulfide
1-bromo ethyl benzene	2-dodecanone	Ethanethiol
1-ethyl-2-methyl benzene		Methanethiol
1,2,3-trimethyl benzene	Alcohols	Propanthiol
1,2-dimethyl cyclohexane	Ethyl hexanol	
2,4-dimethyl hexane	3-methyl-3-pentanol	N-compounds
2-Decane	2-ethyl-1-hexanol	Propyl amine
Undecane		Benzyl amine
Tridecane	Halogenated compounds	Acetonitrile
2-nonane	Tetrachloro ethylene	2-chloro-2-nitro propane
	Methylene chloride	4-methyl-2-hexanamine
	Chloro benzene	
Aldehydes	Esters	Acids
2,3-dimethyl pentanal	Methyl acetate	Mercapto acetic acid
2-methyl pentanal		Carbamic acid
2-ethyl butanal	2-propenyl acetate	Isobutyric acid

Table 3. Distribution of pollutant concentrations (ppm) in rendering plant A

Compound	Mean \pm SD				
	A1	A2	A3	A4	A5
Acetone	31.33 \pm 44.31	7.94 \pm 11.23	ND	0.58 \pm 0.82	0.43 \pm 0.86
Benzene	5.99 \pm 1.74	ND	ND	ND	ND
Toluene	128.03 \pm 134.37	79.38 \pm 89.17	27.69 \pm 25.02	15 \pm 15.1	8.8 \pm 11.92
Pyridine	8.9 \pm 12.58	2.92 \pm 4.13	2.47 \pm 3.5	2.49 \pm 1.21	2.38 \pm 1.69
Carbon disulfide	9.45	5.06	ND	3.72	4.02 \pm 0.56

Table 4. Distribution of pollutant concentrations (ppm) in rendering plant B

Compound	Mean \pm SD			
	B1	B2	B3	B4
Acetone	62.70 \pm 16.21	30.39 \pm 42.98	3.59 \pm 5.08	5.46 \pm 7.91
Benzene	6.54 \pm 2.5	ND	ND	ND
Toluene	14.22 \pm 24.63	12.95 \pm 22.43	1.47 \pm 2.55	0.46 \pm 1.09
Pyridine	ND	ND	ND	ND
Carbon disulfide	39.72	23.06	27.2	19.03 \pm 23.1

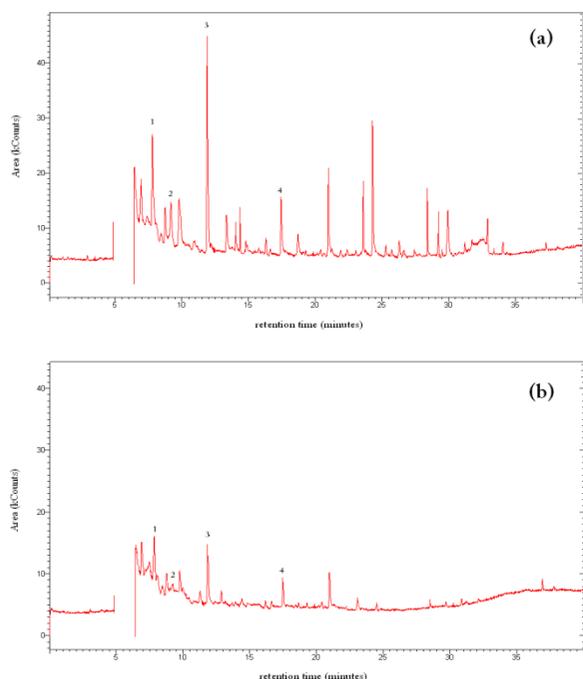


Figure 1. Typical chromatograms of the gas samples from the exhaust of the cooker in rendering plant A. Prepared by solvent carbon disulfide. Identified peaks: 1, acetone 7:74 min; 2, benzene 9:11 min; 3, toluene 11:78 min; 4 and a pyridine 17:44 min. From 5 to 6:40 min to remove the solvent (carbon disulfide) was off mass spectrometer.

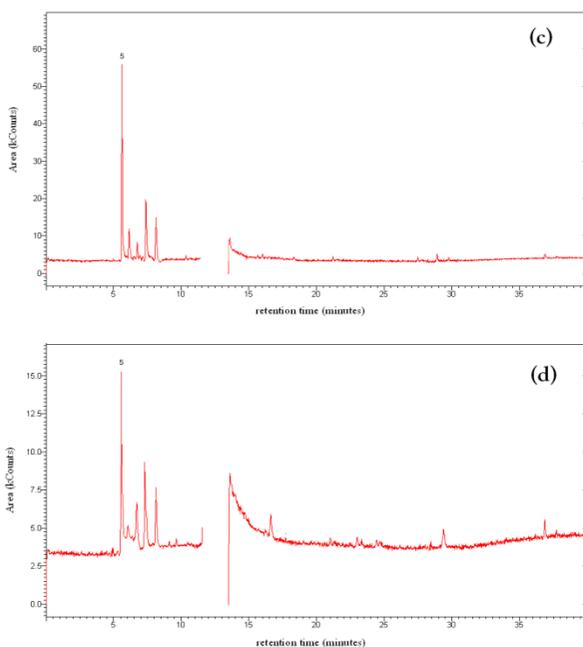


Figure 2. Typical chromatograms of the gas samples from the exhaust of the cooker in rendering plant B. Prepared by solvent toluene. Identified peaks: 5, carbon disulfide 5:61 min. From 11:50 to 13:50 min to remove the solvent (toluene) was off mass spectrometer.

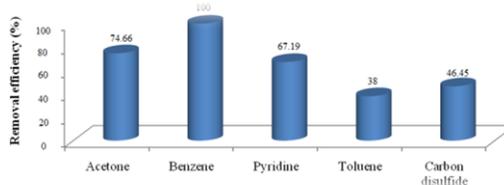


Figure 3. The efficiency of pollutants removal by the condenser in rendering plant A

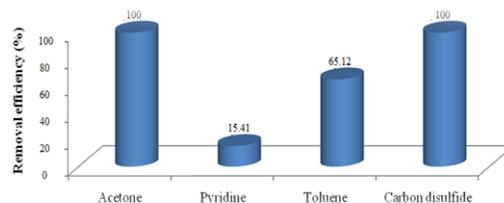


Figure 4. The efficiency of pollutants removal by the thermal oxidation in rendering plant A

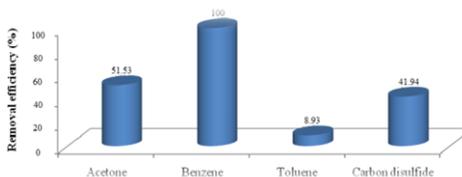


Figure 5. The efficiency of pollutants removal by the water tank in rendering plant B

Discussion

Many studies have been completed for identifying pollutants released by a rendering plant. The major compounds identified in our study, include hydrocarbons, aldehydes, ketones, alcohols, esters, halogenated compounds, sulfur compounds, nitrogen compounds, acids, and hormones. Most of these compounds have also been reported in other studies.^{4,6,12,13} However, some compounds such as hormones have not been reported in previous studies due to the low temperature of the column.² The difference between pollutant emissions and concentrations of pollutants in different studies can be based on different materials from poultry organic wastes and the differences in the cooking process. In some studies, the feather was firstly hydrolyzed, and then it was mixed with offal; however, in some other studies, feather was combined with offal without hydrolyzing, and then the cooking was carried out. These differences could have an effect on the pollutant emissions.^{2,3}

The cooking processes in two slaughterhouses had several main differences. The time of adding zeolite and the time of filing the cooker are two main differences in the rendering plants. Zeolite is added for increasing the absorption of nutrients and increases the nutritional value of meat powder. In rendering plant B, zeolite is added to cooking meat powder at the end of cooking and at discharge cooker, but in rendering plant A, zeolite will be added to meat powder during cooking (2 h after the cooker starts). Zeolite heating during cooking

may reduce some pollutants and produces other contaminants. Also in rendering plant B, slaughterhouse organic wastes are accumulated from the outside and 1 h before cooking, cookers are filled, whereas in rendering plant A, cooker filling is performed after the discharge of the cooker and cooking process takes place the next morning (17 h later cooker filing). Accumulation of waste products in the cooker for 17 h causes the accumulation of pollutants resulting from the enzymatic degradation of microorganisms and their protein oxidation which affects the type and concentration of pollutants.¹

Previous studies have identified the presence of benzene and toluene, however, the presence of benzene has been attributed to the environment.^{14,15} Benzene and toluene are aromatic hydrocarbons that often simultaneously occur in the workplace or in the environment. Benzene has been classified as a group 1 carcinogen contaminant by the International Agency for Research on Cancer (IARC) because it can cause leukemia in humans. Toluene is toxic to the central nervous system but is not carcinogenic.¹⁶ The odor threshold for benzene and toluene, respectively, are 8.65 and 0.16 ppm and their threshold limits value (TLV) are 0.5 and 20 ppm. Kastner and Das (2002), for instance, identified benzene and toluene in air released cookers (entry scrubber), but for very low concentrations, it cannot quantify.² Dincer et al. (2006), on the other hand, reported that the benzene and toluene concentrations in ambient air of rendering plants are 0.1-0.4 ppb and 0.25.2 ppb, respectively. They believed that benzene and toluene in the air of rendering plants is probably due to traffic machines.⁶ In our study, the concentrations of benzene and toluene released by the cooker are much higher than personal and environmental exposure. Availability of benzene and toluene in air emissions from the cooker in our study and from studies such as Kastner² indicates that the main source of benzene and toluene environment is directly from the waste cooker.

Carbon disulfide and acetone were reported in previous studies in the air of a rendering plant.^{6,12} Carbon disulfide is a volatile liquid with a pungent odor and is classified as a dangerous pollutant under categories III in the United States Clean Air Act Amendment (CAAA).¹⁷ Acetone is also a clear fluid with a nauseating odor at high concentrations which causes eye, nose, and throat irritation.¹⁸ As well as this, carbon disulfide is produced naturally as a result of microbial activity in a low oxygen environment.^{17,19} Acetone can be produce by the breaking down of starches and sugars by bacteria.²⁰ Correlation between contaminants and odor of the rendering plant showed that acetone, carbon disulfide and aldehydes are responsible for the smell.⁶ Odor thresholds in carbon disulfide and benzene were 0.096 ppm and 4.58 ppm, respectively, and TLV is 500 and 1 ppm. Anet et al. (2013) reported diffused acetone concentrations of a cooker (entry biofilter) to be 0.29-0.78 ppm,¹² and Dincer et al. (2006) reported environmental concentrations of acetone and carbon disulfide in the rendering plant to be 1.7-11 ppb and 0.1-0.6 ppb, respectively.⁶ Acetone and carbon disulfide concentrations in our study for personal, environmental and diffused exposure was found to be higher than the cooker which is likely due to differences in the cooking process.

Pyridine is volatile liquid with an odor threshold of 0.17 ppm and TLV is 1 ppm. Pyridine manufacturing and industrial operations in which pyridine is used has caused severe odor problems. Pyridine is a carcinogen and mutagen and is as a dangerous pollutant classified by the USEPA.^{21,22} Pyridine is found in certain medicines, vitamins, and food flavorings²³ and can also be produced in reactions with the carbonyl group of a sugar in the heat.²⁴ Dincer et al. (2006) reported the environmental concentration of pyridine in the rendering plant as 0.1 ppb.⁶ Sato et al. (2001), however, reported the diffused pyridine concentration of human wastes to be 0.03-0.23 ppm.²⁵ In our study, pyridine was detected only in the rendering plant A, which may be due to the retention time being much higher in the cooker. After unloading the cooker, wastes poured in the cooker which was still hot and can react with amines and carbonyl to produce pyridine.

Use of the condenser, thermal oxidation, and wet scrubber for removal of VOCs in the rendering plant has been performed in previous studies.^{2,3,26} Sironiet al. (2007), for example, reported that the thermal oxidation and scrubber efficiency in removing pollutants released by a rendering plant were more than 99 and 41%-60%, respectively.¹ In our study, the removal rate in the condenser and water tank was 38%-100% and 8.93%100%, respectively. The highest removal efficiency of the condenser and water tank is the benzene pollutant and the lowest was for toluene pollutant. Thus, there was a lower boiling point and higher solubility of benzene to toluene in water²⁷ and these lower concentrations of benzene to toluene are mostly due to the 100% removal efficiency of benzene and lower removal efficiency of toluene.

Removal efficiency of thermal oxidation was 16%-100%. The highest removal efficiency was for contaminants acetone and carbon disulfide, and lowest had been for pyridine pollutants. The higher flame point of pyridine to acetone and carbon disulfide is the reason for the lower efficiency of pyridine thermal oxidation. In most studies, proper combustion temperatures are needed to incinerate VOCs and turn them into carbon dioxide and water vapor. This was suggested to occur between 700°C and 1400°C. Using a platinum, palladium, and rubidium catalyst, the required temperature reduced between 300°C and 700°C.²⁸ A lower combustion point of thermal oxidation in our study was, therefore, due to the low efficiency of thermal oxidation.

This study showed that the gases released from the rendering plant are made up of a complex mixture of chemical compounds. Quantification was made for five compounds from the 56 detected compounds in rendering plant A and 41 detected compounds in rendering plant B. Personal exposure to carbon disulfide and pyridine in rendering plant A and carbon disulfide in rendering plant B were found to be more than the threshold values. The concentration of toluene, carbon disulfide, and pyridine in rendering plant A and the concentration of toluene, acetone, and carbon disulfide in rendering plant B were also higher than the odor threshold.

The results showed that using two refiner's condenser and thermal oxidation, a large volume of diffused gases could be removed. Using these two methods, refiners were able to remove three pollutants out of the five quantified pollutants,

with an efficiency of 100%, 72.24%, and 78.37%. Low temperature thermal oxidation has been the main reason for the low removal efficiency of some compounds. Removal efficiency of the water tank for four quantified compositions was approximately 50%.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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