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ODOR EMISSION MANAGEMENT IN A FEATHER TREATMENT PLANT

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ABSTRACT

Karoliina Lahti: Odor emission management in a feather treatment plant
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Gas emissions from the process industry vary depending on the treatment methods, equipment and raw materials used in the process. The rendering process generates malodorous and harmful gases that need to be controlled. The formation of odorous gases is often prevented at the process stage or controlled by removing odorous compounds from the process off-gas by various chemical, physical, and biological techniques. The purpose of the off-gas treatment is to avoid the release of emissions harmful to human health and the environment into the surrounding air.

The objective of the thesis was to determine which regulations and emission limit values govern the odorous emissions from the treatment of animal by-products, and which off-gas treatment methods are suitable for this sector. The odorous compounds generated by the feather treatment process of Honkajoki Ltd, an animal by-products processing plant, were characterized. In addition, the operation of an existing off-gas treatment process, including a chemical scrubber and a biofilter, was optimized to minimize odor emissions by improving the removal efficiencies of hydrogen sulfide and ammonia. The topic is relevant with the update of the new BAT document, which defines the best available techniques for gas collection and treatment and at the same time sets emission levels for environmental permits for plants operating in EU Member States. The new document will require factories to review their emission levels and re-evaluate the adequacy of their gas treatment systems.

Among the 32 compounds identified from feather processing, the most significant odorous compounds were hydrogen sulfide, ammonia, and methyl mercaptan, due to their high concentrations of 12.9–55.8 mg/Nm³ and low odor thresholds. The characterization of the process off-gas showed that most of the ammonia is formed during the drying of the feather material and most of the hydrogen sulfide is formed during hydrolysis. The removal efficiency of the plant's chemical scrubber for hydrogen sulfide reached a maximum of 74 %, while the removal efficiency for ammonia remained between 90–100 % throughout the entire study. The hydrogen sulfide removal efficiency of the biofilter was close to 80 % at its highest but decreased to less than 20 % in the short term. The characterization of the biofilter bed material indicated that too low pH was responsible for the decrease in H₂S removal efficiency in the biofilter.

The results of this work show that the current treatment system, when operating normally, is adequate for the BAT limit values that will be established. It is recommended that the bed material of the biofilter is limed in order to improve its functioning. Possible increases in production volumes in the future could cause the capacity of the off-gas treatment system to be exceeded, so based on the literature, the off-gas treatment could be improved, e.g., using a supplemental treatment such as a bioscrubber, which is particularly suitable method for hydrogen sulfide.

Keywords: BAT, odor, condenser, thermal oxidation, wet scrubber, biofilter, bioscrubber

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TIIVISTELMÄ

Karoliina Lahti: Hajupäästöjen hallinta höyhentenkäsittelylaitoksella
Diplomityö
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Prosessiteollisuuden kaasupäästöt vaihtelevat teollisuudessa käytettävistä käsittelymenetelmistä, -laitteista ja raaka-aineesta riippuen. Renderöintiprosessista muodostuu voimakkaasti haisevia haitallisia kaasuja, joiden hallinta on välttämätöntä. Haisevien kaasujen muodostumista pyritään ehkäisemään usein jo prosessivaiheissa tai hallitsemaan poistamalla hajua aiheuttavia yhdisteitä prosessin poistoilmasta erilaisten kemiallisten, fysikaalisten ja biologisten menetelmien avulla. Käsittelyn tavoitteena on estää ihmisille ja ympäristölle haitallisten päästöjen vapautuminen ympäristöön.

Työn tavoitteena oli selvittää millaiset säädökset ja päästöraja-arvot ohjaavat eläinperäisten sivutuotteiden käsittelystä aiheutuvia haisevia päästöjä, ja mitkä ovat kyseiselle sektorille soveltuvia poistoilman käsittelymenetelmiä. Eläinperäisiä sivutuotteita käsittelevän laitoksen, Honkajoki Oy:n, höyhenten käsittelyprosessista syntyvät hajua aiheuttavat yhdisteet karakterisoitiin. Lisäksi optimoitiin olemassa olevan kaasunkäsittelyprosessin, johon kuuluivat kemiallinen pesuri ja biosuodatin, toimintaa hajupäästöjen minimoimiseksi rikkivedyn ja ammoniakkin poistotehokkuuksia parantamalla. Aihe on ajankohtainen uuden BAT-asiakirjan päivittymisen myötä, sillä asiakirja määrittelee parhaiten käytettävissä olevan tekniikan kaasujen keräilylle, käsittelylle ja samalla määrittää päästötasot EU jäsenmaiden alueella toimivien tehtaiden ympäristöluville. Uusi asiakirja laittaa tehtaat tarkastelemaan päästötasojaan ja arvioimaan uudelleen kaasunkäsittelyjärjestelmiensä riittävyttä.

Höyhenten prosessoinnista muodostuneista tunnistetuista 32 yhdisteestä, merkittävimmät hajua aiheuttavat yhdisteet olivat rikkivety, ammoniakki ja metyylimerkaptani, koska niiden pitoisuudet olivat korkeat 12,9–55,8 mg/Nm³ ja hajukynnys matala. Prosessin poistoilman karakterisoinnin perusteella saatiin selville, että ammoniakista suurin osa muodostuu höyhenmateriaalin kuivausvaiheesta ja rikkivedystä suurin osa hydrolysoinnista. Laitoksen kemiallisen pesurin poistotehokkuus rikkivedylle oli parhaimmillaan 74 %, kun taas ammoniakkin poistotehokkuus pysyi koko tutkimuksen ajan 90–100 %. Biosuodattimen rikkivedyn poistotehokkuus oli parhaimmillaan lähes 80 %, mutta laski lyhyellä aikavälillä alle 20 %:iin. Biosuodattimen petimateriaalin karakterisoinnin perusteella havaittiin, että liian alhainen pH oli syynä biosuodattimen H₂S poistotehokkuuden laskuun.

Työn tulosten perusteella voidaan todeta nykyisen käsittelyjärjestelmän, toimiessa normaalisti, olevan riittävä voimaan tuleviin BAT-raja-arvoihin nähden. Biosuodattimen petimateriaalin kalkitsemista suositellaan sen toiminnan elvyttämiseksi. Mahdollisesti tulevaisuudessa lisääntyvät tuotantomäärät saattaisivat aiheuttaa poistoilmankäsittelyjärjestelmän kapasiteetin ylittymisen, joten kirjallisuuskatsauksen perusteella, poistoilman käsittelyä voitaisiin tehostaa esimerkiksi laiteliäyskellä, kuten biopesurilla, joka on etenkin rikkivedylle soveltuva menetelmä.

Avainsanat: BAT, haju, lauhdutin, terminen hapetus, märkäpesuri, biosuodatin, biopesuri.

Tämän julkaisun alkuperäisyys on tarkastettu Turnitin Originality Check -ohjelmalla.

PREFACE

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LIST OF SYMBOLS AND ABBREVIATIONS

ABP	Animal by-product
BAT	Best Available Technique
BAT-AELs	BAT-Associated Emission Levels
BSE	Bovine spongiform encephalopathy
CaCO ₃	Calcium carbonate
CH ₃ SH	Methyl mercaptan
ClO ₂	Chlorine dioxide
CO ₂	Carbon dioxide
EBRT	Empty bed residence time
FTIR	Fourier-transform infrared spectroscopy
H ₂ O ₂	Hydrogen peroxide
H ₂ S	Hydrogen sulfide
H ₂ SO ₄	Sulfuric acid
HNO ₃	Nitric acid
IED	Industrial Emissions Directive
LPG	Liquefied Petroleum Gas
mV	Millivolt
Na ₂ CO ₃	Sodium carbonate
Na ₂ S ₄	Sodium tetrasulfide
NaHSO ₃	Sodium bisulfite
NaOCl	Sodium hypochlorite
NaOH	Sodium hydroxide
NH ₃	Ammonia
NO _x	Nitrogen oxides
O ₃	Ozone
ou _E /m ³	European odor unit
ppm	Parts per million
ppmv	Parts per million volume
Redox	Reduction-oxidation / oxidation-reduction
SA-BREF	Slaughterhouses, Animal By-products and/or Edible Co-products Industries – BAT reference document
SO _x	Sulfur oxide
TBRT	True bed residence time
TVOC	Total volatile organic compounds
VOC	Volatile organic compound
WWTP	Waste water treatment plant

1. INTRODUCTION

The utilization of organic waste to recover important resources, such as proteins from animal by-products, is important for the circular economy (Tesfaye et al., 2017). Animal by-products are processed in rendering plants to produce fat and high-protein meat and bone meal, for example for animal feed (Sironi et al. 2007). The rendering process involves the separation of fat and protein-rich material from animal tissues by heating them to a temperature that breaks down the cellular structure and releases the fat, which is then separated from the solid fraction (Woodgate & Van der Veen, 2004).

The growing interest in the use of renewable and sustainable raw materials and environmental concerns are forcing industry to find ways to process raw materials such as animal by-products. For example, feathers, can be processed into feather meal and fertilizers (Tesfaye et al. 2017). The main problem in processing feathers is the low digestibility of the raw material due to keratin. To improve the digestibility, the protein structure of feathers is converted into shorter peptide chains through thermal pressure hydrolysis. The keratin protein in feathers contains high levels of sulfur-containing amino acids, which causes the release of compounds that cause unpleasant odors during thermal treatment processes such as hydrolysis and drying of feathers. (Haerens et al. 2022)

Odorous compounds released from the rendering process often have low water solubility, such as hydrogen sulfide (Bhatti 2013; Shareefdeen 2005). Odorous air pollutants are more sensitive to being detected than, for example, carcinogenic compounds, although they are not less harmful (Kennes et al. 2001). The most common direct health effects of odor and malodorous compounds are related to eye, nose and throat irritation, shortness of breath, headache, and nausea. Fatigue, sleep problems and mood changes also occur with long-term exposure. Not only the intensity of the odor, but also its nature and frequency of occurrence affect the perceived annoyance of the odor (Manni et al. 2023, 26). For people living near rendering plants, emissions that cause unpleasant odors can be problematic, so one of the most important aspects of the rendering process is emission control (Sironi et al. 2007).

The odor emission limits for environmental permits are based on Industrial Emissions Directive (IED) 2010/75/EU, which aims to prevent and reduce pollution and to harmonize permitting practices across the EU. Under the IED, emission limit values are set according to Best Available Techniques (BAT). (Ympäristö.fi 2023) In Finland, this EU

legislation is included in the Environmental Protection Act (2014, 1 §), which aims to control emissions from industry. The purpose of the law is to prevent pollution, reduce emissions and ensure a healthy and comfortable environment. To minimize odor-causing compounds, different chemical, biological, and physical treatments techniques have been developed (Kymäläinen & Pakarinen 2015).

The objective of the literature review in this thesis is to determine what regulations and emission limit values exist in relation to air emissions from the treatment of animal by-products and what are the appropriate off-gas treatment methods for the sector, and to compare the advantages and disadvantages of these treatment methods. The objective of the experimental part of the study is to investigate the quality of the off-gas from the treatment of feathers by characterizing the odorous compounds, as there is not enough information available on the compounds resulting from the treatment of this raw material. In addition, the objective is to optimize the operation of the chemical scrubber and the biofilter in order to improve the removal efficiencies of H_2S and NH_3 . The results of the work will also be used to examine the suitability of the current off-gas treatment process at the investigated plant for the odorous compounds from the treatment of feathers and to ensure that the treatment system is adequate for the BAT mandatory limit values.

Chapter 2 of this thesis describes the treatment of animal by-products and the typical odorous compounds resulting from the processing. Chapter 3 discusses the legislation on industrial emissions and the off-gas treatment methods suitable for rendering plants according to the BAT recommendations. Chapter 4 presents the feather treatment process of the case study company and the experimental studies carried out during this thesis. The results of these studies are presented in chapter 5. Chapter 6 presents the conclusions of the thesis.

2. ODOROUS GASES FROM THE TREATMENT OF ANIMAL BY-PRODUCTS

In this chapter the legislation on the treatment of animal by-products and the rendering process in general are introduced. The typical sources of odor emissions from the rendering process are presented, including the main odorous compounds resulting from the treatment of animal by-products.

2.1 Processing of animal by-products

Animal by-products (ABPs) are regulated by EU legislation, supplemented by national legislation. Regulation (EC) No 1069/2009 of the European Parliament and the Council and its implementing Commission Regulation ((EU) No 142/2011) contain regulations on ABPs. The scope of the animal by-products Regulation is wide, covering the collection, transport, treatment, marketing, and disposal of ABPs and their derivatives. It also applies to the import, export, and transit of ABP. The Regulation and the implementing Commission Regulation are directly applicable EU legislation. However, national legislation may provide for some limited exceptions to the requirements of the ABP Regulation. The ABP Regulation sets strict health rules for the use of ABPs to guarantee a high standard of health and safety, as ABPs may contain pathogens or chemical contaminants which, if spread in animal feed, can be harmful to animals and pose a risk to human health. When handled correctly, there is no risk to human or animal health. (Ruokavirasto 2023)

According to Guerra et al. (2017), up to 50 % of the livestock's weight is not consumed by humans but must be processed by rendering. Rendering is an industry that recycles by-products from slaughtering operations, such as fractions separated from meat such as bones, viscera, and lard, turning them into value-producing usable products such as meat bone meal and fat (Shareefdeen et al. 2005). Rendering is the process of treating inedible animal by-products with heat and pressure to separate the proteins, fat, and water from the by-products to produce value-added circular economy products. The raw material is brought to the rendering plant, for example from slaughterhouses. Typically, only one type of raw material is used per processing line in the rendering plant so that the control of process conditions does not require significant changes during processing. (Prokop 1992, 557)

Animal by-products are classified in categories 1, 2 and 3 according to their health risk to humans or animals under the EU animal by-products regulation. Category 1 by-products include bovine heads, including the brain and spinal cord, which are the highest risk material as they may contain prion-causing diseases. Therefore, they cannot be used as food or animal feed. The end products are used as fuel by combustion or in biodiesel. Category 2 by-products include, for example, the contents of the digestive tract and carcass parts rejected during meat inspection. By-products in this category are not intended for human consumption or pet food, but may be used as feed for fur animals, fertilizer, fuel, biogas fuel or biodiesel. In addition to other parts suitable for animal consumption category 3 by-products include blood, hides and skins, hooves, and tallow. These materials can be used for pet food, but not for human consumption. Category 3 final products can also be used as fish feed, in the chemical industry and for the same uses as Category 1 and Category 2 final products. (EU 1069/2009) Depending on the category of the by-product, there are seven different EU approved processing methods for the treatment of raw materials, which define maximum particle size ranging from 20–150 mm, core temperature ranging from 70–133°C and time at core temperature ranging from 3–125 minutes, as well as certain special details, such as pressure, pH, and processing instructions (Karlis et al. 2024, 332-333).

In rendering, the raw material is pumped through closed pipes or fed by screw conveyors either through a metal detector or directly into a mechanical crusher, where the raw material is reduced to meet the particle size specifications in the processing method applied and approved by the authorities. From the crusher, the raw material is fed into a cooker where it is heated to the temperature specified by the chosen method for the required residence time. The design and operating parameters of the cooker depend on whether it is a continuous or batch process and whether pressure sterilization is used. In pressure sterilization, the process involves maintaining a pressure of at least 3 bar by eliminating air from the sterilization chamber and replacing it with steam. (Karlis et al. 2024, 332) The sterilization process was added to rendering plants after the bovine spongiform encephalopathy (BSE) i.e. mad cow disease problem to ensure that the product did not contain the active prion that caused BSE. Sterilization is carried out at high temperature with the substance for a few minutes. And because of this additional treatment, air emissions from rendering plants are estimated to have increased compared to when no sterilization was carried out. (Bhatti et al. 2013)

Rendering can be conducted either as a continuous process or as a batch process. For high volumes of raw materials, a continuous process is typically used, while batch cooker

systems are more often used for processing lower-capacity raw materials such as feathers and blood. (Karlis et al. 2024, 332) In a batch cooker system, a certain amount of material is fed into the cooker and processed under selected conditions, after which the entire batch is discharged. Typically, it takes 1.5–2.5 hours to cook a single batch. Often a batch process involves several cookers, while a continuous system involves only one. In a continuous rendering system, the raw material is fed into the digester in a continuous feed and the cooker is discharged likewise. The continuous process requires a shorter cooking time and less space for a single cooking unit. (Prokop et al. 1992) The cooking phase produces strong odorous gases, which are discharged to an odor removal system (Karlis et al. 2024, 334).

After cooking, the material is separated from the fat and the solids mixture, i.e., the melting residue, which is transferred by screw conveyors to the grinding plant. Category 1 and 2 raw material is called meat and bone meal (MBM) and Category 3 processed animal protein (PAP). The fat is separated from the cooked material by a feed screw conveyor through a plate screen or two-stage decantation. The solid material is pressed, and the separated fat is centrifuged to remove solid particles. The solid material is passed to a hammer mill where it is chopped into small pieces and passed through sieves to achieve the desired particle size. The remaining product is homogenized and packed in bags or transported by screw conveyor to a silo to be distributed. (Karlis et al. 2024, 334)

In wet rendering, the fat is separated from the raw material using boiling water or steam. After cooking, the material is centrifuged to separate the water and proteins from the fat. When the raw material reaches 90°C, it is separated by a press, leaving fat, stick water containing glue and protein solids. The stick water is centrifuged to separate the proteins and fats and the protein solids are processed into flour. Wet rendering causes costs due to high energy consumption and evaporation of additional water. In addition, the process method has adverse effects on the quality of the fat, for example, conduct of the fact with excess water under boiling temperature tends to increase the free fatty acid content of the fat. Therefore, dry rendering is often used, in which the fat is separated from the raw material by dehydrating. In dry rendering, the fat is separated by dehydrating the animal by-product with steam. The heating breaks down the cell structure, releasing the fat and causing the product to dry out. The fat is discharged, and the remaining solids are fed into a press where the remaining fat is separated. Moisture and solid particles are separated from the fat. The advantage of dry rendering is that no excess water or steam must be added. Less fatty materials such as blood and feathers are treated in a separate

process, for example feathers are treated by hydrolysis, which is a chemical reaction that uses water to break down the bonds of the material. (Prokop et al. 1992, 557)

Feathers contain keratin, which is a long-chain, highly cross-linked, low-digestibility protein (Prokop et al. 1992, 560). To convert feathers into easily digestible feed (68–93 % digestibility), they must be hydrolyzed under pressure (National Renderers Association 2023; Anderson 2006). The keratin protein in the feathers contains high levels of sulfur-containing amino acids, which means that heat treatment of the feathers produces odor-causing compounds such as sulfur (Haerens et al. 2022). The heat treatment stages of the feather treatment process utilize steam (Figure 1).

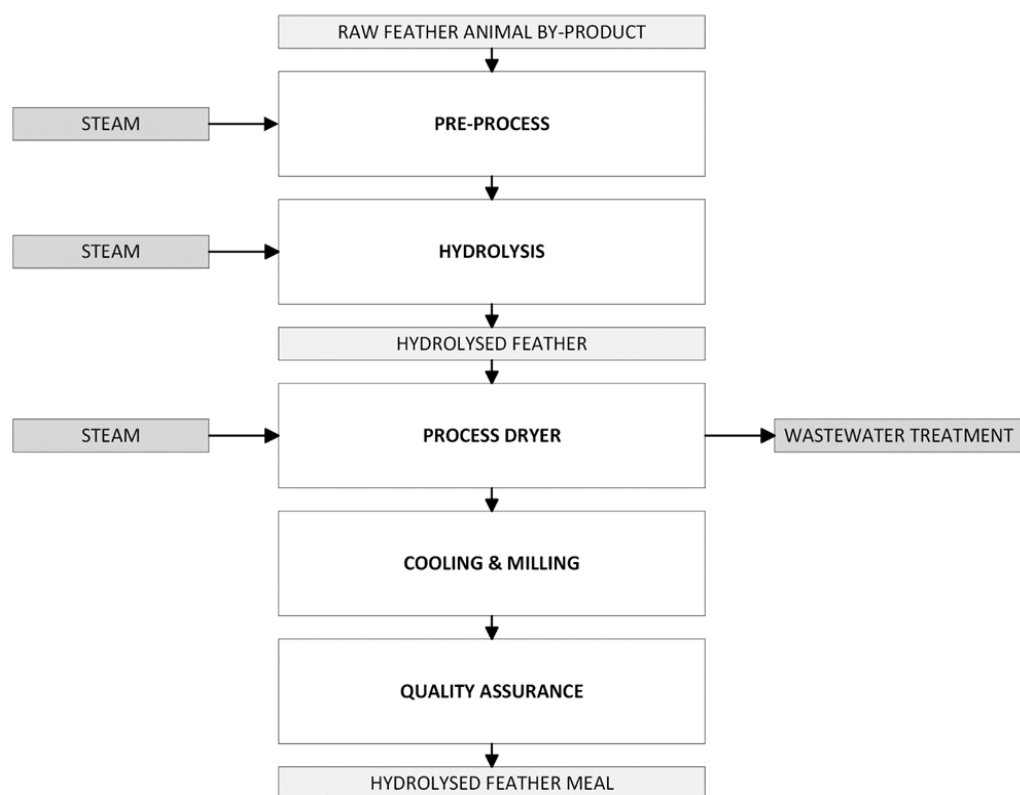


Figure 1. Feather treatment process (adapted from Karlis et al. 2024).

The raw materials are fed from the raw material silo to a hydrolyzer where they are treated at 138–149°C using steam and 2,7–3,5 bar pressure. After hydrolysis, the moisture content of the material is about 50 %. (Prokop et al. 1992, 560) Sterilization is carried out either in the hydrolysis stage or in the following stage of drying. After drying, the material is ground to a meal. (Karlis et al. 2024, 343) The final product is hydrolyzed feather protein which can be used, for example, in animal feed (Prokop et al. 1992, 557). The crude protein content of pure feather meal is normally 80 % and fat 3–5 % (North

Renderers Association 2023). The process equipment is usually designed to be completely enclosed so that the off gas can be efficiently directed to the odor removal unit (Karlis et al. 2024, 343).

2.2 Typical odorous compounds from the animal by-product treatment process

The further processing of animal by-products generates a high number of odorous compounds, which are mainly the degradation products of proteins caused by heat treatment (Mattila 1986, 55). In the batch rendering process, the primary sources of high intensity odors are the process steps where the material is heated, such as the cooker, where most of the compounds are released when the cooker is emptied (Prokop et al. 1992, 560-561). The number of odorous compounds depends on the temperature used and the type of process. By following an approved cooking method and avoiding excessive temperatures, odor generation can be reduced (Karlis et al. 2024, 344). Other sources of high intensity emissions are for example screw presses, centrifuges, tallow handling tanks (Prokop et al. 1992, 560-561) and cooler condensate and storage and handling of animal meal (Karlis et al. 2024, 344). In addition, for example, dry rendering releases more odorous compounds than wet rendering, where some odor-causing compounds condense with the water (Mattila 1986, 55). Closed equipment is one way to prevent high-intensity odor release to buildings (Karlis et al. 2024, 344). Other factors affecting the number of odorous compounds is the type of raw material, for example blood and feather raw materials typically produce high amounts of these compounds. In addition, the freshness of the raw material has a significant impact on the number of odorous compounds, as spoiled raw material produces more odor during the cooking and pressing processes than fresh raw material. It is therefore recommended to treat the raw material without delay. (Prokop et al. 1992, 560-561)

The malodorous gaseous emissions from the processing of animal by-products usually include highly concentrated process gases and vapors from the cooking process (Karlis et al. 2024, 344). Both the cooking and drying vapors are passed through condensers to separate condensable and non-condensable gases. The non-condensable gases are passed to the off-gas treatment, for example through wet scrubbers, to remove the non-condensable fraction in the condensers. (Kastner et al. 2005) The condensate is treated at a wastewater treatment plant (Karlis et al. 2024, 158). Rendering can have a negative impact on the environment because of the harmful odorous compounds released. Heat treatment reactions such as the Maillard reaction and Strecker decomposition release odorous compounds. (Anet et al. 2013) The range of compounds formed by rendering is

quite wide. Their formation is the result of the breakage of the animal cell during heating, the release of volatile substances and the degradation of proteins by heat. (Mattila 1986, 55) In addition, Rappert et al. (2005a) indicated that the degradation of lipids, involving deamination and decarboxylation of amino acids during pyrolysis, and the oxidation of lipids result in the formation of odorous compounds. Odor-causing compounds from rendering include sulfurous compounds, e.g. hydrogen sulfide, mercaptans and organic sulfides, nitrogenous compounds, e.g. ammonia, amines and amides, oxygenated compounds, e.g. ketones, esters, alcohols, aldehydes and acids, and aliphatic and aromatic compounds, e.g. oils and fats. (Karlis et al. 2024, 344) Odorous compounds released during cooking from rendering unit processes include hydrogen sulfide, mercaptans, ammonia, amines, aldehydes, and organic acids. The off-gases from drying mainly contain nitrogen compounds such as ammonia and amines, mercaptans and hydrogen sulfide. However, the odor content of drying off-gas is often lower than from cooking (Mattila 1986, 55) Both cooking and drying produce volatile organic compounds (VOCs), some of which are also odorous (Kastner et al. 2005). VOCs is a class of pollutants that includes any organic compounds that can exist in air as vapors (Cooper 2007).

People smell different odors depending on their individual characteristics. The olfactory sensitivity to different compounds can be measured by the threshold of odor. The odor threshold is the lowest concentration of a compound that a human detects in an odorless dilution gas. Odor quality is defined by different descriptive terms as in Table 1 for typical rendering compounds. When assessing odor nuisance, it is important to consider whether the odor produced by the different compounds, alone or in mixture, is perceived as pleasant or unpleasant. For example, unpleasant odors are often perceived as a sign of danger (Mattila 1986).

Table 1. Odor description and threshold of typical compounds released from rendering process.

Compound	Odor threshold (ppm)	Odor description
Acetaldehyde	0,21 ^[1]	pungent, fruity ^[2]
Acetic acid	1 ^[2]	sour ^[2]
Ammonia	37 ^[1]	pungent, irritating ^[2]
Dimethyl disulfide	0,008 ^[1]	decayed cabbage ^[3]
Dimethyl sulfide	0,001 ^[2]	decayed cabbage ^[3]
Hydrogen sulfide	0,0047 ^[1]	rotten eggs ^[3]
Methyl mercaptan	0,001 ^[1]	rotten cabbage ^[1]

^[1] Prokop et al. (1992), ^[2] Cooper (2007), ^[3] Rappert et al. (2005b)

Sulfurous compounds such as mercaptans, sulfides and disulfides are formed from sulfur-containing amino acids by both aerobic and, even more so, anaerobic degradation (Albers et al. 2003, 16). Methyl mercaptan (CH_3SH), dimethyl sulfide and dimethyl disulfide has low odor threshold values (Table 1) (Prokop et al. 1992, 562; Cooper 2007). The hydrogen sulfide (H_2S) produced by the thermal treatment of rendering is mainly formed by the anaerobic degradation of organic matter in the presence of sulfate or the anaerobic degradation of proteins (Albers et al. 2003, 16). H_2S is a colorless toxic gas, which is heavier than air at room temperature (Andrés et al. 2023). It is combustible and hydro soluble (Xie et al. 2022, 141). The H_2S recognition threshold is 0.0047 ppm (Prokop et al. 1992, 562) and its odor is described by Rappert et al. (2005b, 943) as an obvious smell of rotten eggs. The health effects of the H_2S vary with different concentrations, e.g. 1-5 ppm causes a moderately unpleasant odor, headache, nausea, and watery eyes; 20-50 ppm causes a very strong odor and irritation of the eyes and respiratory tract; 100 ppm causes loss of the sense of smell and 150-200 ppm paralyses the sense of smell and can cause cognitive and motor impairment. Exposure to 500 ppm H_2S can cause serious health effects such as severe eye damage after 30 minutes of exposure, severe lung irritation, sudden unconsciousness, pneumonia and even death within 4-8 hours. High concentrations close to 1000 ppm can cause immediate collapse after a few breaths and death after 30 minutes of exposure (Guidotti 2010; Andrés et al. 2023).

Nitrogenous compounds such as amines are formed mainly by anaerobic and/or heat-induced degradation of proteins and amino acids. Ammonia (NH_3) is formed mainly as a degradation product of proteins and amino acids during aerobic degradation. (Albers et al. 2003, 16) NH_3 is lighter than air (Chai et al. 2021) and reacts sensitively with water. In water, the compound is present either as dissolved ammonia or as ammonium ion. Increases in water temperature and pH reduce the solubility of ammonia and therefore increase the evaporation of ammonia into the air. (Manni et al. 2023, 26) NH_3 recognition threshold is 37 ppm (Prokop et al. 1992, 562) and the odor is described as pungent and irritating (Cooper 2007). Exposure to ammonia via the breathing air can cause physical health effects such as eye, skin and respiratory tract irritation and more severe upper respiratory tract damage (Manni et al. 2023, 26).

Of oxygenated compounds acetaldehyde odor is described as pungent, fruity, and acetic acid odor description is sour. Exposure to these kinds of harmful compounds may cause toxicological effects. Typical physical symptoms caused by such compounds include headache, eye and throat irritation, cough, shortness of breath, rhinitis, and nausea due to exposure to the odor. (Cooper 2007)

3. TREATMENT OF ODOROUS GASES

This chapter reviews the legislation affecting air emissions from animal by-product processing plants and reviews the best available techniques for the treatment of air emissions from this industry. A comparison of the treatment techniques considered is then made with a view to their advantages and disadvantages and their suitability for the treatment of odorous compounds typical for rendering plants.

3.1 The impact of BAT on the operation of directive plants

Industry contributes a large share of emissions to air and water, which is why the European Union has adopted the IED 2010/75/EU. The main objective of the IED is to protect the environment and health and to regulate the environmental impact of industrial plants through environmental permitting. In Finland, the IED requirements have been enacted as part of the Environmental Protection Act 527/2014, which specifies that BAT must be used to prevent pollution (Ympäristönsuojelulaki 2014, 8 §). Emission limit values are set in accordance with the BAT method. In addition, BAT aims to improve energy efficiency and increase the use of side streams in industrial installations. BAT documents are managed through the BAT Reference Document (BREF) by the European IPPC Bureau. An essential part of preparing BAT guidelines is the exchange of information between industry and public authorities. (Ympäristö.fi 2023) The aim of the BREF is to provide information on efficient methods and technical solutions. It highlights the cross-effects of methods in different contexts to generate the best practices. (Puheloinen et al. 2011, 33)

According to the IED, the emission levels of the plant should not be exceeded under normal operating conditions. Applications for an environmental permit shall include the results of emission monitoring and additional information to allow comparison of the operation of the plant applying for a permit with the best available techniques and emission levels defined in the BAT. The environmental permit application will indicate the techniques and means that the plant intends to use to protect the environment. (Ympäristö.fi 2023) The environmental permit for an industrial plant must be reviewed when the European Commission publishes a decision on the conclusions of the main operation of the industrial plant, i.e. the new BREF (Ympäristönsuojelulaki 2014, 80 §). The operator must comply with the conclusions on the main operation at the earliest four years after the publication of the conclusions (Ympäristönsuojelulaki 2014, 81 §). Although the emission limit value and emission prevention permit requirements must be based on BAT, the

operator cannot be obliged to use only a certain technique (Ympäristönsuojelulaki 2014, 52 §).

Rendering industry follows the Best Available Techniques (BAT) Reference Document for the Slaughterhouses, Animal By-products and/or Edible Co-products Industries (SA-BREF), which provides recommendations for odor removal systems for rendering of animal by-product operation. In addition, the SA-BREF has defined BAT-associated emission levels (BAT-AELs), for channeled emissions to air of odor, organic compounds, NH₃ and H₂S from rendering, fat melting, blood and/or feather processing. It defines a limit value for odor concentration of 200–1 100 ou_E/m³. By exception, this limit value does not necessarily apply to combustion e.g. thermal oxidizer. For other treatment processes, the limit value may be higher, up to 3 000 ou_E/m³ if the abatement efficiency is ≥ 92 % or no odor is observed in the treated gases. The Total volatile organic compounds (TVOC) limit value is 0.5–16 mgC/Nm³, while NH₃ is 0.1–4 mg/Nm³, with an upper limit that can also be higher, up to 7 mg/Nm³ in the case of combustion of malodorous gases. For H₂S, the BAT-Associated Emission Levels (BAT-AELs) range applies where the compound is identified as a relevant contributor to the emission in the sector in question, in which case the limit value is < 0.1–1 mg/Nm³. (Karlis et al. 2024, 431)

3.2 Odor treatment techniques for animal by-product processing plants

The techniques described in this chapter have been selected based on the BAT techniques presented in the SA-BREF and the techniques found in literature survey. The selected odor removal systems are condensation, thermal oxidation, wet scrubbing, bio-filtration, and bioscrubbing.

3.2.1 Condensation

In condenser, impurities in the waste gas stream are removed by lowering the temperature of the gas below the condensation point using a heat exchanger, causing the vapor to liquefy, and be removed from the gas (Mattila 1986, 73). The lower the normal boiling point of a compound, the more volatile it is. In this case, cooling must be used to achieve a sufficiently low temperature. (Schnelle et al. 2015, 239) In this process, condensable and non-condensable gases are separated. The condensate that separates as a liquid phase is directed to wastewater treatment and the non-condensable gases to further treatment. (Karlis et al. 2024, 158) Condensers are typically used to remove VOCs and

hazardous air pollutants from the emission streams (Schnelle et al. 2015, 239). For example, in rendering plants, condensation is used because of the high intensity of the cooking vapors (Karlis et al. 2024, 159).

Condensers can vary from simple condensers to complex installations that maximize energy and steam recovery. Vertical shell and tube heat exchanger arrangements is shown in Figure 2, with condensation inside the tubes. Typical surface condensers are shell and tube or finned heat exchangers. Condensation is achieved by direct cooling, such as surface condensers, or indirect cooling, such as contact condensers.

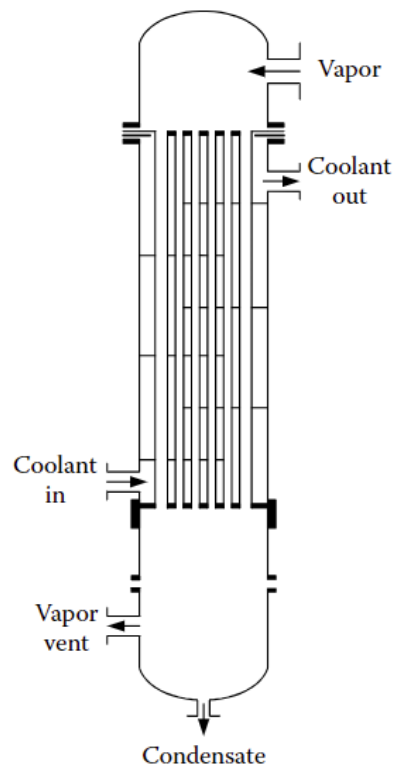


Figure 2. Vertical shell and tube heat exchanger arrangements (Schnelle et al. 2015).

In both cases, the condensed vapor forms a film on the cooled surface, flowing as a liquid phase into a collection tank for further treatment, such as reprocessing or disposal. In surface condensers, the contaminated gas is not in contact with the refrigerant, but the refrigerant passes through the system's tubes, with VOCs condensing outside the tubes inside the shell of the unit. The system coolant can then be reused, as there is no risk of contamination. In contact condensers, the evaporating gas stream is cooled by spraying a cooler liquid directly into the gas stream. Due to the contact between the contaminated gas stream and the coolant, the coolant cannot be recirculated and is treated before being disposed of. Coolants are usually cooling water, chilled water, and refrigerants. (Karlis et al. 2024, 159; Schnelle et al. 2015, 239–241)

Condensation alone is usually not sufficient to reduce the gas to be purified to the level required by emission limits (Devinny et al. 1999, 3), which is why this method is often used as a preliminary cleaning technique when the off gas contains high concentrations of pollutants. Thermal oxidation often has to be used after air-cooled condensers as a secondary treatment method to ensure that the off gas is treated to the required emission limits (Schnelle et al. 2015, 239). In contrast, residual air from high-efficiency condensers, such as chilled water condensers or glycol systems, can be cleaned by a chemical scrubber or biofilter instead of the typical energy-intensive thermal oxidation. (Karlis et al. 2024, 158 & 345) The odor removal efficiency of condensation varies between 50–90 %, but gas flow pressurization can achieve higher removal efficiencies than conventional condensation (Schnelle et al. 2015, 239 & 240).

The advantage of condensation is the simplicity and cost-effectiveness of the process. It is a viable solution for VOCs and the removal efficiency of the system improves with higher VOC content in the gas to be treated (Schnelle et al. 2015, 240). The environmental benefit achieved is a reduction in odors (Karlis et al. 2024, 159). However, the method does not necessarily eliminate odor problems completely, as odor-causing compounds may be part of a non-condensable gas phase (Nabais 2006, 116). From an economic point of view, condensation is most profitable for concentrated vapors with recycling or recovery value. Mixed impure gas is difficult to recycle, making combustion more profitable. One disadvantage of condensation is that it causes secondary emissions as wastewater, which must be treated by wastewater treatment. The high ammonia content and chemical oxygen demand of the condensate can overload the wastewater treatment plant if it is not treated in a controlled manner. (Karlis et al. 2024, 158) In addition, condensate wastewater causes secondary odors (Mattila 1986, 73). The heat exchangers can form ice (Schnelle et al. 2015, 240) and maintenance can be problematic. In addition, contaminated exhaust gas can cause fouling of the heat exchanger. The costs of condensation are related not only to the investment costs of the equipment and operational costs but also to the disposal of secondary effluents. (Nabais 2006, 116)

3.2.2 Thermal oxidation

According to Nabais (2006, 118), the process of thermal oxidation is an exothermic reaction where, in the presence of oxygen, hydrocarbon compounds are converted to carbon dioxide and water vapor and released heat. The combustion of the odorous gases can be carried out either in a separate combustion chamber or in a process unit designed for the combustion of other fuels. The odorous gas containing impurities is fed to a combustion chamber, where an oxidizing flame is maintained by burning a supporting fuel, often natural gas, or fuel oil. (Krogerus 1992, 26) Typical thermal oxidation process is presented in Figure 3. According to Mattila (1986, 64), the consumption of supporting fuel is directly proportional to the quantity of impure gas. To make the process more economical, a heat exchanger or steam boiler can be placed after the combustion chamber to recover part of the energy used for oxidation as hot water or steam (Krogerus 1992, 27). However, the implementation of a waste heat recovery system requires capital costs (Karlis et al. 2024, 163).

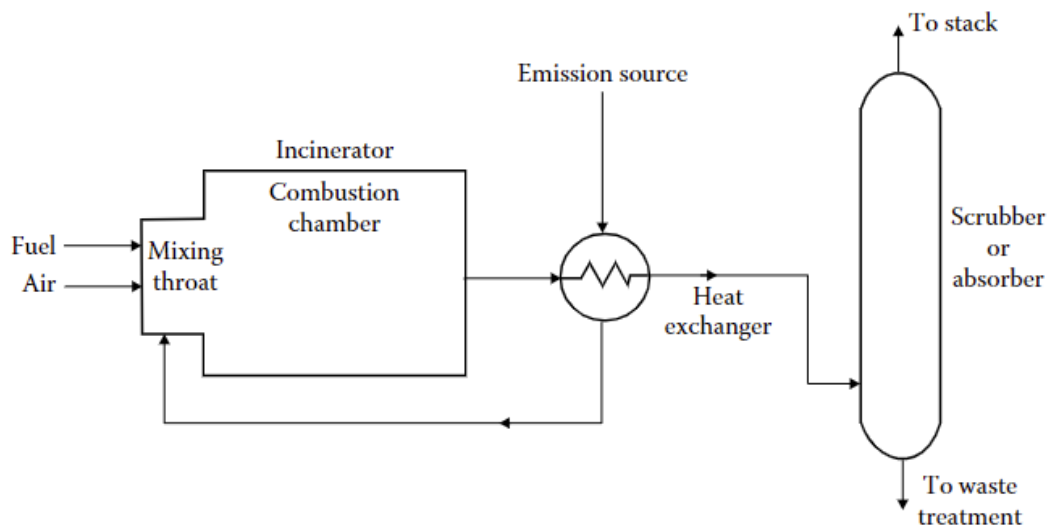


Figure 3. Thermal oxidation process (Schnelle et al. 2015).

The oxidation of decomposable compounds in the gas is successful if they are in contact with a sufficient amount of oxygen at a temperature above the autoignition point of the compound (Karlis et al. 2024, 163). The temperature of thermal oxidation can vary between 500–1200°C (Nabais 2006, 118). For odorous compounds, a typical temperature is 750–850°C and a sufficient residence time of 1–2 seconds, with enough turbulence and oxygen (Karlis et al. 2024, 163). The method can achieve up to 99 % reduction of odorous compounds (Mattila 1986, 64).

In thermal oxidation of odorous gases, the aim is to oxidize the combustible gases entirely. The process generates pollutants such as carbon dioxide (CO₂), nitrogen oxides (NO_x), sulfur oxides (SO_x) and water. Emission levels are affected by the properties of the gas being processed and the basic combustion conditions of the used fuel. For example, NO_x is generated by the decomposition of substances in the process air fed into the combustion chamber. The level of these emissions is influenced by the amount of NH₃ in the gases, which is related to the freshness of the raw material used for rendering. This can be influenced by paying attention to storage and by treating the raw material as fresh as possible. (Karlis et al. 2024, 163) When sulfur compounds are oxidized to sulfur dioxide, the chemical structure changes, but emissions are not reduced. This is why sulfur dioxide is often separated before the combusted gas is released into the atmosphere. (Krogerus 1992, 26) SO_x emissions can be high, especially in the treatment of feathers (Karlis et al. 2024, 165). If the impure gas is high in organic matter, it can be fed to the combustor chamber as a fuel, as the high concentration will cause it to burn in the same way as the fuel itself. Dilute gas streams are fed into the combustion chamber with the combustion air, as the low organic content will not cause the gas to burn independently but may smother the flame. (Krogerus 1992, 26) Depending on the oxygen content of the odorous gas, air must sometimes be fed into the burner (Mattila 1986, 64).

The advantages of thermal oxidation are a very high oxidation rate, even at low concentrations, and the possibility to recover the part of the used energy. The method should be used when the gas to be oxidized has very low concentrations of odor causing compounds or when a high oxidation rate is difficult to achieve by other methods. (Krogerus 1992, 27) Burners have a fast start-up time, which makes them well suited for batch and shift processes (Nabais 2006, 118). In some cases, however, it may take some time to reach the minimum temperature for start-up or shutdown, causing steam to be released before complete combustion is achieved. In this case, partially evaporated organic matter may still cause odor nuisance. (Karlis et al. 2024, 163 & 345)

The investment cost of the process depends on the heat recovery system and the capacity of the combustion chamber, where the size is determined by the volumetric flow and residence time of the gas. The operating costs depend on the price and consumption of the fuel and the working hours required for monitoring. Electricity is consumed when the gas flow is blown into the burner. However, the benefit of the recovered energy can be considered to reduce the operating costs. (Krogerus 1992, 27) The method is widely used by rendering plants in Europe (Karlis et al. 2024, 165).

3.2.3 Wet scrubber

The wet scrubber is based on absorption of compounds to scrubbing liquid because the solubility of odorous compounds in the liquid is higher than in the off gas. In a wet scrubber, the pollutants in the gas stream are transferred to the liquid phase using an adequate detergent (Table 2). In a wet scrubber, the contaminants in the gas and the liquid from the separator are brought into contact with each other, whereby the high gas velocity or the velocity of the liquid injected into the scrubber causes the liquid to break down into small droplets that dissolve compounds in the gas. (Nabais 2006, 109–111) The absorption technique is well suited for odorous compounds that are easily soluble either in water or in acidic or alkaline solutions. For instance, such compounds include hydrogen sulfide, ammonia, amines, ketones and acetic acids. In addition to gas scrubbing, absorption can be used to recover the wanted compounds. (Mattila 1986, 68) In a wet scrubber, the adsorption process and chemical oxidation are responsible for H₂S removal, so the selected scrubbing liquid, inlet flow rate and gas contact time are crucial factors for the removal efficiency of compounds from the gas phase through mass transfer to the liquid phase (Alinezhad et al. 2019).

Table 2. Classification of scrubbing liquids (Brinkmann et al. 2016, 362–363).

Detergent	Active substance	Targeted towards
Water	H ₂ O	Hydrogen halides, NH ₃
Alkaline solution	NaOH, Na ₂ CO ₃	Acidic compounds such as: hydrogen halides, H ₂ S, SO ₂ , phenols, chlorine
Alkaline oxidizing solution	Basic solution with NaOCl, ClO ₂ , O ₃ , or H ₂ O ₂	Odorous pollutants
Oxidizing solution	H ₂ O ₂	NO _x emissions
Sodium hydrogen sulfite solution	NaHSO ₃	Odor removal (aldehydes)
Sodium tetrasulfide solution	Na ₂ S ₄	Mercury from waste gas
Acidic solution	H ₂ SO ₄ , HNO ₃	Alkaline compounds such as: NH ₃ , amines, esters
Monoethanolamine and diethanolamine solutions	Ethanolamine	H ₂ S
Organic solvents	Chilled nonane (C ₉ H ₂₀)	Light VOCs such as: butanes and pentanes

The selection of the scrubbing liquid is essential for cleaning efficiency. A more reactive detergent will provide more effective absorption, which in turn has a beneficial effect on the size of the washer. When washing with a reactive detergent, a much smaller washing column can be used than with a less reactive detergent. The detergent can be either water, a solution containing an acidic, alkaline, or oxidizing chemical, or a combination of these. The use of these detergents is based on the fact that many odor-causing compounds are acids or bases. (Krogerus et al. 1992, 32) In Table 2 is a list of the most common types of gas scrubbing detergents and examples of the chemicals they are intended to absorb.

According to Nabais (2006, 109) it should also be noted that the odor problem does not necessarily disappear when using scrubbing liquids, as odor compounds remain in the liquid and can be released again in gaseous form when conditions change. To prevent this, strongly oxidizing chemicals such as hydrogen peroxide, ozone, potassium permanganate or chlorine oxide can be added to the scrubbing liquid, causing the odorous compounds to react with the oxygen atoms in the solution to form odorless water-soluble compounds. This prevents the formation of secondary odors. Wet scrubbers also generate other secondary emissions because the primary gaseous emissions are absorbed into the liquid phase, producing a waste solution. (Krogerus et al. 1992, 33)

In general, scrubbers are used as countercurrent-flow scrubbers, with the liquid phase passing from top to bottom and the gas being blown against the liquid from bottom to top (Figure 4). Examples of such scrubbers are the packed bed scrubber and the spray tower scrubber. (Mattila 1986, 67) In a packed bed scrubber, the gas flows upwards through the packing material and the water flows downwards against the gas. The wetted packaging material forms a large surface area for contact between the gas and the water. (Bhave et al. 2008) In a spray tower scrubber, the gas flows upwards against a droplet stream which is sprayed downwards, causing compounds in the gas phase to be transferred to the liquid phase (Bandyopadhyay et al. 2007). There is also the multi-stage scrubber, which consists of several scrubbing units. It is often a crossflow type but can also be constructed from countercurrent-flow scrubbers. In a crossflow scrubber, the gas flows horizontally through a layer of filler and the scrubbing liquid is sprayed from above. The different scrubbing units in a multi-stage scrubber can operate with their own detergents to remove different types of compounds. (Mattila 1986, 67)

The advantage of a multi-stage scrubber is its versatility, as the unit is assembled from scrubbing units that can use their own liquid cycle and remove different compounds in

their own stages. (Mattila 1986, 67) Multi-stage wet scrubbers using various scrubbing liquids are often the preferred option for rendering plants that produce high levels of odors. Parameters related to the design and operation of a wet scrubber include fillers shape, liquid spray locations, gas residence time, flow rate, both gas and liquid temperature, pressure drop and liquid-to-gas flow ratio. The gas flow rate provides a preliminary estimation of the footprint of the system, the inlet contaminant concentrations, and the overall removal efficiency. (Nabais 2006, 111)

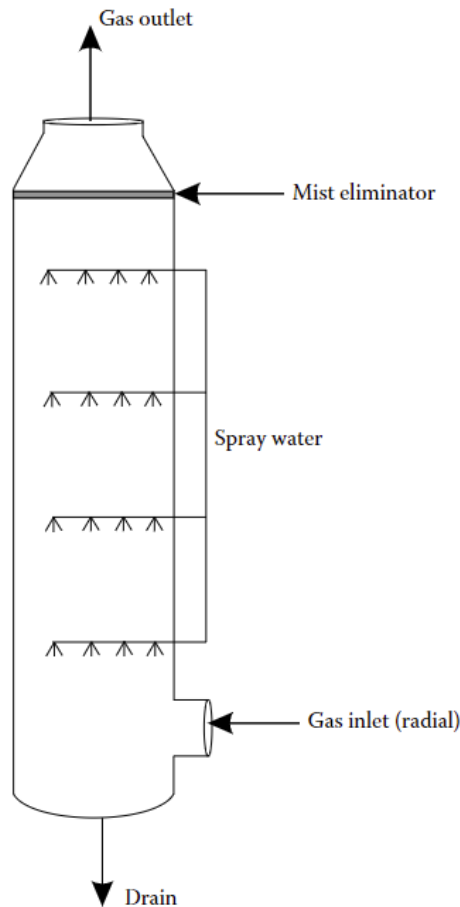


Figure 4. A vertical countercurrent tower (Schnelle et al. 2015).

Scrubbers are well suited to different gas flows and the addition of chemicals can provide a more targeted impact on scrubbing efficiency. Scrubbers can achieve up to 99 % removal efficiency for odorous compounds. The attractiveness of the method is enhanced by the relatively small space taken up by the equipment and the relatively low cost of operation, consisting of investment costs, which are influenced by factors such as column size, operating costs, including detergent chemicals, and energy costs associated with gas blowing and liquid pumping. (Nabais 2006, 109–110; Krogerus et al. 1992, 33)

One advantage of the wet scrubber is its cooling effect on hot gas streams (Brinkmann et al. 2016, 373).

Other disadvantages of using wet scrubbers are high chemical consumption, which is costly and requires the handling of hazardous substances. Scrubber equipment is complex and requires frequent maintenance. In addition, scrubbers require internal monitoring of the chemicals in the gases and liquids, and calibration and replacement of various sensors such as pH. The equipment can also suffer from internal clogging, corrosion. (Nabais 2006, 110)

3.2.4 Biofiltration

In biofiltration, the off gas is passed through a humidifier to moisturize the gas so that it does not dry out the bed material. Then the off gas is passed through the bed material, whereby the pollutants in the odorous gas are transferred to the biologically active water phase and adsorbed on the surface of the filter material to be used by the biofilm formed by microbes (Figure 5). (Revah et al. 2005, 44 & 54) Microorganisms get the carbon and energy they need from the impure inlet gas, while nutrients such as nitrogen, phosphorus, minerals, and trace elements come either from the natural biofilter bed material or by adding them separately (Kennes et al. 2001, 74–75). The function of microorganisms creates more biomass and carbon dioxide, water, sulfate, and nitrate as a by-product. Odor-causing compounds are oxidized by microbial metabolism to become odorless and harmless. (Datta et al. 2005 128) Biofiltration is used in the treatment of organic gases such as VOC compounds, other hydrocarbons, and gases containing ammonia or hydrogen sulfide. Biofiltration is most effective with low molecular weight compounds that are highly water soluble and contain simple molecular bonds. (Sercu et al. 2006, 127)

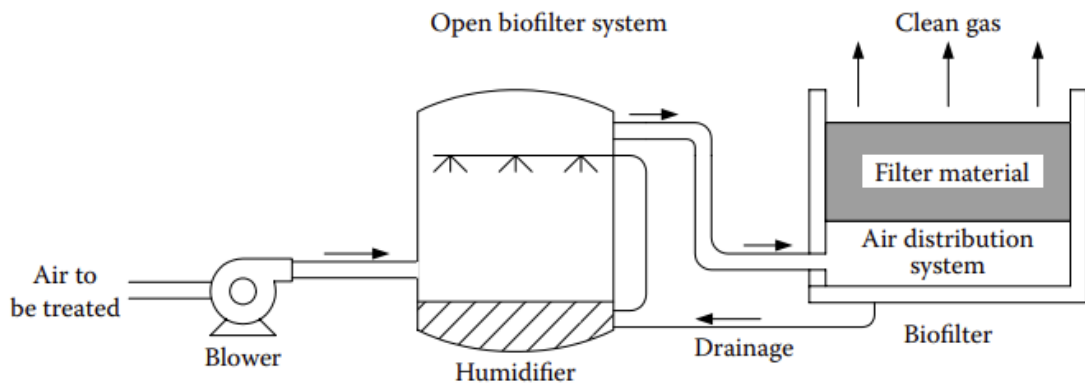


Figure 5. Typical open biofilter configuration (Schnelle et al 2015).

Natural materials such as compost, peat, wood chips, fertilizer and soil can be used as the bed material of the biofilter, but also adsorbents like activated carbon can be added in bed material (Kennes et al. 2001, 66). Natural bed materials contain a sufficient number of different microorganisms to biodegrade air pollutants. Several groups of microorganisms such as bacteria and fungi are involved in the degradation of pollutants in the supply air in biofilters. (Kennes et al. 2001, 68–71) Microbial populations in biofilters are estimated to be 1 billion microorganisms per gram of organic matter. The efficiency of the biofiltration process improves after the growth during the acclimation phase. (Datta et al. 2005, 135–136) The thickness of the biofilm formed by microorganisms varies from tens of micrometers to more than 1 cm, but the average thickness is less than 1 mm. The activity of microorganisms increases as the thickness of the biofilm increases up to a certain level, until nutrient diffusion becomes a limiting factor once this level is exceeded. The functionality of the biofilm is determined based on its microbial density, bed material, and the physical and chemical conditions in the operating environment. (Datta et al. 2005, 129) According to Datta and Allen (2005, 135) bio-oxidation of organic substrates causes aging and mineral accumulation in the system, which eventually requires changing the media.

The factors to be considered in biofiltration to ensure favorable conditions for microorganisms are moisture content, pH, temperature, and the sufficiency of nutrients and oxygen. The optimal moisture level of the biofilter depends on the surface area and porosity of the filter bed material. Depending on the material used, 30–60 % is considered as a typical moisture content to create an ideal operating environment for microorganisms. (Datta et al. 2005, 131) Too low a moisture content will cause the bed material to dry out and crack, forming escape channels for gas. In this case, the contact time decreases, and the microorganisms do not have time to clean the air of impurities sufficiently efficiently. The desired moisture content of the biofilter can be maintained with a pre-humidifier of the feed gas stream. In addition to this, sprinklers located above the bed can be used, the addition of water can be regulated automatically with, for example, a load sensor that detects the weight of the filter bed. Too high a moisture content prevents the transport of oxygen and hydrophobic contaminants into the biofilm, promoting the development of anaerobic zones and limiting the reaction rate. (Datta et al. 2005, 131; Kennes et al. 2001, 81)

Oxygen is essential to support the function of aerobic micro-organisms, which need oxygen for their metabolic processes. The survival of aerobic heterotrophic bacteria in the filter bed requires an oxygen content of at least 5-15% in the incoming gas stream. However, the lack of oxygen is not considered a typical problem in exhaust gases, but in

overloaded filters it can nevertheless act as a limiting factor. (Datta et al. 2005, 132–133) The recommended temperature for microbial activity in biofiltration is considered to be in the mesophilic range 20–40°C, which promotes the growth of microorganisms (Verein Deutscher Ingenieure, 15). If the temperature of the contaminated gas is above 40°C, the gas should be cooled before being fed to the biofilter. Correspondingly, a cold gas stream below 10°C should be heated to the desired temperature to maintain micro-organism activity. According to Datta et al. (2005, 132) biological activity almost doubles for every 10°C increase in temperature. Thermal regulation can help to avoid thermal shocks in biofiltration. In terms of the activity of microorganisms, the most optimal pH is typically 5–9. (Singh et al. 2005a, 113) The pH value of biofiltration is influenced by choosing a bed filter material suitable for microorganisms, for example compost with a pH of 7–8. Carbon dioxide produced from the metabolism of aerobic microorganisms can lower the pH of the system. If the incoming gas stream or its intermediate products do not provide sufficient buffer capacity, the pH can be adjusted by adding alkali such as sodium and magnesium hydroxide or by changing the filter material. The pH value of the biofilter can be maintained by adding solid buffer substances during the bed addition phase. (Datta et al. 2005, 133)

Biofilter operation can be optimized by selecting a biofilter of sufficient size, taking care of physical stability, moisture balance and pH buffering capacity. In addition, ensuring nutrient sufficiency and low pressure loss will improve the functioning of the process. (Datta et al. 2005, 131) Factors limiting the functioning of a biofilter include too high flow rates, high levels of contaminants in the inlet gas, short residence times or difficultly degradable compounds. It has been established that the accumulation of biomass is greater in the inlet parts of the biofilter, which causes the bed properties to change. The reduction of the empty space between the particles and the compaction of the natural packing materials cause channeling and increase the pressure loss. Similar problems can be caused by a large filter depth when the bottom of the filter bed becomes too compact, for example when using multilayer biofilter media, which operates at high load rates with less surface area. Therefore, the depth of the biofilter medium typically varies between 0.5 and 2.5 m, and a depth of about 1 m is commonly used to ensure sufficient residence time and minimum filter surface area. (Datta et al. 2005, 134)

Biofiltration performance can be monitored with the help of various parameters, such as true bed residence time (TBRT) which means actual residence time. This takes into account the average porosity of the biofilter material when calculating the intake air per unit of time. Depending on the material, the porosity can vary from 20 to 80 %. The higher the TBRT value, the better the efficiency of the biofilter, while a low value suggests that

the efficiency of the biofilter should be improved, for example by increasing the size of the biofilter. (Wang et al. 2004, 424–428) Another parameter affecting the efficiency of the biofilter is the empty bed residence time (EBRT), which relates the flow rate to the size of the biofilter. EBRT is directly correlated with the size of the plant and the construction and operating costs. (Mirmohammadi et al. 2014)

The advantages of biofiltration compared to other treatment technologies can be considered its simple structure, low capital costs and inexpensive bed material. It is a viable choice for large volumes of low-concentration impure gases due to low energy costs. In addition, the method does not necessarily require the addition of chemicals. Biofiltration does not create a secondary waste stream, as, for example from a gas scrubber. Disadvantages of the method can be considered the regularity of the need to replace the filter material at least every few years and the large surface area required by the structure, which can be problematic in industrial areas where construction area is not cheaply available. (Datta et al. 2005, 136–137)

3.2.5 Bioscrubber

The principle of the bioscrubber is based on physical and biochemical mechanisms. Absorption involves the transfer of odorous compounds from the gas to the liquid phase. At this stage, the bubble surface area, contact time and diffusion coefficient are important. One mechanism is that higher molecular weight compounds with lower water solubility can adsorb to biological flocs. In condensation, a relatively warm odorous gas is transferred to an aqueous solution at a lower temperature, causing it to condense. During biodegradation, the active micro-organisms in the bioreactor are responsible for a substantial transformation of the odorous compounds as they are absorbed, adsorbed and concentrated in the aqueous phase. Heterotrophic microbes need an organic carbon source for energy and carbon for cell growth and synthesis. Autotrophic organisms use carbon dioxide from the air stream as carbon, and the oxidation of sulfide to sulfate or elemental sulfur provides energy to the cells for growth and respiration. Typical odor-causing compounds such as hydrogen sulfide, acetone and propionaldehyde are highly biodegradable. Bioscrubbers are less popular for the treatment of a large proportion of VOCs due to their low water solubility. (Singh et al. 2005b, 173–174) This treatment method can achieve odor removal efficiencies of up to 90–99 % (Potivochayanon et al. 2006).

The bioscrubber is a two-stage system in which the odor-causing compounds are absorbed into the aqueous solution by the absorber (Figure 6). The packed bed inside the

absorber creates more contact surface between the absorber and the aqueous solution. The aqueous solution is passed into a bioreactor containing active biomass, where suspended micro-organisms decompose the contaminants. The water in the bioscrubber is continuously recirculated between the absorber and the bioreactor. The purified gas is passed through a demister to reduce the moisture content. (Singh 2005b; Morral et al. 2023) The principle of operation of the bioscrubber is similar to the biofilter, but it can be used with a higher inlet gas concentration and gas flow rate than the biofilter. Bioscrubber systems require less space and have lower construction costs than a biofilter. (Potivochayanon et al. 2006)

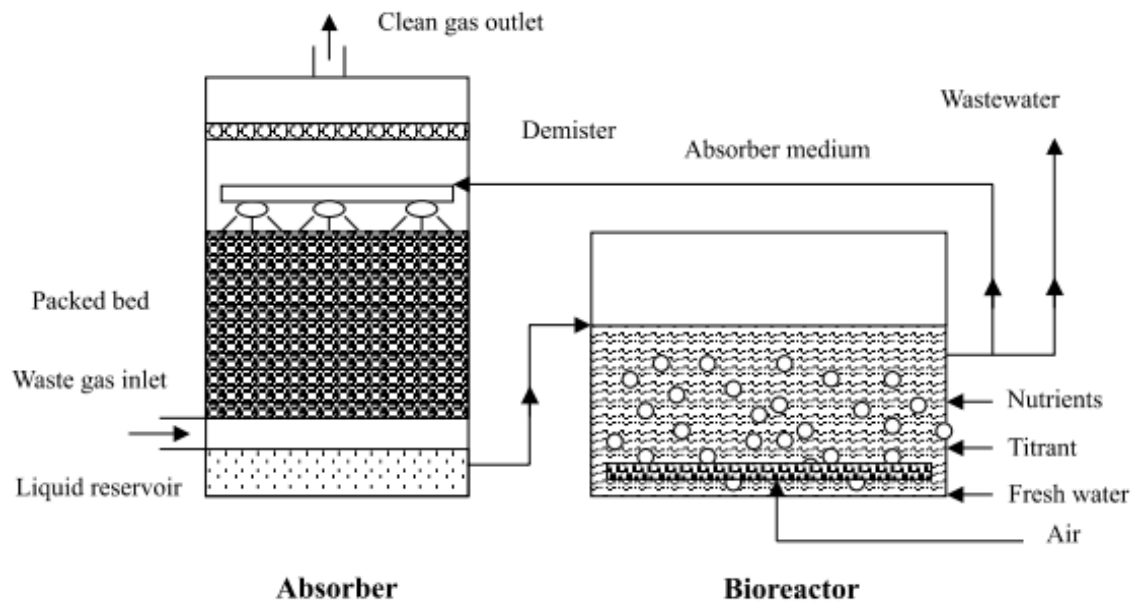


Figure 6. Design of the suspended-growth bioscrubber (Singh 2005b).

The absorber unit of a bioscrubber acts as a gas-liquid contactor, where the gas is divided into small bubbles in the liquid phase (Singh et al. 2005b, 175). According to Le Cloirec (2013), the absorber is usually packed with randomly oriented plastic elements with more than 70 % porosity. The packing material elements size typically range from 2 to 8 cm. The surface area of the packing material usually ranges from 100 to 300 m²/m³, of which about 2/3 is wetted at the time. (Van Groenestijn 2001, 135) The packed tower absorbers are recommended as bioscrubbers, as the others have a lower removal efficiency for poorly water-soluble compounds. Countercurrent packed towers are preferred over co-current and crossflow towers due to higher absorption efficiency, lower pressure drop and energy cost. (Singh et al. 2005b, 175)

The absorbed contaminants are transferred with the liquid to a bioreactor containing suspended activated sludge, which is aerated by air bubbles (Van Groenestijn 2001, 134).

In the bioreactor, microbial activity breaks down the contaminants into CO₂, H₂O, and biomass (Singh et al. 2005b, 177). In most cases, the solid and liquid phases are separated, for example by filtering (Singh 2005b, 183), to avoid clogging of the contactor, and then water is recycled back to the absorber for reuse (Le Cloirec 2013). Bioreactors volume varies between 7 and 1000 m³. The balanced average for gas flow rate and bioreactor is 1000, although there can be variations between 100 and 3000. (Singh et al. 2005b, 177)

The bioscrubber produces and maintains microbial biomass while retaining high odorous compounds utilization rates. The start-up of the bioreactor's microbiological activity can take some time, but this can be reduced by inoculating the activated sludge from the wastewater treatment plant or by using acclimatized inoculum from the mixed cultivation. For example, Thiobacillus and Hyphomicrobium strains have been found to be effective for the degradation of sulfur-containing compounds. The bioreactor biomass is sensitive to periods without substrate and therefore the supply of nutrients and aeration must be ensured even when the bioreactor is not being fed with gas. This ensures that microbial activity is maintained. The micro-organisms obtain trace metals from gas or water, while N and P sources are added as nutrients. One source of nutrients can be the effluent from a wastewater treatment plant. Oxygen is added by spraying air into the bioreactor. A minimum dissolved oxygen concentration of 1–2 mg/l is considered necessary to maintain biological activity. In order to maintain the functioning of the bioscrubber, the pH is kept constant by using titrant. An optimal pH value for biological activity and H₂S removal is considered to be 8.5–9, while a pH value of 6–7 is recommended for VOCs. (Singh et al. 2005b, 180–183) Solution acidification can occur due to the metabolites and carbon dioxide production resulting from the complete bio-oxidation of VOCs (Le Cloirec 2013), which requires pH adjustment, for example with sodium hydroxide. The optimum operating temperature for microbial activity varies for different compounds, but for sulfide oxidation efficiency, 25–35 °C is recommended. Bioscrubber operation results more harmless sludge and in lower quantities than wastewater treatment plants. The sludge consists of small solid particles, which may require filtration or centrifugation instead of sedimentation or flocculation for separation. Sludge may be discharged with the effluent to sewers, if permitted. The water has a residence time of 20 to 40 days. It is recommended to discharge 0.2 % of the tank volume per hour. (Singh et al. 2005b, 183)

One advantage of a bioscrubber is its small size, although the capital and operating costs are slightly higher than for example a biofilter. Bioscrubbers can handle high gas flow rates and high contaminant concentrations. Its process control of pH and nutrients is easier than a biofilter. (Singh et al. 2005b, 172) Bioscrubber has no risk of clogging the

packaging material (Van Groenestijn 2001, 134). The operation is reliable, predictable, and stable (Van Groenestijn 2001, 134). The microbial mass has a good adaptability to the gas composition. The process is well suited for the removal of water-soluble compounds such as H₂S, SO₂, alcohols, aldehydes, and fatty acids. However, the importance of pH control for optimum performance must be taken into account. Nevertheless, the dissolution of gaseous contaminants in absorption columns takes place over a short residence time, making it less suitable for compounds that are less soluble in water. (Singh et al. 2005b, 172) In addition, the method has the potential for leaching of slower growing micro-organisms. The start-up procedure is complicated by microbial activation, so breaks in production should be avoided. (Van Groenestijn 2001, 134) Sludge generated in the bioreactor may need to be controlled due to excessive biomass formation (Singh et al. 2005b, 173).

3.2.6 Comparison

All other treatment methods, besides condensation, can achieve almost as high odor removal efficiencies with more than 90 %. The condenser has the lowest odor removal efficiency, but on the other hand it is inexpensive and suitable for high concentrations of odor causing compounds, but it is not reaching target emission limits when used as a single technology. Table 3 summarizes the different techniques of off-gas treatment technologies and their advantages and disadvantages. In addition to not being a sufficient treatment method for odor removal, the condenser generates secondary emissions in the form of condensate and non-condensable gas. Thermal oxidation, on the other hand, is very effective for odor removal, but the operation consumes fuel and electricity. When only technology is taken into consideration, cost-efficiency of thermal oxidation is lower than condenser. However, thermal oxidation is an efficient technology, and it can reach target emission limits, used as a single technology. Comparing condenser against other technologies, its simplicity is emphasized. Condenser doesn't require monitoring, like wise wet scrubber which demands constant monitoring.

The wet scrubber is well suited for intensive odor causing compounds. Benefits of wet scrubber are low capital costs, operating efficiency and required space. Wet scrubber has high operating costs, and its chemical processes are complicated, claiming regular maintenance. In addition, this method is associated with safety risks due to the handling of chemicals.

Table 3. Comparison of off-gas treatment technologies.

Gas treatment technology	Odor removal efficiency	Advantages	Disadvantages
Condenser	-	+ Simple method ^[5] + Cost-effective ^[5] + Suitable for high concentrations ^[6]	- Not sufficient technique to achieve the emission limit values on its own ^[8] - Odor emissions in non-condensable gas phase ^[7] - Secondary emissions as wastewater ^[9]
Thermal oxidation	95–99 % ^[2]	+ High oxidation rate ^[2] + Possibility to recover used energy ^[2] + Fast start-up time, suited for batch processes ^[7]	- May cause odor nuisance before reaching minimum operating temperature ^[9] - Operating needs fuel and electricity ^[2] - Requires monitoring ^[2]
Wet scrubber	> 95 % ^[4]	+ Low capital costs ^[8] + Can operate with moist gas stream ^[8] + Ability to handle variable loads ^[8] + Takes up relatively small space ^[7] + Cooling effect on hot gas streams ^[13]	- High operating costs ^[8] - Complex chemical feed system ^[8] - Requires frequent maintenance ^[8] - High chemical consumption ^[7] - Can suffer from clogging and corrosion ^[7]
Biofilter	up to 98 % ^[1]	+ Low operating and capital costs ^[8] + Simple structure ^[13] + Suitable for large volumes of low-concentration gases ^[13]	- Large surface area ^[13] - Less suitable for high concentrations ^[8] - Operating conditions difficult to control ^[8] - Bed material need to be replaced ^[13]
Bioscrubber	90–99 % ^[3]	+ Small equipment size ^[10] + Suitable for high flow rates and high contaminant concentrations ^[10] + Stable and reliable operation ^[11]	- Complicated start-up procedure ^[11] - Need to control biomass formation in some cases ^[10]

^[1] Mattila (1986), ^[2] Krogerus et al. (1992), ^[3] Potivochayanon et al. (2006), ^[4] Prokop et al. (1992), ^[5] Schnelle et al. (2015), ^[6] Cooper (2007), ^[7] Nabais (2006), ^[8] Devinny et al. (1999), ^[9] Karlis et al. (2024), ^[10] Singh et al. (2005b), ^[11] Van Groenestijn (2001), ^[12] Brinkmann et al. (2016), ^[13] Datta et al. (2005).

Benefits of biofilter are simplicity, low operating and capital costs combined with odor removal efficiency. It works well on large volumes of low-concentration gases. However, its equipment requires a large surface area, and the operating conditions are not easy to control. Compared to a biofilter, a bioscrubber takes up very little space and its operating conditions such as pH and humidity are easier to control. However, in a bioscrubber the start-up procedure is complicated by microbial activation and production breaks of process should be avoided. A similar problem has not been observed in the use of a biofilter.

4. MATERIALS AND METHODS

This chapter presents the experimental works carried out during this study and the information on the feather treatment plant processes and off-gas treatment. Since the selection and optimization of suitable odor treatment methods is essentially influenced by the quality of the off-gas to be treated, the pollutants and their quantity, the aim of the experimental work was to investigate the quality of the off-gas by characterization and to optimize the operation of the off-gas treatment process to remove hydrogen sulfide and ammonia and to optimize the consumption of chemicals.

4.1 Honkajoki Ltd

Honkajoki Ltd is a company that handles animal by-products and processes them into products for various industries, using the nutrients in the by-products as raw materials for the circular economy. The company processes category 1–3 by-products from slaughterhouses and the food industry according to EU Regulation 1069/2009. In 2021, Honkajoki Ltd and its subsidiary Findest Protein Ltd processed a total of 234 000 tons of animal raw materials. The final products produced include meat-and-bone meal, fat, proteins as raw material for production animal and pet feed, fertilizer raw material and material for energy production. There are currently 7 different processing lines in Honkajoki, where different animal fractions are processed. Process differences between plants are related to the chosen treatment methods. The main processes also include emission control, which for all plants consists of the control of wastewater emissions and odor emissions in the process off-gas. The process vapors from Honkajoki Ltd's production facilities are condensed to reduce odor emissions and the non-diluted part is incinerated in a nearby energy production plant or, depending on the characteristics of the treated air stream, discharged through a chemical scrubber or directly to a biofilter.

4.1.1 Process description of the feather treatment

The most recent treatment plant is a feather plant, completed in 2023, which treats category 3 poultry feather raw material. A simplified process diagram of feather processing is shown in Figure 7. First, the quality of the raw material is checked, the material must not contain other by-products, foreign matter or be contaminated. The aim is to feed the raw material into the process as fresh as possible. The feathers are fed through a metal

remover into a hydrolyzer, where their protein structure is processed for better digestibility. Approximately 6000 kg of feathers and additional water are fed in one hydrolysis batch. Hydrolysis is carried out by using heat and pressure in the method required by the authorities. During hydrolysis, the feathers are sterilized, ensuring a microbiologically safe product. The material discharged from the hydrolyzer is homogeneous. After hydrolysis, the feather material is conveyed by feed screws to a dryer where it horizontally passes through an air dryer to a discharge screw at a temperature of 125°C as hot air circulates through the dryer, drying the material to near the desired meal moisture content. Drying is a continuous process. From the dryer, the feather meal passes through a sieve to a cooler and from there on to the meal processing stage, which consists of further mixing, milling, and sieving. The final product meal has a moisture content of 6–8 %. Finally, the meal is packed in large bags and stored awaiting transport. The annual technical processing capacity of the feather production line is 21 000 t/a.

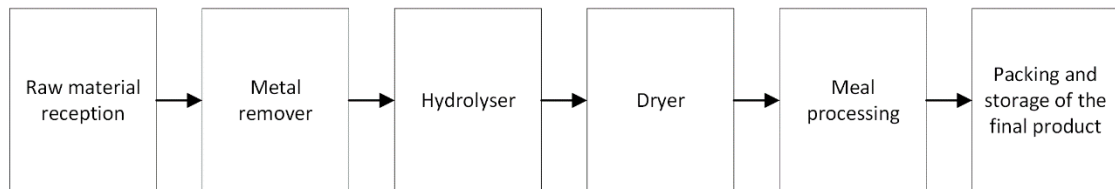


Figure 7. Simplified schematic for the production of feather meal.

The off-gas from the feather plant is divided into concentrated and diluted target off-gas. The concentrated off-gas includes non-condensable gases i.e. NCG's and selected process air for dilution. This includes the air leaving from the condenser of the hydrolyzer and the dryer. In addition, the concentrated off-gas includes the target off-gas from the metal detector and the target off-gas from the wastewater heating and holding tanks. The dilute off-gas is collected from target off-gas from other process steps, such as the raw material silo, screw conveyors, and meal handling. The concentrated off-gas is routed to a chemical scrubber, where it is combined with the diluted off-gas and then further through a humidifier to a biofilter.

4.1.2 Off-gas treatment process

The off-gas from the Honkajoki Ltd feather processing plant is treated in two stages. The plant is equipped with a chemical scrubber and a biofilter, to where the air is led by a humidifier. The different stages of the off-gas treatment process are shown in Figure 8.

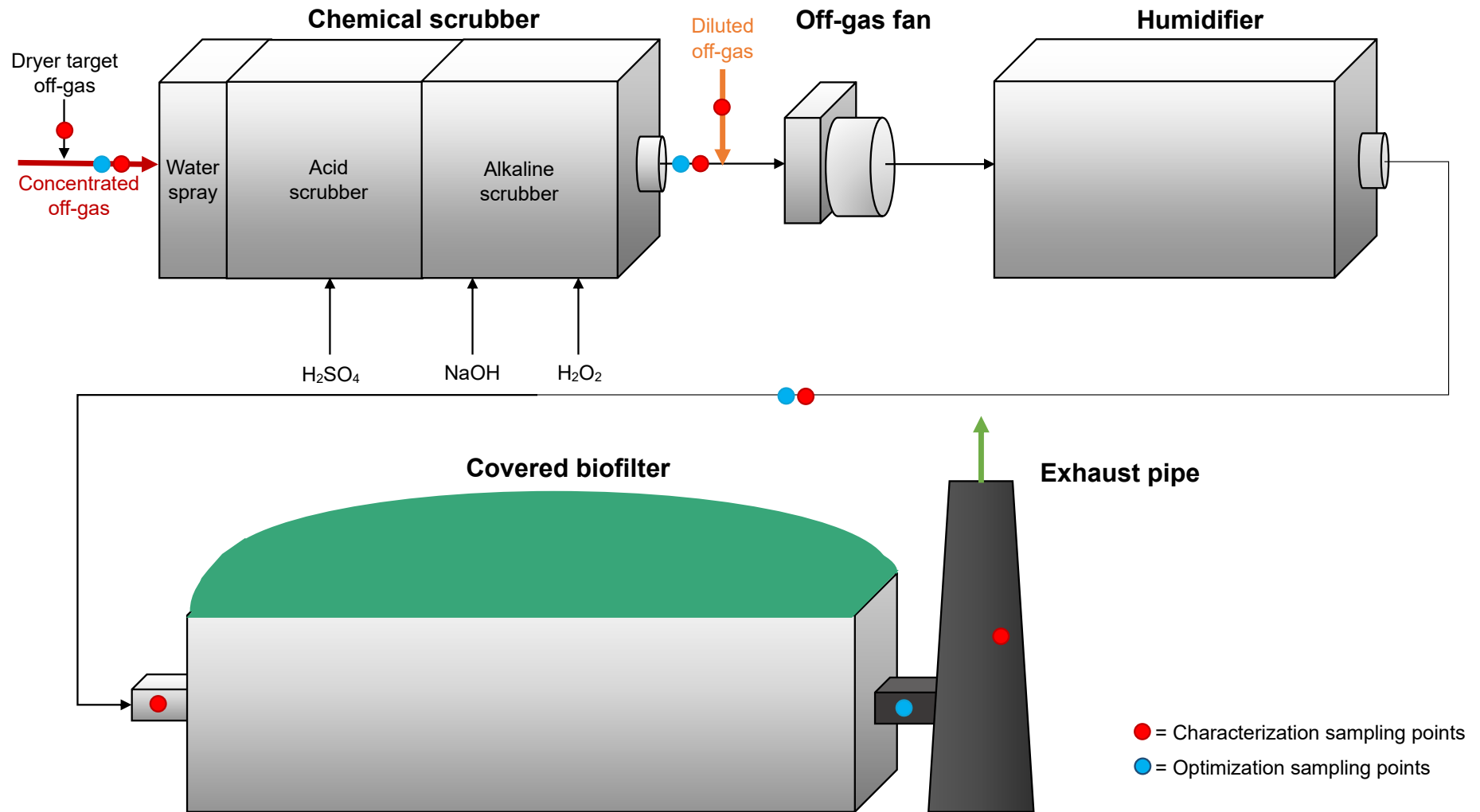


Figure 8. Off-gas treatment process of Honkajoki Ltd feather processing plant, the chemicals to be added to the chemical scrubber and the sampling points for the experimental work of the thesis.

The first stage of the treatment of the off-gas in a feather plant is a chemical scrubber with a three-stage system to treat the concentrated off-gas. In the chemical scrubber, the off-gas passes through a water spray to an acid scrubber, where 93 vol% sulfuric acid (H_2SO_4) is fed into the process to remove ammonia (NH_3). Next, the off-gas is passed to the alkaline scrubber, which is fed with 50 vol% sodium hydroxide (NaOH) to remove hydrogen sulfide (H_2S). An additional oxidizer for the alkaline scrubber is 50 vol% hydrogen peroxide (H_2O_2) which aims to improve the removal of H_2S . The supply of the oxidant is controlled by adjusting the redox value. The cycle of the washing water in both the acid and base water basins is determined by automatically operated outlet valves which operate on different cycles depending on whether production is running or not.

After the chemical scrubber, the treated off-gas is mixed with the diluted off-gas and the mixed gas is fed to a humidifier. The humidifier aims to raise the relative humidity of the off-gas to 100 % before it is fed to the biofilter. As the water in the humidifier is contaminated by dilute target effluents and the off-gas from the scrubber, the water in the humidifier is changed regularly. The outlet valve of the humidifier opens in certain cycles depending on whether production is running or not.

From the humidifier, the off-gas is directed to a biofilter with a bed consisting of a mixture of wood chips. The volume of the biofilter is 450 m^3 . The temperature of the biofilter is maintained at $10\text{--}50^\circ\text{C}$ to ensure the activity of micro-organisms that reduce pollutants. The biofilter watering valve dispenses a controlled amount of water onto the surface of the biofilter bed material. Empty bed residence time of the biofilter is 54 s, based on maximal air flow capacity which is $30000 \text{ m}^3/\text{h}$. The biofilter is covered to maintain optimum conditions. The exhaust air cleaned by the biofilter is fed through a pipe into the atmosphere. The treatment of the off-gas results in secondary emissions in the form of wastewater. Wastewater from the different stages is discharged to the factory's own wastewater treatment plant.

4.2 Characterization of the feather treatment off-gas

4.2.1 Sampling points and conditions

Characterization of the off-gas was carried out at the Honkajoki Ltd feather processing plant to determine the odor-causing compounds formed during the heat treatment stages of the feather treatment process, i.e., hydrolysis and drying. In addition, odor concentration was determined, and volumetric flow and gas temperature measurements were carried out. The measurements and sampling were performed by A-Insinöörin and samples were analyzed by the Institute of Occupational Health. Measurements and sampling

were carried out under normal operating conditions of the feather plant. Before the samples were taken by A-Insinöörin, the chemical scrubber was maintained by washing the filters and calibrating the pH sensors. At the same time, the humidifier before the biofilter was cleaned. During the measurements, the pH adjustments of the chemical scrubber and the addition of the oxidant were kept constant. The pH setting for the acid scrubber was kept at 4.2 and for the base scrubber at 9.7. The redox measurement, which controls the addition of oxidant, was set at 100 mV.

A total of 7 sampling points were selected to provide comprehensive information on the different qualities of concentrated and diluted off-gases entering the off-gas treatment, and on the effects of the different treatment steps. The sampling points are represented by red circles in Figure 8. In Chapter 4.1.2. These included the dryer target off-gas line, the concentrated off-gas line before the scrubber, the line after chemical scrubber, the dilute target off-gas line, the line after humidifier, the line before biofilter, and the pipe after biofilter. Each sampling point, excluding the dryer, had three separate sampling connections, allowing continuous and grab sampling at the required sampling points simultaneously.

The selected sampling time was the beginning of the depressurization of the hydrolysis, which has been found to cause spikes in emission concentrations. In addition, a continuous measurement of the emissions from the dryer was performed, which represents most of the emissions from the production process over time. The measurements were carried out during three different hydrolysis batches, except sampling from the dryer, which was carried out outside the hydrolyzer depressurization. During the depressurization of the first hydrolysis batch, samples were taken from the line to the biofilter after the humidifier, from the sampling point before the biofilter and from the pipe leaving the biofilter. This was the first hydrolysis batch of the day at the feather plant, so drying process was not running simultaneously during the hydrolysis depressurization, as it was during the second and third hydrolysis depressurizations. As an alternative, sampling during drying was carried out by taking a sample directly from the target off-gas channel. During the second hydrolysis depressurization, measurements were taken from the concentrated off-gas channel before the chemical scrubber and from the sampling point after the chemical scrubber. During the third depressurization, samples were taken from the dilute off-gas channel that connects to the off-gas treatment system after the chemical scrubber. The samples were taken during one working day and delivered the same day to the laboratory of the Institute of Occupational Health for analysis.

4.2.2 Analysis and measurement methods

The components to be analyzed were the odorous sulfur compounds, i.e., hydrogen sulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide, and ammonia, amines, ketones, aldehydes, VOCs and odor concentration. The components were selected according to both the literature and upcoming BAT requirements (Karlis et al. 2024). Table 4 shows the measurement principles and equipment as well as analytical methods used for the compounds to be analyzed.

Table 4. Measurement equipment and analytical methods used for characterization.

Parameter	Measurement principle	Equipment	Analytical method
TVOC	Fourier-transform infrared spectroscopy (FTIR)	FTIR DX 4000	MEN 101 CEN/TS 17337:2019
	Adsorption	Activated carbon tubes LFS sampling pump	CEN/TS 13649:2015
Ketones	Adsorption	Activated carbon tubes LFS sampling pump	CEN/TS 13649:2015
Amines	Adsorption	Anasorb 747 adsorption tubes SKC sampling pump	CEN/TS 13649:2015
Aldehydes	Adsorption	Seppak collector SKC sampling pump	
Sulfur compounds	FTIR	FTIR DX 4000 online analyzer	MEN 101 CEN/TS 17337:2019
		Laminate bags and vacuum equipment SKC sampling pump	
Ammonia	Absorption	Gas washing cylinders Sampling pump	MEN 126 VDI 3878:2017
Odor concentration	Olfactometric analysis	Olfactometer TO8 Odor sampling bags and vacuum equipment Gilian sampling pump	SFS-EN 13725:2003
Off-gas volume flow, temperature, and humidity		DP Measurement- micromanometer S-pitot-tube L-pitot-tube Testo 511 pressure meter Testo 175 temperature logger Fluke 52-2 thermometer K type thermocouple	MEN 021 ISO 10780:1994 SFS-EN 14790:2017 MEN 022 MEN 023

Sampling was carried out according to the principles presented in table 4. The Fourier-transform infrared spectroscopy (FTIR) analyzer samples were continuous measurements, while the adsorption and absorption samples were taken either in sampling tubes

or in bags. Odor concentrations were determined from the off-gas by using a dynamic olfactometer. The olfactometer does not directly measure odor concentrations but dilutes the sample with clean air for evaluation by members of the odor panel. The odor panel organized by A-Insinöörin determined the odor concentration by diluting the sample until 50 % of the panel members could no longer sense the odor. At this point the odor threshold of 1 ouE/m³ is reached. The odor unit therefore determines the intensity of the odor relative to the odor threshold of the average human sensation. Samples taken before and after the scrubber have a higher uncertainty than usual, as samples had to be diluted 100 times before the odor panel.

4.3 Optimization of the off-gas treatment process

For the optimization of the off-gas treatment process of the feather treatment plant, chemical scrubber parameter changes were carried out to improve the efficiency of the hydrogen sulfide and ammonia removal and to optimize the consumption of chemicals. In addition, a sample of the biofilter bed material was sent for analysis to an external laboratory to investigate the condition of the bed material. Single samples of the off-gas were taken for internal laboratory analyses to compare the H₂S and NH₃ concentrations before and after the unit processes of the off-gas treatment system, i.e. both the chemical scrubber and the biofilter. In addition, the reduction of the whole off-gas treatment process was calculated. H₂S and NH₃ were chosen as the compounds to be measured, as qualitative analyses showed that they were significant odor causing compounds from hydrolysis and drying processes. In addition, the selected compounds are within the future limit values defined in the EU SA-BREF BAT-associated emission levels (Karlis et al. 2024).

4.3.1 Description of the sampling

Sampling was carried out during the depressurization of the hydrolysis, which has previously been identified as the peak time for odor emissions from the feather treatment process. Sampling after each operating value change was repeated both only during the depressurization of the hydrolysis process and also while drying was in progress. This was important because it was already noted before the experimental period that the drying of feather meal was the main source of ammonia emissions, so the efficiency of the chemical scrubber for NH₃ removal had to be examined also during the drying process.

The selected sampling points were the concentrated off-gas line before the chemical scrubber, the line after the chemical scrubber, the line to the biofilter where the off-gas line from the chemical scrubber and the dilute off-gas line join and pass through the

humidifier before the sampling point, and the exiting line from the biofilter. The sampling points are shown in Chapter 4.1.2 Figure 8. The sampling equipment used were 10-liter Nalophan bags and a flow-through pump with a flow rate of 3,3 l/s. During one sampling session, three samples were taken from each sampling point at approximately 5-minute intervals, resulting in a total of 12 samples from all four sampling points over a time period of approximately 16 minutes. The depressurization of the hydrolyzer is set to last 30 min, so sampling was performed in the first half of the depressurization period. The first sample was taken one minute after the beginning of the depressurization in the order of the process flow of the off-gas treatment system, i.e. before the chemical scrubber, after the scrubber, before the biofilter and after the biofilter.

4.3.2 Optimization of chemical scrubber

To optimize the efficiency of the chemical scrubber and the consumption of chemicals, the dosage of chemicals was adjusted. In addition, optimization was improved by adjusting the duration of the hydrolysis depressurization process and the operation of the oxidizer feed pump. The adjustments made to the chemical scrubber and the process during the experimental period are shown in Table 5.

On the fifth sampling day, a process change was made to increase the duration of the hydrolysis depressurization from 30 minutes to 40 minutes, in order to influence the reaction time of opening the vent valves. On the sixth sampling day, the set points were not changed compared to the previous day, but the redox pumping settings were changed. The speed of the feed pump control was increased to improve the efficiency of the pump run. The aim was to speed up the pumping of the oxidizer so that it would react more quickly to the hydrogen sulfide load peak at the beginning of the hydrolysis depressurization. On the seventh sampling day, the oxidizer pumping was adjusted so that the pump output signal was forced to run 10 % higher than the current dosage would normally be, one minute before the hydrolysis depressurization began. The purpose was to predict a coming hydrogen sulfide load peak by increasing the oxidizer feed.

During the measurements, data on the operational parameters were collected from the automation system to obtain information on the consumption of sulfuric acid, sodium hydroxide and hydrogen peroxide and changes in pH and redox measurements relative to the desired set value.

Table 5. Operating value changes while optimizing chemical scrubber.

Sampling day	Operational conditions of the chemical scrubber			Other operational changes	Purpose of the changes to set values
	Acid scrubber pH set value	Base scrubber pH set value	Redox set value		
1.	4,2	9,7	100 mV		
2.	4,5	9,7	140 mV		To enhance the reduction of hydrogen sulfide. To investigate the dosage of sulfuric acid in relation to sufficient ammonia removal.
3.	5	9,5	No input		To examine the effect of the amount of oxidizer on the removal of hydrogen sulfide. To examine the effect of base feed on hydrogen sulfide removal. To investigate the sufficient level of acid feed in relation to ammonia removal.
4.	5	9,5	200 mV		To compare the effect of hydrogen peroxide feeding on hydrogen sulfide removal and chemical consumption compared to a third set of experiments where no oxidizer was fed to the chemical scrubber.
5.	4,5	9,5	100 mV	Slowing down the depressurization of the hydrolysis, increasing the setting time by 10 minutes = total duration 40 min	To reduce the consumption of hydrogen peroxide compared fourth set of experiments and based on the results of previous experiments, to adjust the pH of the acid side to a suitable value.
6.	4,5	9,5	100 mV	Increasing the speed of the oxidizer dosing pump	To speed up the pumping of the oxidizer so that it would react more quickly to the hydrogen sulfide load spike at the start of hydrolysis depressurization.
7.	4,5	9,5	100 mV	Predicting the feed of an oxidizer dosing pump	The aim was to predict a coming hydrogen sulfide load peak by increasing the oxidizer feed.
8.	4,5	9	100 mV		To study the change in base consumption in relation to hydrogen sulfide removal.

The analysis of the samples was carried out in Honkajoki Ltd's internal laboratory. Both the sampling and analysis method and the necessary equipment were specified by an external consultant, but the analyses were performed internally. The analyses were carried out using a Dräger X-act 5000 Basic automatic tube pump and Dräger short-term tubes for hydrogen sulfide and ammonia, which are reagent tubes interpreted by color change, in different ranges. The standard deviation of the results of the analyses carried out with short term tubes for ammonia is $\pm 10\text{--}15\%$ and $\pm 5\text{--}10\%$ for hydrogen sulfide.

4.3.3 Analysis of biofilter bed material

To evaluate the current state of the biofilter bed material, that has been in use for just over six months, a sample of it was sent to the external laboratory. The sample was analyzed for sulfur, hydrogen, nitrogen, carbon, potassium, phosphorus, pH and in a laboratory of Honkajoki Ltd for humidity. Table 6 shows the methods used for the analyses performed by external laboratory.

Table 6. *Analyses of biofilter bed material.*

Parameter to analyze	Method
Sulfur (S) dry sample	SFS-EN ISO 16994:2016
Carbon (C) dry sample	
Hydrogen (H) dry sample	
Nitrogen (N) dry sample	SFS-EN ISO 16967:2015 mod.; SFS-EN ISO 16968:2015 mod.
Potassium (K)	SFS-EN ISO 11885:2009; SFS-EN ISO 16967:2015 mod.; SFS-EN ISO 16968:2015 mod.
Phosphorus (P)	SFS-EN ISO 11885:2009; SFS-EN ISO 16967:2015 mod.; SFS-EN ISO 16968:2015 mod.
pH	SFS-EN 13037:2011

The humidity measurement of biofilter bed material was carried out in Honkajoki Ltd's laboratory with a Precisan XM 50 humidity analyzer based on thermogravimetry.

5. RESULTS AND DISCUSSION

The objective of the qualitative study in this thesis was to characterize the off-gas from the treatment of feathers in order to identify effective off-gas treatment methods for this type of raw material. This chapter presents the results of the characterization measurements, which cover the qualitative change of the off-gas during the different process steps of the off-gas treatment system. The other aim of the study was to optimize the performance of the current off-gas treatment system in terms of H₂S and NH₃ removal efficiencies. The results of the optimization tests are considered for both the chemical scrubber and the biofilter. The results of the tests aimed to provide new information on odor emissions from the treatment of feathers, which could serve as a basis for the treatment of off-gases from other similar facilities. Based on the results, recommendations were made to improve the efficiency of the treatment process and to develop an off-gas treatment system to comply with future BAT regulations at the study site.

5.1 Characterization tests

The aim of the characterization was to carry out a qualitative study of the off-gas from the feather treatment process, divided into concentrated off-gas, which also includes the off-gas from the drying process, and diluted off-gas (Table 7). The results confirm the complexity of gaseous emissions from the treatment of animal by-products, as reported in previous studies (Rappert et al. 2005a). In total, 32 compounds were identified in the process off-gases. The most significant odor causing compounds were hydrogen sulfide, which was also one of the most odorous compounds in a study by Anet et al. (2013), ammonia and methyl mercaptan due to their high concentrations of 12.9–55.8 mg/Nm³. Both hydrogen sulfide and methyl mercaptan have low odor thresholds, hydrogen sulfide recognition threshold is 0.0047 ppm (Prokop et al. 1992, 562) and methyl mercaptan it is 0.001 ppm (Cooper 2007). Ammonia threshold is higher with 37 ppm (Prokop et al. 1992, 562). Quantitatively, butane was the most abundant, but its odor detection threshold is high, up to 2700 ppm (Amoore et al. 1983), and the concentration did not exceed this value.

Table 7. Compounds identified by characterization and their concentrations in different fractions of process gases from the feather treatment plant.

Compound	CAS Number	Dryer (mg/Nm ³)	Concentrated off-gases (mg/Nm ³)	Dilute off-gases (mg/Nm ³)	Uncertainty (%)
VOCs determined from adsorption samples					
Benzene	71-43-2	<0,10	<0,15	<0,08	±17
Ethanol	64-17-5	<0,35	<0,51	0,89	±17
Acetone	67-64-1	1,0	0,8	<0,25	±17
Dimethylaminoacetonitrile ¹	926-64-7	1,2	<1,02	1,1	±17
Dimethyl disulfide	624-92-0	<0,35	<0,51	0,51	±17
Dimethyl sulfide	75-18-3	<0,35	<0,51	<0,25	±17
Dimethyl trisulfide ²	3658-80-8	<0,35	<0,51	<0,25	±17
Butane ³	106-97-8	470	135	0,64	±17
Allyl alcohol	107-18-6	0,87	0,26	0,13	±17
Propylene Oxide	75-56-9	1,7	1,0	<0,25	±17
Other VOCs ⁴	-	1,0	0,51	<0,13	±17
Total		478	141	4,5	
Sulfur compounds					
Hydrogen Sulfide	7783-06-4	<0,05	47	24,3	±40
Methyl mercaptan	74-93-1	<0,06	1,7	12,9	±40
Dimethyl sulfide	75-18-3	<0,08	<0,08	<0,08	±40
Dimethyl disulfide	624-92-0	<0,13	<0,13	0,84	±40
Carbonyl sulfide	463-58-1	0,54	2,4	<0,08	±40
Ethanethiol	75-08-1	<0,08	1,1	<0,08	±40
Total		0,9	52,4	38,3	
Aldehyde compounds determined from adsorption samples					
Formaldehyde	50-00-0	1,9	0,72	0,83	±21
Acetaldehyde	75-07-0	3,6	8,4	0,28	±21
Acetone	67-64-1	<0,01	0,64	0,15	±21
Acrolein	107-02-8	0,31	2,2	0,02	±21
Propionaldehyde	123-38-6	0,28	0,62	0,01	±21
Crotonaldehyde	4170-30-3	0,02	0,06	0,01	±21
Methyl ethyl ketone	78-93-3	<0,01	0,1	0,04	±21
Methacrolein	78-85-3	<0,01	0,08	<0,01	±21
Butyraldehyde	1123-72-8	0,12	<0,02	0,11	±21
Benzaldehyde	100-52-7	0,08	0,12	0,03	±21
Valeraldehyde	110-62-3	0,04	0,05	0,01	±21
m-Methylbenzaldehyde	2880-05-9	0,02	<0,02	<0,01	±21
Hexanal	66-25-1	0,15	0,13	0,03	±21
Total		6,5	13,2	1,5	
Ammonia	7664-41-7	50,3	55,8	3,1	±27
Other compounds determined from adsorption samples					
Ethanol	64-17-5	0,1	0,25	0,97	±25
Acetone	67-64-1	0,8	0,76	0,14	±25
Acetic acid	64-19-7	<0,48	<0,76	1,4	±25
Propionic acid	79-09-4	<0,16	<0,25	1,2	±25
Allyl alcohol	107-18-6	0,8	0,51	0,07	±25
Total		2,3	2,5	3,8	

¹ Dimethylaminoacetonitrile has been answered with the response of dimethylethylamine; the result is semi-quantitative.

² Dimethyl trisulfide has been answered with the response of dimethyl disulfide; the result is semi-quantitative.

³ Butanes have been calculated as pentane; the result is semi-quantitative. Butanes contain probably also propane.

⁴ Other VOCs are calculated as n-heptane; the result is semi-quantitative.

The off-gas from the drying process is combined with the concentrated off-gas, but was analyzed separately outside the hydrolysis depressurization, as it is the longest lasting heat treatment step in the batch process. While the hydrolysis depressurization lasts 30–40 min, the drying process takes up to 1.5 h. Based on the characterization, drying produces 89 % of VOCs. Majority of VOCs was butane, which also had the highest concentration of compounds identified from concentrated off-gas (53 %), because the off-gas from the dryer combines in concentrated off-gases fed to the chemical scrubber. The off-gas after the chemical scrubber contained 43 % VOCs, with butanes being still the most abundant. The dilute off-gas, which is fed into the off-gas treatment process after the chemical scrubber, contained about 9 % of VOCs, with the highest concentration of dimethylaminoacetonitrile. Sample taken before biofilter consisted 39 % of VOCs, most of which were also butane as in sampling point after biofilter, where VOCs accounted for 69 % of the identified compounds.

The second highest concentration of drying is ammonia, 9 % of the identified compounds. Samples of drying and concentrated off-gas were not taken during the same batch, so the measured concentrations are not directly comparable, but the results indicate that a large amount of the ammonia entering the off-gas treatment is expected to be caused by drying. The concentrated off-gas contains about 20 % of ammonia. Ammonia was not detected after the chemical scrubber. Dilute off-gas contains 6 % ammonia. Ammonia was below the analytical limit of quantification before or after biofilter.

Sulfur compounds in the drying phase were measured at 0.2 %, with the highest concentration of carbonyl sulfide. The concentrated off-gas contains about 20 % of sulfur compounds, mostly hydrogen sulfide, but other odorous sulfur compounds such as methyl mercaptan, carbonyl sulfide and ethanethiol were also present. Drying process did not produce much hydrogen sulfide, it indicates that hydrogen sulfide is mainly formed by hydrolysis. After chemical scrubber off-gas contained 47 % of sulfur compounds, most of which was hydrogen sulfide. The diluted off-gas contained the highest concentration in relation to the compounds found was sulfur compounds, 75 %, mostly hydrogen sulfide and methyl mercaptan. The off-gas analyzed before the biofilter contained almost 59 % of sulfur compounds, most of which were hydrogen sulfide. This was also the highest concentration of the identified compound at the corresponding stage, according to a study on rendering emissions by Anet et al. (2013). The off-gas after biofilter still contained sulfur compounds, almost 30 %, of which hydrogen sulfide was the most abundant.

The drying off-gas contains 1 % aldehydes. The highest concentration of aldehydes was observed in acetaldehyde, which was also the highest single compound of the total 5 %

aldehydes found in concentrated off-gas. The off-gas after chemical scrubber contained almost 7 % aldehydes, most of which were acetaldehyde, formaldehyde and acrolein. The proportion of aldehydes in the diluted off-gas was 3 %, most of which consisted of formaldehyde. Other compounds found in drying phase were allyl alcohol and acetone, of which the latter was also observed in the concentrated off-gas. Acetic acid and propionic acid were identified from the diluted off-gas.

The results of the characterization confirm that the off-gas from the treatment of animal by-products contains a wide variety of odor-causing compounds, including compounds resulting from thermal decomposition and drying. The compounds identified in this study correspond to odor compounds identified in the literature from rendering, including sulfur compounds such as hydrogen sulfide, mercaptans and sulfides, nitrogen compounds such as ammonia and oxidized molecules such as aldehydes (Anet et al. 2013). The off-gas from the study site contained the highest levels of butane at all stages, which is not a typical compound formed from animal based material, but it is assumed to be due to the unburned Liquefied Petroleum Gas (LPG) from the dryer burner, because it is used as a fuel of the burner and LPG consists 25 % of butane (Kaliya et al. 2001). Hydrogen sulfide was found at all sampling points except for the drying stage, but its contribution decreases during the off-gas treatment. Ammonia is found in the concentrated off-gas entering the off-gas treatment system and in the drying process but is effectively removed before the biofilter. A study by Anet et al. (2013) achieved similar results, which showed that ammonia was nearly 100 % removed, by maintaining the pH of the scrubber at 4, with no further emissions of ammonia or amine-like alkaline compounds detected in the gas entering the biofilter. The pH of the acid scrubber was 4,2 at the time of characterization sampling which seems to be an essential parameter for ammonia removal efficiency.

The chemical scrubber and biofilter used at the site are suitable treatment techniques for the compounds found, supported by theory. The chemical scrubber is an effective solution for water-soluble odorous compounds such as ammonia (Nabais 2006, 109). Based on the characterization, ammonia is already almost completely removed by the chemical scrubber at the study site, but concentrations entering the biofilter could also be removed with a removal efficiency of 83–85 %, depending on the bed material (Kennes & Veiga 2001, 88). Biofilters can achieve removal efficiencies of up to more than 80 % for aldehydes at concentrations of less than 20 mg/Nm³ in the treated off-gas Anet et al. 2013). For example, acetaldehyde has good biodegradability in a biofilter (Devinny et al. 1999, 6) and was more efficiently removed by a biofilter than by a chemical scrubber at the site. The oxidizing agents in a chemical scrubber do not always react quickly enough

with VOCs or aldehydes, unlike hydrogen sulfide, which typically reacts strongly with the scrubber oxidant (Kastner J. & Das K. 2002. 460). The chemical scrubber is therefore well suited to handle high hydrogen sulfide concentrations, up to more than 200 ppm (Nabais 2006, 110). With a biofilter, the hydrogen sulfide removal efficiency can be larger than 99 % when for example ceramic bed material is used. On the other hand, compost-hog fuel-perlite (2:2:1) has achieved only 30 % removal efficiency, illustrating the importance of the suitability of the bed material. Other sulfur compounds can also be efficiently removed by biofilter, e.g. for methyl mercaptan a removal efficiency of up to > 99 % can be achieved when using activated carbon fabric as bed material (Kennes & Veiga 2001, 89).

The characterization results cannot be used to assess the overall performance of the off-gas treatment system, nor can any far-reaching conclusions be drawn about the quality or efficiency of the system, as sampling was carried out during several different batches at different stages of the off-gas treatment system. Although the amount of raw material treated remained constant during each batch, differences in the quality of the raw material, e.g. between chicken and turkey feathers, may affect the concentrations of the compounds tested. Compound concentrations may also vary depending on the freshness of the raw material (Anet et al. 2013). In addition, during the first batch, the drying process was not yet running, so the quality of the concentrated off-gas fed into the off-gas treatment system was not exactly the same during all batches. This qualitative study was also carried out before the optimization of the off-gas treatment system, only months after the start-up of the plant. Therefore, the results after the different phases of the treatment system do not fully reflect the current situation.

In addition to the characterization, the odor content of the off-gas air was determined using an odor panel by A-Insinöör. The odor concentrations were calculated for standard conditions of 20°C, 101.3 kPa for a humid gas. Sampling for the evaluation of odor concentration was carried out during the hydrolysis depressurization of the different treatment batches, which prevents a direct comparison between them and the odor discrimination for the different unit processes cannot be determined. Although both the concentrated off-gas and the off-gas to be released to the atmosphere after the biofilter were sampled during different batches, both samples were taken approximately 15 minutes after the start of the hydrolysis depressurization. The odor concentration of the concentrated off-gas was 164 777 ou_E/m³. This is a typical result, because according to Anet et al. (2013) odor concentration from the treatment of animal by-products is usually between 20000 and 1100000 ou_E/m³. After the biofilter, the odor concentration was 5709 ou_E/m³. Based on these results, it can be estimated that the odor removal efficiency of

the whole treatment process of the site is up to 96 % at the middle of the hydrolysis depressurization. For example, according to Prokop et al. (1992; 566–567), 99 % odor removal efficiency can be achieved with multiple-stage scrubber systems alone, suggesting that even higher odor removal efficiencies could be achieved at the study site.

5.2 Optimization tests

The aim of the optimization tests was to improve the functioning of the off-gas treatment system at the study site in terms of H₂S and NH₃ removal efficiencies. The results provided information on the input concentrations of the mentioned compounds to the off-gas treatment system and on how their concentrations change during hydrolysis depressurization.

5.2.1 Chemical scrubber

The measured ammonia concentrations in the off-gas entering the chemical scrubber ranged from 5.6 to 10.5 mg/Nm³. The ammonia concentrations entering the scrubber were detected when the drying process was running simultaneously with the hydrolysis depressurization. Therefore, the ammonia concentrations are assumed to originate mainly from the drying process. The concentration of NH₃ also did not change during the depressurization, the load remaining steady. The ammonia concentration in the off-gas after the chemical scrubber was between 0 and 0.7 mg/Nm³. Ammonia was removed by the chemical scrubber in the same quantity regardless of the parameter values used in the optimization test. For all acid scrubber pH values between 4.2 and 5, a removal efficiency of 90–100 % of NH₃ was achieved. Based on research by Alinezhad et al. (2019), NH₃ removal efficiency is affected by the loading rate, but with optimal practices, a 99.8 % removal efficiency is generally achieved. Increasing the acid scrubber pH to 4.5 reduced H₂SO₄ consumption by 20 % compared to the starting pH setpoint, while increasing the pH to 5 reduced chemical consumption by 40 % compared to the starting pH. The use of an oxidizer had no effect on NH₃ removal efficiency. Similar results have been obtained using different oxidants with a chemical scrubber, where NH₃ removal efficiency remained at 95–100 % (Alinezhad et al. 2019).

H₂S removal efficiency of the chemical scrubber varies depending on consumption of oxidizer (Table 8). 13 % removal efficiency was observed when the supply of H₂O₂, the oxidizer affecting the redox value, was completely stopped. Only the highest H₂S peak value, 274,1 mg/Nm³ showed a 39 % removal efficiency, while lower concentrations, 27

mg/Nm³, were not affected at all. Increasing the redox value, i.e. by increasing the oxidizer feed to the alkaline scrubber, improved the H₂S removal efficiency, especially at lower concentrations of H₂S during the hydrolysis depressurization, but before the process and pumping changes on sampling days 4–6, the H₂S removal efficiency at the highest concentration remained almost the same as without feeding H₂O₂.

Table 8. Optimization test operational settings, H₂S concentrations and removal efficiencies at different settings before and after the chemical scrubber.

Sampling day	Redox (mV)	Acid scrubber pH	Alkaline scrubber pH	Concentrated off-gases before chemical scrubber (mg/Nm ³) ¹	After chemical scrubber (mg/Nm ³) ¹	Removal efficiency	Average removal efficiency	
1.	100	4,2	9,7	260,4	193,6	26 %	45 %	
				54,8	27,7	50 %		
				27,4	11,1	60 %		
2.	No input	5	9,5	274,1	165,9	39 %	13 %	
				27,4	27,7	-1 %		
				27,4	27,7	-1 %		
3.	200	5	9,5	191,9	110,6	42 %	63 %	
				82,2	27,7	66 %		
				27,4	5,5	80 %		
4.	100	4,5	9,5	274,1	165,9	39 %	51 %	
				Depressurization time of the hydrolysis + 10 min	27,4	13,8		50 %
				27,4	9,7	65 %		
5.	100	4,5	9,5	191,9	55,3	71 %	74 %	
				Increasing the speed of the oxidizer dosing pump	41,1	8,3		80 %
				27,4	8,3	70 %		
6.	100	4,5	9,5	219,3	83,0	62 %	69 %	
				Predicting the feed of an oxidizer dosing pump	54,8	13,8		75 %
				27,4	8,3	70 %		
7.	100	4,5	9	342,7	221,2	35 %	50 %	
				Same oxidizer pump settings as in sampling days 5. & 6.	109,7	55,3		50 %
				82,2	27,7	66 %		

¹ Both before and after chemical scrubber samples were taken in the same way for each sampling session. The first sample was taken 1 min after the beginning of the hydrolysis depressurization, the second sample 6 min after the beginning of the depressurization and the third sample on average 13 min after the beginning of the depressurization.

Increasing the 100 mV redox value to 200 mV showed a 3–20 % improvement in H₂S removal efficiency. Depending on the moment of hydrolysis depressurization, the 200

mV redox value reached 3–81 % higher removal efficiencies than the complete lack of H_2O_2 feeding. The results show that H_2O_2 feed, adjusted by increasing the redox value, has a relatively small effect on the removal efficiency of the high H_2S content in the initial phase of the hydrolysis depressurization, but as the load decreases, the oxidizer feed significantly improves the removal efficiency. Increasing the redox value from 100 mV to 200 mV increased H_2O_2 consumption by up to 29 %. According to Li et al. (2013) H_2S is a reductant that can only be oxidized. The reduction potential of H_2S is measured at -280 mV (pH 7.0 compared to the standard hydrogen electrode) for the redox pair involving two-electron HS^-/S^0 . Additionally, it is measured -230 mV for the redox pair involving $\text{H}_2\text{S}/\text{S}^0$. This contributes to clarify the beneficial effect of higher H_2O_2 consumption on H_2S removal.

The process change made on the fourth sampling day, increasing the duration of the hydrolysis depressurization, slightly improved the H_2S removal efficiency, especially in the initial phase of the hydrolysis depressurization, up to 13 %, when comparing the results with the first day initial situation at a redox setting of 100 mV, respectively. On average, the removal efficiency improved by 6 % compared to the initial situation with the process modification. However, the process change increased the duration of the hydrolysis depressurization by 10 minutes, which could be problematic if the plant's production volumes would increase a lot. In the batch process, this would slow down the feeding of the next batch of feathers into the process, which would also reduce the production capacity. The operational setting change for the oxidizer feed pump at the fifth sampling time improved the H_2S removal efficiency significantly, on average up to 29 % higher than the beginning of the optimization tests. The removal efficiency for the highest H_2S concentration at the beginning of the hydrolysis depressurization was improved by 45 % compared to the initial situation. The technical change on sampling day 6 for the prediction of the oxidizer feed did not improve the removal efficiency compared to the change in the operation of the oxidizer feed pump. But when comparing the results from the oxidizer feed prediction with the initial results from the first sampling day, it can be seen that H_2S removal efficiency also improved with this change, by almost 24 %. However, contrary to expectations, the change did not improve the removal efficiency at the highest H_2S concentration, but at lower H_2S concentrations it achieved removal efficiencies almost equivalent to those achieved by the earlier change in the speed of the oxidizer pump. The changes in the setting of the oxidizer dosing pump did not increase H_2O_2 consumption, but mainly affected the dosing reaction rate by changing the redox value under the influence of H_2S concentrations.

The optimization of the alkaline scrubber with a moderate pH adjustment did not have a major impact on H₂S removal efficiency. At both pH 9.5 and 9.7, with a constant redox setpoint of 100 mV, removal efficiencies averaged close to 50 % depending on the sampling time. In the final test, the alkaline scrubber pH setpoint was lowered to 9, but the previously made changes to the oxidizer feed pump were kept the same. Using H₂O₂ at too low a pH, such as 7.8–8.1, is not favorable, but as the pH of the scrubbing liquid increases, the alkalinity of the oxidant increases, resulting in improved H₂S solubility, but also increased mass transfer between the gas and water phases (Alinezhad et al. 2019). Comparing the H₂S removal efficiencies of the sixth and seventh sampling days, it is noted that lowering the pH decreased the results by an average of 19 %. The results show that lowering the pH of the alkaline scrubber from the initial 9.7 to 9.0 is not profitable, although it would reduce the NaOH input by almost 35 %. However, a moderate pH changes from 9.7 to 9.5 is cost-effective, as H₂S removal efficiency remains almost as good and chemical consumption is reduced by about 5 %. The chemical consumption values are based on data from the automation of the feather treatment plant. The reliability of the chemical calculators has not been tested and the reported change figures are based on data from only one sampling run at a given setting values, so they mainly give an indication of the potential change in consumption as the setting changes.

Based on these results, the aim was to find an optimum setpoint value that would provide H₂S and NH₃ removal efficiencies sufficient for the capacity of the biofilter and keep chemical consumption at a moderate level. Based on the results, the best removal efficiency (74 %) on average was achieved with a redox setting of 100 mV, an acid scrubber pH of 4.5, an alkaline scrubber pH of 9.5 and an oxidizer feed pump speed above the initial condition. However, with optimal practices, removal efficiencies of up to 98 % of H₂S can be achieved (Lebrero et al. 2012), for example removal efficiency of more than 99 % of H₂S has been achieved at pH 12 (Nisola et al. 2017). However, such a high pH value as 12 would increase the chemical consumption of the NaOH, which is not economically advantageous. Also increasing the redox value to 200 mV would provide even better results, but this would not be viable due to the significant increase in H₂O₂ consumption.

5.2.2 Biofilter

The off-gas from the chemical scrubber is combined with the diluted off-gas after the chemical scrubber and this combined gas is passed through the humidifier to the biofilter. H₂S concentration decreased after the chemical scrubber as compared to the samples taken before the biofilter, so that the H₂S removal efficiency averaged 43 %, ranging from

0–80 %. Since no separate sampling of dilute off-gas was performed, it is not possible to say for sure how much the water-fed humidifier alone contributes to H₂S removal in this case and how much the dilute off-gas dilutes the concentration of the off-gas fed to the humidifier before the concentrations were measured at the sampling point entering the biofilter. Research by Anupoju et al. (2009) indicates that the humidifier increased the efficiency of the biofilter operation by up to 35 %, achieving over 99 % H₂S removal efficiency.

H₂S concentrations measured before the biofilter ranged from 2.7 to 139.4 mg/Nm³. At the beginning of the sampling period, H₂S concentrations in the off-gas after the biofilter varied between 0 and 2 mg/Nm³. Based on the results from the biofilter, it was soon noticed that the H₂S removal efficiency dropped suddenly nearly 60 % (Figure 9). The efficiency of the biofilter in H₂S removal has been monitored regularly since the start-up of the feather treatment plant. However, Figure 9 presents only the results of the monitoring period carried out during the experimental part of the thesis. At the beginning H₂S removal efficiency from the biofilter averaged 78 %. After two months, the removal efficiency had dropped to 13 %. Research by Alinezhad et al. (2019) showed that under favorable operating conditions, a biofilter can achieve removal efficiency of more than 92 % for H₂S.

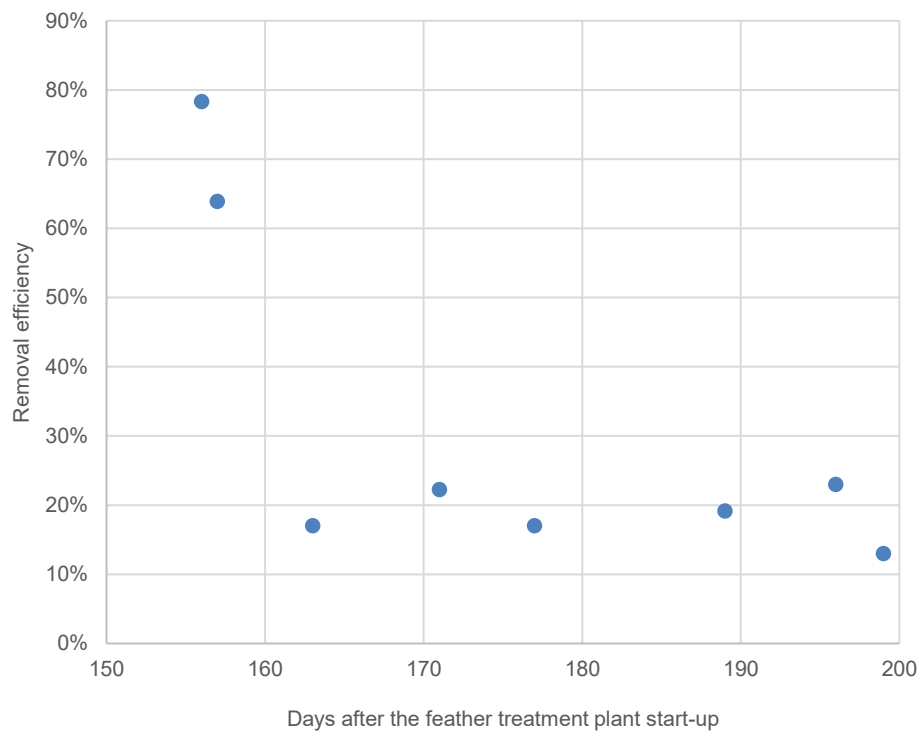


Figure 9. Average H₂S removal efficiency of three daily samples from the biofilter.

Due to the decreased H₂S removal efficiency, it was decided to perform characterization analyses on the biofilter bed material. The results of the characterization of the biofilter bed material are presented in Table 9. The results show that the pH of the biofilter bed material is 3.1 which is too low compared to the typical 4–8 (Kennes & Veiga 2001, 81). The biofilter can be shown to have been operational for less than six months since the plant start-up in the spring. Omri et al. (2013) present that a biofilter with wood chips as bed material and an input H₂S concentration of 30–450 ppm achieved up to 75–99 % removal efficiency. Although the biofilter can handle such high concentrations, according to Kennes & Veiga (2001, 82), biodegradation of compounds containing chlorine, sulfur or nitrogen is often expected to lead to a decrease in pH through the formation of acidic by-products. The results show that the raw material treated at the study site generates high concentrations of H₂S, which was also discharged directly to the biofilter during the commissioning phase of the plant. This is likely to have contributed to the decrease in the pH of the bed material in the biofilter. The humidity of the bed material was measured to be 55 %, which is sufficient, as Kennes & Veiga (2001, 78) suggest that a suitable humidity is typically 40–60 %.

Table 9. Biofilter bed material characteristics 190 days after the start-up of the feather treatment plant.

Parameter	Results	Measurement uncertainty
Sulfur (S) dry sample (%)	0,14	0,01
Carbon (C) dry sample (%)	54,1	1,1
Hydrogen (H) dry sample (%)	6,2	0,3
Nitrogen (N) dry sample (%)	0,23	0,1
Potassium (K) (mg/kg)	130	70
Phosphorus (P) (mg/kg)	27	14
pH	3,1	0,5
Humidity (%)	55	± 0,05

Nutrient levels of the biofilter bed material were measured because microbial cells contain carbon, nitrogen, oxygen, and hydrogen as major elements and therefore they need to be available to the microorganisms. Barona et al. (2004) study had the corresponding nutrient ratio when using horse manure C/H/N content (%) was 53.2/5.4/0.5. Other important nutrients are for example sulfur, potassium, and phosphorus. (Kennes & Veiga

2001, 74–75) Biofilters sometimes produce leachate, either intentionally or inadvertently, and this will carry dissolved nutrients out of the biofilter. Growing biomass in high-load biofilter needs nutrient additions and typically operators add fertilizers on a regular schedule. (Devinny et al. 1999, 66–67)

NH₃ concentrations were also measured at the biofilter, although the removal efficiency with the chemical scrubber was generally 100 %. NH₃ concentrations measured before the biofilter ranged from 0 to 0.7 mg/Nm³. After the biofilter the result was always 0 mg/Nm³ when using short term tubes.

5.3 Current state of the off-gas treatment system and suggestions for improvement

The off-gas treatment system was optimized to reduce air emissions and ensure that odor emissions are not released into the environment. Based on the results, it appears that the future BAT-associated emission levels can theoretically be achieved with the current off-gas treatment system at the study site. Based on the characterization results, a chemical scrubber and a biofilter have been shown to be suitable options for the removal of the identified compounds. Based on the qualitative study, the most odorous compounds were hydrogen sulfide, ammonia, and methyl mercaptan. According to the literature part of the study, a chemical scrubber and a biofilter are suitable odor emission treatment techniques for these compounds. Chemical scrubbers can achieve removal efficiencies of more than 98 % for H₂S and NH₃ (Nisola et al. 2017) and 80 % for CH₃SH (Zhou et al. 2018). Depending on the bed material, a biofilter can achieve removal efficiencies of up to 98 % for CH₃SH (Wani et al. 1998), 95–99 % for NH₃ and (Chen et al. 2005) and about 92 % for H₂S (Rabbani et al. 2015).

The current environmental permit requires the plant to achieve a 90 % reduction in odor concentrations. The results of the odor panel, which are based on a single sampling and not on continuous monitoring, however, confirm that the requirements of the environmental permit are complied with. The BAT-associated emission level (Karlis et al. 2024, 423) specifies that if purification methods other than the combustion of malodorous gases are used, the limit value may be higher and up to 3000 ouE/m³ if the abatement efficiency is ≥ 92 % or, as an alternative, process odor is not perceptible in the treated waste gases. In this regard, the results of the odor panel for odor concentration also appear to be acceptable for the future limit values.

When comparing the results for H₂S and NH₃ with the future EU-wide BAT-associated emission levels, it is found that for NH₃ the concentrations are already below the required

limit value. For H₂S, on the other hand, the required limit value (0.1–4 mg/Nm³) has not yet been reached, due to the non-functionality of the biofilter due to the low pH. However, the required values were achieved at the beginning of the sampling period, suggesting that the current off-gas treatment system can also achieve the required limit values for H₂S. The first action to improve the efficiency of the off-gas treatment system is to return the biofilter to operational condition. This can be achieved by adding base to the biofilter bed material, which raises the pH closer to 4–8, which is favorable for most microorganisms (Kennes & Veiga, 2001, 81). In the long term, consideration could also be given to selecting a different type of bed material suitable for H₂S removal. For example, according to Chaiprapat et al. (2011), in one case a sea mineral containing CaCO₃ was used as a carrier to achieve 82 % H₂S removal efficiency. It also improved the pH buffering capacity. A study by Omri et al. (2013) achieved up to 99 % H₂S removal efficiencies in a pilot scale biofilter with a bed material consisting of peat. Peat provides a nutrient-rich environment for microbial growth due to its good water retention and buffering effect.

In order to prevent a pH decrease in the biofilter due to high H₂S concentrations at the study site, actions to further increase the capacity of the chemical scrubber could be considered, or attention could be paid to the humidifier before the biofilter. The effectiveness of the humidifier for odorous compounds was not investigated in this study, but developing its performance could improve the removal efficiency of odorous compounds such as H₂S. For example, adding NaOH to the humidifier water could raise the pH slightly, enhancing H₂S removal, although the humidifier does not have the same contact time as a chemical scrubber. In addition, it might be beneficial to further optimize the performance of the chemical scrubber by testing different changing interval of the scrubbing water. The frequency of adding pure water or changing larger volume of water at a time and measure how this affects the removal of the compounds studied. In a chemical scrubber, the scrubbing liquid and flow rate have an impact on the removal efficiency of odorous compounds, according to a study by Alinezhad et al. (2019), high H₂S removal efficiencies have been achieved by using sodium hypochlorite (NaOCl) in the scrubbing liquid at a flow rate of 7 l/min. Therefore, it would be advisable to test different chemical options to find the best option to minimize odor compounds.

In general, when designing the off-gas treatment system, characterization should be carried out to be prepared, for example, for high H₂S concentrations when sizing an off-gas treatment device such as a chemical scrubber. The purchase of a new chemical scrubber is not always possible, for example due to lack of space. In this situation, other options are considered, such as diluting the concentrated off-gas with a more dilute off-gas before the scrubber. When identifying the target off-gas collection, it is taken into account

that concentrated and diluted gases are in principle discharged in separate lines. However, at the consideration, a share of dilute off-gases may be combined with the concentrated off-gas line, if routing is possible. This could reduce the load on the system without modifying the equipment. However, if capacity is reached for high concentrations of compounds and odors, additional capacity could be considered through equipment modifications or applying additional technologies such as a bioscrubber. Bioscrubber can achieve H₂S removal efficiencies of 85–94 %, for a case with a starting H₂S concentration of 5000 ppmv, at an inlet flow rate of 0.091–0.247 l/min, with a residence time of 6.6–2.4 min (San-Valero et al. 2019). According to Morral et al. (2023), the bioscrubber is a functional solution for treating NH₃ as well, because with an ammonia concentration of 80 ppmv, almost 95 % removal efficiency was achieved.

A further issue for investigation could be the secondary emissions from the off-gas treatment system, as the removal of hydrogen sulfide from the various treatment steps in the effluent can cause a load to the waste water treatment plants (WWTP). The effluent may contain sulfide, which can cause loading to the WWTP. Dissociated odorous compounds in the wastewater solution leaving the chemical scrubber can be re-released in gaseous form as conditions change. Release can be prevented by the use of oxidizing chemicals such as hydrogen peroxide or sodium hypochlorite. When oxygen or chlorine atoms in the oxidizer react with odorous compounds, less odorous soluble compounds are formed. (Mattila 1986, 66–67)

6. CONCLUSIONS

The aim of the study was to clarify which regulations and emission limit values regulate odorous emissions from the treatment of animal by-products, and which are the suitable off-gas treatment methods for this sector. In addition, the aim of this study was to characterize the off-gases from the feather treatment plant and to optimize the performance of the current off-gas treatment system in terms of H₂S and NH₃ removal efficiencies. In addition, the results of the optimization experiments provided information on the input concentrations of these compounds into the off-gas treatment system and how their concentrations change during hydrolysis depressurization. Based on qualitative studies, 32 compounds were identified in the off-gases from feather treatment process, of which the most odor-causing compounds were hydrogen sulfide, ammonia, and methyl mercaptan due to their high concentrations and low odor thresholds. Characterization results showed that the gaseous emissions from the rendering plant consist of a complex mixture of chemical compounds. The most abundant odorous compound in the off-gas from the drying process was ammonia (50.3 mg/Nm³). This off-gas fraction contained high concentration of butane (470 mg/Nm³), which was assumed to be caused by unburned LPG from the burner. Concentrated off-gases, which also included the drying off-gas, also contained hydrogen sulfide (47 mg/Nm³). The most abundant odorous compounds in dilute off-gases were hydrogen sulfide (24.3 mg/Nm³) and methyl mercaptan (12.9 mg/Nm³).

The qualitative study included odor concentration measurements, which provided an indicative value that the case study off-gas treatment system achieves 90% removal efficiency in terms of odor concentration when treating feathers. The study reveals that the high sulfur concentrations released from the feather raw material require efficient treatment methods that are also capable of reducing the peak concentrations caused by the batch process.

Optimization results showed that H₂S removal could be improved by adding H₂O₂ in scrubbing liquid of the chemical scrubber and increasing the speed of the oxidizer dosing pump. At the highest, an average removal efficiency of 74 % of H₂S was achieved. NH₃ removal with the chemical scrubber ranged from 90–100 % at all tested operational values. Further optimization of the performance of the chemical scrubber could be achieved by increasing the frequency of the scrubbing water or by diluting the concentrated off-gases fed to the scrubber by mixing it with more diluted off-gases.

Based on samples taken from the biofilter, it was found that in a short period of time, less than two weeks, the H₂S removal efficiency dropped from almost 80 % to less than 20 %. Based on this result, it was decided to have characterization analyses of the biofilter bed material carried out by an external laboratory. The results showed that the pH of the bed material had dropped to 3.1, which was significantly below the optimum pH of 4–8. The operating conditions of the biofilter were unfavorable, highlighting the need to correct the pH by adding for example CaCO₃. The sudden drop in the pH of the bed material may be explained by the high H₂S concentrations entering the biofilter, which could have been caused by the high concentrations released during the commissioning phase of the chemical scrubber or by other malfunctions during its operation. In the effluent off-gas entering the biofilter, NH₃ remained very low, below 0.7 mg/Nm³ and the removal efficiency was 100 % at each sampling test.

The results of the experimental part were compared with the EU-wide BAT-associated emission levels published in December 2023. Increasingly stringent regulation is requiring industry to develop their operations and technologies to control odor emissions. The results provide confidence that the BAT-AELs limit values are achievable for the target company, especially if the biofilter function is recovered by increasing the pH of the bed material by adding a base such as CaCO₃. The H₂S off-gas concentrations measured during the experimental part in the off-gas fed to the chemical scrubber were already at the upper limit of the capacity of the device. Despite the fact that the chemical scrubber was now effectively removing the studied compounds, if production volumes increase in the future, the capacity of the off-gas treatment system may be limited. As the batch size of the hydrolysis process increases, more emissions are released quantitatively.

When designing new treatment systems, it is useful to be prepared for tightening emission limits, as this will allow for optimization and development of the system through a back-up solution. Examples of such contingency options could include space reservations for additional treatment systems or precautions related to off-gas collection systems, such as distributing the process gases in separate ducts instead of one combined duct. This would allow, for example, only high intensity gases to be directed to additional systems, which would allow them to be sized more economically than if all process gases were collected in the same unit. In this case, off-gas treatment can be made more efficient either by re-sizing the existing equipment or by purchasing an additional unit to fold the load before the existing system. For example, a bioscrubber is a potential alternative for water-soluble compounds such as H₂S.

REFERENCES

- A-Insinöörit. (2023). Höyhentenkäsittelylaitoksen hajukaasuselvitys. Internal report.
- Albers, M., Helle, H., Varpula, T., Itävaara, M., Kapanen, A. & Vikman, M. (2003). Kompostointiprosessin monitorointi ja ohjaus. VTT. <https://www.vttresearch.com/sites/default/files/pdf/tiedotteet/2003/T2207.pdf>
- Alinezhad, E., Haghghi, M., Rahmani, F., Keshizadeh, H., Abdi, M. & Naddafi, K. (2019). Technical and economic investigation of chemical scrubber and bio-filtration in removal of H₂S and NH₃ from wastewater treatment plant. *Journal of Environmental Management*, Vol. 241, pp. 32–43. Available at: <https://doi.org/10.1016/j.jenvman.2019.04.003>
- Amoore, J. & Hautala, E. (1983). Odor as an aid to chemical safety: odor thresholds compared with threshold limit values and volatilities for 214 industrial chemicals in air and water dilution. *Journal of applied toxicology*, Vol. 3, Iss. 6, pp. 272–290.
- Anderson, D. Edited by Meeker, D. (2006). *Essential Rendering – All About The Animal By-Products Industry*. The National Renderers Association. Available at (cited 23.4.2023): http://assets.nationalrenderers.org/essential_rendering_book.pdf
- Andrés, C., Lastra, J., Juan, C., Plou, F. & Pérez-Lebeña, E. (2023). Chemistry of Hydrogen Sulfide—Pathological and Physiological Functions in Mammalian Cells. Available at (cited 8.2.2024): <https://doi.org/10.3390/cells12232684>
- Anet, B., Lemasle, M., Couriol, C., Lendormi, T., Amrane, A., Le Cloirec, P., Cogny, G. & Fillières, R. (2013). Characterization of gaseous odorous emissions from a rendering plant by GC/MS and treatment by biofiltration. *Journal of Environmental Management*, Vol. 128, pp. 981-987. Available at: <https://doi.org/10.1016/j.jenvman.2013.06.028>
- Anupoju, G. & Jetty, A. (2009). Hydrogen Sulfide Removal in Biofilter: Evaluation of a New filter Material by Immobilization of Thiobacillus sp. *International Journal of Chemical Reactor Engineering*, Vol. 7. Available at: <https://doi.org/10.2202/1542-6580.1848>
- Bandyopadhyay, A. & Biswas, M. (2007). Modeling of SO₂ scrubbing in spray towers. *Science of The Total Environment*, Vol. 383, Iss. 1–3, pp. 25-40. Available at: <https://doi.org/10.1016/j.scitotenv.2007.04.024>
- Barona, A. Elías, A., Arias, R. & González, R. (2004). Biofilter response to gradual and sudden variations in operating conditions. *Biochemical Engineering Journal*, Vol. 22, Iss. 1, pp. 25–31. Available at: <https://doi.org/10.1016/j.bej.2004.07.006>
- Bhatti, Z., Maqbool, F. & Langenhove, H. (2013). Rendering plant emissions of volatile organic compounds during sterilization and cooking processes. *Environmental Technology*, Vol. 35, Iss. 11, pp. 1321–1327. Available at: <https://doi.org/10.1080/09593330.2013.867364>
- Bhave, A., Vyas, D. & Patel, J. (2008). A wet packed bed scrubber-based producer gas cooling–cleaning system. *Renewable Energy*, Vol. 33, Iss. 7, pp. 1716-1720. Available at: <https://doi.org/10.1016/j.renene.2007.08.014>

Brinkmann, T., Giner, Santonja, G., Yükseler, H., Roudier, S. & Delgado Sancho, L. (2016), Best Available Techniques (BAT) Reference Document for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector. European Union. Available at: <https://doi.org/10.2791/37535>

Chai, W., Bao, Y., Jin, P., Tang, G. & Zhou, L. (2021). A review on ammonia, ammonia-hydrogen and ammonia-methane fuels. *Renewable and Sustainable Energy Reviews*: Volume 147. Available at: <https://doi.org/10.1016/j.rser.2021.111254>

Chaiprapat, S., Mardthing, R., Kantachote, D. & Karnchanawong, S. (2011). Removal of hydrogen sulfide by complete aerobic oxidation in acidic biofiltration. *Process Biochemistry*, Vol. 46, Iss. 1, pp. 344–352. Available at: <https://doi.org/10.1016/j.procbio.2010.09.007>

Chen, Y., Yin, J. & Wang, K. (2005). Long-term operation of biofilters for biological removal of ammonia. *Chemosphere*, Vol. 58, Iss. 8, pp. 1023–1030. Available at: <https://doi.org/10.1016/j.chemosphere.2004.09.052>

Cooper, C. (2007). Air Pollution Control Methods. *Kirk-Othmer Encyclopedia of Chemical Technology*. Available at: <https://doi.org/10.1002/0471238961.01091803181503.a01.pub2>

Datta, I. & Allen, G. Edited by Shareefdeen, Z. & Singh, A. (2005). Springer. *Biofilter Technology. Biotechnology for odor and air pollution control*. Available at: <https://doi.org/10.1007/b138434>

Deshusses, M. & Shareefdeen, Z. Edited by Shareefdeen, Z. & Singh, A. (2005). *Modeling of Biofilters and Biotrickling Filters for Odor and VOC Control Applications. Biotechnology for odor and air pollution control*. Available at: <https://doi.org/10.1007/b138434>

Devinny, J., Deshusses, M. & Webster, T. (1999). *Biofiltration for air pollution control*. CRC Press, Boca Raton Florida, USA, 299 p.

EU:n sivutuoteasetus 1069/2009. (2009). Available at: <http://data.europa.eu/eli/reg/2009/1069/oj>

Guerra, F., Smith, G., Alexis, F. & Whitehead, D. (2017). A Survey of VOC Emissions from Rendering Plants. *Aerosol and Air Quality Research*, Vol. 17, Iss. 1. Available at: <https://doi.org/10.4209/aaqr.2016.09.0391>

Guidotti, T. 2010. Hydrogen Sulfide: Advances in Understanding Human Toxicity. *International Journal of Toxicology*, Vol. 29, Iss. 6. Available at: <https://doi.org/10.1177/1091581810384882>

Haerens, K., Baerdemaeker, N., Wispelaere, J., Raes, N. & Van Elst, T. (2022). Optimisation of Odour Treatment of a Feather Processing Plant using Activated Carbon. *Chemical Engineering Transactions*, Vol. 95. Available at: <https://doi.org/10.3303/CET2295004>

Honkajoki Ltd. Website. Available at (cited 14.3.2023): <https://honkajokioy.fi/>

Industrial Emissions Directive (IED) 2010/75/EU. (2010). Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control). Available at: <http://data.europa.eu/eli/dir/2010/75/2011-01-06>

Kaliya, M., Malinovskaya, O., Landau, M., Herskowitz, M. & van den Oosterkamp, P. (2001). Kinetics of Oxidative Dehydrogenation of Lpg to Olefins on Dy-Li-Ci-Zr-O Catalyst. Reaction Kinetics and the Development and Operation of Catalytic Processes, Vol. 133, pp. 113–121. Available at : [https://doi.org/10.1016/S0167-2991\(01\)81953-4](https://doi.org/10.1016/S0167-2991(01)81953-4)

Karlis, P., Presicce, F., Giner-Santonja, G., Brinkmann, T. & Roudier, S. (2024). Best Available Techniques (BAT) Reference Document for the Slaughterhouses, Animal By-products and/or Edible Co-products Industries. European Union. Available at: <https://eippcb.jrc.ec.europa.eu/sites/default/files/2024-02/SA%20BREF.pdf>

Kastner, J. & Das, K. (2002). Wet Scrubber Analysis of Volatile Organic Compound Removal in the Rendering Industry. Journal of the Air & Waste Management Association, Vol. 52, pp. 459-469. Available at: <https://doi.org/10.1080/10473289.2002.10470800>

Kastner, J. & Das, K. (2005). Comparison of chemical wet scrubbers and biofiltration for control of volatile organic compounds using GC/MS techniques and kinetic analysis. Journal of Chemical Technology & Biotechnology, Vol. 80, Iss. 10, pp. 1170–1179. Available at: <https://doi.org/10.1002/jctb.1308>

Kennes, C. & Veiga, M.C. (2001). Bioreactors for Waste Gas Treatment. Environmental Pollution. Kluwer Academic Publishers, Dordrecht, Netherlands, 312 p.

Krogerus, M. & Hynninen, P. (1992). Sellu- ja paperiteollisuuden päästöjen käsittelyvaihtoehdot ja kustannukset. Vesi- ja ympäristöhallitus, Helsinki, Finland, 226 p.

Kymäläinen, M. & Pakarinen, O. (2015). Biokaasuteknologia: Raaka-aineet, prosessointi ja lopputuotteiden hyödyntäminen. Suomen Biokaasuyhdistys ry. Hämeen ammattikorkeakoulu, Hämeenlinna, Finland. Available at: https://www.theseus.fi/bitstream/handle/10024/104180/HAMK_Biokaasun_tuotanto_2015_ekirja.pdf?sequence=1&isAllowed=y

Le Cloirec, P. & Humeau, P. Edited by Kennes, C. & Veiga, M. (2013). Bioscrubbers. Air Pollution Prevention and Control: Bioreactors and Bioenergy. Available at: <https://doi.org/10.1002/9781118523360.ch6>

Lebrero, R., Gabriela, M., Rangel, L. & Muñoz, R. (2012). Characterization and biofiltration of a real odorous emission from wastewater treatment plant sludge. Journal of Environmental Management, Vol. 116, pp. 50–57. Available at: <https://doi.org/10.1016/j.jenvman.2012.11.038>

Li, Q. & Lancaster Jr., J. (2013). Chemical foundations of hydrogen sulfide biology. Nitric Oxide, Vol. 35, pp. 21–34. Available at: <https://doi.org/10.1016/j.niox.2013.07.001>

Manni, K., Luostarinen, S., Virkkunen, E. & Grönroos, J. (2023). Paras käyttökelpoinen tekniikka kotieläintaloudessa. Ympäristöministeriön julkaisuja 2023:12. Ympäristöministeriö, Helsinki, Finland. Available at: https://julkaisut.valtioneuvosto.fi/bitstream/handle/10024/164817/YM_2023_12.pdf?sequence=1&isAllowed=y

Mattila, T. (1986). Teollisuuden hajupäästöt Suomessa. Kirjallisuusselvitys. Ympäristöministeriö, Helsinki, Finland, 93 p.

Morral, E., Dorado, A. & Gamisans, X. (2023). A novel bioscrubber for the treatment of high loads of ammonia from polluted gas. Environmental Science and Pollution Research, Vol. 30, pp. 8698–8706. Available at: <https://doi.org/10.1007/s11356-022-19065-6>

Nabais, R. Edited by Nicolay, X. (2006). Odors Treatment: Physicochemical Technologies. *Odors in the Food Industry*, pp. 105–123. Available at: https://doi.org/10.1007/978-0-387-34124-8_7

National Renderers Association, INC. North American Rendering – The Source of Essential, High-Quality Products. Available at (cited 10.9.2023): http://assets.nationalrenderers.org/north_american_rendering_v2.pdf

Omri, I., Aouidi, F., Bouallagui, H., Godon, J-J. & Hamdi, M. (2013). Performance study of biofilter developed to treat H₂S from wastewater odour. *Saudi Journal of Biological Sciences*, Vol. 20, Iss. 2, pp. 169–176. Available at: <https://doi.org/10.1016/j.sjbs.2013.01.005>

Potivochayanon, S., Pokethitiyook, P. & Kruatrachue, M. (2006). Hydrogen sulfide removal by a novel fixed-film bioscrubber system. *Process Biochemistry*, Vol. 41, Iss. 3, pp. 708–715. Available at: <https://doi.org/10.1016/j.procbio.2005.09.006>

Prokop, W., Sweeten, J. & Blandford, J. Edited by Davis, W. & Buonicore, A. (1992). *Air Pollution Engineering Manual*. Van Nostrand Reinhold, New York, USA, 918 p.

Puheloinen, E., Ekroos, A., Warsta, M., Watkins, G., Harju-Oksanen, M. & Dahl, O. (2011). Teollisuuden päästödirektiivin (IED) voimaansattaminen ja muita ympäristönsuojelulain kehittämisajatuksia. Ympäristöministeriö. Available at: https://julkaisut.valtioneuvosto.fi/bitstream/handle/10138/41377/YMra_6_2011.pdf?sequence=2&isAllowed=y

Rabbani, K., Charles, W., Kayaalp, A., Cord-Ruwisch, R. & Ho, G. (2015). Pilot-scale biofilter for the simultaneous removal of hydrogen sulphide and ammonia at a wastewater treatment plant. *Biochemical Engineering Journal*, Vol. 107, pp. 1–10. Available at: <https://doi.org/10.1016/j.bej.2015.11.018>

Rappert, S. & Müller, R. (2005a). Odor compounds in waste gas emissions from agricultural operations and food industries. *Waste Management*, Vol. 25, Iss. 9, pp. 887–907. Available at : <https://doi.org/10.1016/j.wasman.2005.07.008>

Rappert, S. & Müller, R. (2005b). Microbial degradation of selected odorous substances. *Waste management*, Vol. 25, Iss. 9, pp. 940–954. Available at: <https://doi.org/10.1016/j.wasman.2005.07.015>

Revah, S. & Morgan-Sagastume, J. Edited by Shareefdeen Z. & Singh A. (2005). *Methods of Odor and VOC Control. Biotechnology for odor and air pollution control*. Available at: https://doi.org/10.1007/3-540-27007-8_3

Ruokavirasto. Eläimistä saatavat sivutuotteet. Available at (cited 14.3.2023): <https://www.ruokavirasto.fi/elaimet/elaimista-saatavat-sivutuotteet-ja-kuolleet-elaimet/elaimista-saatavat-sivutuotteet/>

San-Valero, P., Peña-roja, J., Álvarez-Hornos, F., Buitrón, G., Gabaldón, C. & Quijano, G. (2019). Fully aerobic bioscrubber for the desulfurization of H₂S-rich biogas. *Fuel*, Vol. 241, pp. 884–891. Available at: <https://doi.org/10.1016/j.fuel.2018.12.098>

Schnelle, K., Russel, D. & Ternes, M. (2015). *Air Pollution Control Technology Handbook*. CRC Press, Boca Raton, Florida, USA, 446 p.

Sercu, B., Peixoto, J., Demeestere, K., van Elst, T. & Langenhove, H. Edited by Nicolay X. (2006). *Odors Treatment: Biological Technologies. Odors in the Food Industry*. Available at: <https://doi.org/10.1007/978-0-387-34124-8>

SFS-EN 13037 (2011). *Soil improvers and growing media. Determination of pH*. Finnish Standard Association SFS, 8 p.

SFS-EN ISO 11885 (2009). *Water quality. Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)*. Finnish Standard Association SFS, 28 p.

SFS-EN ISO 16967 (2015). *Solid biofuels. Determination of major elements. Al, Ca, Fe, Mg, P, K, Si, Na and Ti*. Finnish Standard Association SFS, 13 p.

SFS-EN ISO 16968 (2015). *Solid biofuels. Determination of minor elements*. Finnish Standard Association SFS, 11 p.

SFS-EN ISO 16994 (2016). *Solid biofuels. Determination of total content of sulfur and chlorine*. Finnish Standard Association SFS, 16 p.

Shareefdeen, Z., Herner, B., Webb, D., Verhaeghe, L. & Wilson, S. (2005). *An odor predictive model for rendering applications*. *Chemical Engineering Journal*, Vol. 113, Iss. 2–3, pp. 215–220. Available at: <https://doi.org/10.1016/j.cej.2005.03.006>

Singh, A. & Ward, O. Edited by Shareefdeen, Z. & Singh, A. (2005a). *Microbiology of Bioreactors for Waste Gas Treatment. Biotechnology for odor and air pollution control*. Available at: https://doi.org/10.1007/3-540-27007-8_5

Singh, A., Shareefdeen, Z. & Ward, O.P. (2005b). *Bioscrubber Technology. Biotechnology for Odor and Air Pollution Control*. Available at: https://doi.org/10.1007/3-540-27007-8_8

Sironi, S., Capelli, L., Céntola, P., Del Rosso, R. & Grande, M. (2007). *Odour emission factors for assessment and prediction of Italian rendering plants odour impact*. *Chemical Engineering Journal*, Vol. 131, Iss. 1–3, pp. 225–231. Available at: <https://doi.org/10.1016/j.cej.2006.11.015>

Tesfaye, T., Sithole, B. & Ramjugernath, D. (2017). *Valorisation of chicken feathers: a review on recycling and recovery route – current status and future prospects*. *Clean Technologies and Environmental Policy*, Vol. 19, pp. 2363–2378. <https://doi.org/10.1007/s10098-017-1443-9>

Van Groenestijn, J. Edited by Kennes C. & Veiga M.C. (2001). *Bioscrubbers. Bioreactors for Waste Gas Treatment*. *Environmental Pollution*, pp. 133–162. Available at: https://doi.org/10.1007/978-94-017-0930-9_5

Verein Deutscher Ingenieure. (2016). *Biological waste gas treatment Biofilters*. VDI 3477.

Wang, L., Pereira, N., & Hung, Y. (2004). *Air Pollution Control Engineering. Handbook of Environmental Engineering*, Vol. 1. Available at: <https://doi.org/10.1007/978-1-59259-778-9>

Wani, A., Lau, A. & Branion, R. (1998). Performance of Compost and Hog-Fuel Bio-filters: Impact of Periods of Non-Use and Varying Methyl Mercaptan Loading. *Environmental Technology*, Vol. 21, Iss. 3, pp. 271–283. Available at: <https://doi.org/10.1080/09593332108618116>

Woodgate, S. & Wilkinson, R. (2021). The role of rendering in relation to the bovine spongiform encephalopathy epidemic, the development of EU animal by-product legislation and the reintroduction of rendered products into animal feeds. *Annals of Applied Biology*, Vol. 178, Iss. 3, pp. 430–331. Available at: <https://doi.org/10.1111/aab.12676>

Xie, Y., Corpas, F. & Li, J. (2022). Hydrogen Sulfide and Reactive Oxygen Species, Antioxidant Defense, Abiotic Stress Tolerance Mechanisms in Plants. Available at: <https://doi.org/10.3390/books978-3-0365-5375-7>

Ympäristö.fi. (2023). Paras käyttökelpoinen tekniikka BAT. Suomen ympäristökeskus. Available at: <https://www.ymparisto.fi/fi/kestava-kierto-ja-biotalous/kestava-tuotanto/paras-kayttokelpoinen-tekniikka-bat>

Ympäristönsuojelulaki, 27.6.2014/527. (2014). Available at: <https://www.finlex.fi/fi/laki/ajantasa/2014/20140527>

Zhou, J, Jiang, Y., Li, W. & Liu, Y. (2018). Kinetics and removal formula of methyl mercaptan by ethanol absorption without neglecting solute accumulation. *Journal of Environmental Science and Health, Part A. Toxic/Hazardous Substances and Environmental Engineering*, Vol. 53, Iss. 14, pp. 1229–1234. Available at: <https://doi.org/10.1080/10934529.2018.1528036>