Volatile Organic Compounds Abatement: A Critical Discussion of Destruction Techniques

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Abstract—This paper critically discusses volatile organic compounds destruction techniques. The methods discussed are thermal and recuperative oxidation, catalytic oxidation, regenerative oxidation, flares and bioreactors. Examples of bioreactors discussed are bio-filters, bio-trickling filters and bio-scrubbing filters. The principle of operation as well as the strength and weaknesses of each methods are given.

Keywords—Bio-filters, catalytic, destruction, flares, recuperative, regenerative.

I. INTRODUCTION

ACCORDING to the European Commission's Best Available Techniques reference document [1], there are three classes of waste gas emissions in the chemical industry, namely fugitive, diffusive and ducted emissions. Fugitive emissions originate from equipment leaks and the sources include pump and compressor seals, valves, vent plugs, flanges and as well as connectors and other piping items. Diffuse emissions are from point, linear, surface or volume sources during normal process operations such as non-deducted emissions released from storage equipment or during material handling, process emissions from large surfaces or openings during normal process operations, emissions from flares and secondary emissions released during the handling or disposal of waste. Ducted emissions are emissions those which are intentionally captured for the purposes of abatement or recovery. Sources include: process emissions captured via venting and purging of process equipment during normal operations; flue gases from energy-generating equipment process equipment such as furnaces, steam boilers, gas turbines and gas engines; waste gases emitted from emission control equipment; tail gases from reaction vessels and condensers; waste gases captured during catalyst or solvent regeneration; discharges from safety relief devices and those waste gases captured during storage and handling of process materials. Only ducted emissions can be treated using recovery or destructive abatement techniques. Fugitive and diffuse emissions can only be minimized and controlled

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through good maintenance and operating practices.

The two main options for ensuring high quality air are the application of control (end-of-pipe) technologies and prevention methods [2]. Prevention methods include technology or plant modifications, product design and raw material changes as well as in-process recycling and reuse [3]. Good operating practices can limit emissions but cannot entirely prevent them. The benefits of prevention methods include reduced capital investment for end-of-pipe technologies, lower waste-disposal costs through reduced waste volumes, and lower annual operating and maintenance costs [3]. End-of-pipe treatment technologies are classified as recovery and destructive techniques, which are add-on processing units to an existing production facility. Prevention at source is the preferred and more cost-effective than end-of-pipe treatment technologies. However prevention is not always possible, and in many instances control technologies represent the only feasible option to managing air pollution problems [2]. End-of-pipe control technologies can be classified as either recovery or destructive depending on the ultimate fate of the emission being treated. Destructive techniques are employed when the VOC waste stream is odorous, toxic or carcinogenic. The treatment results in either the alteration or the destruction of VOCs. Typical destructive techniques include oxidation (thermal or catalytic with regenerative or recuperative technologies), flaring, bio filtration, bio scrubbing and bio trickling. The disadvantage with oxidisers and flares is that while totally destroying the VOC, they emit CO_2, NOx and CO as by-products of the combustion process. These gases have negative implications for global warming and overall air quality.

II. DESTRUCTIVE TECHNIQUES

A. Thermal and Recuperative Oxidation [4]

Principle of operation

Thermal oxidation (also known as incineration) employs the use of a heat source, several hundred degrees Celsius above the auto-ignition temperature of the VOC-laden gas stream, to oxidise the gas stream in the presence of oxygen. The high temperature is maintained for sufficient time to allow complete combustion of the VOCs to carbon dioxide and water. A typical straight thermal oxidiser comprises only of a combustion chamber. In order to make thermal oxidisers more energy efficient, a waste gas preheater (and if appropriate, a secondary energy recovery heat exchanger) are added. Then, such thermal oxidisers are classified as

recuperative incinerators. The two types of heat exchangers most commonly used are plate-to-plate and the shell-and-tube. The heat is used mainly to preheat the incoming waste gas stream prior to entering the combustion chamber. Remaining heat is often used to generate steam in the energy recovery heat exchanger. In this way, approximately 70% of the waste heat from the exhaust gases can be recovered, making the use of a recuperative exchanger usually more economical than straight thermal incinerators.

A combination of auxiliary fuel, air and waste gas are introduced into the combustion chamber as a nozzle-stabilized flame. While passing through the flame, the waste gas is heated to its ignition temperature. The efficiency of VOC destruction depends on design criteria such as chamber temperature, residence time of the gas in the chamber, the inlet VOC concentration and composition, and oxygen availability. Mixing which is enhanced by turbulence improves the destruction efficiency. Waste gas flow rates range from 0.24 to 24 standard cubic meters per (sm^3/sec). Most hazardous waste thermal incinerators can be operated at 980^0C to 1200^0C. Inlet concentrations of around 1500 to 3000 ppm/v are recommended for economic limitations. A flow diagram of a typical thermal recuperative incinerator is shown in Fig. 1.
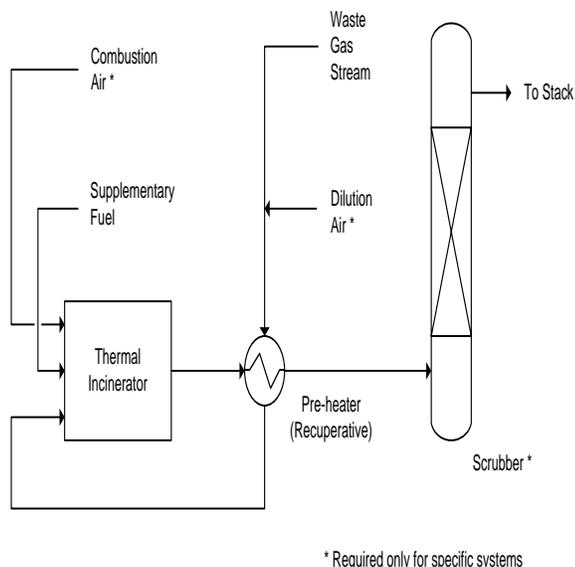

Fig. 1 Thermal incinerator with recuperative pre-heater

Strengths

Thermal incinerators can be used to reduce emissions from almost all VOC sources, such as reactor and distillation vents, gas streams from solvent, ovens, dryers, and kilns operations. Incinerators have efficiencies of up to 99.9999%. Can be applied over a fairly wide range of organic vapour concentrations.

Weaknesses

Incinerators are not generally recommended for halogenated or sulphur-containing VOCs due to the formation of highly corrosive acid gases after oxidation. The installation of a post-oxidation acid gas treatment scrubber would be required, making the application of incinerators economically unjustifiable. They can only handle minor fluctuations in flow. For excessive fluctuations in gas stream flow rate, a flares will be better suited. Due to their high fuel consumption, thermal incinerators are not as economical as recuperative incinerators. Even with the use of a recuperative heat exchanger, incinerator operating costs are relatively high. Thus, thermal oxidisers are best suited for smaller process applications with moderate-to-high VOC loads. The concentration of the organics in the waste gas stream must be substantially below the lower explosive limit (LEL) of the specific VOC being controlled and normally a safety factor of four (i.e. 25% of the LEL) is used.

B. Catalytic Oxidation [4]

Principle of operation

Catalytic incinerators operate in a similar manner to thermal oxidisers; however the waste gas passes through a catalyst bed after passing through the flame area. The waste gas usually passes through a recuperative heat exchanger (where it is preheated by post combustion gas) before passing through the catalyst bed. Oxygen and the VOC migrating to the catalyst surface via gas diffusion are adsorbed onto the catalyst active sites. The oxidation occurs on the surface of the catalyst and products are desorbed from the active sites by the gas and re-enter the gas stream via diffusion. The purpose of the catalyst is to increase the oxidation rate, thereby enabling conversion at lower oxidation temperatures compared to thermal oxidisers. Typical catalysts used in VOC treatment include platinum, palladium and mixed metal oxides.

VOC destruction efficiency for catalytic oxidation dependent on VOC composition and concentration, operating temperature, oxygen concentration, catalyst characteristics as well as space velocity. The space velocity is defined as incoming gas volumetric flow rate divided by catalyst bed volume. The relationship between space velocity and VOC destruction efficiency is strongly influenced by catalyst operating temperature. VOC destruction efficiency increases with an increase in catalyst operating temperature and a decrease in space velocity. Catalytic incineration systems can further be classified as either fixed-bed or fluid-bed systems. Fluid-bed catalytic incinerators have much higher mass transfer rates and are also more tolerant to particulate matter (PM) in the gas stream than fixed bed systems. However the overall pressure drop is higher for fluid bed systems than for fixed bed systems. Fig. 2 shows a typical catalytic incinerator setup. Gas flow rates range from 0.33 to 24 standard cubic meters per second (sm³/sec). Inlet gas pre-treatment is not usually required but particulate matter may be removed before the waste gas enters the incinerator. Most hazardous catalytic waste incinerators are operated at 320°C to 430°C. Catalytic incinerators can be operated at inlet concentrations of around 1 ppm/v or less.
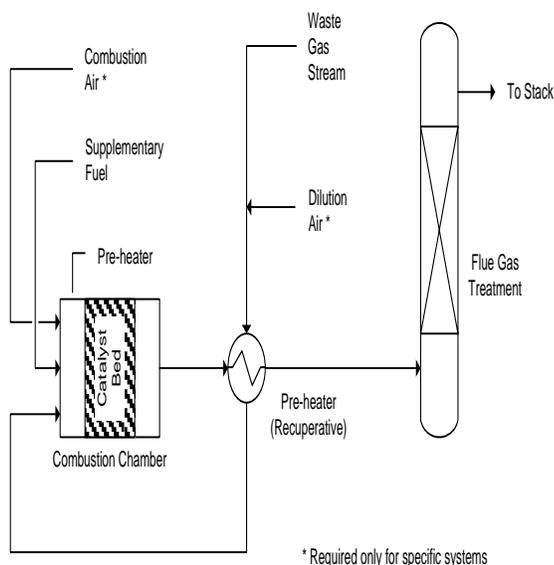
Fig. II Catalytic incinerator with optional recuperative exchanger setup

Strengths

Catalytic incinerators have similar advantages as thermal incinerators. Catalysts allow the oxidizing reaction to occur at a lower temperature than is required for thermal incinerators. Thus a smaller catalytic incinerator can achieve similar efficiencies at the same waste gas flow rate as large thermal units. Lower operating temperatures also reduce fuel requirements and insulation requirements.

Weaknesses

Catalytic incinerators suffer similar weaknesses as thermal incinerators. Particulate matter can blind the catalyst by blocking the catalyst active sites, resulting in deactivation over time. Catalysts can be poisoned by silicon, phosphorous, arsenic, or other heavy metals. Spent catalyst that cannot be regenerated may require disposal. The concentration of VOCs in the waste gas stream must be substantially below the lower explosive limit (LEL) and a safety factor of four (i.e. 25% of the LEL) is used.

C. Regenerative Oxidation [4]

Principle of operation

Regenerative incinerators can be operated as either thermal or catalytic units, hence they can be called regenerative thermal oxidizers (RTOs) or regenerative catalytic oxidizers (RCOs) depending on the operating principle. RTOs use a high-density media such as a ceramic-packed bed, still hot from a previous cycle to preheat the incoming VOC-laden waste gas stream before entering the combustion chamber and this partially oxidise the gas stream. The purified, hot gases exiting the combustion chamber are directed to one or more different ceramic-packed beds cooled by an earlier cycle and the heat is recovered. The reheated packed bed then begins a new cycle by heating a new incoming waste gas stream. RCOs operate in the same manner as RTOs, using a precious metal based catalyst (typically platinum or palladium) rather than ceramic material as the

packed bed. This allows for destruction of VOC at a lower oxidation temperature. Fig. 3 shows a typical flow diagram for a fixed-bed regenerative oxidise with ceramic packed beds. Inlet gas pre-treatment is not usually required but for some RCOs operation, particulate removal is necessary to limit catalyst blinding. Gas flow rates range from 2.4 to 240 standard cubic meters per second. Typical regenerative incinerator design efficiencies range from 95 to 99% for RTO systems and 90 to 99% for RCO systems, depending on waste gas stream characteristics and system design parameters. Most regenerative thermal incinerators are operated at 760°C to 820°C, but can be operated at as high as 1100°C if maximum destruction is required. RCOs use a precious metal catalyst and thus operate at approximately 400°C. Inlet concentrations range from about 100 ppm/v to 1000 ppm/v.
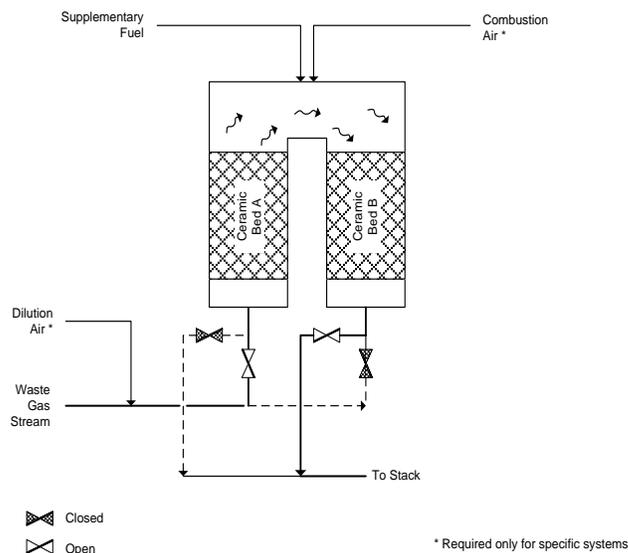

Fig. 3   Fixed-bed regenerative oxidiser

Strengths (RTOs)

Lower fuel requirements due to high energy recovery of up to 95%. Higher temperature capability (up to 1100°C) than recuperative incinerators (820°C maximum) and catalytic incinerators (limited to 600°C). Less sensitive to chlorinated compounds than other oxidisers.

Strengths (RCOs)

Lower fuel requirements than RTOs due lower temperature operation. Catalyst capable of destroying CO in waste stream.

Less sensitive to chlorinated compounds than other oxidisers.

Weaknesses (RTOs)

High capital cost. Installation is costly and difficult. High maintenance equipment with a lot of moving parts which require periodic replacement.

Weaknesses (RCOs)

These oxidisers experience the same weaknesses as RTOs. Particulate removal is often required before treatment. Possibility of catalyst poisoning.

D. Flares [4]

Principle of operation

Flaring, a thermal oxidation procedure is also known as direct-flame combustion. There are two main types of flares – elevated flares and ground flares. Elevated flares are most common and have larger capacities than ground flares. Flares are further classified by the method of enhanced mixing at the flare tip (i.e. steam-, air-, pressure-assisted or unassisted). Steam, air and pressure are added to enhance gas flow rate in order to improve flame stability.

In elevated flares, the waste gas stream is fed through a stack ranging in height from 10 metres to over 100 metres. Combustion occurs at the tip of the stack. In ground flares, combustion occurs at ground level. Ground flares vary in complexity, consisting either of conventional flare burners discharging horizontally with no enclosures or of multiple burners in refractory-lined steel enclosures.

The waste gas stream is routed to the stack via a collection header. A knock-out drum located at or close to the base of the flare removes water and condensed hydrocarbons before they enter the stack. Liquids can extinguish the flame or cause irregular combustion, hence the need for their removal. The waste gas usually passes into the stack via a flame arrestor, which prevents possible flame flashback. Flashback occurs when the waste gas flow rate is too low, resulting in the flame front dropping down into the flare stack. Purge gases (e.g. nitrogen, carbon dioxide or natural gas) are also often used for this purpose. Once the waste gas stream enters the base of the flame, it is heated by fuel and pilot burners at the flare tip. The pilot burners, positioned around the outer perimeter of the flare tip, ensure reliable ignition of the vent stream. The vent stream then flows into the combustion zone where it is oxidized. Whilst flares can be used for continuous, batch and variable-flow waste gas stream applications, their principle purpose is their use as a safety device (i.e. they are designed to relieve emergency process upsets that require the release of large volumes of gas). The VOC destruction efficiency of flares is influenced by flame temperature, residence time in the combustion zone, oxygen availability and the degree of turbulence in the air/ fuel mixing process. The waste gas stream must have a heating value greater than 11 MJ/sm³ otherwise supplementary auxiliary fuels will be required. Max gas flow rate is about 500 standard cubic meters per second (sm³/sec). The discharge temperature from the flare ranges from 500°C to 1100°C and this influenced by the composition of the waste gas stream. Ground flares can handle up to approximately 50 000 kg/hr of waste gas and elevated flares are capable of handling more than 1 million kg/hr of waste gas. A typical flare arrangement is shown in Fig. 4.
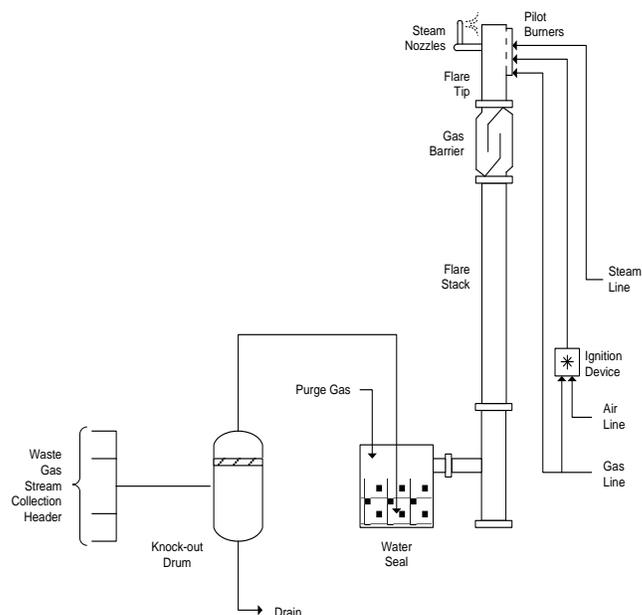

Fig. 4   Typical steam-assisted vertical flare arrangement

Strengths

Flares can be used to control almost any VOC/ HAP stream. Flares have few controls, resulting in lower maintenance costs than other VOC /HAP control devices. Flares can handle large fluctuations in VOC/ HAP concentration, flow rate, heating value and inert species content. Flares can handle waste gases above the lower flammable limit unlike incinerators as they are not enclosed and thus, the explosion risk of a confined chamber is non-existent.

Weaknesses

Flares cannot be used to treat waste gas streams containing halogenated compounds. Flares can produce undesirable noise, smoke, heat radiation and light.

E. Bio-reactors [4]

Principle of operation

Microbes are utilized to consume pollutants from a contaminated waste gas stream. Almost any substance, including VOCs and inorganic gases such as NO_x and hydrogen sulphide decompose with the help of microbes under ideal conditions. Low molecular weight, water-soluble compounds which contain oxygen atoms can easily be decomposed through bio-reaction. Examples of such VOCs are aldehydes, ketones, alcohols, ethers, esters and organic acids which degrade rapidly in bio-filters. However halogenated hydrocarbons and poly-aromatic hydrocarbons do not degrade easily.

Temperature control is very important in the operation of a bio-reactor. When the waste gas stream is too hot, it is passed through a humidifier that cools the gas stream by evaporative cooling and this also increases the moisture content of the gas stream. Waste gas streams having low moisture content are treated similarly. An adequate moisture level is also very important for the proper functioning and efficiency of a bio-

reactor as the degradation reactions are exothermic and tend to dry the filter beds.

In order to ensure good microbe growth, macronutrient dosing is required. Essential macronutrients include nitrogen, phosphorus, potassium, sulphur, magnesium, calcium, sodium and iron. The bed should be operated at a pH as close to 7 (neutral pH) as possible. The bed becomes acidic with as time as a result of the decomposition of halogenated and organic sulphur compounds. Inlet waste gas stream may require pre-treatment for example high temperature and low moisture gas streams require conditioning in a humidifier. Maximum gas flow rate is about 48 standard cubic meters per second (sm³/sec). The temperature of the incoming waste gas stream must be within the limits of 30°C to 41°C and lower temperatures will result in microbe dormancy.

Bio-filters

Original bioreactor consist of a rectangular housing that contains an enclosed plenum on the bottom, a support rack above the plenum, and several feet of media (bed) on top of the support rack. The bed is made of natural materials such as compost, soil peat, gravel or bark which also serve to provide macronutrients to the microbes. Activated carbon and polystyrene may also be added to minimise bed pressure drop. The perforated support rack allows air from the plenum to move through the bed media allowing contact with the microbes in the bed. Excess, condensed moisture can drain out of the bed via the perforations to the plenum for removal. The waste gas stream is pumped to the plenum and then distributed into the bed via the perforated support rack. As the waste gas stream flows through the bed media, VOCs and other pollutants are absorbed by moisture on the bed media and come into contact with microbes. The microbes consume and metabolise the pollutants from the waste gas stream, thus reducing the exiting gas stream pollutant concentration. During the digestion process, enzymes in the microbes convert the VOCs into energy, CO_2 and water. The indigestible material remains as sludge residue. Optimum bed media moisture ranges from 40% to 60% water. Flooding a bio-filter increases bed pressure drop and reduces efficiency. Bio-filters should be operated at inlet pollutant concentrations of less than 1000 ppm/v, 500 ppm/v is ideal.
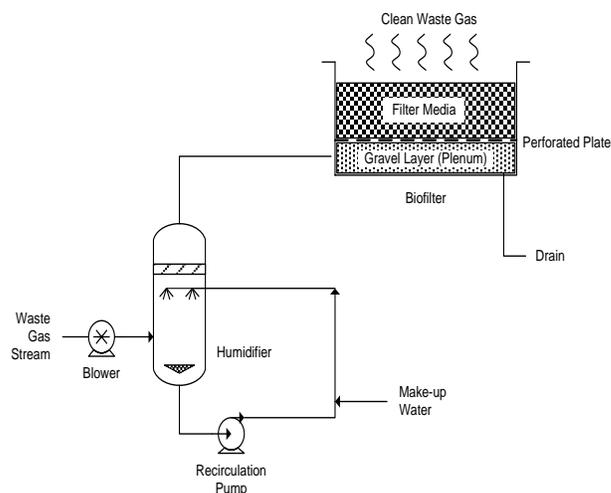

Fig. 2   Bio-filter equipped with humidifier

Bio-trickling filters

A bio-trickling filter is a modification to the original bio-filter concept consisting of a vertical tank that contains a support rack for the packing. The vessel is filled with packing in the form of aggregate, ceramic or plastic media, to a height of between 0.9 to 4.5 metres. The use of ceramic or plastic packing rings achieves a void space of up to 95%, which greatly reduces the pressure drop across the packing. A spray arm containing spray nozzles is attached to the discharge side of a recirculating pump, which pumps liquid from the reservoir at the bottom of the vessel to the spray nozzles. The liquid level in the reservoir is maintained with an automatic effluent make-up system. A biofilm of microbes forms on the packing surface.

The waste gas stream is fed co-currently or counter-currently to the effluent flow through the filter. As the waste gas stream passes through the packing, the pollutants are absorbed from the air into the liquid phase to achieve maximum contact with the microbes. Bio-sludge is periodically drained from the reservoir and discarded. A typical bio-trickling filter setup is shown in Fig. 6.
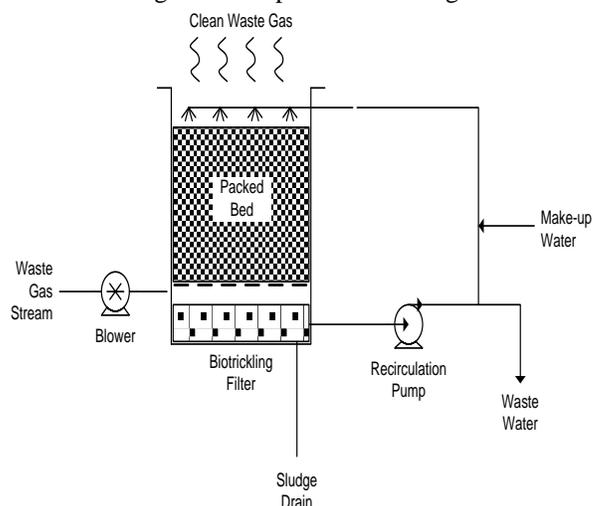

Fig. 3   A typical bio-trickling filter system

Bio-scrubbing filters

Bio-scrubbing filters are modifications to the principal operation of bio-trickling filters. The bio-scrubber was designed to overcome two problems experienced with bio-trickling filters, namely improving the absorption of pollutants into the liquid, and prolonging the contact time of the microbes with the pollutants. In a bio-scrubber, the tower packing is flooded with a liquid and the discharge effluent from the bio-scrubber is collected in activating tanks prior to recycling back to the bio-scrubber. As the waste gas stream is bubbled through the bed media, it forms tiny bubbles that greatly increase the interfacial surface-area between the gas and liquid phases. Increasing the interfacial surface-area improves the liquid phase's ability to absorb pollutants. The activating tank acts as a reservoir for the liquid phase, allowing for additional reaction time for the microbes to consume the pollutants. Macronutrient feed is often introduced into these tanks under controlled conditions. A typical bio-scrubber arrangement is shown in Fig 7.
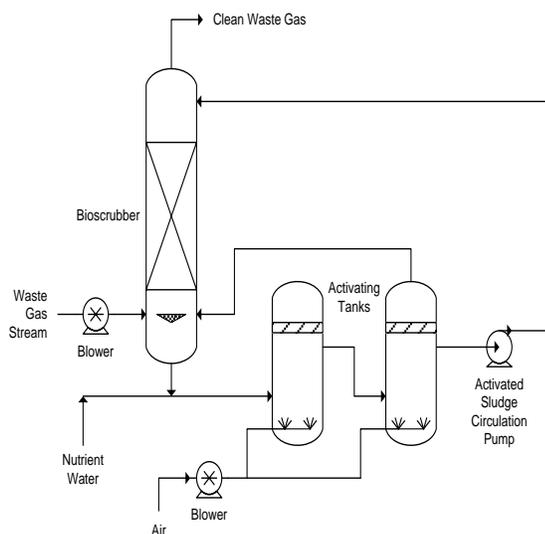

Fig. 4   Bio-scrubber arrangement using two activating tanks

Strengths (Bio-filters and Bio-trickling Filters)

Bio-reactors usually do not generate hazardous pollutants or CO, NO_x and SO_2 gases unless fuel gas is used as a waste gas stream preheater. The products of a bio-reactor are usually water and CO_2. Much lower installation costs compared to traditional destructive technologies. Operating costs are usually low as fuel and energy requirements are much lower than for traditional destructive technologies. Bio-filters have high removal efficiencies in particular for aldehydes, organic acids, nitrous oxide, sulphur dioxide and hydrogen sulphide. Bio-filters are ideal for treating low VOC concentration waste gas streams.

Weaknesses (Bio-filters and Bio-trickling Filters)

Pilot testing is necessary prior to implementation on a process scale. Traditional bio-filter designs require large surface areas. The uniform distribution of macronutrients, and pH control of bio-filter beds, is difficult due to the large

surface area of the beds. Natural bio-filter bed media must be replaced every 2 to 5 years. Bed replacement can take up to six weeks for larger bed sizes. Occasional washing of the bed can extend its life in some cases. Absorption of pollutants into the liquid phase in bio-trickling filters is not as efficient as for bio-filters. Contact time between the microbes and the pollutants is less than that of bio-filters.

Strengths (Bio-scrubbers)

Bio-scrubbers usually do not generate hazardous pollutants or CO, NOx and SO_2 gases unless fuel gas is used as a waste gas stream preheater. Bio-filters can treat low VOC concentration waste gas streams with high gas volume. Humidification of emissions prior to treatment is not necessary. The bio-scrubber has a smaller footprint than other bio-reactors. Nutrient feeding and pH control can be automated. Ideal for emissions which produce acids upon treatment and for waste gas streams which contain particulate matter.

Weaknesses (Bio-scrubbers)

More expensive to install compared to other bio-reactors. Have high operating costs. Over feeding can cause excessive biomass growth and this can in turn plug the system. Natural bed media must be replaced every 2 to 5 years. Expensive, complex feeding and neutralizing systems need to be installed.

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