A Critical Discussion of Volatile Organic Compounds Recovery Techniques

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Abstract—This paper discusses 4 volatile organic compounds recovery technologies. The study focusses on the principle of operation as well as the strengths and weaknesses of each abatement technique. The four techniques discussed are absorption, adsorption, condensation and membrane separation.

Keywords—Abatement, absorption, adsorption, condensation, membrane separation, recovery.

I. INTRODUCTION

VOLATILE organic compounds (VOCs) recovery abatement techniques are utilized when the VOCs in the waste stream are valuable and can be either recycled or converted into other useful compounds. Recovery is also required when flammable VOCs waste stream concentrations exceed Upper Explosive Limit (UEL) specifications. Separation technologies are used in the recovery of VOC emissions and these include: phase change processes (distillation, stripping or condensation); mass separating agent-based processes (adsorption or membrane-based absorption technologies); equilibrium-based mass separation (absorption) and rate-governed membrane processes (vapour permeation). According to [1], activated carbon adsorption, condensation, liquid absorption and membrane separation are the most common recovery techniques. In most situations, 2 or more techniques are integrated into single waste stream processing unit.

II. ADSORPTION

A. Principle of Operation

VOC gas molecules are retained (adsorbed) on a solid surface (adsorbent) which possesses a high surface area per unit mass, thus achieving the removal of VOC molecules from the waste gas streams. Once the adsorbent is saturated with the pollutant VOC, the adsorbent is regenerated by desorption of the VOC. When desorbed, the contaminants are usually at a higher concentration and can either be recovered or abated. Adsorption processes are utilized mainly for maximum recovery of a maximum of three VOCs from a waste stream and pre-concentration of dilute VOC streams prior to thermal or catalytic oxidation [2]. Pre-concentration reduces the oxidiser fuel requirements. Pre-concentration adsorbers are generally smaller recovery absorbers. The design of an adsorber is influenced by the chemical characteristics of the VOC or HAP being recovered, the temperature, pressure and volumetric flow rate of the inlet stream as well as the physical properties of the adsorbent. Most common adsorbents include granular activated carbon, zeolite, macro-porous polymers, silica gel and sodium-aluminium silicates. Granular activated carbon is the most widely used with a wide efficiency range. It is applicable to both polar and non-polar VOCs, thus can be used to both hydrophilic and hydrophobic compounds. Pretreatment may be required before the waste gas stream enters the adsorber. Filters are used to remove particulate matter as well provide cooling. Cooling of the waste gas stream helps maintain the bed at optimum operating temperature; this prevents bed fires or polymerisation of the hydrocarbons.

The basic operating principle of adsorption is based on potential energy between the adsorbent and the pollutant molecule. When the waste gas stream is passed through the adsorbent bed, a repulsive force occurs between the electron clouds of the adsorbent surface and that of the VOC molecule. According to [1], activated carbon adsorption, condensation, liquid absorption and membrane separation are the most common recovery technologies. In most situations, 2 or more techniques are integrated into single waste stream processing unit.
rate is about 27 normal cubic meters per second (nm³/sec). Well-designed adsorption systems may achieve recovery efficiencies of about 95% - 98%. Thermal swing regeneration occurs at a maximum temperature of approximately 175°C [3]. Adsorber should not normally operate above this temperature limit due to the risk of bed fires. Adsorption system can handle a wide range of VOC concentrations from approximately 10 – 10,000 ppm/v [2].

B. Fixed-Bed Adsorption

Fixed – bed adsorbers are the most commonly used in industry. The waste gas stream is initially preheated and water vapour is removed. Thereafter the VOC gas enters the adsorber at a temperature of approximately 40°C and a purified gas stream exits the adsorber. Adsorber beds are inoperable during regeneration, thus adsorbers are normally operated as multiple bed facilities. Whilst one bed is in adsorption mode, the other bed is being regenerated. Ideally, a third bed will be on stand-by.

C. Fluidised-Bed Adsorption

Fluidised bed processes utilise the velocity of the waste gas stream to maintain the adsorbent in a fluidised state. Only abrasion-resistant adsorbent beads are used. The gas stream velocity is usually maintained in the region of 0.8 – 1.2 m/s. The adsorbent is regenerated in a heat exchanger positioned underneath the adsorber and subsequently returned pneumatically to the fluidised bed as a continuous process.

D. Continuous Moving-Bed Adsorption

The adsorbent entering via the top of the adsorber is continuously fed counter-current to the waste gas stream. The saturated adsorbent exits the bottom of the vessel and is continuously transferred to a moving-bed regenerator.

E. Pressure-Swing Adsorption (PSA)

The PSA process is characterised by four distinct steps which are (i) pressure built up by the gas entering into the adsorber (ii) adsorption occurs once the target pressure has been attained (iii) once the bed becomes saturated, the adsorption chamber is de-pressurised (iv) the adsorption chamber is purged at either low pressure or under vacuum.

This four-step process causes a separation of components according to their bond strength to the adsorbent. Since two chambers are employed in simultaneously, VOCs in a waste gas mixture are adsorbed in one chamber whilst bed regeneration occurs simultaneously in the second chamber. With downstream treatment facilities this technique improves the ability of waste gas mixtures to be recovered and re-used. Fig. 1 shows a typical PSA system with a vacuum pump.

F. Continuous Moving-Bed Adsorption

This process uses steam, microwaves, heaters or hot inert stripping gas as heat sources to regenerate adsorbents. The use of superheated steam is favourable especially for granular activated carbon. The heating agent passes downward through the adsorbent, stripping the adsorbent of its VOC load. The VOCs are then transferred to a condensation and separation unit for further processing.

G. Vacuum Regeneration

Regeneration under vacuum allows the desorption process to occur at ambient adsorbent temperature and this is preferred for recovering temperature-sensitive VOCs. This method can be used to regenerate granular activated carbon, zeolite and polymer adsorbents.

H. Strength and Weaknesses

Strengths

Adsorbers can handle a wide range of VOC concentrations in waste gas streams and can also cope with fluctuations in VOC concentration and waste gas flow rate.

Weaknesses

Adsorption is not recommended for high humidity or particulate matter containing streams due to possible blinding of the adsorbent over time resulting in bed efficiency reduction. Adsorption systems are generally restricted to VOCs with molecular weight of 50 – 200kg/kmol. Lower molecular weight VOCs do not adsorb efficiently while higher molecular weight compounds adsorb too strongly, making desorption difficult to achieve [2]. Adsorption systems are less efficient when handling streams containing a mixture of low – and high molecular VOCs as lighter organic compounds are displaced from the adsorbent surface by heavier components [4]. VOCs with high heats of adsorption for example ketones can cause bed fires.
III. CONDENSATION

A. Principle of Operation

Condensation is a technique that removes VOC vapours from a waste gas stream by saturating the VOC components in the waste gas stream. Condensation, refrigeration, and cryogenic systems are usually used on gas streams that contain only volatile organic compounds. Saturation (dew point temperature) occurs when the partial pressure of the volatile organic compound is equal to its vapour pressure. Once saturation temperature has been attained, separation via condensation occurs by either increasing the system pressure (known as compression condensation) or by lowering the temperature at constant pressure (known as refrigerated condensation) [4]. Most commercial condensers are of the refrigeration type and these are discussed in more detail. Refrigerated condensation occurs by means of direct contact between gas and cooling liquid or indirect contact via heat exchanger with a cooling medium. For direct contact applications, a cryogenic gas such as liquid nitrogen is injected into the gas stream. Indirect condensation is preferred because direct condensation requires an additional separation stage. The cooling medium is usually recycled, re-cooled, and reused for additional VOC condensation. The cooling medium used is usually cooling water or chilled water or a freon-based refrigerant. The coolant condenser systems consist of a condenser, heat transfer unit and auxiliary equipment such as a pre-cooler; recovery or storage tank; pumps; blowers and piping. Cryogenic condensation systems consist of a pre-condenser which make use of chilled water or glycol as coolant; the main process condensers; the waste gas economiser; the nitrogen economiser; and the nitrogen vapouriser. Selection of a condensation technology is influenced by the operating temperature range for example (i) Coolant condensation is utilized when a minimum temperature of about 25°C is required (ii) Refrigerant condensation is used when minimum condensation of approximately 2°C are acceptable (iii) Ammonia brine condensation is utilized to lower condensation temperature down to -40°C for a single stage process or -60°C for a two stage process (iv) Cryogenic condensation is utilized to drop the minimum condensation temperature down to about -120°C. Condensation recovery systems vary from simple, single condensers to more complex, multi-condenser systems which have been designed to maximise energy and vapour recovery. The most popular condenser remains the conventional shell-and-tube condenser, which is either water-cooled or air-cooled. The condensation efficiency is often improved by employing a two-stage operation – cooling water is used as coolant in the first stage and refrigerated liquid is used as coolant in the second stage. Condensation processes are widely used for both raw material and product recovery applications. Coolant condensation is used in the treatment of more or less saturated gas streams of VOCs or odorous substances. An essential application of coolant condensation is the pre-treatment or post-treatment of waste gas streams for upstream or downstream waste gas treatment facilities. Cryogenic condensation is often applied for final VOC emission control, as the low temperatures attained result in very high condensation efficiencies. Cryogenic systems cope with all VOCs and HAPs, irrespective of their individual vapour pressures, even under varying flow rate and solvent loading conditions. The waste gas stream feed must however be essentially free of water vapour.

A pre-cooler may be required to remove the moisture and high boiling point solvents before the waste gas stream enters the condenser. Inlet gas streams should also be free of particulate matter as this may contribute to exchanger fouling. Maximum gas flow rate is about 27 normal cubic meters per second (nm³/sec) for coolant systems and 1.35 nm³/sec for cryogenic operations. VOC recovery efficiencies of 90 – 99% can be achieved when using coolant condensation depending on volatile organic compounds vapour pressures while for cryogenic processes; recovery efficiencies often exceed 99%. Temperatures range from 25°C for coolant systems, to –120°C for cryogenic systems. Both coolant and cryogenic systems can handle a maximum waste gas feed temperature of 80°C. Condensation systems are especially suited to high VOC concentration waste gas streams exceeding 1000 ppm/v. The VOC recovery efficiency improves as the VOC concentration in the inlet gas increases.

B. Strengths and Weaknesses

Strengths

Condensation processes can handle both intermittent waste gas feed and flow rates. They can be used for recovering both non-halogenated and halogenated VOCs / HAPs from waste gas streams without the need for expensive auxiliary equipment. Condensation processes are also ideal for high boiling point VOCs.

Weaknesses

The freezing of water vapour and VOCs such as benzene in condenser tubes reduces the heat transfer efficiency and hence recovery efficiencies. The condensation process can generate a waste water stream. There can be challenges with the disposal of the spent coolant.

IV. MEMBRANE SEPARATION

A. Principle of Operation

Membrane separation is based on selective permeability of organic vapours over other gases such as oxygen, nitrogen, hydrogen or carbon dioxide. This is because VOCs have permeation rates of up to 100 times higher than other gases. In a typical membrane separator, the waste gas stream is compressed and fed to an array of membrane modules, where organic solvents preferentially permeate through. The concentration of VOCs in the enriched permeate stream is increased up to fifty times the inlet membrane stream concentration depending on system design. The enriched permeate stream is then recovered by methods such as condensation or adsorption, or abated using appropriate...
oxidation technologies. The pressure differential required to drive the permeate through the membrane is usually created by using excess pressure on the feed side and approximately 0.2 kPa vacuum on the permeate side. Membrane life can be as long as three years. Membrane processes are usually equipped with membrane modules, a compressor, a vacuum unit, a recovery unit such as a condenser or adsorber, ducting and a possible second stage unit for further treatment. Membrane separations are ideally suited for purification of low flow, high-concentration waste gas streams, where condensation or adsorption processes are either uneconomical or unable to attain the required VOC recovery efficiency. Additional VOC treatment is usually required to achieve VOC concentration levels that are within acceptable discharge limits. Membrane process is often used as a pre-concentrator step prior to further recovery or treatment operations. There is a possibility of residual emissions from cooling water or the treated waste gas recovery or treatment operations. There is a possibility of exceeding 5000 ppm/v [4]. Fig. 2 shows a typical membrane separation system with a vacuum pump to draw permeate through the membrane.

Inlet gas streams should be free of particulate matter as this may blind the membranes. Condensation is mainly used for treating low inlet gas flow rates of up to approximately 0.8 normal cubic meters per second (nm³/sec). The limiting flow rate is determined by the surface area of the membrane. VOC recovery efficiencies of up to 90% can be achieved using membrane systems. Most membranes accommodate feed waste gas temperatures of up to 60°C. Membrane processes are especially suited to high VOC concentration waste gas streams exceeding 5000 ppm/v [4]. Fig. 2 shows a typical membrane separation system with a vacuum pump to draw permeate through the membrane.

**B. Strengths and Weaknesses**

**Strengths**

Membranes can handle most volatile organic compounds including halogenated hydrocarbons. VOCs from membrane separation processes are usually recycled and hence no waste is generated. In addition, membrane processes are simple to operate.

**Weaknesses**

The increase in vapour concentration above the lower exposure limit during VOC permeation can result in the accumulation of an explosive mixture. Membrane processes are usually not capable of treating waste gas streams to acceptable disposal limits and hence additional treatment is required.

**V. Absorption**

**A. Principle of Operation**

Absorption, also known as wet scrubbing, is a diffusion-controlled, mass transfer process between a soluble gas and a solvent. During absorption, the waste gas stream pollutants are efficiently removed by contacting the gas stream with suitable scrubbing liquor in an absorption tower. Contact between gas and solvent can occur via three flow patterns (i) co-current flow (ii) counter – current flow (iii) cross-current flow. The most widely used scrubbing flow pattern is the counter – current and this briefly discussed in this section. The gaseous VOC stream flowing into the scrubber via the bottom of the tower is distributed throughout the absorption column. Absorbent scrubbing liquor, usually a heavy hydrocarbon liquid, is introduced into the top of the tower and flows down the tower to exit at the bottom of the tower. The VOC is transferred from the gas to the liquor via direct contact with the liquid flowing down the column, thereby ‘scrubbing’ the waste process stream. The VOC/ liquor mixture exiting the bottom of the column is subsequently stripped at elevated temperature or under vacuum to separate the VOC from the liquor, thereby regenerating the liquor for reuse in the process. The VOC-free scrubbed waste gas stream exits via the top of the absorber. Water is the most commonly used solvent because of its cheap and readily available. Its main weakness is that it quickly saturates, this necessitates the use of alkaline and acidic solutions or polymeric solvents.

The amount of VOC absorbed from the waste stream is influenced by density and viscosity of the waste gas stream and absorbent. VOC characteristics in both liquid and gas streams, such as diffusivity and equilibrium solubility also affect the absorption efficiency. Absorption is also enhanced by greater contacting surface, higher liquid-gas ratios, and higher concentrations in the gas stream. Packed towers are usually used for low temperature inlet waste gas streams due to their cost effectiveness. However, impingement plate design is preferred over packed columns when internal cooling is required or when low liquid flow rates result in inadequate wetting of the packing.

Pre-coolers may be required to saturate the gas stream or to lower the inlet waste gas temperature to improve absorption rates or to avoid solvent evaporation. A particulate matter removal device may be required to avoid plugging of nozzles and packing. Typical waste gas flow rates for packed-bed
absorbers are 0.25 to 35 standard cubic meters per second (sm³/sec), and 0.47 to 35 sm³/sec for impingement-plate scrubber units [3]. VOC removal efficiencies depend on the absorber type and the VOC-solvent system. Most systems achieve above 90% removal efficiency. Packed-tower absorbers can achieve efficiencies exceeding 99% for some VOC-solvent systems. However, typical recovery efficiencies range from 70% to greater than 99% [3]. Operating temperatures range from 4°C to 38°C for gas absorption applications. Excessively high gas temperatures can result in significant scrubbing liquid loss through evaporation. Furthermore, increases in waste gas temperature usually result in lower absorption rate [3]. Absorbers can handle waste gas pollutant concentrations ranging from 250 to 10000 ppm/v [3].

B. Absorption Types

Chemical absorption

Chemical absorption is utilized utilised exclusively to absorb acid gases through chemical reaction of these gases with the scrubbing solvent. The scrubbing solvents are mainly amine based aqueous solutions. Chemical absorption is particularly suitable when the amount of pollutant to be removed is small, and when the raw gas contains no impurities. However, due to the irreversibility of chemical reactions, chemical scrubbing is restricted to the abatement of gaseous compounds.

Physical absorption

Physical absorption processes are used to absorb acid gas components as well as higher hydrocarbons and other components. Physical processes accomplish effective absorption by utilising the difference in solubility of the respective waste stream components with the scrubbing agent. Physical scrubbing is preferred when VOC recovery is required. The VOC is recovered by regeneration of the solvent, which is then reused in the process. Physical scrubbing processes are particularly suitable for treating large gas volumes at high pressures, and streams containing a high concentration of impurities.

Physical-chemical absorption

Physical-chemical absorption processes combine the advantages of both chemical and physical absorption. The pollutant, whilst dissolving into the absorbing liquid, simultaneously reversibly reacts with the absorbent enabling the recovery of the gaseous component. Physical-chemical processes result in higher load ability than purely physical processes and an acceleration of mass transfer as a result of the chemical reactions. The organic absorbents utilized in such processes can also dissolve trace impurities. Optimum design of scrubbing systems include (i) Achieving the lowest economically feasible pollutant exit concentration (ii) Selecting the correct scrubber for a particular application (iii) Select a suitable solvent to give the best mass transfer (iv) Ensuring high reliability of the scrubbing process. Scrubbers are normally operated with pre-coolers. The pre-cooler lowers the inlet waste gas stream temperature this also saturates the gas stream resulting in increased absorption rates. Some common absorbers are discussed in the following section.

A. Scrubbers

Packed Bed Scrubbers

Packed-bed scrubbers consist of packed bed, liquid distributors, gas and liquid, inlets and outlets as well as a demister. Packing can be structured for example proprietary designs such as gauze, corrugated or honeycomb. Random packing such as raschig rings, spiral rings, or berl saddles may also be utilized. The packing provides a large surface area for liquid-gas contact. The packing is held in place by wire mesh retainers and supported by a plate positioned near the bottom of the scrubber. The scrubbing liquid is evenly introduced above the packing via distribution arms and nozzles and flows down through the bed. The liquid coats the packing and establishes a thin film. The waste gas stream flows through the packing, in the process contacting the liquor which absorbs the soluble VOC. Plugging and scaling caused by particulate matter are serious problems for packed-bed scrubbers as they are more difficult to access compared to other scrubber designs. Thus a particular matter removal add-on device is required for the pre-treatment of inlet waste gas stream. Packed-bed absorbers are generally limited to waste gas streams where particulate concentration is less than 0.45 grams per standard cubic meter (g/sm³) to avoid clogging of the packing.

Fibrous Packing Scrubbers

These contain mats of fibrous packing material made from glass, plastic or steel. Pre-cooling of the waste gas stream before it enters the scrubber assists in condensing some of the volatile pollutants, thereby optimising the absorption process. However, the efficient operation of such columns is plagued by the blockage of nozzles and plugging of the fibrous mats, especially if the waste gas stream contains solid contaminants. Mal-distribution of the absorbent over the fibrous mats and fouling of the tower by solid pollutants are challenges.

Moving-Bed Scrubbers

Moving-bed scrubbers consist of zones of mobile packing in the form of low-density plastic spheres, which are held in place by support grids. A mist eliminator is also installed inside these scrubbers. The spherical plastic balls are kept in a constant state of agitation and fluidisation. This prevents plugging and clogging of the packing as well as scale build-up. Moving-bed scrubbers are used in the removal of sulphur dioxide, hydrogen fluoride, odours and dust from waste gas streams and also where scaling is a challenge.

Impingement Plate Scrubbers

Impingement plate scrubbers consist of several bubble-cap or sieve trays stacked in a vertical tower. Baffles are situated a short distance above the plate apertures. The scrubbing liquid flows down the tower while the waste gas stream flows upward. Contact between the liquid and the VOC-laden gas occur on the plates with openings which allow the gas to pass through. As the gas bubbles through the liquid layer, the froth generated creates the contact point between the absorbent and the soluble VOC, where mass transfer occurs. The velocity of the waste gas stream prevents the absorbent from flowing down through the openings. Plate scrubbers are highly efficient and are easier to maintain compared to packed columns. Plate towers however exhibit larger pressure drops.
than packed scrubbers. A further drawback of plate scrubbers is the large liquid hold-ups at high gas flow rates. Plate scrubbers are usually used in the absorption of acids, sulphur dioxide and odours. They are not suitable for foaming liquids, and are less cost-effective than packed towers in terms of VOC abatement.

### Spray Towers

Spray towers make use of spray nozzles, situated at the top of the tower, to inject a mist of liquid solvent into the chamber. The waste gas stream entering the tower near the bottom contacts the solvent as the waste gas stream passes counter-current up the column. Spray towers are used to remove acid gases and odours. They are generally limited to the removal of highly soluble gases of concentrations ranging from 100 to 10000 mg/Nm³ due to their poor mass transfer. Spray towers are preferred when high pressure drop across the column is a concern. Spray tower wet scrubbers are not as prone to fouling as packed scrubbers, but their nozzles are susceptible to plugging. Fig. 3 shows a typical scrubbing – stripping system.

![Diagram of a conventional absorption system including a stripping section](image_url)

**Fig. 3 A conventional absorption system including a stripping section**

### C. Strengths and Weaknesses

#### Strengths

Scrubbers can handle a wide variety of waste gas flow rates and high humidity (>50% relative humidity) air streams. They are relatively simple to maintain and are able to process flammable and explosive gases with low risk.

#### Weaknesses

Most scrubbers are susceptible to particulate matter plugging. Entrainment of the liquid absorbent in the exit gas stream could pose new pollution challenges. Only absorbent soluble VOCs are recovered, other treatment options may be required for those which are insoluble.

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### REFERENCES


### Biography: Edison Muzenda

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