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Review

Removal of Volatile Organic Compounds from polluted air

Faisal I. Khan *, Aloke Kr. Ghoshal

Department of Chemical Engineering, Birla Institute of Technology and Science, Pilani-333 031, Rajasthan, India

Abstract

Volatile Organic Compounds (VOCs) are among the most common air pollutants emitted from chemical, petrochemical, and allied industries. VOCs are one of the main sources of photochemical reaction in the atmosphere leading to various environmental hazards; on the other hand, these VOCs have good commercial value. Growing environmental awareness has put up stringent regulations to control the VOCs emissions. In such circumstances, it becomes mandatory for each VOCs emitting industry or facility to opt for proper VOCs control measures. There are many techniques available to control VOCs emission (destruction based and recovery based) with many advantages and limitations. Therefore, deciding on a particular technique becomes a difficult task. This article illustrates various available options for VOCs control. It further details the merits, demerits and applicability of each option. The authors hope that this article will help in critically analysing the requirements and accordingly decide on the appropriate strategy to control VOCs. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Adsorption; Bio-filtration; Membrane; Oxidation; RFR; Volatile Organic Compounds (VOCs)

1. Introduction

Volatile Organic Compounds (VOCs) include most solvent thinners, degreasers, cleaners, lubricants, and liquid fuels. A brief list of some common VOCs are presented in Table 1, which includes methane, ethane, tetrachloroethane, methyl chloride, and various chlorohydrocarbons and perfluorocarbons. VOCs are the common air pollutants emitted by the chemical and petrochemical industries. Emissions of VOCs originate from breathing and loading losses from storage tanks, venting of process vessels, leaks from piping and equipment, wastewater streams and heat exchange systems. Control of VOCs emission is a major concern of the industries' commitment towards the environment.

Table 1
Some of the common VOCs

Serial Number	Volatile Organic Compounds
1	Acetaldehyde
2	Acetone
3	Benzene
4	Carbon tetrachloride
5	Ethyl acetate
6	Ethylene glycol
7	Formaldehyde
8	Heptane
9	Hexane
10	Isopropyl alcohol
11	Methyl ethyl ketone
12	Methyl chloride
13	Monomethyl ether
14	Naphthalene
15	Styrene
16	Toluene
17	Xylene

From an environmental point of view, it is necessary to limit and control vapour emissions because they affect the change of climate, the growth and decay of plants, and the health of human beings and all animals. For example, according to a report of the National Academy of Sciences, the release of chlorofluoromethanes and chlorine-containing compounds into the atmosphere increases the absorption and emission of infrared radiation. If the heat loss from the earth is retarded, the earth's temperature and climate are affected. Studies on carcinogenicity of certain classes of hydrocarbons indicate that some cancers appear to be caused by exposure to aromatic hydrocarbons found in soot and tars. Hydrocarbons in combination with NO_x, in the presence of sun-

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* Corresponding author. Fax: +91-01596-44183.
E-mail address: khan@bits-pilani.ac.in (F.I. Khan).

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light, undergo photochemical oxidation, producing a photochemical smog that is environmentally hazardous.

1.1. Regulation to control VOCs emission

Regulations on controlling organic vapour pollutants in air have been issued world-wide. In the ambient air quality standards produced by the US Environmental Protection Agency, the maximum 3-hour concentration of hydrocarbon content is 1.6×10^{-4} kg/m^3 (0.24 ppm), not to be exceeded for more than a year.

VOCs react with nitrogen oxides and other airborne chemicals, in the presence of sunlight (photochemically), to form ozone, which is a primary component of smog. Reduction of VOCs emissions that exceeds the current national ambient air quality standard for ozone of 0.12 ppm is mandated under Title I of the US Clean Air Act Amendment of 1990. In addition, Title III of the amendments requires reduction of the emissions of 189 hazardous air pollutants, most of which are included under the definition of VOCs as well (Ruddy & Carroll, 1993). Thus, some sources of VOCs may be controlled under two separate sets of regulations with potentially differing requirements.

The recently passed European Community stage emissions limit is 35 grams total organic compounds (TOC) per cubic meter gasoline loaded (35 g TOC/m^3). Similarly, the United States Environmental Protection Agency Standard 40 CFR Part 63 has established an emission limit of 10 g TOC/m^3. The German TA-Luft Standard, the most stringent known gasoline emission regulation, has set an emissions limit to 150 mg TOC (excluding methane) per cubic meter of loaded product (0.15 g TOC/m^3) (USEPA, 1991; Ruddy & Carroll, 1993; Pezolt, Collick, Johnson & Robbins, 1997). Like any third world country, in India there is no separate regulation as such to control VOCs emissions. However, the Clean Air Act, 1990 (Amendment) and the Factory Act, 1986 (Amendment) limit the release/emission of commonly hazardous chemicals that include most of the VOCs.

After a detailed analysis of an emission inventory, an appropriate technique for their control should be decided on. This paper aims to present state-of-the-art technologies available to control VOCs emissions with their relative merits and demerits. The article further analyses the applicability of each technique in different situations.

2. Available techniques/technologies for VOCs control

There are many different techniques available to control VOCs emissions. These techniques are basically classified into two different groups: (i) process and equipment modification and (ii) add-on-control techniques. In the first group, control of VOCs emissions are achieved by modifying the process equipment, raw material, and/or change of process, while in the other class an additional control method has to be adopted to regulate emissions. Though the former is the most effective and efficient method, its applicability is limited, as usually it is not possible to modify the process and/or the equipment. The techniques in the second group are further classified into two sub-groups, namely the destruction and the recovery of VOCs. An organisational tree diagram showing various VOC control techniques is presented in Fig. 1.

The first task in evaluating VOC control techniques is to prepare a comprehensive emissions inventory. The emissions inventory provides the basis for planning, determining the applicability of regulations permitting the selection of control options for further consideration (USEPA, 1986; Kuhn & Ruddy, 1992). The inventory should cover the entire facility source-by-source, considering:

- pollutants emitted,
- the individual chemical species within each vent stream (to identify any non-VOC materials that may have determined effects on particular types of control equipment),
- hourly, annual, average, and worst case emissions rates,
- existence and condition of certain pollution control equipment, and
- regulatory status.

3. Process and equipment modification

Process and equipment modifications are usually the most preferred alternative for reducing emissions. Modifications include the substitution of raw materials to reduce VOCs input to the process, changes in operating conditions to minimise the formation or volatilisation of VOCs and the modification of equipment to reduce opportunities for escape of VOCs into the environment. The first two mechanisms vary with the process being addressed and are not further discussed here. Equipment modification can take many forms, but the objective is always to prevent the escape of VOCs. VOCs can be emitted through open vessel tops, vents, or leaks at flanges or valves, or they may be the result of process conditions. The starting point is the vessel or structure in which the operation takes place. Vessels can be capped or equipped with rupture disks or pressure/vacuum vent caps to contain vapour emissions. Monitoring and repair programs can be instituted to consistently reduce emissions due to leaks from valves, pumps, and process piping connections in order to

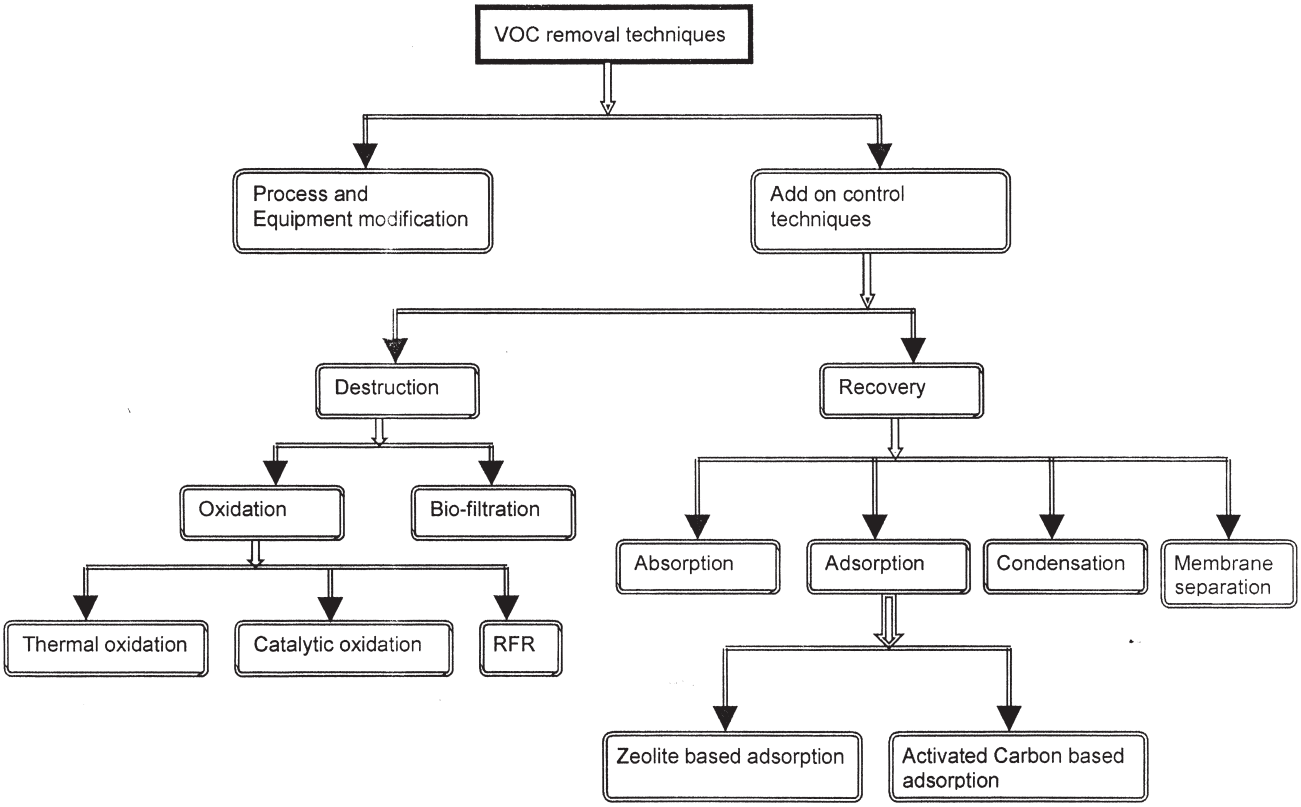

Fig. 1. Classification of VOC control techniques.

reduce emissions. Similarly, process enclosures can be designed to reduce emissions. By enclosing the source, a positive means of collecting the emissions can be provided. However, simply providing an enclosure is not enough to reduce the emissions. If emissions are captured in the enclosures but no additional measures are taken, the pollutants will eventually escape into the environment. Typically, this situation is handled by end-of-pipe solutions (Chadha & Parmele, 1993; Ruddy & Carroll, 1993; William & Lead, 1997). An overall approach to develop collection and control strategies to reduce VOCs emissions is via a stepwise analysis. The first step is to quantify air emissions by developing an understanding of the process steps and material balances, followed by sampling, measuring or estimating vent flows. Then, significant sources can be identified and strategies and designs are developed to address the issues.

4. Add-on-control techniques

Add-on control techniques are broadly classified into two types: destruction and recovery, details of which are presented in subsequent sections.

5. Destruction of VOCs

In this step, VOCs are destroyed by different types of oxidation such as thermal and catalytic, and digestion of VOCs under aerobic conditions by microbes (Bio-filtration).

5.1. Oxidation of VOCs

5.1.1. Thermal oxidation

Thermal oxidation systems, also known as fume incinerators, are not simple flares or afterburners. The modern thermal oxidiser is designed to accomplish from 95% to 99% destruction of virtually all VOCs. These systems can be designed to handle a capacity of 1,000 to 500,000 cfm (cubic feet per minute) and VOC concentration ranges from 100 to 2,000 ppm. Nominal residence time ranges from 0.5 to 1.0 s. Available with thermal energy recovery options to reduce operating costs, thermal oxidisers are very popular (Marks & Rhoads, 1991; William & Lead, 1997).

Thermal oxidation systems combust VOCs at temperatures of 1,300–1,800°F. Actual operating temperature is a function of the type and concentration of material in the vent stream and the desired DRE (Destruction and Removal Efficiency). Compounds that are difficult to combust or that are present at low inlet concentrations will require greater heat input and retention time in the combustion zone to ensure that the desired DRE is accomplished. High DRE requirements will also require higher temperatures and longer retention times. Inlet concentrations in excess of 25% of the LEL (Lower Explosive Limit) are generally avoided by oxidiser manufacturers because of potential explosion hazards (AIChE, 1992; Ruddy & Carroll, 1993).

Operating temperatures near 1,800°F can produce elevated levels of nitrogen oxides (from nitrogen in air), a secondary pollutant that may, in turn, require further treatment. Halogenated compounds in the vent stream are converted to their acidic counterparts. Sufficient quantities may necessitate the use of expensive corrosion resistant materials of construction and the use of additional acid gas controls, such as scrubbing, as follow-up treatment.

Two types of thermal energy recovery systems are in common use today, regenerative and recuperative (Fig. 2). Both use the heat content of the combustion exhaust stream to heat the incoming gas stream prior to entering the combustion zone.

Regenerative systems use ceramic beds to capture heat from gases exiting the combustion zone. As the bed approaches the combustion zone temperature, heat transfer becomes inefficient and the combustion exhaust gas stream is switched to a lower temperature bed. The incoming gas stream is then passed through the heated bed where it recovers the captured heat prior to entering the combustion zone (Fig. 2(a)). By using multiple beds, regenerative systems have achieved up to 95% recovery of the thermal energy input to the system as fuel and the heat content of the combusted VOCs. Where the incoming gas stream contains sufficient thermal energy potential from VOC combustion, regenerative systems can operate without external fuel (excluding the need for a pilot light). The efficiency of the thermal recovery system depends on the process operating characteristics. A process where the flow rate and VOC content are relatively constant has a good potential for achieving virtual no-fuel operation. Cyclic processes generally are not as compatible with regenerative oxidation systems. The absorbed heat is lost to the environment during periods of low activity. Operation with insufficient VOC content to supply thermal input requirements necessitates the use of external fuel sources.

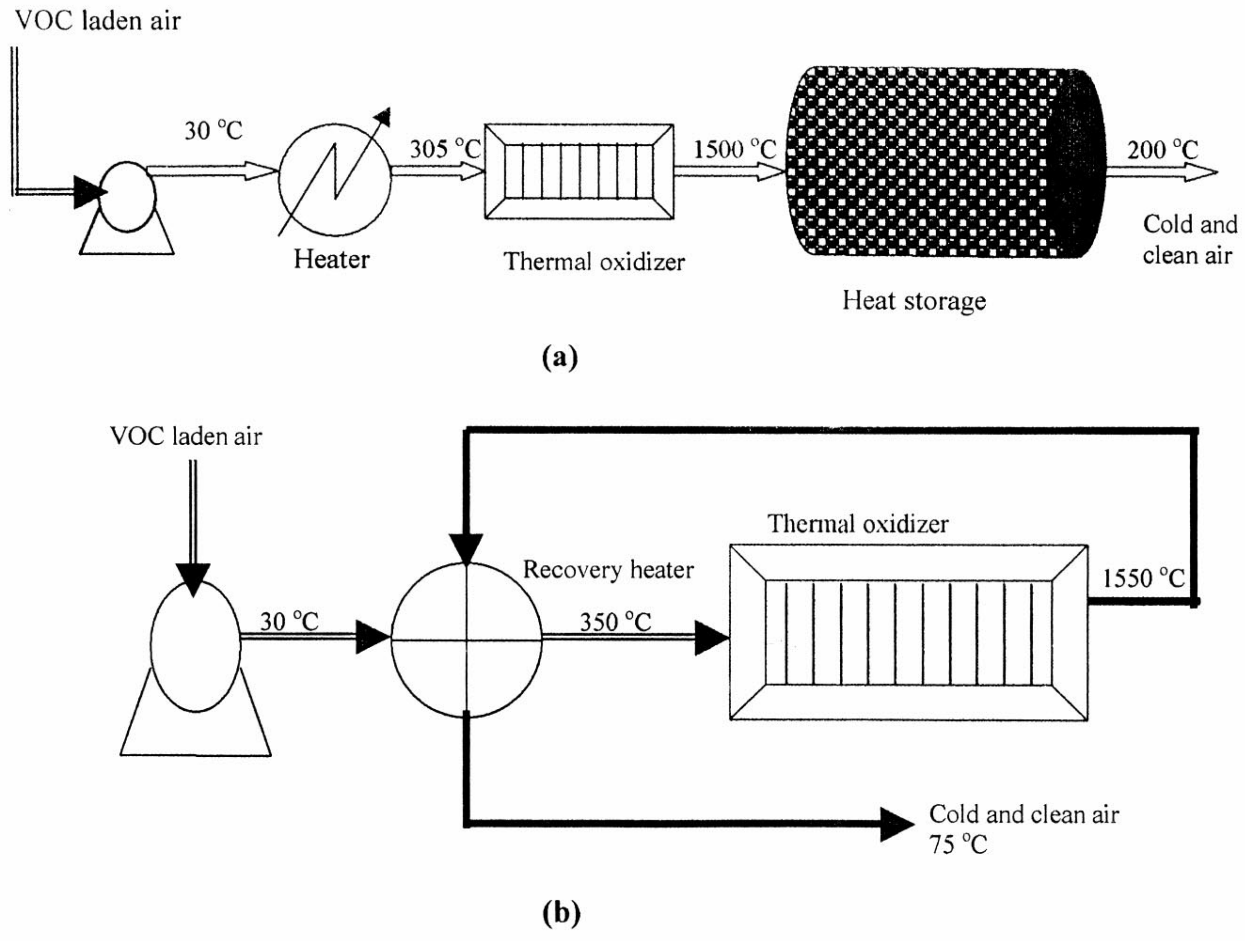

Fig. 2. Schemes of thermal oxidation. (a) Regenerative thermal oxidation; (b) recuperative thermal oxidation.

Recuperative thermal oxidation systems recapture thermal energy with a simple metallic heat exchanger, typically a shell-and-tube design (Fig. 2(b)). The maximum thermal energy recovery of a recuperative system is around 70% of the fuel and VOC combustion energy input to the system. The advantage over the regenerative system comes from the relatively short period required for the heat exchanger to reach operating conditions. The larger mass of the regenerative heat recovery system requires time and relatively large initial fuel inputs to reach operating conditions, while the recuperative heat exchanger reaches operating conditions within several minutes of start up. Recuperative systems are best suited to cyclic operations where the versatility of an oxidation system is required along with the ability to respond to cyclic operating conditions.

The high concentrations of organics in the regeneration stream, combined with the short duration of the desorption cycle, permits economical destruction of the VOCs in a thermal oxidiser. Thermal oxidation is a costly disposal method for treating low concentrations of organics contained in the process exhaust. A properly designed thermal oxidiser, which incorporates an effective heat exchanger and advanced refractory lining, is able to utilise the calorific value of the desorbed VOCs to generate the temperatures required for destruction with minimum auxiliary fuel consumption. A destruction efficiency of more than 99% can be achieved for most organics at temperatures ranging from 1,400°F to 2,000°F with residence times of 0.5 s to 2.0 s (Marks & Rhoads, 1991; Ruddy & Carroll, 1993).

5.1.2. Catalytic oxidation

Catalytic oxidation systems directly combust VOCs in a manner similar to thermal oxidisers. The main difference is that the catalytic system operates at a lower temperature—typically about 700–900°F. This is made possible by the use of catalysts that reduce the combustion energy requirements. The incoming gas stream is heated, most often in a recuperative heat exchanger followed by additional input from a burner if needed, and passed through a honeycomb or monolithic support structure coated with catalyst. Catalyst systems can be designed to handle a capacity of 1,000 to 100,000 cfm and VOC concentration ranges from 100 to 2,000 ppm (Fig. 3). The catalytic system is well suited to low concentration operations or those that operate in a cyclic manner. They are often used for vent controls where flow rates and VOCs content are variable. Destruction efficiencies in excess of 90% are common with a maximum DRE of 95% (Patkar & Laznow, 1992; Ruddy & Carroll, 1993). High concentration vent streams can also be treated with catalytic technology; however, as with thermal oxidation, it is not advisable for concentrations in excess of 25% of LEL. Lower operating temperatures, combined with a recuperative heat exchanger, reduce the start up fuel requirement. Large catalytic systems have been installed, but are not as popular as direct thermal oxidation systems, mainly due to the high costs of catalyst replacement. Catalyst systems, like thermal oxidisers, can produce secondary combustion wastes. Halogens and sulphur compounds are converted to acidic species by the catalytic combustion process; these are treated by using acid–gas scrubbers. Also, the spent catalyst materials can require disposal as a hazardous waste if they are not recyclable. Catalyst materials can be sensitive to poisoning by non-VOC materials such as sulphur, chlorides and silicon. Many catalyst manufacturers have overcome sensitivity to some of these substances, but every catalyst has susceptibilities that must be considered at the process selection stage. For example, some catalysts are sensitive to deactivation by high-molecular-weight hydrocarbons or polymerising materials. Also, the catalyst support may become deformed at high temperatures and high concentrations. Researching these issues should be part of the process selection activity if catalytic oxidation is under consideration (William & Lead, 1997).

5.1.3. Reverse Flow Reactor (RFR)

A Reverse Flow Reactor (RFR) is an adiabatic packed bed reactor in which the direction of the feed flow is reversed periodically (Fig. 4). Thus, the reactor is forced to operate under transient conditions. RFR is becoming a strong alternative for the removal of VOCs from polluted air because unsteady-state reactor operation can be profitable for the chemical process (Matros, 1989; Matros, Noskov & Chumachenko, 1993). The RFR, if operated on a large scale, will behave close to adiabatically. For the RFR the dynamics of the system should be well defined and not influenced by its surroundings. This excludes the use of insulation to obtain adiabatic conditions, because for a reasonable resistance against heat losses the amount of insulation needed is very large. The heat capacity of the insulation can easily be larger than that of the packed bed and thus a significant additional heat buffer is created. Also, applying compensation heating has to be avoided, because in that case the dynamics of the system are certainly influenced and no more well defined. The best way of achieving adiabatic conditions and minimising the influence of surroundings is making use of an evacuated jacket with the provision of a radiation shield at higher operating temperatures (Van de Beld, Borman, Derkx, Van Woezil & Weserterp, 1994). Table 2 gives a brief review of experimental studies of RFR in different applications.

5.1.4. Important parameters influencing the performance of RFR

5.1.4.1. Cycle period The maximum temperature inside the reactor is almost insensitive to a change in the

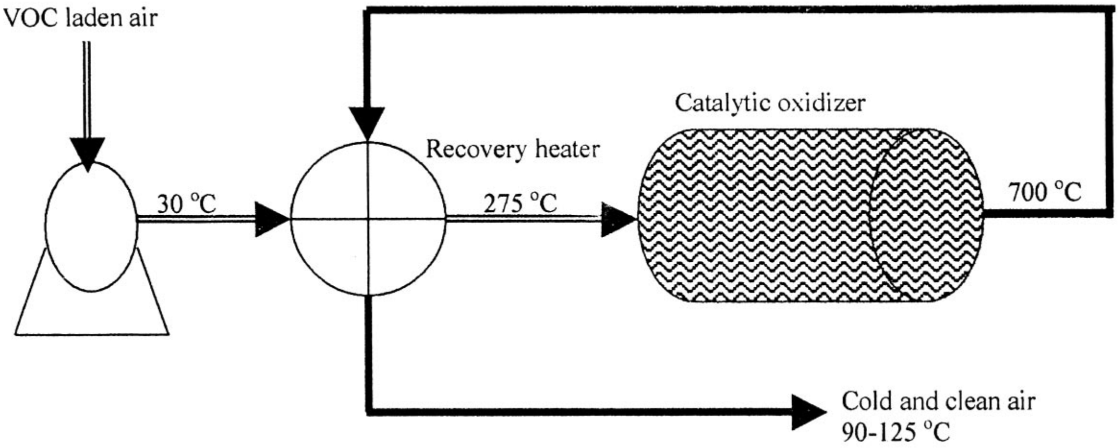

Fig. 3. Scheme of catalytic oxidation.

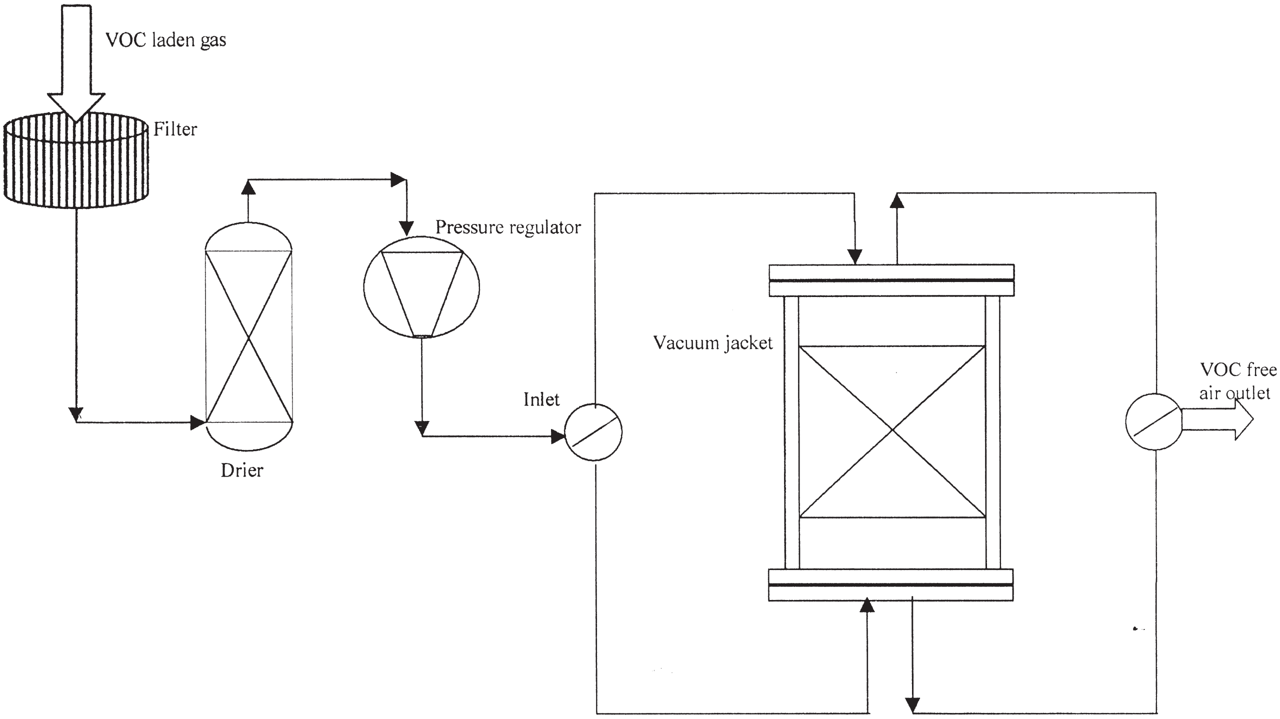

Fig. 4. Schematic diagram of a reverse flow reactor.

cycle period. If the cycle period is very high, too much heat will be removed from the reactor and at the end of the cycle the conversion starts decreasing so an autothermal process is no longer possible. Again, at a particular axial position of the reactor the temperature changes over a wide range within one cycle, and perhaps these temperature fluctuations will shorten the age of the catalyst. On the other hand, for a very small cycle period the temperature profiles hardly move. Now the overall efficiency of the process will be lowered, because large amounts of feed gas will bypass the reactor at the moment of flow reversal. So, the optimum cycle period is such that it allows the heat front to move over a certain distance, but not too far so that the whole heat reserve is removed during one cycle.

5.1.4.2. Influence of the gas velocity If the gas velocity changes, the relative change in the heat front velocity is the same. For low adiabatic temperature rises, a monotonously increasing plateau temperature is observed with increasing gas velocity. For high gas velocities the plateau temperature remains nearly constant.

Table 2
A brief-review of the experimental studies for the reverse flow reactor in different applications (Van de Beld et al., 1994)

Application	Reactor dimension	Radial heat loss prevention	Important references
SO_2 oxidation	D=175 mm, L=0.44–1.8 m	200 mm insulation	Boreskov, Bunimovich, Matros & Ivanor (1982) and Bunimovich, Strots & Goldman (1990)
Air purification	D=175 mm, L=3 m	200 mm insulation	Matros et al. (1993)
Methanol production	D=68 mm, L=0.77 m	Insulation thickness not specified	Matros (1989)
Selective reduction of NO_x	D=175 mm	Not mentioned	Bobrova, Salvinskaya, Noskov & Natros (1988)
Air purification	D=570 mm, L=4 m	630 mm insulation	Eigenberger & Nieken (1988)
Methanol production	30 g of catalyst	Evacuated jacket	Neophytides & Forement (1992)
Air purification	D=136 mm, L=0.594 m	Insulation+heat loss compensation	Van de Beld et al. (1994)
Air purification	D=145 mm, L=1.0 m	Evacuated jacket	Van de Beld et al. (1994)

5.1.4.3. Influence of adiabatic temperature There lies a critical adiabatic temperature inside the reactor below which no reaction occurs, and the plateau temperature equals the feed temperature. Above this critical value a high conversion is obtained and the temperature rise in the reactor reaches values several times the adiabatic temperature rise. A further increase in the inlet concentration will lead to an increase in the plateau temperature larger than the increase in adiabatic temperature. The minimum required adiabatic temperature rise can be much lower under really adiabatic temperatures, such as those found in industrial conditions. It is only slightly sensitive to the kind of combustible used.

5.1.4.4. Different components and mixtures A reverse flow reactor exhibits self-controlling behaviour: lowering the reaction rate will result in a higher plateau temperature (Eigenberger & Nieken, 1988). If extra combustibles have to be added to the feed to attain higher bed temperatures and thus high conversions of all components, then it depends upon the temperature level required as to which active additive to use. Most likely the component itself or a component which reacts in the same temperature range should be added.

5.1.4.5. Influence of pressure The combustion reactions can often be described by first order reaction kinetics with respect to the hydrocarbon. Therefore increasing the pressure will lead to an increase in the reaction rate. Because the gas hold up increases with increasing pressure and the cycle period remains unchanged, at the moment of flow reversal an increase in bypass of the reactor hold up takes place leaving the system unconverted. Due to this reactant loss the total heat production in the reactor and the overall conversion is reduced.

5.1.4.6. Response to variations in inlet concentration

For industrial air purification processes obviously the inlet conditions, like concentration and chemical character of the contaminants and the flow rate, are subject to fluctuations. When switching from one component to another component, if the new component is easier to oxidise and the concentration is high enough then the process continues without any trouble. But if the new component is more difficult to convert, the situation is completely different. It depends on the temperature of the reactor whether the reaction starts at all. The inlet concentration determines whether enough heat is released to achieve a stable ignited pseudo steady state, or otherwise it may be necessary to supply additional heat to the system. In a reverse flow reactor the catalyst is exposed to high temperatures and rapid temperature changes. This may cause a severe deactivation of the catalyst, in which case the plateau temperature will increase.

So, it may be emphasised here that though the reverse flow reactor is still in the development stage, if oxidation is to be chosen as a VOCs removal technique, then the reverse flow reactor is becoming a stronger option because of its certain advantages. One advantage of applying an RFR is the possibility of purifying polluted air with an autothermal process without any external energy supply. To this end a minimum amount of combustibles should be present in the feed. Instead of a minimum feed concentration it is better to consider a minimum adiabatic temperature rise. It also enables the reactor to handle fluctuations in the inlet conditions like gas flow and inlet concentration, as they occur in industrial practice. Though the RFR involves complexity in design, higher initial investment costs, and higher maintenance costs, yet in the near future it is going to replace the conventional oxidation techniques as it relies upon using less energy.

5.2. Biological treatment of VOCs

5.2.1. Bio-filtration

The bio-filtration process, which was originally developed for the odour abatement of waste gases, has proven recently to be an effective and inexpensive method for the removal of VOCs produced during various industrial activities (Ottenger & van den Oever, 1983). This technique is based on the ability of micro-organisms (generally bacteria) to convert, under aerobic conditions, organic pollutants to water, carbon dioxide and bio-mass. The bio-filter consists generally of a simple structured packed bed, intensively surrounded with an immobilised micro-flora (Fig. 5). The contaminated gas is directed through a bio-layer around the packing material. In practice, various types of packing material are used, e.g. compost, soil, peat, etc. (Leson & Winer, 1991; Jol & Dragt, 1995; Kiared, Bieau, Brzezinski, Viel & Heitz, 1996). The filter bed material should have certain mechanical and physical properties (structure, void fraction, specific area, flow resistance and water retention capacity), and biological properties (provision of inorganic nutrients and specific biological activity).

In the past decade increasing attention has been paid to bio-filtration as a waste gas purification process due to some important advantages this technique has compared to conventional purification methods. In addition to the mild operating conditions, a biological decontamination process does not generally transfer the pollution problem to another environmental compartment (gas to solid and/or gas to liquid), which is often the case with many other purification methods. Moreover, biological treatment is especially effective when the odours or toxic waste gas emission are in the lower concentration range, i.e. at few ppm levels.

Bio-filtration is a process in which contaminated air is passed through a porous packed medium that supports a thriving population of micro-organisms. The contaminants are first adsorbed from the air to the water/bio-film phase of the medium (Fig. 5). The degree of adsorption is a function of the chemical characteristics of the specific contaminant (water solubility, Henry's constant, and molecular weight). Once the contaminants are adsorbed, the micro organisms convert them to carbon dioxide, water, inorganic products and bio-mass (Ottenger & van den Oever, 1983; Liu et al., 1994).

Bio-filter success is dependent upon the degradability of the contaminants (Leson & Winer, 1991; Kiared et al., 1996). Anthropogenic compounds may contain complex bonding structures that resist microbial enzymatic reactions. Oxidation may not be complete, and may even form degradation by-products more toxic than the original compounds (Tahraoui et al., 1994; Webster, Devinny, Torres & Basrai, 1996). For example, during the aerobic transformation of trichloroethylene, the highly toxic by-product vinyl chloride may be formed (Webster, Torres & Basrai, 1995; Devinny & Hodge, 1995). A successful bio-filter must also provide a benign environment for micro-organisms. The moisture content of the medium should be maintained at optimum values to support microbial growth without clogging the pores. Acceptable values of the medium pH at which micro-organisms can thrive must be maintained.

Bio-filtration is effective in simultaneously removing hydrogen sulphide, VOCs and toxic air emissions from discharges of publicly owned treatment works (POTW). In order of degradability, data suggest that the order of removal efficiency appears to be hydrogen sulphide>aromatics>aldehydes and ketones>chlorinated hydrocarbons. The preference for compounds with low molecular weights, higher solubilities and less complex

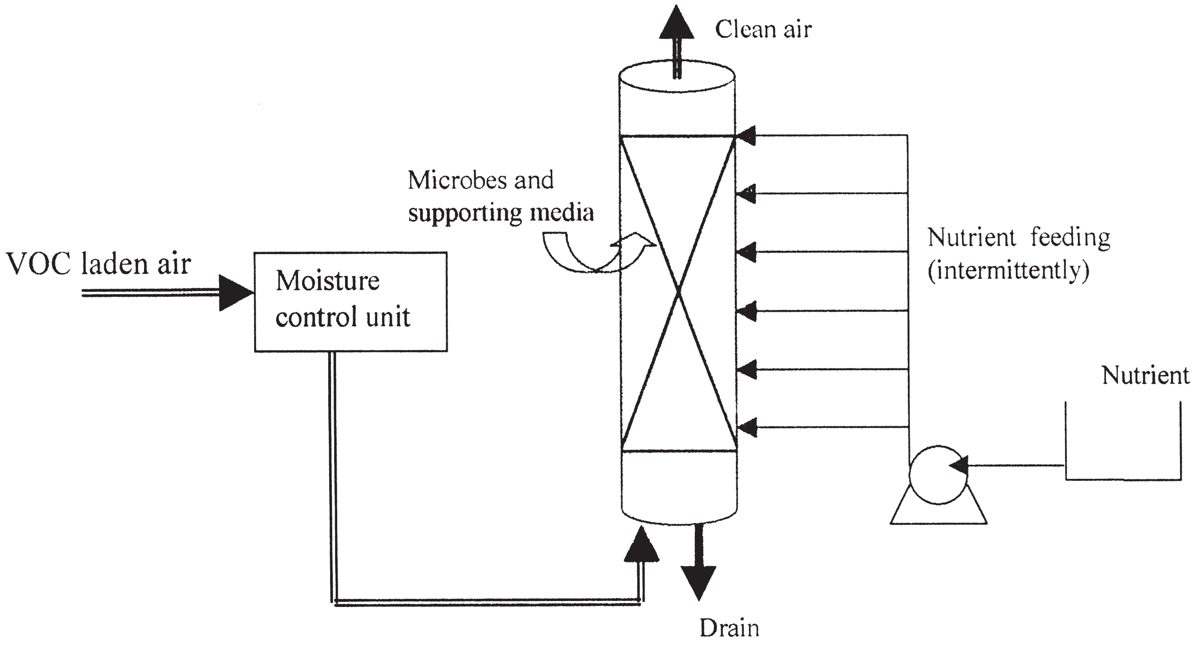

Fig. 5. A simple schematic sketch of a bio-filtration system.

structures is evident in the data (Webster et al., 1995). For both the bench and pilot-scale reactors, TGNMO (Total Gaseous Non-Methane Organics) data suggest that more than 65% removal is possible regardless of reactor pH conditions. Removal efficiencies for aromatics ranged from 53 to 98%, aldehydes and ketones from 43 to 96% and chlorinated compounds from 0 to 98%. Complete oxidation of hydrogen sulfide occurred at both the bench and pilot-scale levels (Liu et al., 1994).

A recent laboratory scale bio-filtration study was conducted by Kiared et al. (1996) to remove vapours of ethanol and toluene present in air. Peat was chosen to serve as filter material. Under typical operating conditions, the following conclusions have been drawn:

- The commercial peat offered a favourable life environment for micro-flora, at moist conditions.
- The pH of the medium, measured regularly, was stable around the neutral value (pH=7), hence, no acid intermediates were produced and consequently no buffering agent was needed.
- The pressure drop was also minimal, i.e. less than 6 cm H_2O per meter of bio-filter, for most of the experimental periods.
- The RTD (Residence Time Distribution) measurement showed that the gaseous phase was in plug flow affected by axial dispersion.

Good performance was obtained in terms of removal efficiency and elimination capacity. The micro-organism selected and used here maintained a good level of activity even under local dryness conditions (as has generally been the case in bio-filtration).

Overall, bio-filtration of POTW waste air appears to be effective, while being resistant to changing environmental conditions. This increases confidence in a technology which must be used under conditions which are not always optimal.

6. Recovery of VOCs

Several techniques for recovery of VOCs such as condensation, absorption, adsorption and membrane separation are discussed here in detail.

6.1. Condensation of VOCs

The driving force for condensation is over-saturation, which is achieved by chilling or pressurisation (or both) of the waste gas stream. Condensation is most efficient for VOCs with boiling points above 100°F at relatively high concentrations above 5,000 ppm. Low-boiling VOCs can require extensive cooling or pressurisation, which sharply increases operating costs. Exceeding the 25% LEL threshold is more common with condensation systems. In fact, some systems begin operation above UEL (Upper Explosive Limit). This is dangerous, because the concentration will likely fall through the explosive range during the condensation process. Therefore, inert gas blanketing of the vessels or unmanned process enclosures is advised to avoid the explosion hazard associated with high VOC concentration. However, this causes additional operating costs. Polymerisation materials should also be avoided in the condensation system due to the potential for fouling the heat-exchanger surface. Best suited to mono solvent systems, condensation produces a liquid product that must be treated to remove condensed water and possibly to separate various chemical species. Recovered VOCs can be reused within the process, used as wash solvents during equipment cleanup, burned as an alternative boiler fuel, shipped off-site for disposal or resold for reuse by others. Recovered water should be sent to a wastewater treatment plant prior to discharge, if exposed to miscible VOCs.

6.2. Absorption of VOCs

Absorption is used to remove VOCs from gas streams by contacting the contaminated air with a liquid solvent. Any soluble VOCs will transfer to the liquid phase. In effect, the air stream is scrubbed. This takes place in an absorber tower designed to provide the liquid vapour contact area necessary to facilitate mass transfer. Using tower packing and trays as well as liquid atomisation can provide this contact. Packed bed and mist scrubbing absorption systems are detailed here.

An absorption system can be designed to handle a capacity of 2,000 to 100,000 cfm and VOCs concentration ranges from 500 to 5,000 ppm. An absorber can achieve VOC removal efficiencies of 95 to 98% (William & Lead, 1997). The design of an absorption system for VOC control is similar to the design of an absorber for process application, using vapour liquid equilibrium (VLE) data, liquid and vapour flux rates, liquid and vapour handling information, and material balances.

Packed bed scrubbing uses packing material to improve vapour–liquid contact. Packing can either be randomly dumped or stacked in the tower. Packing varies widely in size, cost, contact surface area, pressure and material of construction, and each packing design has its own advantages under different conditions. Packed bed scrubbers can be used well with a low solubility system due to the high liquid and vapour residence time ($>$10 s) associated with the entraining nature of packing. Packed bed scrubbers should, however, be used when liquid flow rates are low which causes inadequate wetting of the packing material. Also, the particulates on entering the air stream or absorbent create absorbate/reaction products which can foul or plug the packing.

Mist scrubbers use spray nozzles to atomise the liquid stream into tiny droplets. These droplets provide the surface area for liquid–vapour contact. Mist scrubbers require a very low-pressure drop and must not be fouled by particulate in the incoming gas stream (Ruhl, 1993; Ruddy & Carroll, 1993). The residence times of liquid and vapour are low (1–10 s). Therefore, mist scrubbing should only be applied to highly soluble systems. Absorption is not particularly suitable for cyclic operation due to start-up time constraints. It is, however, good for a high humidity air stream (>50% RH).

6.3. Membrane based recovery process

Membrane based separation has been reported over a long period. This technique initially was used back in 1960 for desalination purposes. Since then a number of applications have been reported. According to various requirements, this technique has been classified in many groups. Table 3 presents different classes of this technique and modes of transport and separation. Gas permeation and reverse osmosis are the techniques used in the application of solvent recovery (recovery of VOCs) from air. This technique is in the field of experimental research and has yet to be commercialised, though a few pilot plants have been developed and are continuously monitored for performance. A simplified process diagram of VOC recovery using the membrane technique is presented in Fig. 6. A brief analysis of this is presented below:

Baker, Yoshioka, Mohr & Khan (1987) conducted air and vapour permeation experiments for various polymeric films, most of the experimental work reported so far is concentrated on composite silicon rubber membranes. Pinnau, Wijmans, Blume, Kuroda & Peinemann (1988), Kimmerle, Bell, Gudernatch & Chmiel (1988) and Paul, Philipen, Gerner & Strathmann (1988) tested silicon rubber membrane coated on a porous polysulfone substrate. Behling (1986) and Behling, Ohlrogge, Peinemann & Kyburz (1988) have chosen poly (ether imide) as the supporting material because it is much more stable to organic vapours than polysulfone. Buys, Martens, Troos, Van Heuven & Tinnemans (1990) used polyhydantoine and polyimide as the porous support to the silicon rubber-coating layer in their study. A membrane system for the treatment of low-volume, high vapour concentration gas streams was tested, but information was disclosed concerning the membrane materials by Wijmans & Helm (1989). The resistance of silicon rubber to some organic vapours, for example gasoline, is however poor. An attempt was made, therefore, by Deng, Sourirajan & Matsuura (1996) to prepare membranes from a single polymeric material of high organic resistance. In their previous studies, asymmetric aromatic polyimide membranes were investigated for the purpose. It was shown that controlling the conditions of the membrane preparation properly could produce membranes of both high selectivity and reasonably high permeability.

Deng et al. (1996) have conducted a thorough experimental study on the recovery of organic solvent from air with the help of an aromatic poly membrane. The study promises encouraging results. The important outcomes of the study are as follows:

- Hydrocarbon mixtures can be effectively separated from air by an asymmetric aromatic poly (ether imide) membrane without a silicone rubber coating.
- Water permeability is higher than hydrocarbon permeability.
- The presence of water vapour in the feed does not affect the hydrocarbon permeability. In other words, water and hydrocarbon molecules permeate through the membrane independently.
- Gasoline vapour can be separated effectively by an asymmetric aromatic poly (ether imide) membrane.
- Aromatic poly membranes are very good commercial value for removing volatile organic compounds when the amount of air to be treated is relatively small.

Although the membrane-based recovery system promises good results at the experimental stage, its adaptability is dependent on many factors, a few of which are discussed below.

Table 3
Basic type of membrane processes involved in industrial applications

Process	Driving Force	Transport Mechanism
Gas permeation	Concentration gradient	Diffusion transport
Reverse osmosis	Pressure differential	Diffusive solvent transport
Dialysis	Concentration gradient	Diffusive solute transport
Electro-dialysis	Electrochemical potential	Selective ion transport
Gel permeation	Concentration gradient	Diffusive solute transport
Pre-evaporation	Concentration	Selective physicochemical transport of solvent/solute

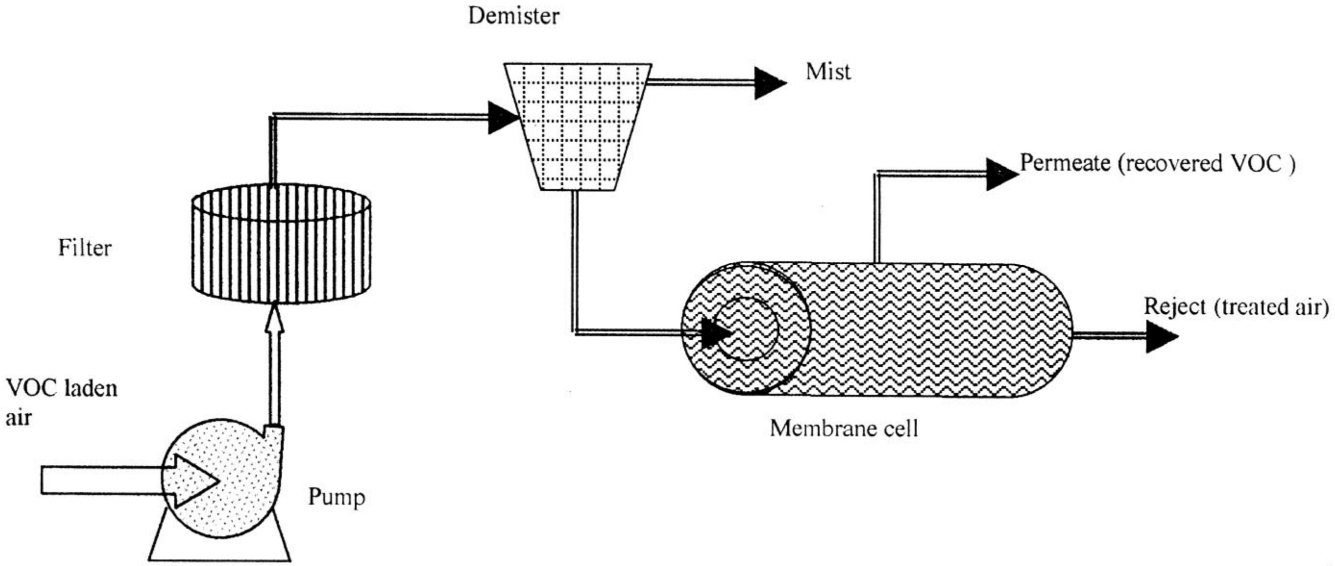

Fig. 6. The simplified process flow diagram for the membrane technique.

6.3.1. Adaptability factors

6.3.1.1. Adaptability to the range of organics Most of the membranes allow selective penetration of the organics, and therefore reduce the efficiency of total recovery of the solvents. As VOCs are comprised of various organics, the membrane has to be designed to allow a range of organics. To some extent progress been made, but it is not yet up to the level of commercial acceptance.

6.3.1.2. Cost of the membrane Most of the membranes are very costly and rarely available. That further limits its use.

6.3.1.3. Maintenance of the membrane Membranes are very susceptible to the operating conditions, fouling, and bacterial growth. These issues have to be resolved for wide acceptability of the technique in commercial use.

6.3.1.4. Process rate Membrane-based recovery is generally considered as a slow process. The increase in the process rate is directly proportional to the operating cost.

6.3.1.5. Rechargeable or reusable membranes Membranes generally have a short life (say, a few years). Their disposal causes further environmental problems. Reusable or rechargeable membranes can off-set this limitation, and to a certain extent reduce the financial burden of the technique.

6.3.1.6. Presence of liquid If liquids are present in the gas separation process, a liquid film can markedly increase the membrane resistance. Liquids can also damage the membrane by chemical action or by swelling or softening.

6.3.1.7. Flow patterns Various investigators have reported detailed parametric studies. They have compared the four flow patterns of complete mixing, cross flow, co-current, and counter-current flow. It is shown that the counter current flow pattern gives the best results. The other patterns of cross-flow, co-current, and complete mixing give lower separation in descending order. The required membrane areas for the same conditions and air feed versus stage cut were also studied. The areas for all four types of flow patterns differ by just 10% of each other. The counter-current flow pattern gives the lowest area required.

6.4. Adsorption of VOCs

The adsorption process is classified into two types, namely, physical adsorption and chemisorption based on the interaction between adsorbate and adsorbent. Physical adsorption has been found to be more significant in the case of separation processes. Physical adsorption is again classified into Thermal Swing Adsorption (TSA) and Pressure Swing Adsorption (PSA), based on the operation of the process. Both the processes have their advantages and disadvantages. Physical adsorption occurs when organic molecules are held on the surface and in the pores of the adsorbent by the weak Van der Waals force of attraction and is generally characterised by low heat of adsorption, and by the fact that the adsorption equilibrium is reversible and rapidly established. For details please refer to Ruthven (1984).

A very low VOC concentration in exhaust air is expensive to treat. For many low-concentration situations it is possible to use adsorption to increase the concentration to a level at which it is more feasible to clean up the air using a reasonable sized recovery plant. Recovery of some organics like 1,1,1-trichloro ethane (TCA) and styrene vapour are not well-suited for steam-regenerated temperature swing adsorption (TSA) or thermal incineration. Because of its thermal sensitivity and tendency to form degradation products, including HCl, TCA could not be recovered with traditional steam-regenerated TSA processes. Thermal incineration of TCA and other chlorinated solvents required tail gas treatment and subsequent wastewater disposal. The potential of styrene to polymerise at elevated temperatures likewise made TSA processes undesirable for styrene vapour recovery (Ruhl, 1993; Hussey & Gupta, 1996; Yun, Park & Moon, 1996; Yun, Choi & Kim, 1998Pezolt et al., 1997). In these situations PSA is the best alternative. The proper adsorbent choice depends upon the application, but activated carbon and styrene/divinylbenzene macroporous resins are the preferred adsorbents for VOCs recovery.

6.4.1. *Activated carbon based adsorption*

Carbon adsorption is a very common method of VOCs emission control. VOCs are removed from the inlet air by physical adsorption onto the surface of the carbon (Fig. 7). The system is sized according to the maximum flow and concentrations expected, and anything less usually improves efficiency. Carbon adsorption systems are flexible and inexpensive to operate. Installation costs are often lower than those of other systems (Ruhl, 1993; Stenzel, 1993). The adsorption capacity of activated carbon for a given VOC is often represented by an adsorption isotherm of the amount of VOC adsorbed (adsorbate) to the equilibrium pressure (concentration) at constant temperature.

VOC molecules are physically attracted and held to the surface of the carbon. Activated carbon is such a good adsorbent because of its large surface area, which is a result of its vast infrastructure of pores and micropores and micro-pores within micro-pores. In a commercial activated-carbon solvent-recovery plant, solvent laden air passes through a tank containing a bed of activated carbon. The solvent is adsorbed on the carbon surface and clean air is exhausted to atmosphere. When all of the available surfaces of the carbon pores are occupied it will not capture any additional solvent. Now, to recover the solvent for reuse, it must be released from the carbon surface. This is most commonly done by heating the carbon with steam. The hotter the carbon, the less solvent it can hold, so as the steam heats the carbon, solvent is released and flushed away by the steam (Fig. 7). The mixture of steam and solvent is condensed by cooling and then separated in the simplest case by gravity decanting. If the solvent is soluble in water, distillation is required instead of decanting. The carbon can then be reused as well. The batch process of adsorption and desorption as described above can be made continuous by the use of multiple carbon beds so that one is off-line for desorption while the other is on adsorption. Regeneration can be done on-site with hot air or hot nitrogen, depending upon process conditions and local utilities.

Moisture is one of the crucial parameters to dictate the efficiency and effectiveness of the adsorption process. In many cases the activated carbon that has adsorbed moisture will lose this moisture by displacement in its preference for organic vapours. Halogenated compounds are strongly affected by increased relative humidity, whereas aromatic compounds are only weakly affected. However, because water vapour competes with the VOCs in the emission stream for adsorption sites on the carbon surface, emission stream humidity levels exceeding 60% RH are not desirable. For these reasons, activated carbon becomes the right adsorbent for high capacity, non-selective adsorption of gases at ambient temperature, suitable for most VOCs with molecular weights between 40 and 150 and boiling points from 100°F to 500°F.

Many parameters need to be studied in detail before deciding about the adsorption process (particularly carbon adsorption), a few important ones are:

(i) description of the process emitting the VOCs, (ii) exhaust volume, (iii) temperature, pressure and relative humidity of the exhaust air, (iv) composition of the VOCs and their concentrations, (v) recovery efficiency required, (vi) quality of recovered solvent required, any contaminants present, such as dust, high boiling components, resins, and so on, (vii) possibility of future expansion of plant, (viii) whether cooling water is available, and if so, its temperature, (ix) whether steam is available, its pressure, and whether it is saturated, and (x) steam costs (which will determine the economy of the steam recovery operation).

6.4.2. *Zeolite based adsorption*

As elaborated in an earlier section, it has been recognised that activated carbon is the most suitable adsorbent for this application (Ruhl, 1993). However, Blocki (1993) pointed out that the applications of activated carbon present some disadvantages as they are flammable, difficult to regenerate for high boiling solvents, promote polymerisation or oxidation of some solvents to toxic or insoluble compounds, and require humidity control. Therefore, it is necessary for a new type of adsorbent to replace the activated carbon. As a result, hydrophobic zeolite is now considered an alternative adsorbent since it has good properties such as thermal stability and hydrophobicity (Blocki, 1993; Takeuchi, Hayato, Miyata & Harada, 1995; Tsai, Chang & Lee, 1996). Hydrophobic zeolite can be manufactured with precise

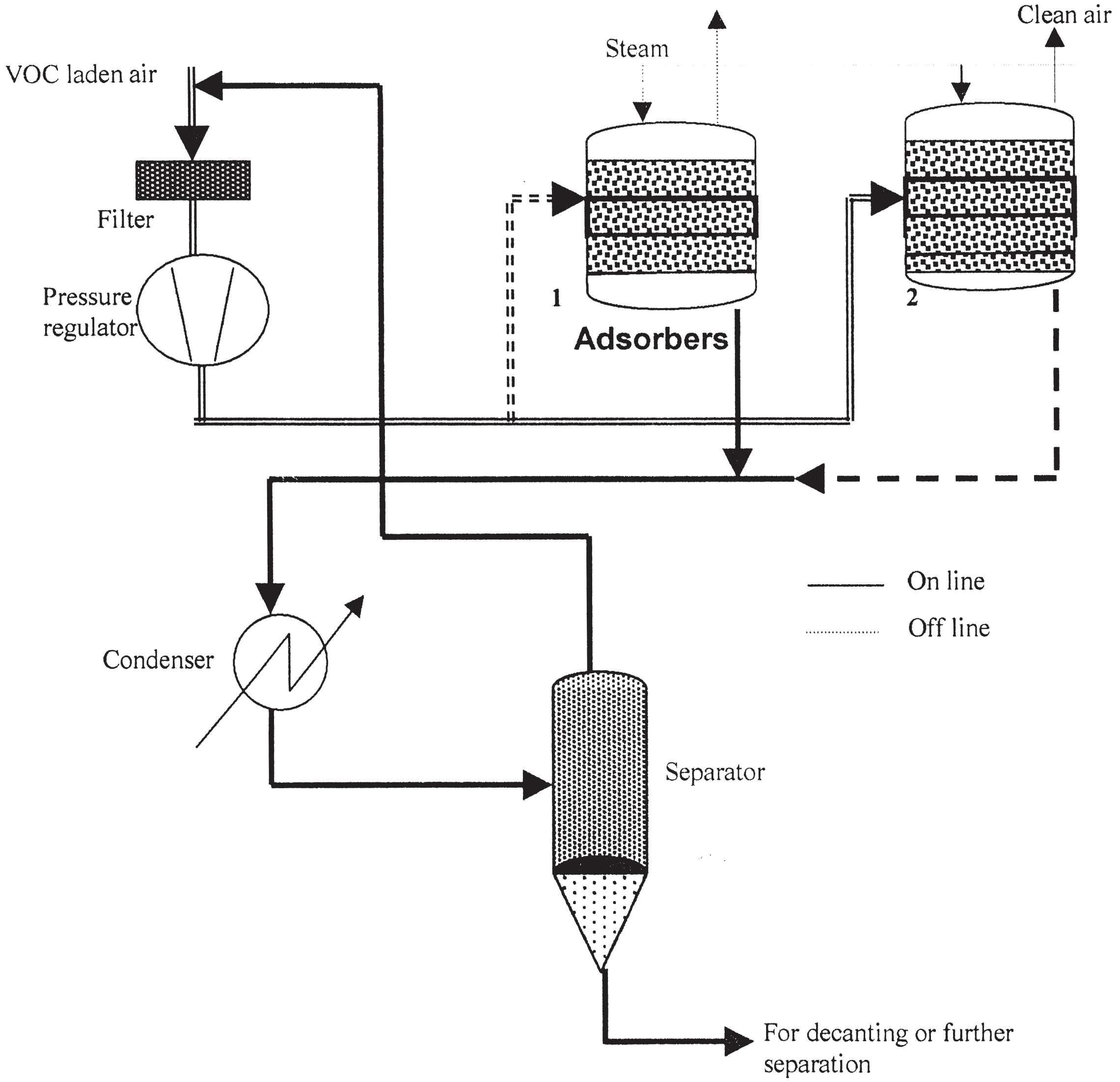

Fig. 7. A typical activated carbon VOC removal (solvent recovery) plant.

pore size, allowing selective adsorption of some compounds while excluding others.

Zeolites are inorganic materials that have a crystalline structure and fixed pore sizes. The homogeneous pore size prevents molecules larger than a certain size from entering the lattice, so zeolites are sometimes called molecular sieves, which allow them to adsorb selectively. The non-flammable, thermal-stable, and hydrophobic characteristics of zeolites can also play an important role in adsorption. The thermal stability and hydrophobicity of zeolites increase with the Si/Al ratio in the zeolite framework. Synthetic hydrophobic zeolite, a pure crystalline silica molecular sieve, is non-flammable and capable of withstanding temperatures as high as 850°C (Deng & Lin, 1995). Furthermore, hydrophobic zeolite has a low affinity for water, which is a useful physical property. Hussey & Gupta (1996) reported that up to 90% relative humidity could be handled with little adverse effect on the capacity of hydrophobic zeolite. Also, Takeuchi et al. (1995) reported that the presence of water was found to reduce the amount of adsorption of the solvent–hydrophobic zeolite system, but water vapour showed no effect on the adsorption kinetics (thus overcoming the major limitation encountered in carbon adsorption). Hydrophobic zeolites are also non-flammable, so it can be used for some compounds that might catch fire with activated carbon (e.g. cyclo-hexane). The cost of hydrophobic zeolite is still very high, so its use is economically limited to applications for which activated carbon is not well suited.

6.4.3. *Important parameters that dictate the performance of adsorption processes*

6.4.3.1. Retentive ability The ability of adsorbate to retain the adsorbed VOCs is an important characteristic that lends itself to industrial and commercial applications for this process. Retentivity, as determined in laboratory studies, represents the amount of adsorbate that, initially saturated with the VOCs, can retain them when pure air is passed through the bed. The application of adsorbtion in air pollution control is a dynamic process. As the contaminated stream is passed through the adsorbate bed and adsorption occurs, the saturation zone with the bed moves forward until the breakthrough point is reached and the VOCs exit concentration begins to rise rapidly.

6.4.3.2. Pressure The pressure needs to be maintained at the recovery plant inlet (both adsorption and desorption processes) and whether or not the recovery plant needs to provide suction to aid in exhausting must be known. Specifically, PSA needs to maintain precise pressure in the column, and this requires sophisticated control accessories. This adds to the total capital cost of the plant.

6.4.3.3. Concentration It is desirable to operate solvent recovery plants at higher concentrations. This minimises the horsepower (by moving less air) and steam consumption, decreasing the required frequency of draining. In general, VOC control systems that are designed always to operate below 25% of the LEL do not require continuous monitoring or control. If continuous monitoring of the exhaust concentration is provided, continuous operation at up to 40% LEL is allowable, with a provision for automatic shut down for concentrations exceeding 40% of LEL.

6.4.3.4. Particulate concentration The presence of dust or other particulates could clog the adsorbent. So it is prudent to install a filter upstream of the adsorbent. An estimate of the particulate loading should be made to determine how frequently the filter medium would have to be cleaned or replaced. The particulate loading and type are the major factors in making the selection of the filter medium.

6.4.3.5. Type of adsorbent In the case of activated carbon as adsorbent, manufactured from coal, wood or coconut shells, it can be given either pellet or granular shapes subject to their specific use. The most important specification is the adsorption isotherm. So for a new application, pilot testing (repeated) is recommended for verifying suitability and predicting commercial performance of each adsorbate–adsorbent system.

6.4.3.6. Desorption methods The most commonly used method for removing adsorbed solvent from the adsorbent is to heat the adsorbent directly with steam. The suitability of this method depends on the solubility of the solvent in water. Hot air or nitrogen can also be used for desorption of the solvent.

6.4.3.7. Fire suppression Since the activated carbon is inflammable, a fire suppression system is included in virtually all activated carbon solvent recovery systems. This system senses high temperature and sounds an alarm, then the adsorber valves are closed causing the fire to be suffocated due to lack of oxygen. The adsorber is then filled with water from the bottom (not by spray) to cool down the carbon. Sprays must be avoided to prevent rapid over pressurising of the adsorber by steam generation as the water spray hits the hot carbon.

6.4.3.8. Steam recovery Inclusion of a steam recovery unit reduces the steam demand by half. This is achieved by using a falling film evaporator in place of the condenser, thus using the latent heat of vaporisation of the adsorbate to generate steam from aqueous condensate. Even a more efficient method is to use a water storage tank to store hot condensed water just below boiling temperature, flashing it off under vacuum with a thermocompressor. This method has the advantage of recovering heat during the entire desorbing cycle and is thus more efficient than the previously described method. A combination of the two methods can achieve even higher efficiencies.

7. Analysis of different available techniques

The available techniques are analysed based on the following important parameters, and the results are summarised in Table 4 and Table 5. The results are briefed as under.

7.1. Source characteristics

Selection of a point-source emission control technique is made on the basis of source characteristics (e.g. VOC concentration, flow rates, etc.) and the desired control efficiency rather than on a particular source type. Table 4 and Table 5 present some specific source characteristics with corresponding control techniques.

7.2. Recycle potential

Recycling presents the opportunity to partially recover costs of control equipment. Before the project has progressed significantly, the viability of this option must be assessed. If recycling is desirable and achievable, further consideration of direct destruction devices such as oxidation systems may be unnecessary.

7.3. Variability of loading

The nature of the process being controlled determines the variability of the loading to which the control device will be exposed. High flow and/or concentration varia-

Table 4
Analysis of various VOC control techniques

Techniques	Annual operating cost $/cfm	Removal efficiency %	Secondary waste generated	Positive remarks	Negative remarks
Thermal oxidation	15–90 for recuperative, 20–150 for regenerative	95–99	Combustion products	Energy recovery is possible (maximum up to 85%)	Hallogenated and other compounds may require additional control equipment downstream
Catalytic oxidation	15–90	90–98	Combustion products	Energy recovery is possible (maximum up to 70%)	Efficiency is sensitive to operating conditions. Certain compounds can poison the catalyst. May require additional control equipment downstream
Bio-filtration	15–75	60–95	Biomass	Requires less initial investment, less non-harmful secondary waste, and non-hazardous	Slow, and selective microbes decomposes selective organics, thus requires a mixed culture of microbes (which is difficult). No recovery of material.
Condensation	20–120	70–85	Condensate	Product recovery can offset annual operating costs	Requires rigorous maintenance. Not recommended for the materials having boiling points above 33°C
Absorption	25–120	90–98	Wastewater	Product recovery can offset annual operating costs	Requires rigorous maintenance. May require pretreatment of the VOCs. Design could be difficult due to lack of equilibrium data
Adsorption					
Activated carbon	10–35	80–90	Spent carbon and collected organics	Recovery of compounds, which may offset annual operating costs	Susceptible to moisture, and some compounds (ketones, aldehydes, and esters) can clog the pores, thus decreasing the efficiency
Zeolite	15–40	90–96	Collected organic, spent zeolite after several cycles	Effective in more than 90% RH, Recovery of compounds offsets annual operating costs	High cost of zeolite, restricted availability.
Membrane separation	15–30	90–99	Exhausted membranes	No further treatment, recovery of solvent may offset the operating costs	Membranes are rare and costly

bility may exist with batch operations, and can produce additional wear and tear on equipment, reduce thermal energy, recovery efficiency, and possibly reduce the actual destruction and removal efficiency (DRE) of the device. The average loading determines the applicability of various processes. Recovery options such as direct condensation require high inlet concentrations to operate successfully. Very low average inlet concentrations require some pre-treatment (increasing the concentration) prior to actual treatment.

7.4. VOCs composition

The mixture or mixtures of VOCs to be treated in the control equipment has an effect on system applicability. The greater the variability of substances to be controlled, the greater the limitations placed upon the selection process. The DRE is dependent upon the “worst player” (that is, the most difficult compound to remove or destroy) in the exhaust stream. Recovery systems may require additional separation equipment to recycle materials.

7.5. Fire and explosion hazards

VOCs are fire-prone chemicals requiring extra precautions and safety measures. This is particularly so in chemical process industries involving bulk storage and operation at extreme conditions of temperature and pressure. Khan & Abbasi (1997, 1998) have discussed these in detail. A brief account of the same has also been presented elsewhere in this paper.

7.6. Presence of non-VOCs

The presence of non-VOCs contaminants in the vent stream can produce problems for VOC control equipment. Particulate matter in the exhaust stream can plug adsorption beds and heat recovery modules on thermal oxidisers. Halogenated materials can be oxidised to form

Table 5
Various operating characteristics of different techniques of VOC control

Techniques	VOC content (ppm)	Moisture content	Capacity range (cfm)	Temperature (°F)	Special remarks
Thermal oxidation	Greater than 20 but less than 25% of LEL	Normal 10–40% RM	1000–500,000	700	Requires elaborate safety measures
Catalytic oxidation	100–1000 but always less than 25% of LEL	Normal 10–40% RM	1000–10,000	300	An elaborate safety measure
Bio–filtration	<5000	>90%	<14,000	50–105	Precaution that VOC should not be toxic to microbes
Condensation	5000–10,000	20–80%	100–20,000	Ambient	–
Absorption	500–15,000	Normal	2000–100,000	Normal	Stripping should be easily possible
Adsorption					
Activated carbon	700–10,000 (but always less than 25% of LEL)	<50%	100–6000	<130	Must be desorbed from another adsorbent
Zeolite	1000–10,000 (but always less than 25% of LEL)	~94–96%	100–6000	ambient	Must be desorbed from another adsorbent
Membrane separation	Very low concentration to 25% of LEL	90–99%	200–1500	ambient	No further operation is required

their acidic counterparts, possibly requiring additional pollution control equipment and costly corrosion resistant materials of construction.

7.7. Maintenance

The level of the maintenance facility available is also an important consideration. If current maintenance is not very sophisticated (for example, the source is neither large nor complete), the choice of a control system requiring continual monitoring and adjustment is not recommended.

7.8. Location

A central plant location may require certain technology applications that include long ductwork runs to reach peripheral locations. Roof mounted systems may require extensive reinforcement of the roof support system as part of the design.

7.9. High discharge temperature

Relatively high vent discharge temperature precludes the use of condensation or adsorption options because of the cost of cooling the gas stream. However, thermal or catalytic oxidation would benefit from such a preheated gas stream.

7.10. Cost

For further screening devices the total cost, consisting of direct capital costs and annual operating costs, should be estimated. Capital costs includes equipment, installation and site preparation costs. Annual costs include utilities, operating and supervisory labour, maintenance labour, and materials.

7.11. Removal efficiencies

Expected emission reductions from the application of control techniques on the basis of the total VOC concentration is identified in Table 4. Combustion devices are capable of providing higher removal (i.e. destruction) efficiencies.

8. Economic analysis of VOC recovery techniques

8.1. Adsorption

The single most important factor affecting the capital costs of a carbon adsorption system is the volumetric throughput, ft^3/min. Typical capital costs for conventional steam-regenerated systems are \$15–20 per ft^3/min. When the VOC concentration in the inlet gas stream is less than about 300 ppm, one vendor reports the use of a “thin bed” to lower this capital cost to about \$10 per ft^3/min for systems greater than 10,000 ft^3/min. The only other capital costs available show that dehumidification to <50% RH may add about \$1 per ft^3/min to the \$15–20 per ft^3/min above. One qualitative observation is that the cost of VOC recovery increases very rapidly as the VOC mass flow rate decreases to below 100 lb of VOC/h. For a VOC of molecular weight 100 at a concentration of 1000 ppm, this mass flow rate corresponds to a total gas flow rate of 6,500 ft^3/min at 1 atm pressure and 75°F. Operating costs include steam, electricity, and condenser water for the conventional system considered here. Steam usage is reported to be 0.25 to 0.35 lb steam (at 15 psig)/lb carbon or about 6lb steam/lb VOC. Electricity usage is about 2.9 to 4.5 kW/1000 ft^3/min. Condenser water is used at about 12 gal/min per 100 lb steam. Replacement carbon, if needed, costs about $3–6/lb, with a typical carbon life being up to 5 years. This results in carbon replacement costs of roughly $7 per lb VOC per h per year.

8.2. Absorption

Absorption costs depend strongly on the VOC absorption equilibrium relationship (it is rarely available), choice of absorbent, and choice of stripping agent, representative economics for VOC recovery from small industrial sources are difficult to determine. Vatavuk & Neveril (1980) have described a procedure to estimate capital and operating costs for absorption processes for pollution control. Zenz (1979) has given a detailed design procedure for absorption towers, but did not discuss economics in detail. The reader should also consult Peters & Timmerhause (1991) for absorption equipment costs. As there is no commercial system and vapour–liquid equilibrium data available for VOC recovery, the authors were unable to quantify the economics of VOC recovery from absorption.

8.3. Condensation

Condensation is a simple heat transfer process, so there are two major capital cost elements: the heat exchanger (condenser) itself and the refrigeration unit. The heat exchanger costs alone are very modest by comparison to the system costs for carbon adsorption. Peters & Timmerhause (1991) have given heat exchanger costs as a function of surface area. For most of the VOC recovery applications, the heat exchanger can be made of carbon steel and designed for modest coolant pressures (coolant is usually on the tube side of a shell and tube condenser) and near atmospheric shell-side pressures. Costs for other materials of construction such as stainless, Monel, or Hastelloy are considerably higher than for carbon steel.

The refrigeration unit cost depends on the heat duty and, to a lesser though significant extent, on the temperature of the coolant at the inlet to the condenser. For typical VOC recovery applications, coolant inlet temperatures of −10 to +10°F are adequate to condense VOCs with boiling points down to about 60 to 80°F.

8.4. Membrane based recovery

This process involves moderate initial capital investment comprising membrane cell, filter, and mister, etc. The operating costs of this process are also comparatively lower than other processes. The capital cost of the process is totally dependent on the type and life of the membrane. Inorganic membranes are more resistive in nature, have relatively high selectivity but are relatively costly. Whereas organic membranes are comparatively cheaper but more susceptible to the operating conditions and shorter in life. Membrane technology has been proved as one of the most efficient and economic options for water treatment (it is also used for recovery of the trace organics from aqueous systems), but this has yet to be proved for air systems. Authors express their inability to give quantitative data for membrane separation technique applications in solvent recovery from waste air.

The comparisons of results of the two most frequently used VOC recovery techniques—carbon adsorption and condensation—are presented in Table 6. These results support the view that condensation is not economical at low VOC concentrations, whereas condensation is more capital-intensive than adsorption, and then at the highest VOC concentration examined (8,000 ppm), condensation is competitive with adsorption. Recovered VOC reuse as a solvent is considerably more economical in all cases (Spivey 1987, 1988). This study also concludes that only carbon adsorption is capable of practical removal efficiencies of 95% or greater (condensation is assumed to achieve typically 90%).

9. Discussion and conclusion

This article reviews various available techniques for VOCs control. The following conclusions have been drawn by a thorough study of the available options for VOCs control.

1. Oxidation is the most commonly used technique, though it destroys the valuable VOCs. Further, the oxidation process with heat recovery is a good economical option. However, this process requires specific operating conditions and design of incinerator depending upon the composition of the VOCs. It may also generate toxic combustion products, which need further processing. These limit its applicability. Catalytic combustion is a good alternative that overcomes some of its limitations. However, the Reverse Flow Reactor is the best alternative to oxidation in today's context of energy management.
2. Adsorption is the next most favoured technique. It has good removal (recovery) efficiency, though it requires higher capital investment and operating costs. Desorption of adsorbent and separation of VOCs from desorbed solution increase the complexity and cost of the process. Activated carbon, though a cheap adsorbent, has many limitations, e.g. the possibility of fire

Table 6
Comparative study of the cost of condensation and fixed-bed carbon adsorption (Spivey, 1988)

		Condensation		Fixed-bed carbon adsorption	
Stack gas emissions (ppm)	Cost item	Removal solvent reused (efficiency)	Recovered solvent used as fuel (efficiency)	Recovered solvent reused (efficiency)	Recovered solvent used as fuel (efficiency)
200	Total capital cost ($)	691,600 (85%)	6,91,600 (85%)	140,000 (94%)	140,000 (94%)
	Annual direct cost ($/yr)	147,600 (85%)	161,900 (85%)	9700 (94%)	24,700 (94%)
3000	Total capital cost ($)	706,800 (90%)	7,06,000 (90%)	140,000 (95%)	140,000 (95%)
	Annual direct cost ($/yr)	175,800 (90%)	3,5,200 (90%)	228,600 (95%)	21,800 (95%)
8000	Total capital cost ($)	613,500 (93%)	6,85,700 (93%)	259,600 (95%)	259,600 (95%)
	Annual direct cost ($/yr)	687,200 (93%)	1,60,000 (93%)	634,800 (95%)	91,800 (95%)

hazard, less selectivity, etc., whereas zeolite is more costly but has many advantages such as no fire hazards, uniform pore size distribution, etc. If VOCs recovery is important, the authors recommend adsorption as a good technique to be implemented. There are many solvent recovery units available commercially based on the adsorption principle.

3. Bio-filtration is a cheap and effective alternative for VOCs elimination. However, due to selective destruction, sluggishness, the applicability of this process is limited in commercial applications. This technique is in current research and the authors feel that in future it would be the most preferred alternative.
4. The absorption process involves high initial investment as well as difficulties in design, due to the lack of availability of vapour liquid equilibrium data. Moreover, stripping of VOCs from the absorbing solvent requires further separation, and thus costs. Along with many limitations (a few cited above), this technique has some advantages, e.g. the ability to handle a wide range of concentrations, simple process and equipment, and good efficiency.
5. Condensation is a safe alternative for VOCs recovery. It does not involve any second component and thus not much separation technology. It is simple. It suffers from many limitations such as it requires high concentration, extreme-operating conditions (temperature and pressure), high boiling VOCs, high operating costs, etc. These limitations have restricted its commercial applicability.

Finally, it is concluded that oxidation (catalytic) is a good option when VOCs recovery is not important (both in terms of efficiency and cost), whereas, if VOCs recovery is important, adsorption is the best alternative. Biofiltration is a bright option, still in research, and we hope that in the near future it will become the most potent technology for VOC control.

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