Reduction of Volatile Organic Compounds to Reduce Air Pollution due to VOCs

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Abstract
Volatile Organic Compounds (VOCs) are among the most common air pollutants emitted from chemical, petrochemical, andallied industries. VOCs are one of the main sources of photochemical reaction in the atmosphere leading to various environmentalhazards; on the other hand, these VOCs have good commercial value. Growing environmental awareness has put up stringentregulations to control the VOCs emissions. In such circumstances, it becomes mandatory for each VOCs emitting industry or facilityto opt for proper VOCs control measures. There are many techniques available to control VOCs emission (destruction based andrecovery based) with many advantages and limitations. Therefore, deciding on a particular technique becomes a difficult task. Thisarticle illustrates various available options for VOCs control. It further details the merits, demerits and applicability of each option.

Keywords: Volatile Organic Compounds (VOCs), removal methods, biofiltration

Introduction:
Volatile Organic Compounds (VOCs) include mostsolvent thinners, degreasers, cleaners, lubricants, andliquid fuels. A brief list of some common VOCs arepresented in Table 1, which includes methane, ethane,tetrachloroethane, methyl chloride, and various chlorohydrocarbons and perfluorocarbons. VOCs are thecommon air pollutants emitted by the chemical andpetrochemical industries. Emissions of VOCs originatefrom 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.[1]

Sr No.	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	Mon methyl ether
14	Naphthalene
15	Styrene
16	Toluene
17	Xylene

Table 1: Some of the common VOCs

From an environmental point of view, it is necessary to limit and control vapour emissions because they affectthe change of climate, the growth and decay of plants, and the health of human beings and all animals. Forexample, according to a report of the National Academyof Sciences, the release of chlorofluoromethanes and chlorine containing compounds into the atmosphereincreases the absorption and emission of infrared radiation. If the heat loss from the earth is retarded, theearth's temperature and climate are affected.[2] Studies on carcinogenicity of certain classes of hydrocarbons indicate that some cancers appear to be caused by exposureto aromatic hydrocarbons found in soot and tars. Hydrocarbons in combination with NOx, in the presence of sunlight, undergo photochemical oxidation, producing aphotochemical smog that is environmentally hazardous.

VOCs are not only outdoor pollutants as high concentrations have been recorded indoors as well. Indoor sources include solvents used in the production and maintenance of building materials, furnishings or equipment e.g., paint, carpets, plastics and photocopying machines. [3] The National Health and Medical Research Council (NHMRC) interim national indoor air quality recommends a maximum hourly average total VOC level of 500 µg m3, where each compound should not contribute more than 50% of the total (NHMRC, 2002). In a study investigating VOC emissions from office furniture, a range of major VOCs emitted over time was found to be in excess of the NHMRC recommendation. Formaldehyde was found to be emitted in highconcentrations from furnishings using reconstituted wood-based panels e.g., particleboards, medium-density fibreboard.

Indoor levels of VOC can be regulated by selecting low-emission materials for furnishing, cleaning and construction. This approach is impractical as many of the materials emitting VOCs are considered standard fixtures and attempting to replace them could prove costly. Furthermore, proper ventilation with outdoor air can help in managing air pollutants indoors by means of dilution. However with the increasing number of high-rise buildings developing in major cities, the problem of VOC pollution becomes both an indoors and outdoors issue that requires a permanent solution.

Common VOCs Removal Methods:

There are physical, chemical and biological treatments available to remove VOCs from air by either recovery or destruction. The contaminated liquid can be aerated either via packed tower aeration or mechanical surface aeration with VOC emissions captured and treated. Traditional primary removal solutions for VOC-contaminated liquids are liquid-phase activated carbon adsorption or air stripping.[1] For soil VOC contamination remediation, Soil Vapour Extraction (SVE) is used.In liquid-phase activated carbon adsorption, the treated liquid is put in physical contact with activated carbon to allow dissolved organic contamination to bind to it. The activated carbon can be either regenerated or removed after treatment. Reactors commonly used for this process are the fixed bed and the pulsed/moving bed. When dealing with halogenatedVOCs and pesticides, this carbon method has limited effectiveness. Economical and logistical issues would arise from disposing or decontaminating the spent carbon, hence carbon adsorption is applied more effectively for "polishing" post-treated liquid discharges with low VOC concentrations (EPA, 1990; 1993; 1995). Similarly VOCs in air emission can be treated with activated carbon by pumping it through activated carbon packed bed reactors. However, problems with spent carbon are the same as the liquid-phase carbon method.

Common permanent solutions to treat extracted VOC emissions would be through oxidation by thermal, internal combustion engine, catalytic or UV. Essentially VOCs are broken down into less harmful compounds such as carbon dioxide, water and hydrochloric gas.

There are many different techniques available to control VOCs emissions. These techniques are basicallyclassified into two different groups: (i) process and equipment modification and (ii) add-on-control techniques. In the first group, control of VOCs emissionsare achieved by modifying the process equipment, rawmaterial, and/or change of process, while in the otherclass an additional control method has to be adopted toregulate emissions. Though the former is the most effective and efficient method, its applicability is limited, asusually it is not possible to modify the process and/orthe equipment. The techniques in the second group arefurther classified into two sub-groups, namely thedestruction and the recovery of VOCs.

The first task in evaluating VOC control techniquesis to prepare a comprehensive emissions inventory. Theemissions inventory provides the basis for planning,determining the applicability of regulations permittingthe selection of control options for further consideration. The inventoryshould cover the entire facility source-by-source, considering:

- Pollutants emitted,
- The individual chemical species within each ventstream (to identify any non-VOC materials that mayhave determined effects on particular types of control equipment),
- Hourly, annual, average, and worst case emissionsrates,
- Existence and condition of certain pollution controlequipment, and
- Regulatory status.

Various strategies exist to control VOC release. The most desirable is to improve processes so that emissions are minimized at the outset. This is the idea behind "environmentally conscious manufacturing", "green engineering", and "benign by design" initiatives in various industries. These initiatives may be applied in two ways: improvements or redesign of processes. Improvements include alteration of unit operations, such as increasing reactor yields, raising separation levels, or simply cutting down on fugitive emissions. Redesign involves more fundamental changes in processes such as switching from an organic phase to an aqueous phase, converting from stoichiometric to catalytic chemistry, or going from batch to continuous operation. In all these cases the concept is to eliminate emissions at the point of creation and avoid "end of the pipe" treatment.

An effective technology for waste minimization which is extremely broad in scope is catalysis. Its use in a wide variety of environmental applications has been reviewed. For example, catalysis can be used to manufacture environmentally safer products like hydro fluorocarbons as replacements for the problematic chlorofluorocarbons (CFCs). It can be used as an alternative to hazardous and toxic chemicals like HCN, HF, HCl, phosgene in a variety of processes.[6] It can be used to improve yields, reduce side-products, and produce unique molecules in a variety of chemical and energy applications.

There are many situations where it is impractical or impossible to avoid production of some waste. This can be due to inherent limitations in selectivity of reactions, or unavoidable inefficiencies in separations. Both kinetic and thermodynamic factors may be involved in these cases. Airborne contaminants may also be generated by the nature of the process itself. For example, manufacturing, painting, cooking, dry-cleaning, and animal rendering operations represent situations in which activities are carried out in relatively open spaces with release of volatile species into the immediate environment. Such operations usually require ventilation to sweep away any noxious substance. Treatment of this air stream containing low concentrations of contaminants now becomes the objective. Again, in this situation catalysis can be very effective [4]. Catalysis is used for the elimination of pollutants from fixed sources like power plants, mobile sources like vehicles, and increasingly in everyday environments like office, home, and retailing outlets.

Condensation

Condensation is the liquefaction of condensable contaminants by the use of low temperatures. Specifically, the compounds to be removed from the gaseous phase are cooled to a temperature at which their partial pressure (fugacity) in the gas stream exceeds their dew point, so that they transform to liquids. Conventional condensers are shell and tube heat exchangers, used because they contain a relatively large amount of surface area for heat transfer, but are fairly compact. Critical parameters which establish the requirements and efficiency of the condenser include: the overall heat transfer coefficient (a function of the hot and cool stream composition, flow characteristics, and the construction material), the difference in temperature between the streams, and the operating pressure.

Condensation is most effective for compounds with high boiling points. However, if a significant portion of the organic material is composed of compounds which solidify at the condenser operating temperature, a standard shell and tube design condenser will not be effective, as these will quickly foul the heat transfer area, plugging the condenser. For those cases, a contact condenser, in which the hot and cool streams come directly into contact with each other would be more appropriate.

Adsorption

Adsorption refers to the trapping of pollutants on a high-surface area material. The process is typically used to remove contaminants in fairly low concentrations from a gas stream. The pollutants are adsorbed onto the surface or interstitial areas of a material such as activated carbon or a molecular sieve by physical or chemical attraction. Once the carbon or adsorbent material is saturated, that is, it can no longer adsorb any more pollutant, the material is regenerated, typically by introducing steam to drive off the pollutants.[15] The vent stream is condensed, decanted if necessary to separate the aqueous layer from the organic layer, and in some cases, further treated. For example, one of the layers may require distillation to further separate the constituents from the aqueous phase or from each other. Because of the subsequent separation required to reuse the solvents, carbon adsorption is not well suited to streams which have a large number of VOCs, nor does it work effectively on streams that have constituents which are difficult to separate. In those circumstances, as well as situations where the adsorbed species has a large molecular weight and is therefore difficult to desorbs, or in cases of low flows, the carbon can be used and then disposed of. This creates a similar dilemma to that of incineration, though, in that it treats a symptom (VOC emissions) but causes other problems such as waste disposal.

Absorption / Scrubbing

Absorption is a physical process consisting of the dissolution of a pollutant in a liquid. In absorbers (or scrubbers), the vapor stream is introduced into a chamber where it is intimately mixed with the liquid. The amount of pollutants remaining in the gas stream as it leaves the scrubber is governed by Henry's law, which establishes the amounts of a component in equilibrium in the gas and water streams for dilute mixtures [14]. By using counter current gas and water flows, the mass transfer between the vapor and liquid phases is maximized. If the vapor and liquid have adequate contact, the gaseous components that are soluble in the liquid are absorbed, where they may react or be removed by discharging the liquid. Some additional removal is accomplished by the evaporative cooling that occurs in the scrubber; some components condense out and are removed as the liquid is removed. Absorption, however, is not effective on constituents which are not soluble in the liquid medium. Therefore, it, too, is not well suited to vapor streams which have a large variety of constituents.

There is a variation of absorption known as wet scrubbing where the gas-phase component undergoes a chemical reaction with a component in the liquid phase. The reactions can be of an acid-base nature, or an oxidation type. The reaction of the liquid phase compound results in a lower concentration of the liquid phase compound than would otherwise exist at equilibrium. Thus, the driving force for removal of the gas-phase component is higher than in simple adsorption. However, a drawback is that the scrubbing agent is consumed in the process, and hence the method is more costly than adsorption where the liquid phase can be reused. Also, in some cases, the process generates a by-product which must be separated and disposed.

Biological Treatment

Biological treatment consists of using microorganisms to biologically degrade contaminants. Biological purification is a relatively new technology in the field of air pollution control, although the same concept has been used for years to treat wastewater streams. Microorganisms are grown on a substrate (bio filtration) or are suspended in a liquid scrubber media (bio-scrubbers). The scrubber liquid or substrate may also serve as an adsorbent for the pollutants, so that the microbes have a constant food supply, even if the process is not operating.[19] In less variable processes, the microbes are contained in compost, peat, or a similar soil and the air stream is passed through the bed for treatment. Just as in water treatment operations, the microorganisms break down the large organic molecules into smaller, less harmful molecules, consuming a portion of the molecules for energy to sustain their microbial activity. Although this technology is still not well accepted in the US, there are several hundred installations operating worldwide. Like adsorption, bio-purification is a good alternative for streams which have relatively low concentrations of organic constituents and is most effective for systems containing alcohols, ethers, aldehydes, and ketones.

Biofiltration offers excellent VOC removal, even from dilute gas streams with relatively low maintenance and operating costs. However, care must be exercised to remove particulates, ensure adequate moisture is present, avoid gas channeling, and maintain a fairly constant temperature. As with wastewater treatment systems, the microbes are susceptible to significant changes in the nature or concentration of pollutants and can be killed by sudden changes. Therefore, highly variable processes, or batch systems in which products change daily or weekly are not well-suited to biofiltration. In addition, design of a biofiltration system generally requires a pilot unit to determine the treatability of the gas stream and the residence time required for effective removal.

Membrane Separation

Membrane technology involves the use of semi permeable membranes to separate VOCs from a process stream [23]. The technology has been used in water purification, and has been adapted for use with gaseous media. Basically, the separation is based on preferential diffusion of VOCs across thin polymer layers wrapped around a perforated central tube. The driving force is a pressure differential between the inner and outer portions of the tube. The method is effective for recovering VOCs such as chlorinated hydrocarbons, chlorofluorocarbons, and hydro fluorocarbons that have been traditionally difficult to separate because of their high volatility.

Conclusion:

The following conclusions have been drawn by a thorough study of the available options for VOCs control.

- 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.

- 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.[22] 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.
- Adsorption is the next most favored 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 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.
- 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.
- The absorption process involves high initial investment as well as difficulties in design, due to the lack of availability of vapor 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.

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