# Chapter 10

# Control of Volatile Organic Compounds (VOCS)

# VOCs: ID

- Volatile organic compounds (VOCs) are liquids or solids that contain organic carbon
  - carbon bonded to carbon, hydrogen, nitrogen, or sulfur,
  - but not carbonate carbon as in CaCO3
  - nor carbide carbon as in CaC2.
- VOCs are probably the *second-most widespread* and diverse class of emissions after particulates.
- VOCs are a large family of compounds:
  - Some (e.g., benzene) are toxic and carcinogenic and are regulated individually as hazardous pollutants.

# Why Control VOCs?

- Direct human health impacts:
  - Some of the VOCs are known Hazardous Air Pollutants (HAPs), or Air Toxics
  - Toxic, carcinogenic, mutagenic effects, e.g. benzene is a known human carcinogen
  - Others related to motor vehicles, e.g. formaldehyde; acetaldehyde;1,3-butadiene; acrolein)
- VOCs are precursors to bad Ozone
  - smog formation in the atmosphere by the reaction of VOCs and NOx in the presence of sunlight
- Some VOCs are powerful infrared absorbers and thus contribute to the problem of global warning.

# VOCs: Sources

- Main sources are:
  - solvent usage (e.g., paint thinners and other similar solvents),
  - the transportation and storage of hydrocarbons,
  - motor vehicles (including autos, airplanes and railroad engines),
  - other sources: incomplete combustion in fireplaces and forest fires, paint spray cans, turpentine and wood smoke.
- Many VOCs are intermediates in production of plastics and other chemicals (e.g. vinyl chloride for PVC).
- VOCs emissions (mainly solvents and motor fuels) are petroleum based.

# VOCs: Sources

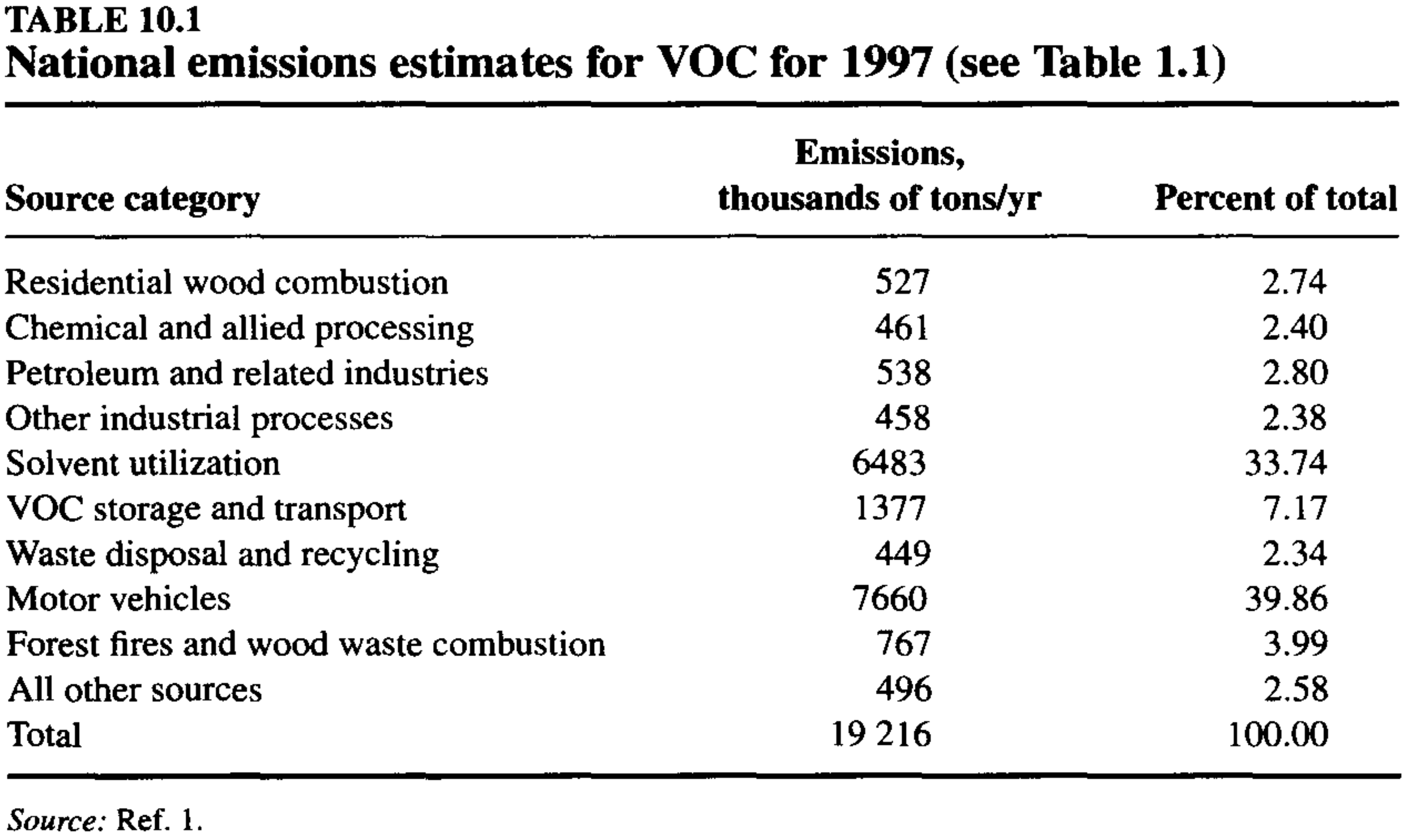


**TABLE 10.1**

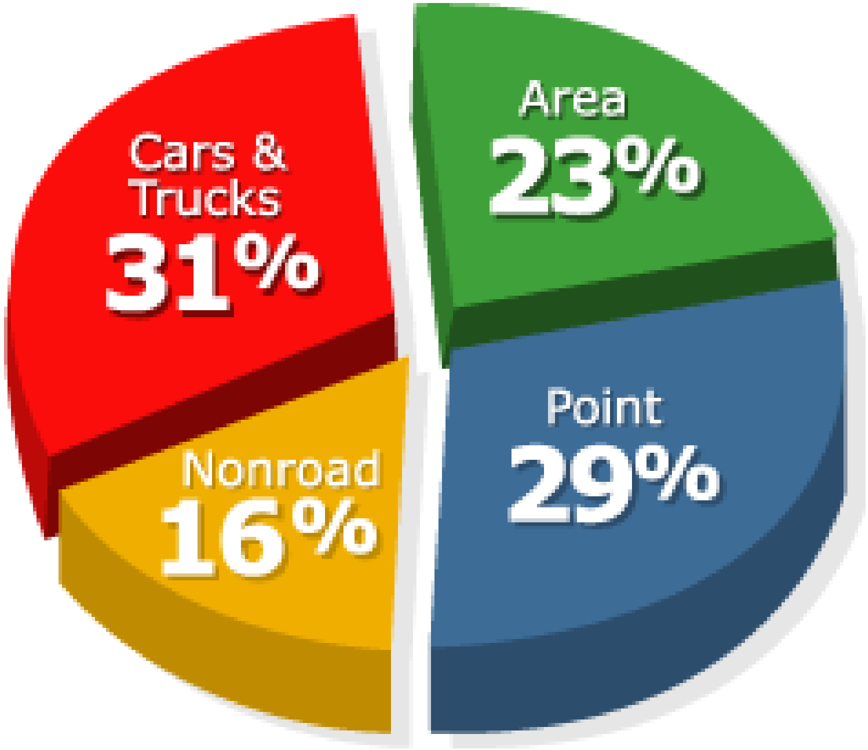
**National emissions estimates for VOC for 1997 (see Table 1.1)**

| Source category | Emissions, thousands of tons/yr | Percent of total |
|---|---|---|
| Residential wood combustion | 527 | 2.74 |
| Chemical and allied processing | 461 | 2.40 |
| Petroleum and related industries | 538 | 2.80 |
| Other industrial processes | 458 | 2.38 |
| Solvent utilization | 6483 | 33.74 |
| VOC storage and transport | 1377 | 7.17 |
| Waste disposal and recycling | 449 | 2.34 |
| Motor vehicles | 7660 | 39.86 |
| Forest fires and wood waste combustion | 767 | 3.99 |
| All other sources | 496 | 2.58 |
| Total | 19 216 | 100.00 |

*Source:* Ref. 1.

# Primary VOC Emitters

- VOCs are emitted from a variety of sources,
  - motor vehicles,
  - chemical plants, refineries, other industries,
  - consumer and commercial products,
  - architectural coatings,
  - natural (biogenic) sources.



*Typical allocation for man-made sources - Specifics will vary by location*

# VOCs Producing Industries

- Adhesive sealant use
- Surface cleaning
- Printing
- Film coating
- Timber preservation
- Crude oil production
- Oil refineries
- Chemical industry
- Alcoholic drinks manufacturer
- Paint manufacturer
- Vehicle manufacturer
- Furniture
- Agrochemical
- Industrial fuel combustion
- Bread baking
- Gas industry
- Rubber processing
- Pharmaceuticals
- OTHER

# VOCs: Vaporization

- Substances like ethane, propane, and n-butane (C2H6, C3H8, and C4H10) have vapor pressures above atmospheric pressure at room temperature.
- These must be kept in closed, pressurized containers or they will immediately boil away at room temperature.
- The vaporization behavior of these materials is summarized in Table 10.2.

## TABLE 10.2

## Behavior of volatile liquids as a function of their vapor pressure $p$ and $P_{atm}$

| Vapor pressure $p$ | Behavior in a container open to the atmosphere | Behavior in a closed, unvented container | Behavior in a closed, vented container |
|---|---|---|---|
| $p > P_{atm}$ | Boils vigorously, cools as it boils, until it cools enough to have $p = P_{atm}$ | Container internal pressure $= p$ | Boils vigorously expelling vapor through container vent |
| $p = P_{atm}$ | Boils, with the boiling rate dependent on the rate of heat input | Container internal pressure $= P_{atm}$ | Boils with the boiling rate dependent on the rate of heat input, expelling vapor through the container vent |
| $p < P_{atm}$ | Evaporates slowly into air | Container internal pressure $< P_{atm}$ unless some other gas is present. May lead to vacuum collapse of vessel | Vapor space in container is mostly air saturated with vapor |

# VOCs: basic properties

- Organic liquid or solid compounds up to 12 carbon atoms
- Boiling points up to 500 F (260 $^0$C)
- Compare with $p^*_{H20}$ = 0.34 psia at 68 F:

$$p^* \geq 0.01 \; psia \; @ \; 68 \; F$$

$$0.0007 \, atm \quad 20 \, C$$

- Pure compounds

$$\log p^* = A - \frac{B}{T+C} \qquad \text{Antoine equation}$$

$$\text{p}^* : \text{vapour (saturation) pressure}$$

(A,B,C: empirical constant)

- Mixtures of similar compounds

$$p_i = y_i P = x_i p_i^* \qquad \text{Raoult's Law}$$

$$P = p_1 + p_2 + p_3 + \ldots$$

# VOCs & H.Cs

- The terms VOC and hydrocarbon (HC) are not identical, but often are practically identical.
- *Strictly* speaking, a hydrocarbon contains *only hydrogen and carbon* atoms.
- But gasoline is *normally* called a "hydrocarbon fuel" because
  - it contains mostly hydrogen and carbon atoms, but
  - also some oxygen, nitrogen, and sulfur atoms.
- Acetone, the solvent and polish remover,
  - is a VOC but is not strictly speaking a hydrocarbon because it contains an oxygen atom.
  - In common usage it would often be grouped with the hydrocarbons.

# VOCs: water solubility

- Hydrocarbons are slightly soluble in water, so we can normally separate liquid HCs from liquid water by simple *phase separation and decantation*.
- Water contains enough dissolved hydrocarbon cannot be discharged to the sewer or natural body of water without *further treatment*.
- Polar VOCs (having N & O plus C & H atoms) including alcohols, ethers, aldehydes and ketones, carboxylic acids, esters, amines, nitriles are much more soluble in water.
- Difference in solubilities makes the *polar VOCs easier to remove* from a gas stream by scrubbing with water, but harder to remove from water once they dissolve in it.
  - Table 10.3 shows some typical values of these solubilities.
- Polar organics are generally about 100 times more soluble than the hydrocarbons (compounds of H and C only) of the same molecular weight
- Within each chemical family, the solubility in water decreases with increasing molecular weight.

## TABLE 10.3
## Solubilities of various categories of VOC in water at 25°C

| Chemical class | Individual compound | $M$, g/mol | Solubility in water, wt % |
|---|---|---|---|
| HC, linear | *n*-Pentane | 72 | 0.0038 |
| | *n*-Hexane | 86 | 0.00095 |
| HC, cyclic | Cyclohexane | 84 | 0.0055 |
| HC, aromatic | Benzene | 78 | 0.18 |
| | Toluene | 92 | 0.052 |
| | Ethyl benzene | 106 | 0.020 |
| Alcohols | Methyl, ethyl, *n*-propyl, isopropyl, | 32, 46, 60, 60, | Totally miscible |
| | ethylene glycol | 62 | Totally miscible |
| | *n*-butanol | 74 | 7.3 |
| | Cyclohexanol | 100 | 4.3 |
| Ketones | Acetone | 58 | Totally miscible |
| | Methyl ethyl ketone | 72 | 26 |
| | Methyl isobutyl ketone | 100 | 1.7 |
| Ethers | Diethyl ether | 74 | 6.9 |
| | Di-isopropyl ether | 102 | 1.2 |
| Esters | Methyl acetate | 74 | 24.5 |
| | Ethyl acetate | 88 | 7.7 |
| | *n*-Butyl acetate | 116 | 0.7 |

*Source:* Ref. 5.

# VOCs CONTROL

***10.3 Control by Prevention***

- *Substitution,*
- *Process modification,*
- *Leakage control*

***10.4 Control by Concentration & Recovery***

- *Condensation ,*
- *Adsorption, Absorption (Scrubbing)*

***10.5 Control by Oxidation***

- *Chemical Oxidation (Burning or Incineration)*
- *Biochemical Oxidation (Biofiltration)*

# VOC Control Technologies

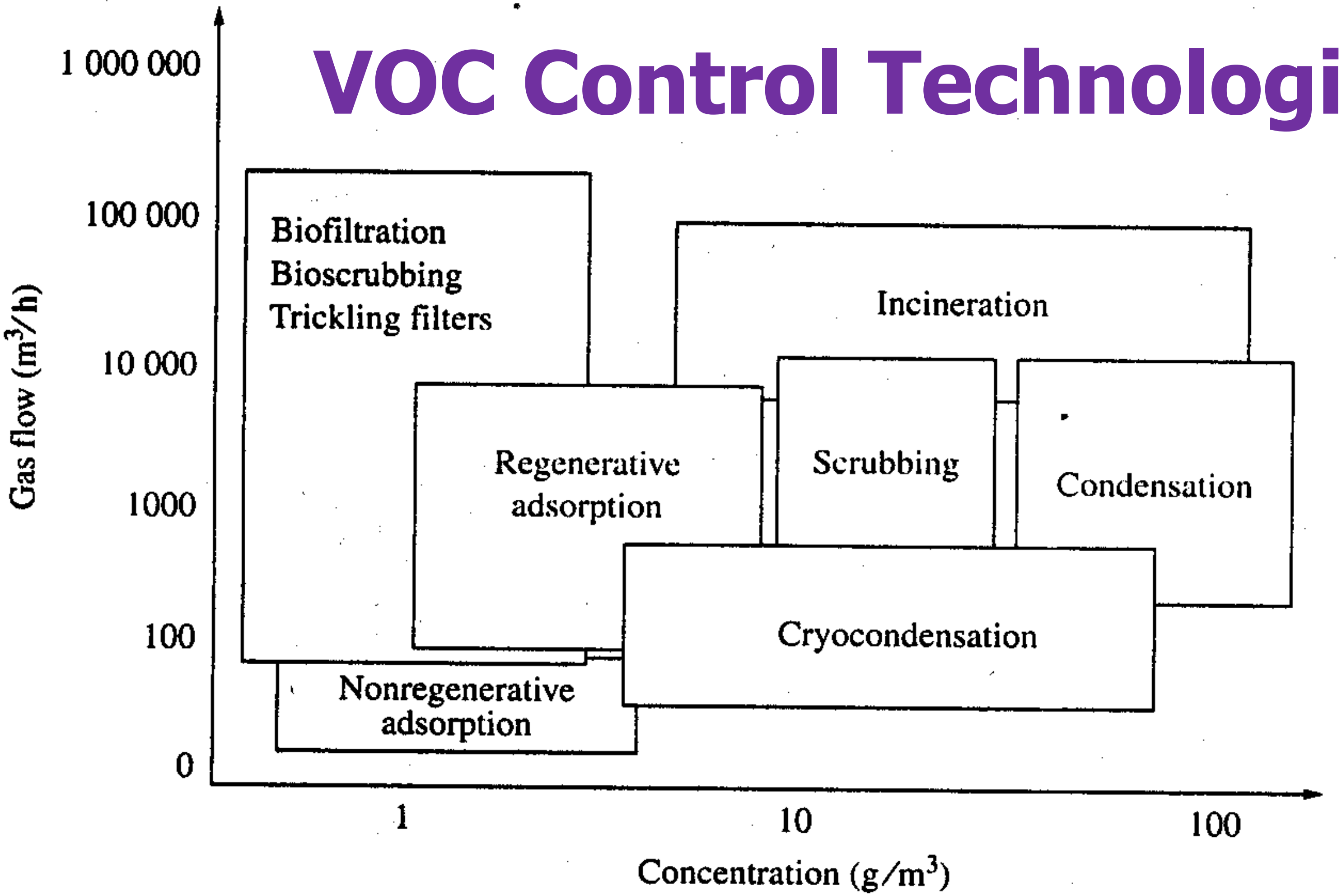


**FIGURE 10.19**

A guide to choosing VOC control technologies, based on flow rate and concentration only [29]. (With permission of KPMG Management Consultants, Ottawa, Ontario.) Cryocondensation is discussed in Problem 10.21. Nonregenerative adsorbers are placed in a landfill or incinerated, instead of being regenerated as shown in Fig. 10.10.

# 10.3 CONTROL BY PREVENTION:

## Substitution

- A less volatile solvent can be substituted for the more volatile one.
  - This normally *reduces but does not eliminate* the emission of VOCs.
- A less toxic solvent can be substituted for a more toxic one.

Examples:

- Gasoline can be replaced as a motor fuel by compressed natural gas or propane to reduce VOCs emissions.
- Petroleum industry is working to improve the burning properties, handling and use of gasoline as to make it a low-emission fuel.

# 10.3 CONTROL BY PREVENTION:

## Substitution

- Oil-based paints, coatings and inks harden by the evaporation of VOC solvents.
- Water-based paints are *concentrated oil- based* paints, emulsified in water.
- Switching from oil- to water-based paints, coatings, and inks greatly reduces but does not totally eliminate the emissions of VOCs.
- Water-based paints have not yet been developed to produce automobile body finishes as bright, smooth and durable as the oil-based paints and coatings now used.

# 10.3 CONTROL BY PREVENTION:
## Process Modification

Examples:

- Replacing gasoline-powered vehicles with electric-powered vehicles or *hybrid* systems are form of process modification to:
    - Reduce vehicle emissions of VOCs
    - Reduce vehicle emission of CO and Nox
    - Causes other emissions where the electricity is generated.
- Improved public transport and car pooling are modifications of the “transport process” that reduce emissions of VOCs (and of CO and NOx).

# 10.3 CONTROL BY PREVENTION:
## Leakage Control

### Working losses

- Tanks containing liquid VOCs can emit VOC vapors because of filling and emptying activities as well as changes in temperature and atmospheric pressure.

- These “working” emissions are three kinds:
  - filling or displacement losses,
  - breathing losses, and
  - emptying losses.

# Leakage Control

<u>1- Filling or displacement losses:</u>

- Figure 10.2 shows a simple tank of some kind being filled with liquid from a pipeline.
- As the liquid enters the tank and the liquid level rises, the vapor space above the tank must decrease in volume.
- Normally that vapor space (called headspace) is connected by a vent to the atmosphere so the vapor, which is mostly air, will be expelled.
- When liquid is withdrawn from the tank, air will flow in through the vent to fill the space made available by the fall in liquid level.
- If the tank were not vented, changing the liquid level would cause an overpressure during filling or a vacuum during emptying.

# Leakage Control

Figure 10 .2 de Nevers

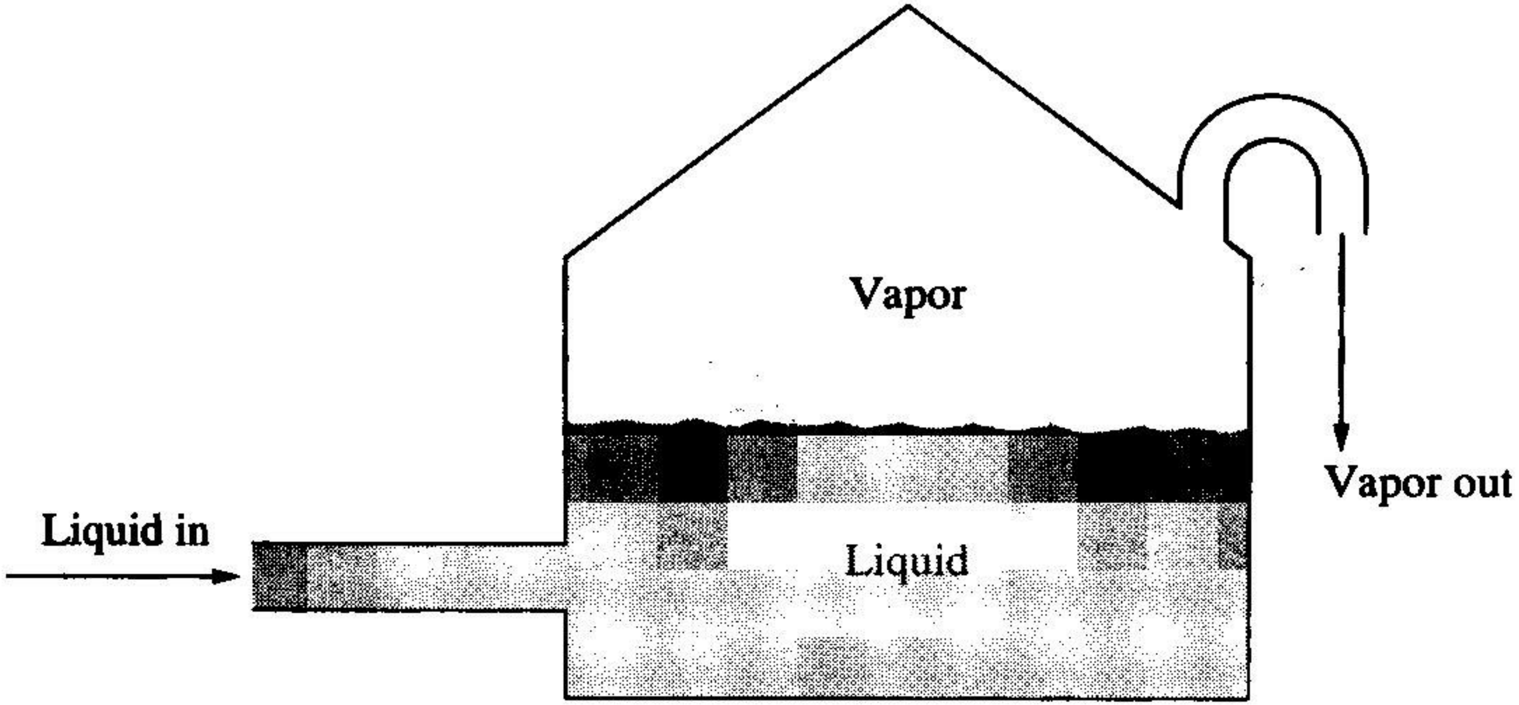


**FIGURE 10.2**
Displacement losses occur when a vented tank is filled with liquid, thus displacing vapor from the tank's headspace. The tank walls support the roofs of small cone-roof tanks; large ones have internal supports. All have some kind of vent on the roof.

# Leakage Control

2- Breathing (diurnal) loss:

- A tank must "breathe" in and out whenever its temperature changes, normally out every day and in every night.
- Assumption of *plug flow displacement* of the vapor is
  - plausible for a *stationary tank*, but
  - not for the fuel tank of a *moving vehicle*, where *sloshing* of the liquid will keep the vapor close to equilibrium at all times.
- Temperature increase causes:
  - increase in vapor pressure
  - expansion of the liquid, the vapor and the tank

# Leakage Control

- Breathing loss due to changes in atmospheric pressure is *normally much smaller* than that due to changes in temperature.

3- Emptying loss:

- arises from slow vaporization of the contents of the tank after partial emptying.

# 10.3 CONTROL BY PREVENTION:
## Leakage Control

For all three kinds of working losses, we can write

$$\text{VOC emission} = \begin{pmatrix}\text{volume of air-VOC mix}\\ \text{expelled from the tank}\end{pmatrix}\begin{pmatrix}\text{concentration of}\\ \text{VOC in that mix}\end{pmatrix} \qquad (10.4)$$

$$m_i = \Delta V c_i$$

where $m_i$ = mass emission of component $i$

$c_i$ = concentration (lb/ft$^3$, kg/m$^3$, or equivalent) in the displaced gas

Concentration $c_i$ can be expressed as

$$c_i = \frac{y_i M_i}{V_{\text{molar, gas}}} \qquad (10.5)$$

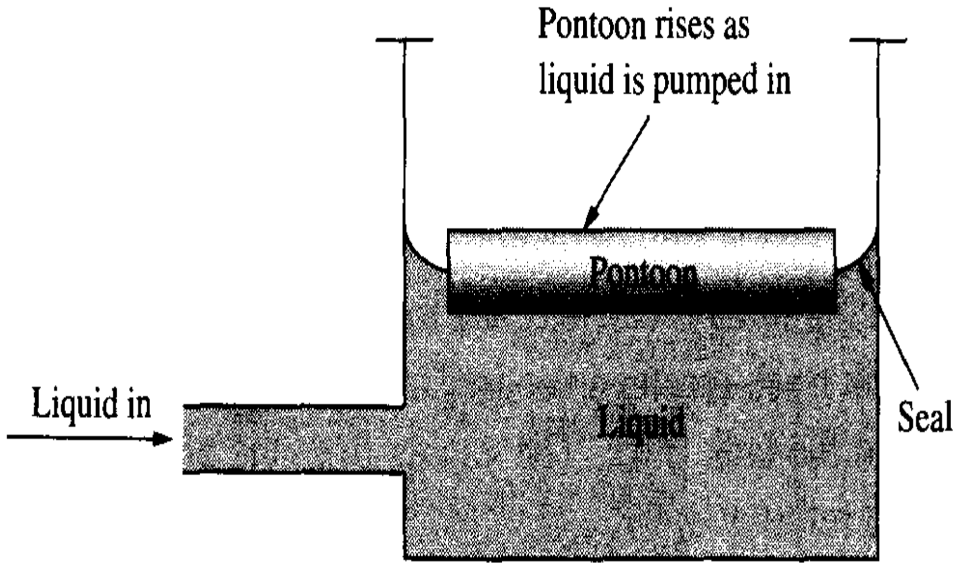
Replacing the vapor mol fraction by Raoult's law, Eq. (10.1), replacing the gas molar volume by the perfect gas law, and substituting in Eq. (10.4), we find

$$\frac{m_i}{\Delta V} = \frac{x_i p_i M_i}{P} \cdot \frac{P}{RT} = \frac{x_i p_i M_i}{RT} \qquad (10.6)$$

# GASOLINE DISTRIBUTION

- The greatest interest in these types of losses concerns **gasoline.**
- Gasoline is a complex mixture, typically containing perhaps 50 different hydrocarbons in concentrations of 0.01 percent or more, plus traces of many others.
  - The smallest molecules have 3 carbon atoms; the largest, 11 or 12.
  - A “typical” gasoline has an average formula of about $C_8H_{17}$ and thus an average molecular weight of about 113.
  - Its composition varies with season of the year and from refinery to refinery.

# Storage Tanks



For large-scale storage, the petroleum industry stores large amounts of such liquids in floating roof tanks, as shown in Fig. 10.4.

**FIGURE 10.4**

Floating roof tank, used to store large amounts of high vapor pressure fluids. The sealed pontoon floats on the fluid, so that there is no headspace. The pontoon moves up and down as fluid is inserted or withdrawn. This completely eliminates the displacement and breathing losses discussed above. However, the seals (normally spring-backed rubber sheets like windshield wiper blades) are not perfect, so that there are *seal losses* at them. This sketch does not show the provisions for removal of rainfall or snowmelt, or various other details.

# Gasoline transfer & storage

- The transfer of gasoline from tank trucks to underground storage tanks at service stations uses the scheme shown in Fig. 10.5.
- Service station tanks are placed underground both to save ground space and to reduce the fire hazard of a leak or spill from such a tank.
  - With time, these tanks corrode and leak, polluting groundwater.
- This has caused conflict between
  - the environmental engineers, who want the tanks aboveground, where leakage can be seen and corrected, and
  - the local fire fighting officers, who want the tanks underground so they cannot cause a fire.

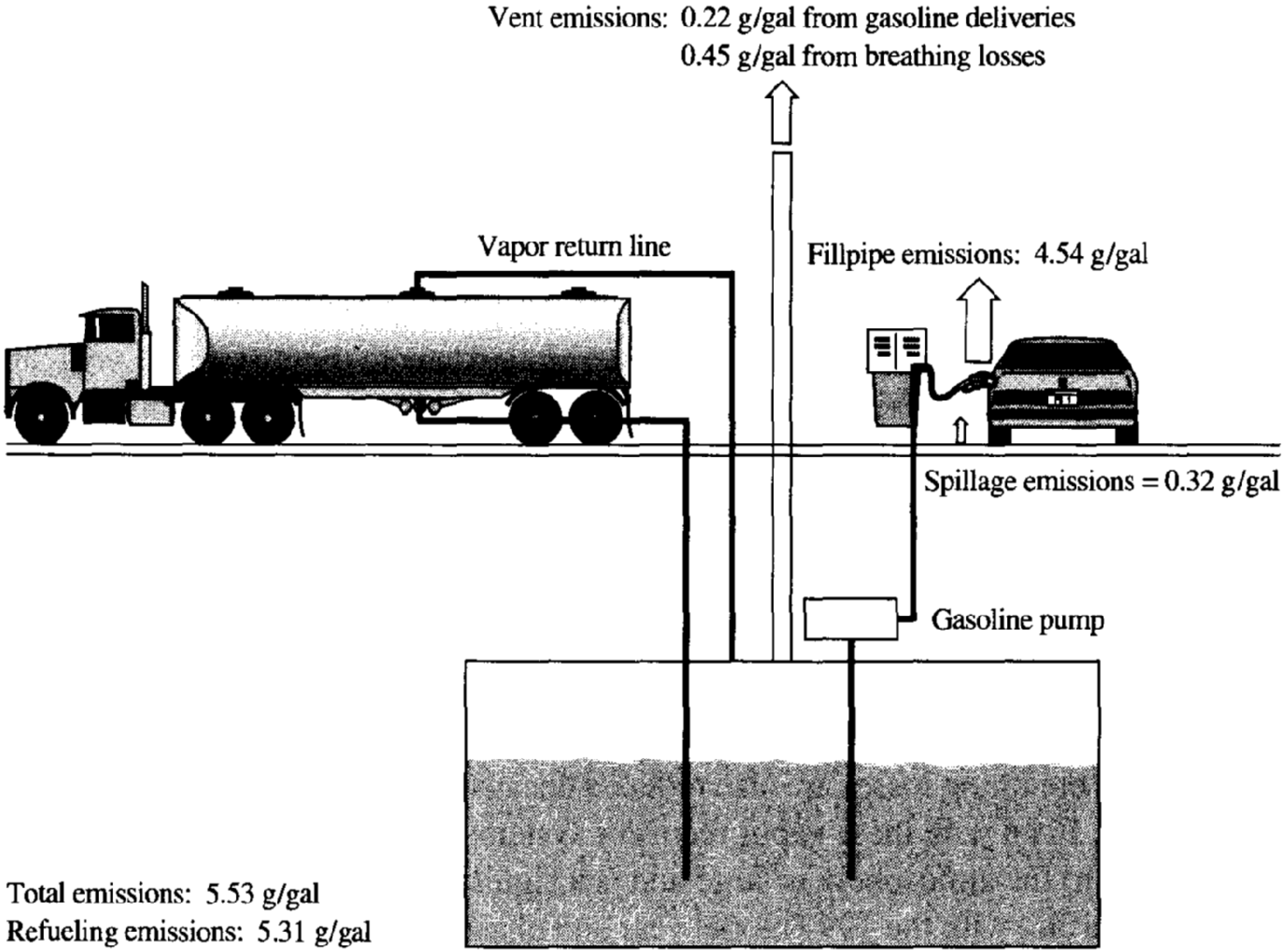


**FIGURE 10.5**
Loading a service station underground storage tank that has a vapor return system. This set of equipment is commonly called *Stage 1 control.* The emissions shown are a mixture of calculated and experimental values, based on work of the California Air Resources Board. (Courtesy of Sierra Research Inc.)

# 10.3.3 Leakage Control: Seal leaks

- Many small emissions of VOCs occur as leaks at seals.
- In recent years these have come under regulatory control because, as the larger sources are controlled, these become a more significant part of the remaining problem.
- Figure 10.7 shows three kinds of seals.

# Kinds of Seals

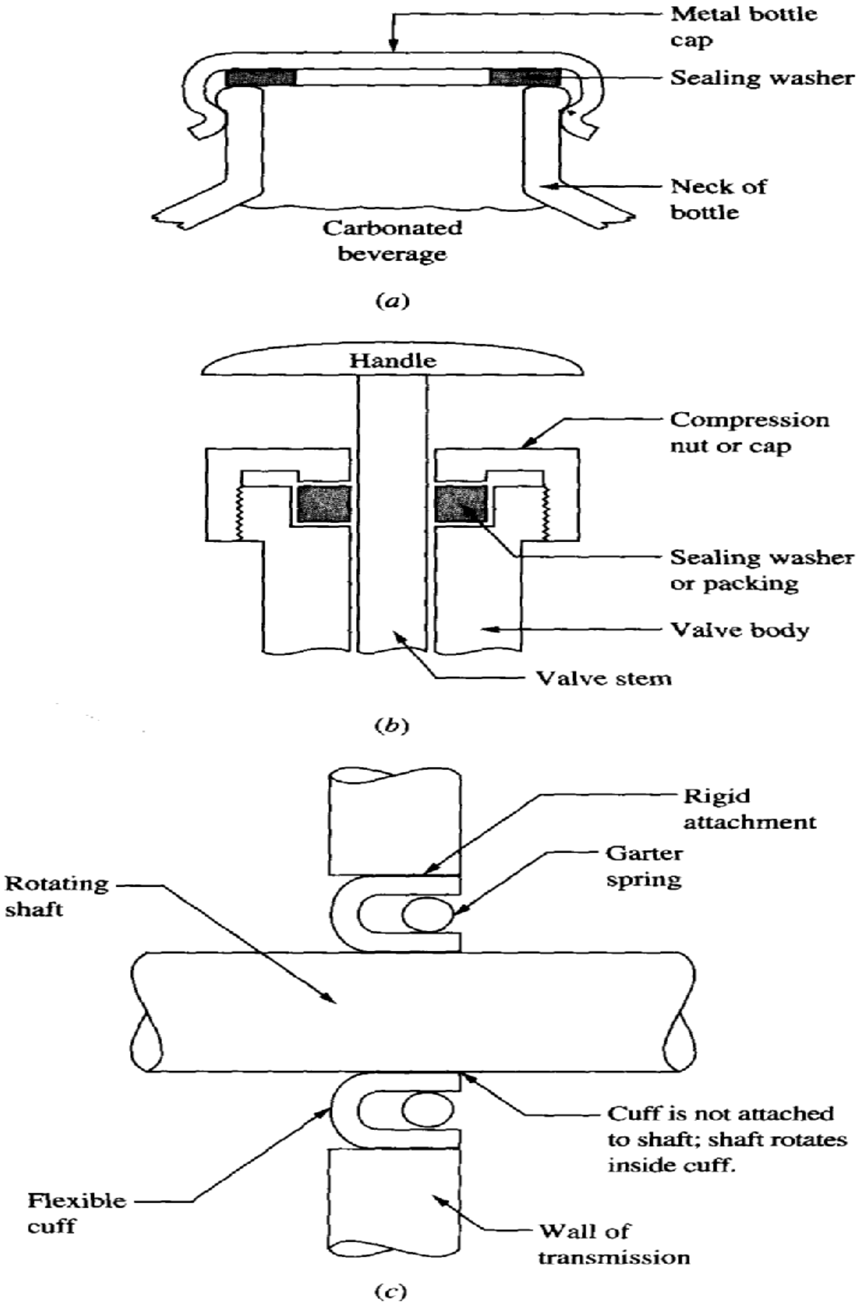


**FIGURE 10.7**
Three kinds of seals: (*a*) a static seal, as exists between a carbonated beverage bottle and its bottle cap; (*b*) a packed seal, as exists between the valve stem and valve body of simple faucets, and as also exists on many simple pumps; (*c*) a rotary seal of the type common on the drive shafts of automobiles and some pumps.

# VOC Control by adsorption

- Adsorption:
  - physical adsorption: reversible attachment of gas (or vapor) molecules to a solid surface
  - Chemisorption: attractive forces between gas molecule and surface are closer to chemical bonding than physical attraction.
- Adsorbents used are high surface area ( ca. 1000 $m^2/g$) micro-porous particles, e.g. Alumina ($Al_2O_3$), Silica ($Si_2O_3$), activated carbon.
- Adsorbent capacity w*: mass of adsorbate per mass of adsorbent

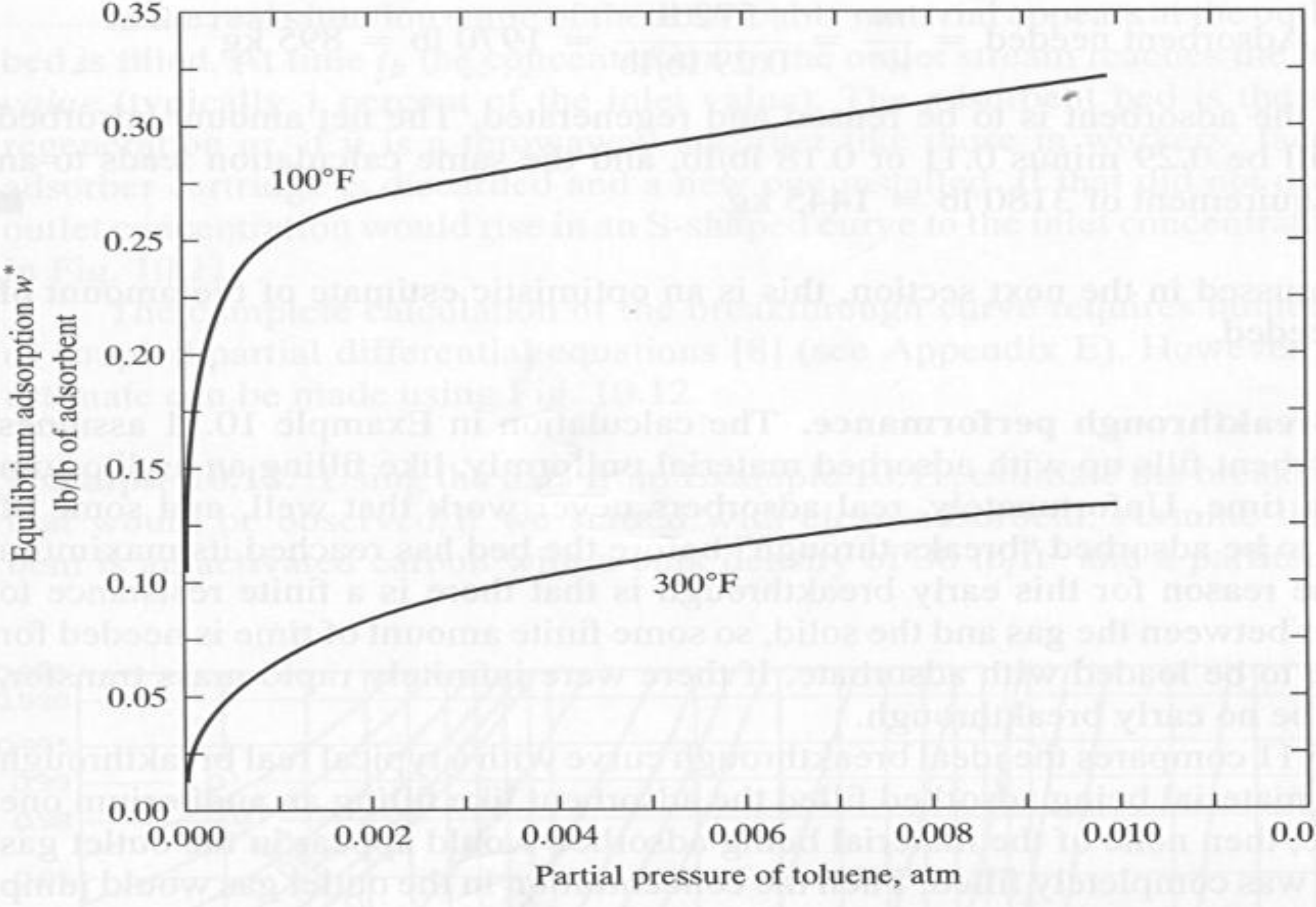


**FIGURE 10.10**
Calculated equilibrium curves (adsorption isotherms) for toluene on a typical activated carbon. See Example 10.10.

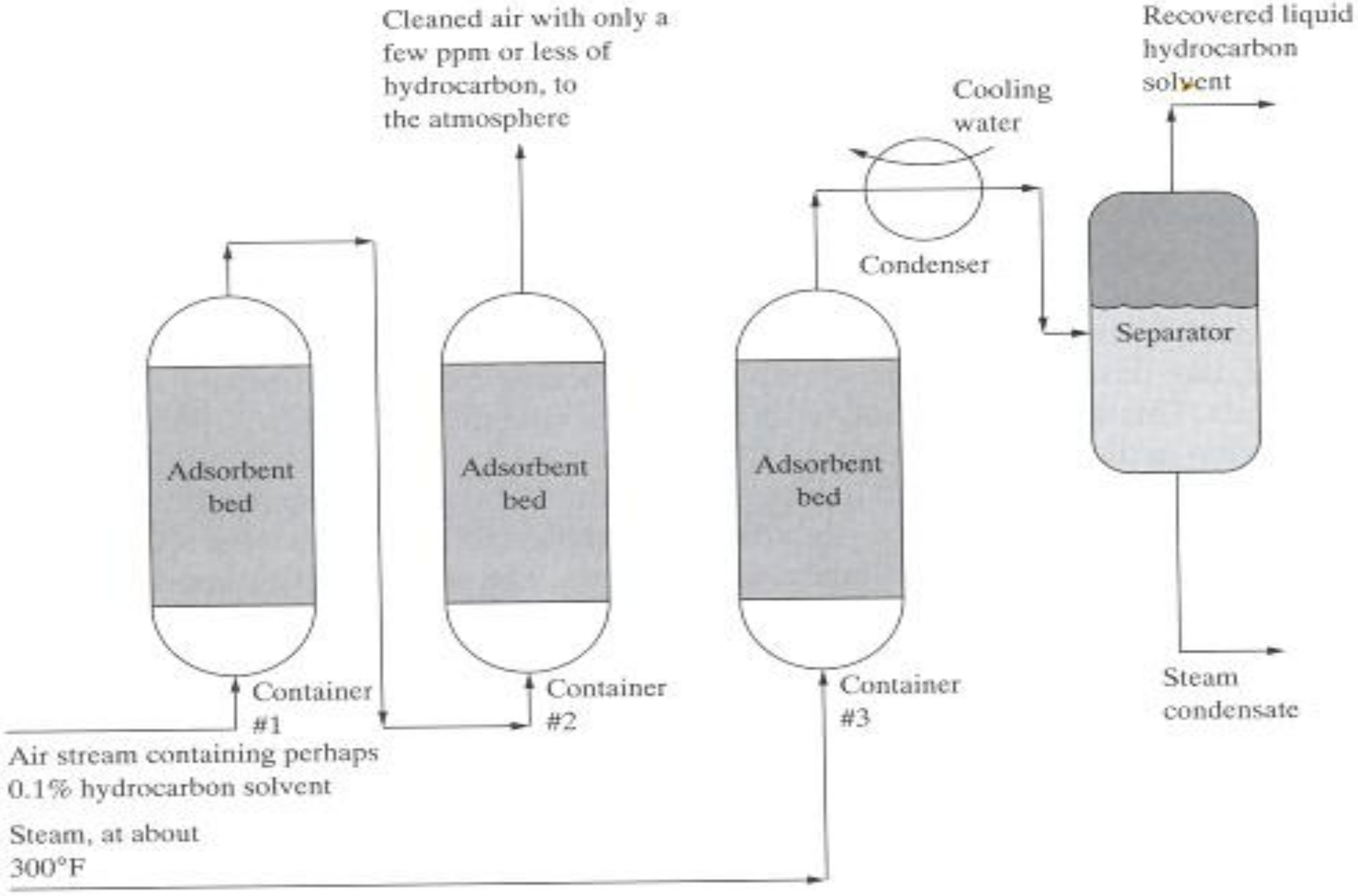


**FIGURE 10.8**
The typical arrangement for adsorption of a VOC from a gas stream, using three adsorbent beds; automatic switching valves; and steam desorption, condensation, and gravity separation.

# VOC control by Absorption (Scrubbing)

- VOC selectively absorbed by bringing gas and solvent in contact in a packed column.
- Solvent and VOC separated in another column operating at lower temperature or pressure.
- Operational principles similar to adsorption but physical basis is different.
- Design principles covered at length in Unit Operations
  - See Fig. 11.1 (deNevers)

# Figure 10.5 de Nevers

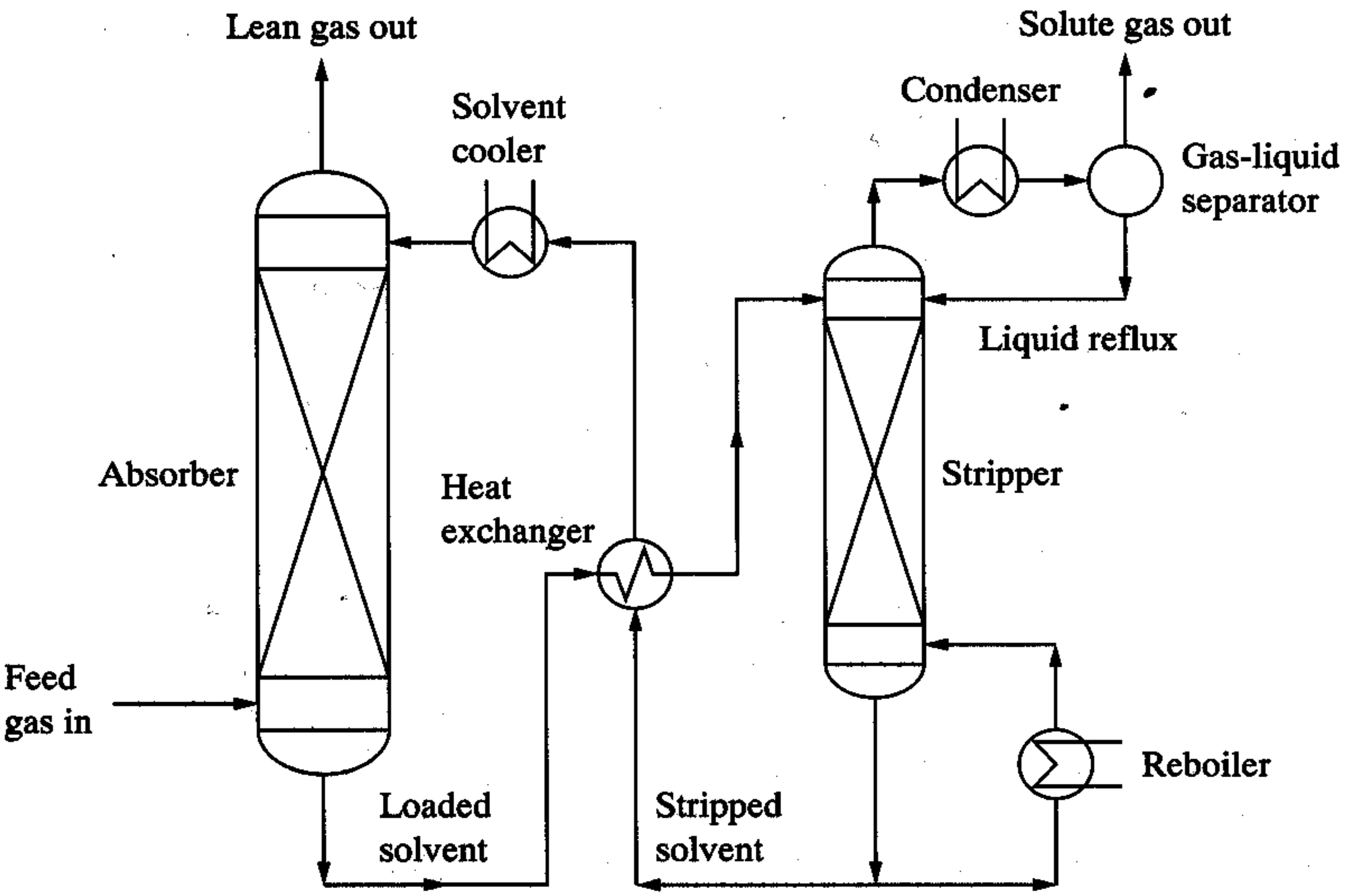


**FIGURE 11.1**
The flow diagram for the most common method for removing one component from a gas stream.

# VOC control by Incineration

- Combustion
  - is responsible for most of the air pollutants of concern.
  - Can be a solution if practiced properly (i.e. sufficiently high temperatures, long residence times, and good mixing)
- Incineration is the term used when the purpose of combustion is the destruction of pollutants rather then energy production.

# COMBUSTION AS A SOLUTION

- Examples of Reactions:

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2$$

$$C_6H_6 + \tfrac{15}{2}O_2 \rightarrow 6CO_2 + 3H_2O$$

$$H_2S + \tfrac{3}{2}O_2 \rightarrow H_2O + SO_2$$

$$VOC + O_2 = CO_2 + H_2O$$

(typically applied for low concentrations of pollutants

# KINETICS OF VOC INCINERATION

- Typically, $C_{O2} >> C_{VOC}$ and does not change
- Thus, for first order kinetics we have:

$$r = kC_{VOC}^{a} C_{O_2}^{b}$$

$$r = kC_{VOC} \quad and \quad \frac{dC}{dt} = -kC$$

- Effect of temperature (Arrhenius equation):

$$k = Ae^{-E_a / RT}$$

$$\ln k = \ln A - E_a / RT$$

# Table (10.3) de Nevers

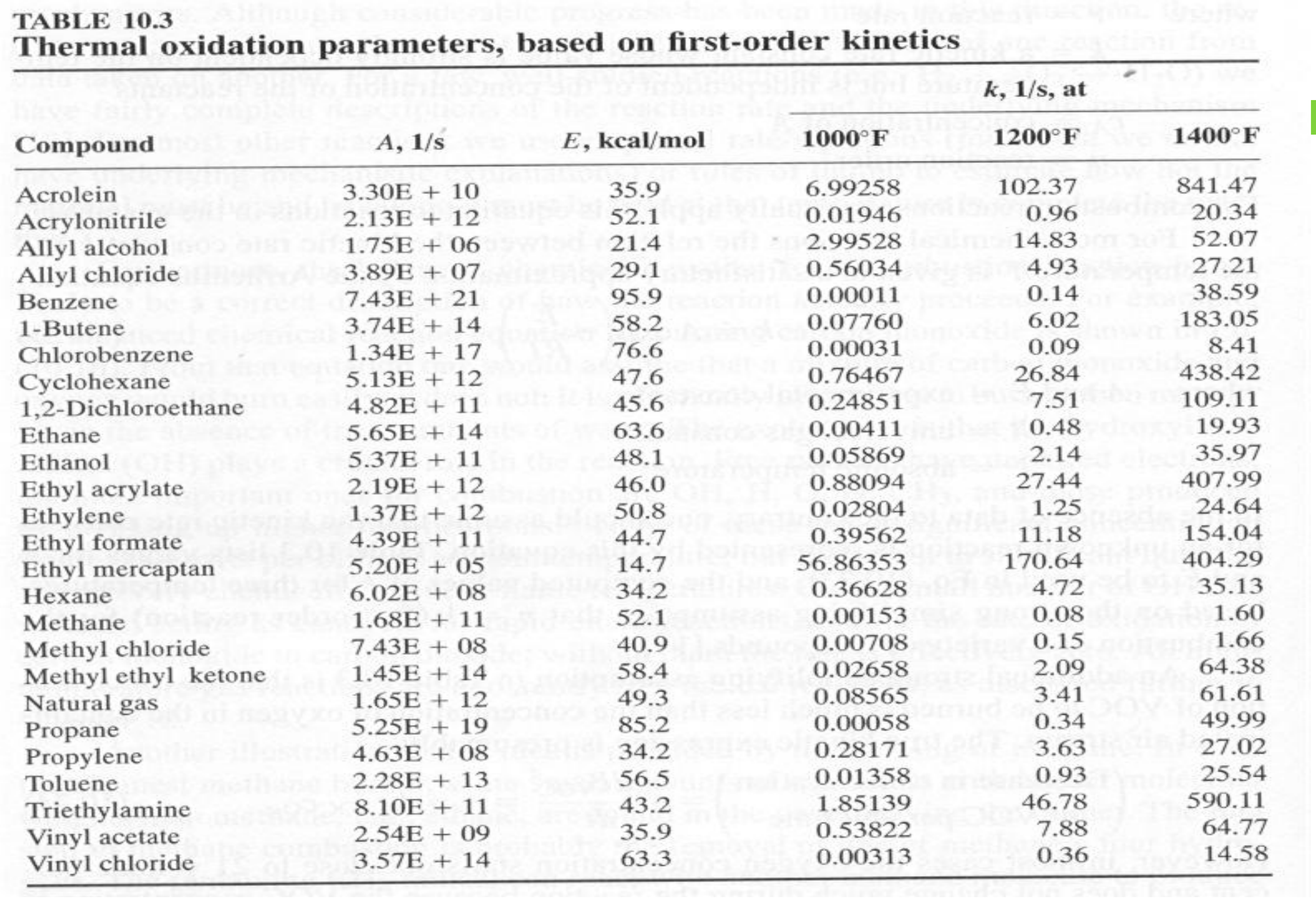


**TABLE 10.3**

**Thermal oxidation parameters, based on first-order kinetics**

| Compound | $A$, 1/s | $E$, kcal/mol | $k$, 1/s, at 1000°F | $k$, 1/s, at 1200°F | $k$, 1/s, at 1400°F |
|---|---|---|---|---|---|
| Acrolein | 3.30E + 10 | 35.9 | 6.99258 | 102.37 | 841.47 |
| Acrylonitrile | 2.13E + 12 | 52.1 | 0.01946 | 0.96 | 20.34 |
| Allyl alcohol | 1.75E + 06 | 21.4 | 2.99528 | 14.83 | 52.07 |
| Allyl chloride | 3.89E + 07 | 29.1 | 0.56034 | 4.93 | 27.21 |
| Benzene | 7.43E + 21 | 95.9 | 0.00011 | 0.14 | 38.59 |
| 1-Butene | 3.74E + 14 | 58.2 | 0.07760 | 6.02 | 183.05 |
| Chlorobenzene | 1.34E + 17 | 76.6 | 0.00031 | 0.09 | 8.41 |
| Cyclohexane | 5.13E + 12 | 47.6 | 0.76467 | 26.84 | 438.42 |
| 1,2-Dichloroethane | 4.82E + 11 | 45.6 | 0.24851 | 7.51 | 109.11 |
| Ethane | 5.65E + 14 | 63.6 | 0.00411 | 0.48 | 19.93 |
| Ethanol | 5.37E + 11 | 48.1 | 0.05869 | 2.14 | 35.97 |
| Ethyl acrylate | 2.19E + 12 | 46.0 | 0.88094 | 27.44 | 407.99 |
| Ethylene | 1.37E + 12 | 50.8 | 0.02804 | 1.25 | 24.64 |
| Ethyl formate | 4.39E + 11 | 44.7 | 0.39562 | 11.18 | 154.04 |
| Ethyl mercaptan | 5.20E + 05 | 14.7 | 56.86353 | 170.64 | 404.29 |
| Hexane | 6.02E + 08 | 34.2 | 0.36628 | 4.72 | 35.13 |
| Methane | 1.68E + 11 | 52.1 | 0.00153 | 0.08 | 1.60 |
| Methyl chloride | 7.43E + 08 | 40.9 | 0.00708 | 0.15 | 1.66 |
| Methyl ethyl ketone | 1.45E + 14 | 58.4 | 0.02658 | 2.09 | 64.38 |
| Natural gas | 1.65E + 12 | 49.3 | 0.08565 | 3.41 | 61.61 |
| Propane | 5.25E + 19 | 85.2 | 0.00058 | 0.34 | 49.99 |
| Propylene | 4.63E + 08 | 34.2 | 0.28171 | 3.63 | 27.02 |
| Toluene | 2.28E + 13 | 56.5 | 0.01358 | 0.93 | 25.54 |
| Triethylamine | 8.10E + 11 | 43.2 | 1.85139 | 46.78 | 590.11 |
| Vinyl acetate | 2.54E + 09 | 35.9 | 0.53822 | 7.88 | 64.77 |
| Vinyl chloride | 3.57E + 14 | 63.3 | 0.00313 | 0.36 | 14.58 |

# Combustion of VOCs: benzene example

- Incineration of benzene with first order kinetics.

| Destruction efficiency | | 99.00% | 99.90% | 99.99% |
|---|---|---|---|---|
| Penetration, C/C0 | | 0.0100 | 0.0010 | 0.0001 |
| T, F | k, 1/s | t, s | t, s | t, s |
| 1000 | 1.10E-04 | 41865 | 62798 | 83730 |
| 1200 | 0.14 | 32.9 | 49.3 | 65.8 |
| 1400 | 38.59 | 0.119 | 0.179 | 0.239 |

a) Relatively *small changes* in temperature result in *large differences* in the time required for a particular efficiency of destruction.

b) In most incinerators the residence times are *of the order of seconds.*

c) If the temperature drops, destruction efficiency drops significantly.

# Combustion of VOCs: benzene example

- ☐ In the above example, penetration increased 100 times by reducing the residence time from 0.24 s to 0.12 s at a temperature of 1400 F.

- ☐ How much does penetration increase by reducing the temperature from 1400 F to 1000 at a residence time of 0.12?

| t, s | T, F | k, 1/s | C/C0 |
|---|---|---|---|
| 0.12 | 1400 | 38.59 | 0.00975 |
| 0.12 | 1000 | 1.10E-04 | 0.99999 |

# Figure 10.14 de Nevers

**Incineration arrangements:**

A) simple thermal incinerator

B) regenerative heat recovery

C) catalytic incinerator

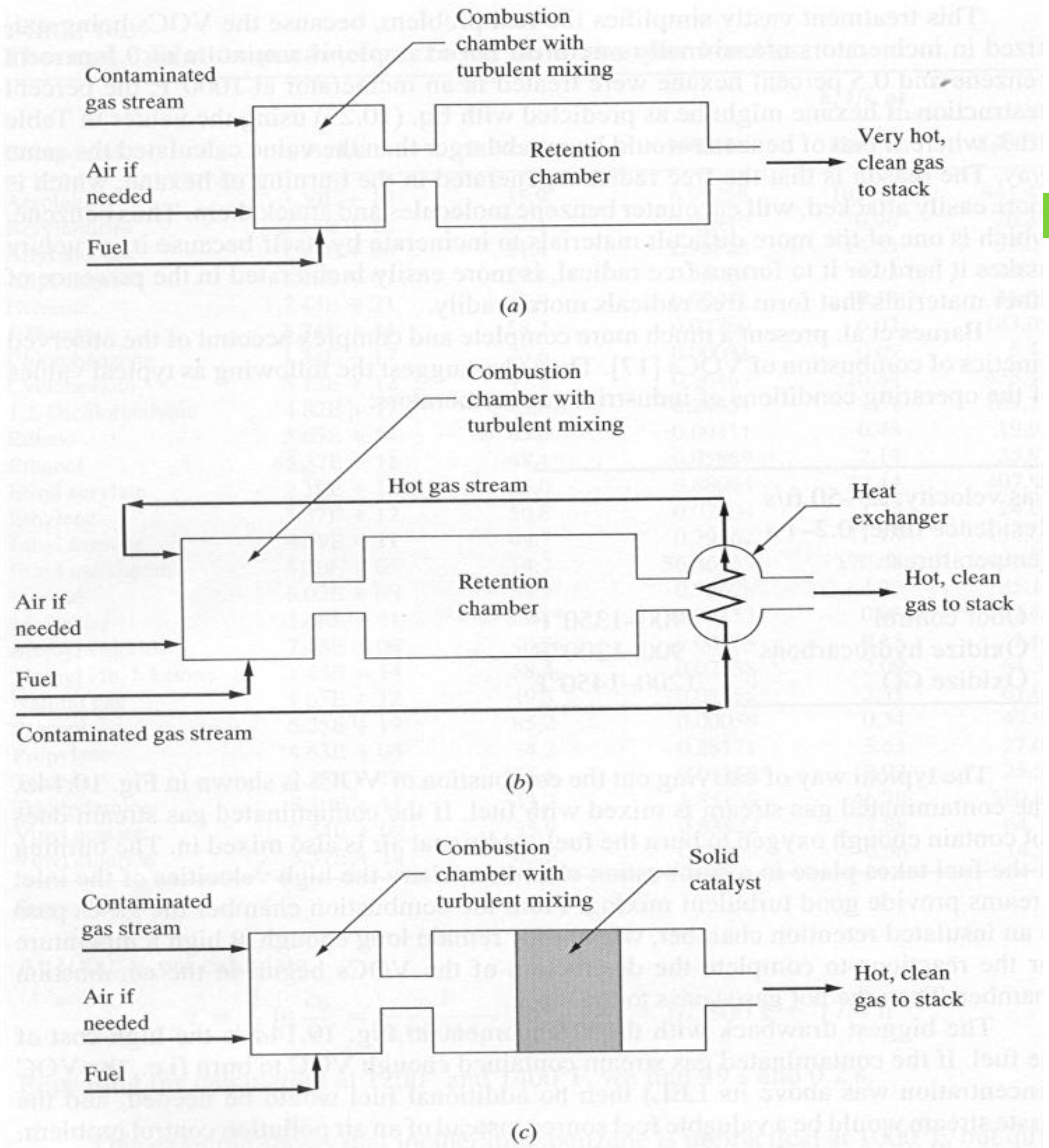


**FIGURE 10.14**
Arrangements for destroying a VOC in a gas stream by incineration: (*a*) simple thermal incinerator, (*b*) thermal incinerator with regenerative heat recovery, and (*c*) catalytic incinerator.

# The Three T's of Combustion*

- We have seen that good mixing is important even in homogeneous systems and that incomplete combustion can result even when we have excess oxygen.
- For heterogeneous systems, large surface area and turbulent mass transfer at that surface become paramount.
- Thus the temperature of reaction, how long the reactants stay at that temperature, and how well they are brought in contact define whether combustion reactions are complete and offer a solution (incineration) to air pollution problems.

* ***Time, Temperature, Turbulence***

**TABLE 1** Characteristics, advantages and drawbacks of the main APCT applied to VOC elimination.

| Technology | Principle and characteristics | Performances and limitations | Costs/($m^3 \cdot h^{-1}$) air |
|---|---|---|---|
| Adsorption | • Transfer of VOC to a porous solid phase, fixed or fluidized<br>• Materials: activated carbons, zeolites and polymers<br>• Ex.: Activated carbon adsorbs 10–30% VOC on a weight basis<br>• Doubled installations: adsorption–desorption cycles<br>• Operating temperature <50–60°C: ignition risks may be present | • Conversion: 90–99%<br>• Possible recovery of VOC (desorption)<br>• Can accept variations of flowrates and shutdown periods<br>But . . .<br>• Treatments for adsorbent regeneration are required<br>• Moisture level of effluents: <50%<br>• Pressure drop<br>• Bed poisoning problems with certain VOC | • Investment: US $15–120<br>• Operation: US $10–35 |
| Incineration | • Thermal oxidation of VOC<br>• 760 < Temperature < 1200°C<br>• 0.3 < Residence time < 2 s<br>• VOC concentration < 25% of explosion limit<br>• Required $O_2$ level ~10% | • Conversion: 98–99.5%<br>• Possible energy recovery<br>• Elimination of halogenated or sulfurated VOC with adequate, additional equipment<br>But . . .<br>• High investment and operating costs<br>• Toxic by-products: CO, $NO_X$, dioxins, furans<br>• Efficiency ↘ for low VOC concentrations | • Investment: US $10–450<br>• Operation: US $20–150 (depends on the quantity of recovered energy) |

| Technology | Principle and characteristics | Performances and limitations | Costs/($m^3 \cdot h^{-1}$) air |
|---|---|---|---|
| Catalytic oxidation | • Thermal, catalytic oxidation of VOC<br>• $300 < \text{Temperature} < 650^\circ\text{C}$<br>• $0.07 < \text{Residence time} < 1$ s<br>• Catalysts: noble metals (Pt, Pd, Rh) on supports (alumina, other ceramics), or metal oxides (Cu, Ti, Ni, Mn, *etc.*)<br>• Catalyst life time: 2–5 years<br>• Usable VOC concentration: far lower than the explosion limit<br>• Required $O_2$ level ~2% | • Conversion: 90–99%<br>• Less energy required than incineration and less toxic by-products<br>But . . .<br>• Catalyst deactivation problems (clogging, poisoning, overheating)<br>• Disposal of used catalyst<br>• Combustion by-products | • Fixed catalyst<br>Investment: US $20–250<br>Operation: US $10–75<br>• Fluidized catalyst<br>Investment: US $35–220<br>Operation: US $15–90 |
| Absorption | • Transfer of the VOC to a liquid phase<br>• Plate tower, bubble column, packed tower, atomizer<br>• Solvents: water (with adjusted pH), high boiling-point hydrocarbons, amines, *etc.*<br>• Counter-current operation (↗ the VOC transfer rate) | • Conversion: 90–98%<br>• Possible recovery and valorization of the dissolved VOC with downstream treatments<br>But . . .<br>• Inadequate for VOC of low solubility<br>• Production of waste water | • Investment: US $15–70<br>• Operation: US $25–120 |

| Technology | Principle and characteristics | Performances and limitations | Costs/($m^3 \cdot h^{-1}$) air |
|---|---|---|---|
| Condensation | • Liquefaction of high boiling-point VOC (>38°C) via cooling and/or compression<br>• Cooling/cryogenic systems: water (5°C), brine (→ −35°C), liquid nitrogen (→ −185°C) | • Conversion: 50–99%<br>• A recovery and valorization way<br>But . . .<br>• Well adapted to saturated VOC only<br>• Disposal of condensates<br>• Problems of frost deposits | • Investment: US $10–80<br>• Operation: US $20–120 |
| Membranes | • Separation of gas mixtures through semi-permeables membranes<br>• Materials: polymers (hollow fibers, silicones), porous ceramics<br>• Gas flow compressed before membrane separation | • Conversion: 50–98%<br>• VOC are concentrated 5–100 times, and valorization (recycle) possible<br>• Selective membranes, resistant to halogenated VOC<br>But . . .<br>• Pressure drop<br>• High operating pressures<br>• Membrane cleaning required | Not available |

| Technology | Principle and characteristics | Performances and limitations | Costs/($m^3 \cdot h^{-1}$) air |
|---|---|---|---|
| UV/photochemical oxidation | • Complete oxidation by oxygenated oxidizers ($O_3$, $H_2O_2$), and initiated by UV radiation<br>• Possible utilization of photocatalysts ($TiO_2$, $Fe_xO_y$, *etc.*)<br>• Operating temperature: ambient | • Conversion: 90–98%<br>• Moderate energetic costs<br>But . . .<br>• Inadequate for halogenated VOC<br>• Deposit of oxidation by-products on the catalysts surface (cleaning)<br>• Complex systems | Not available |
| Biotechnologies (detailed later) | • Biocatalytic oxidation of VOC<br>• 3 configurations: biofilters (most frequent), biotrickling filters and bioscrubbers<br>• Biocatalysts: microorganisms (bacteria, fungi)<br>• 30 s < Residence time < several min<br>• Operating temperature: 20–40°C<br>• Filter-bed life time: 3–5 years | • Conversion: 80–95%<br>• Moderate installation and operating costs<br>• Low maintenance<br>But . . .<br>• Strict control of biological parameters (pH temperature, moisture level, nutrients, *etc.*)<br>• Large spaces required for biofilters<br>• Pressure drop problems | • Investment: US $10–70<br>• Operation: US $3–10 |