

Chapter 6 VOCs, PAHs, soot, tar, CO

6.1 Introduction

Thermal treatment processes such as combustion, gasification, incineration and pyrolysis of fossil fuels, biomass or waste streams will generate carbonaceous and hydrocarbon-rich by-products or “products of incomplete combustion” (PICs). The best examples are CO and carbon-in-ash, but the range of chemical compounds is actually extremely wide. As discussed above (7 chapter 5.12), the particulates emitted by a diesel engine are mainly hydrocarbon, being a mixture of soot, *i.e.* clustered, carbonaceous nano-particles, and unburnt fuel. Similarly, the off-gases of power utilities and waste incinerators contain a wide range of organic and inorganic species which all, excluding O₂, N₂ and H₂O, have an influence on the local or global environment. These effects can be very diverse: water and soil acidification, human health problems (respiratory or cardiovascular diseases, cancer, fertility problems, or in short: long-term or short-term toxicity), ground-level ozone and the enhanced greenhouse effect are the most direct examples (*e.g.* WHO, 1996). Moreover, the presence of combustible species in the off-gases of a combustion or incineration unit in fact indicates inefficient processing.

This chapter considers only the halogen-free, carbon-based species that are found in flue gases, fuel gases and other process off-gases, leaving halogenated compounds such as dioxins/furans to the next chapter. The concentration of many of the species concerned is very low, *i.e.* lower than 1 %-vol. Odorous and/or hazardous off-gases from industrial processes besides the power-related industry, such as processes using organic solvents, are covered here also.

Table 6.1 gives a few definitions that actually have some overlap and seem to exclude some others. Volatile organic compounds (VOCs) are mainly lower (C₁ ~ C₄) paraffins (*i.e.* alkanes, C_nH_{2n+2}) and olefins (*i.e.* alkenes, C_nH_{2n}), and aldehydes (*e.g.* formaldehyde), ketones (*e.g.* acetone) and aromatics (*e.g.* benzene, toluene, benzaldehyde, phenol). A typical tar consists of significant amounts of benzene, toluene and phenol, polycyclic aromatic hydrocarbons (PAHs) like naphtalene and anthracene (see Table 6.7), pyridines (see Figure 4.6) and thiophenes (see Figure 3.3).

During further processing these may be cracked into smaller, gaseous compounds (like VOCs) or they may form soot. The PAH naphthalene (boiling point 218°C) is often regarded as a VOC compound as well: VOCs contain usually ~ 0.1 % PAHs. The definition of VOC, on the other hand, excludes many organic compounds that are not involved in the formation of ground-level ozone, such as methane, CO, and halogenated organics like 1,1,1-trichloroethane and CFCs. Controlling of these non-VOC organic gases will be discussed as well, in this or later chapters.

Table 6.1 Definitions of carbon-based gaseous pollutants

| | |
|------------|--|
| VOC | volatile organic compound: "all organic compounds of antropogenic nature, other than methane, that are capable of producing photochemical oxidants by reactions with nitrogen oxides in the presence of sunlight" (McConville, 1997) |
| PAH | polycyclic aromatic hydrocarbon |
| tar | condensable organic compounds |
| soot | carbonaceous particles produced from gaseous fuel or from volatilised solid or liquid fuel components during combustion |
| THC, TOC | total hydrocarbon, total organic carbon |
| HAP (USA) | hazardous air pollutant |
| POHC (USA) | principle organic hazardous constituents, selected on the basis of difficulties with their incineration (LaGrega <i>et al.</i> , 1994) |

Table 6.2 Organic hazardous air pollutants (HAPs) of interest for thermal power industry (US Clean Air Act 1990, taken from Alvarez Cuenca and Anthony, 1995)

| Volatile organic compounds | Polynuclear aromatic hydrocarbons | Additional polycyclic aromatic compounds |
|----------------------------|-----------------------------------|--|
| Benzene | Acenaphthylene | 1,2-Diphenylhydrazine |
| Toluene | Acenaphthene | 1-Chloronaphthalene |
| Formaldehyde | Anthracene | 1-Naphthylamine |
| | Benzo(a)anthracene | 2-Chloronaphthalene |
| | Benzo(a)pyrene | 2-Naphthylamine |
| | Benzo(b)fluoranthene | 3,3-Dichlorobenzidine |
| | Benzo(g,h,i)perylene | 4-Aminobiphenyl |
| | Benzo(k)fluoranthene | 4-Bromophenyl phenyl ether |
| | Chrysene | 4-Chlorophenyl phenyl ether |
| | Dibenzo(a,h)anthracene | Benzidine |
| | Fluoranthene | Butylbenzylphthalate |
| | Fluorene | Dibenzofuran |
| | Indeno(1,2,3-cd)pyrene | Dibenz(a,j)acridine |
| | Naphthalene | Diphenylamine |
| | Phenanthrene | n-Nitrosodiphenylamine |
| | Pyrene | |
| | 2-Methylnaphthalene | |
| | 3-Methylcholanthrene | |
| | 7,12-Dimethylbenz(a)-anthracene | |

Hazardous air pollutants (HAPs) as defined in the US comprise trace elements (see chapter 8), VOCs, PAHs and other polycyclic aromatic compounds. Organic HAPs of concern for thermal power industry are listed in Table 6.2).

So-called principle organic hazardous constituents (PHOCs), which are selected for a certain process, require 99.99% DRE (destruction and removal efficiency).

6.2 Emission standards for (non-halogenated) organic compounds

Emission standards for non-halogenated organic compounds are generally limited to two compounds: CO, and total hydrocarbons (THC) or total organic carbon (TOC). The three most important processes to be distinguished are power plants, waste incinerators and hazardous waste incinerators. A major difference between the last two are the combustion conditions: a waste incinerator regulation requires a residence time at 850EC of at least 2 seconds after the last air feeding point, for hazardous waste with more than 1 %-wt halogens a minimum temperature of 1100EC is required. For several processes and various countries, emission standards are given in Table 6.3 (Werther, 1999, Wilén, 1999, Foster Wheeler, 1997, Finland, 1994).

Table 6.3 Emission standards for CO and THC for various processes and locations (mg/m³_{STP} @ 11 % O₂, dry)(MSW = municipal solid waste)

| | Power plant Finland (1990+) | MSW incinerator Finland (1994) | MSW incinerator EU (2000) | Power plant Germany (1999) | MSW incinerator Germany (1999) | Hazardous waste incinerator EU (1996) | Waste incinerator USA (1995) |
|-----|-----------------------------------|---|------------------------------------|----------------------------------|---|--|---------------------------------------|
| CO | no limit | 50 | 50 | 250 | 50 | 50 | 76.31 |
| THC | no limit | 10 | 10 | 20 | 10 | 10 | no limit |

6.3 Volatile organic compounds (VOCs) and ground-level ozone

As mentioned above, the term VOC defines carbon compounds that react with NO_x and other chemicals photochemically (*i.e.* with sunlight) to form ground-level ozone. The reaction intermediate peroxy acetyl nitrate (PAN, CH₃-C(=O)-O-NO₂) has been detected as an important reaction intermediate for this process - see also Figure 4.60.

Ozone is a very strong oxidizer. For human health the WHO guide level of 120 µg/m³ (~ 100 ppbv, *i.e.* 0.1 ppmv) should not be exceeded, as was also set as EU regulation target value as of 2010 (Acid News, 1999). Athens, Greece recorded a maximum hourly average of 334 µg/m³ in 2000 (Acid News, 2001). For vegetation, a critical exposure of 3000 ppbv -hours above a 40 ppbv threshold during the growing season was suggested: a 60 ppbv level during 100 hours implies (60 - 40) ppbv * 100 h = 2000 ppbv -h excess (Ågren and Elvingson, 1992). Figure 6.1 shows the emissions of VOC in Europe in 1994; ground-level ozone concentrations as ppbv -h above 40 ppbv during the (warm) summer of 1990 are shown in Figure 6.2.

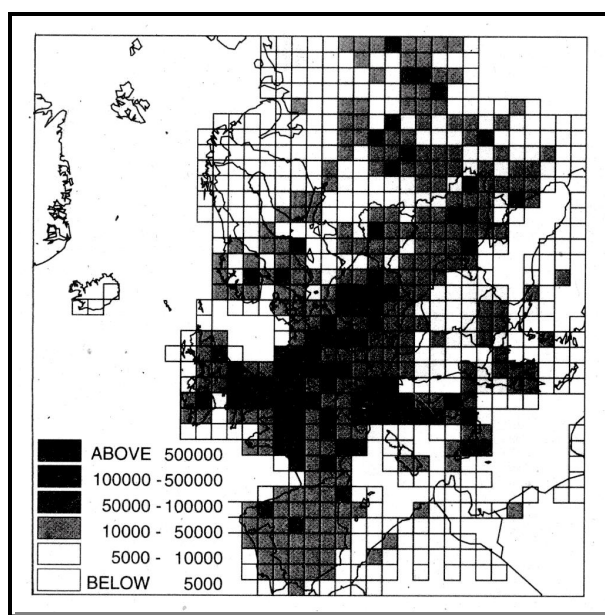


Figure 6.1 Emissions of VOC (incl. methane) in Europe, tonnes 1994 (picture from Ågren and Elvingson, 1997)

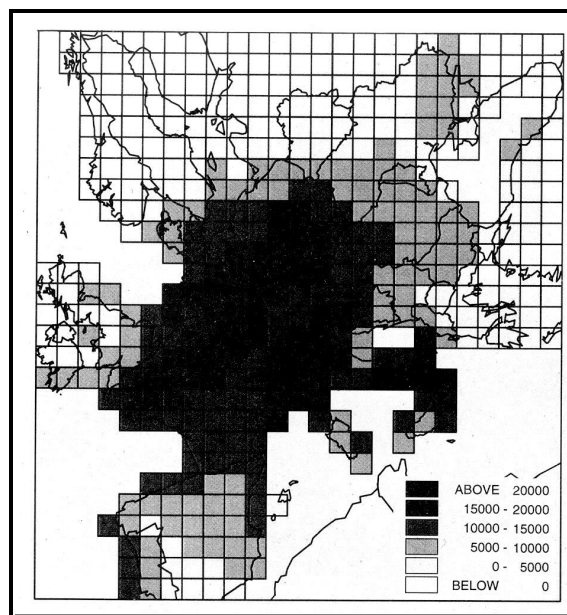


Figure 6.2 Concentrations of groundlevel ozone in Europe, ppb-hours above 40 ppb, summer 1990 (picture from Ågren and Elvingson, 1997)

6.4 Control of volatile organic compounds (VOCs)

The amounts of VOCs as emitted from waste incinerators, for example, vary significantly with plant type: the differences between a grate-fired and a circulating fluidised bed incinerator are illustrated by Table 6.4.

Table 6.4 VOC emissions from waste incineration plants, in mg/m^3 at 10% CO_2 (data from Chagger et al., 2000).

| | benzene | toluene | phenol | m-xylene | 1,3,5 trimethyl benzene | 2-ethyl hexanol | naphta- lene | total VOC |
|--------|---------|---------|--------|----------|-------------------------------|--------------------|-----------------|--------------|
| Grate* | 6.05 | 2.18 | 24.85 | 0.34 | 2.92 | 40.43 | 0.23 | 387 |
| CFB | 0.79 | 1.65 | 7.58 | 0.58 | 2.69 | 22.02 | - | 120 |

* Averaged over 3 facilities

Concentrations of VOCs in gas streams are typically $\ll 1$ %-vol and are usually presented as a “cocktail” of compounds of which only a few (the most hard to handle) will determine what will be the most suitable control process. Important parameters are the lower (and upper) flammability limits (LFL and UFL) of the VOC

/ air mixture, which define whether the mixture may ignite (see *e.g.* Borman and Ragland, 1998). Special caution is taken when the gas mixture composition exceeds 25% of the LFL. For several VOC and other gaseous organic compounds the values for LFL and UFL are given in Table 6.5.

For gas mixtures with VOC contents below the LFL value, the most important options are “VOC combustion”, condensation and carbon absorption. When the concentration of VOC is above the UFL the gas can be oxidised in flares or boilers with air or steam. In this section these options are discussed in more detail (LaGrega *et al.*, 1994, Ruddy and Carroll, 1993). Other, non-VOC components in the gas should be taken into account as well, such as particulate matter or chemical species that may destroy or deactivate catalysts, or are oxidised to aggressive compounds.

Gases containing 100 - 2000 ppmv VOCs can be processed in thermal or catalytic oxidation units, at temperatures 700 - 1000EC and 200 - 500EC, respectively.

Table 6.5 Lower and upper flammability limits (LFL and UFL) for organic gaseous compounds (from LaGrega *et al.*, 1994)

| Gas or vapor | Lower limit % by volume | Upper limit % by volume |
|------------------------|----------------------------|----------------------------|
| Acetaldehyde | 4.0 | 57 |
| Acetone | 2.5 | 12.8 |
| Acetylene | 2.5 | 80 |
| Allyl alcohol | 2.5 | — |
| Ammonia | 15.5 | 26.6 |
| Amyl acetate | 1.0 | 7.5 |
| Amylene | 1.6 | 7.7 |
| Benzene (benzol) | 1.3 | 6.8 |
| Benzyl chloride | 1.1 | — |
| Butene | 1.8 | 8.4 |
| Butyl acetate | 1.4 | 15.0 |
| Butyl alcohol | 1.7 | — |
| Butyl cellosolve | — | — |
| Carbon disulfide | 1.2 | 50 |
| Carbon monoxide | 12.5 | 74.2 |
| Chlorobenzene | 1.3 | 7.1 |
| Cottonseed oil | — | — |
| Cresol <i>m- or p-</i> | 1.1 | — |
| Crotonaldehyde | 2.1 | 15.5 |
| Cyclohexane | 1.3 | 8.4 |
| Cyclohexanone | 1.1 | — |
| Cyclopropane | 2.4 | 10.5 |
| Cymene | 0.7 | — |
| Dichlorobenzene | 2.2 | 9.2 |
| Dichloroethylene (1,2) | 9.7 | 12.8 |
| Diethyl selenide | 2.5 | — |
| Dimethyl formamide | 2.2 | — |
| Dioxane | 2.0 | 22.2 |
| Ethane | 3.1 | 15.5 |
| Ether (diethyl) | 1.8 | 36.5 |
| Ethyl acetate | 2.2 | 11.5 |
| Ethyl alcohol | 3.3 | 19.0 |
| Ethyl bromide | 6.7 | 11.3 |
| Ethyl cellosolve | 2.6 | 15.7 |
| Ethyl chloride | 4.0 | 14.8 |
| Ethyl ether | 1.9 | 48 |
| Ethyl lactate | 1.5 | — |
| Ethylene | 2.7 | 28.6 |
| Ethylene dichloride | 6.2 | 15.9 |
| Ethyl formate | 2.7 | 16.5 |
| Ethyl nitrite | 3.0 | 50 |
| Ethylene oxide | 3.0 | 80 |
| Furfural | 2.1 | — |
| Gasoline (variable) | 1.4–1.5 | 7.4–7.6 |
| Heptane | 1.0 | 6.0 |
| Hexane | 1.2 | 6.9 |

| Gas or vapor | Lower limit % by volume | Upper limit % by volume |
|-----------------------------|----------------------------|----------------------------|
| Hydrogen cyanide | 5.6 | 40.0 |
| Hydrogen | 4.0 | 74.2 |
| Hydrogen sulfide | 4.3 | 45.5 |
| Illuminating gas (coal gas) | 5.3 | 33.0 |
| Isobutyl alcohol | 1.7 | — |
| Isopentane | 1.3 | — |
| Isopropyl acetate | 1.8 | 7.8 |
| Isopropyl alcohol | 2.0 | — |
| Kerosene | 0.7 | 5 |
| Linseed oil | — | — |
| Methane | 5.0 | 15.0 |
| Methyl acetate | 3.1 | 15.5 |
| Methyl alcohol | 6.7 | 36.5 |
| Methyl bromide | 13.5 | 14.5 |
| Methyl butyl ketone | 1.2 | 8.0 |
| Methyl chloride | 8.2 | 18.7 |
| Methyl cyclohexane | 1.1 | — |
| Methyl ether | 3.4 | 18 |
| Methyl ethyl ether | 2.0 | 10.1 |
| Methyl ether ketone | 1.8 | 9.5 |
| Methyl formate | 5.0 | 22.7 |
| Methyl propyl ketone | 1.5 | 8.2 |
| Mineral spirits No. 10 | 0.8 | — |
| Naphthalene | 0.9 | — |
| Nitrobenzene | 1.8 | — |
| Nitroethane | 4.0 | — |
| Nitromethane | 7.3 | — |
| Nonane | 0.83 | 2.9 |
| Octane | 0.95 | 3.2 |
| Paraldehyde | 1.3 | — |
| Paraffin oil | — | — |
| Pentane | 1.4 | 7.8 |
| Propane | 2.1 | 10.1 |
| Propyl acetate | 1.8 | 8.0 |
| Propyl alcohol | 2.1 | 13.5 |
| Propylene | 2.0 | 11.1 |
| Propylene dichloride | 3.4 | 14.5 |
| Propylene oxide | 2.0 | 22.0 |
| Pyridine | 1.8 | 12.4 |
| Rosin Oil | — | — |
| Toluene (toluol) | 1.3 | 7.0 |
| Turpentine | 0.8 | — |
| Vinyl ether | 1.7 | 27.0 |
| Vinyl chloride | 4.0 | 21.7 |
| Water gas (variable) | 6.0 | 70 |
| Xylene (xylol) | 1.0 | 6.0 |

Thermal oxidisers allow for DRE levels above 99% at typical capacities of 0.5 - 250 m³/s, with residence times of the order of 0.5-1 s. Options for heat recovery,

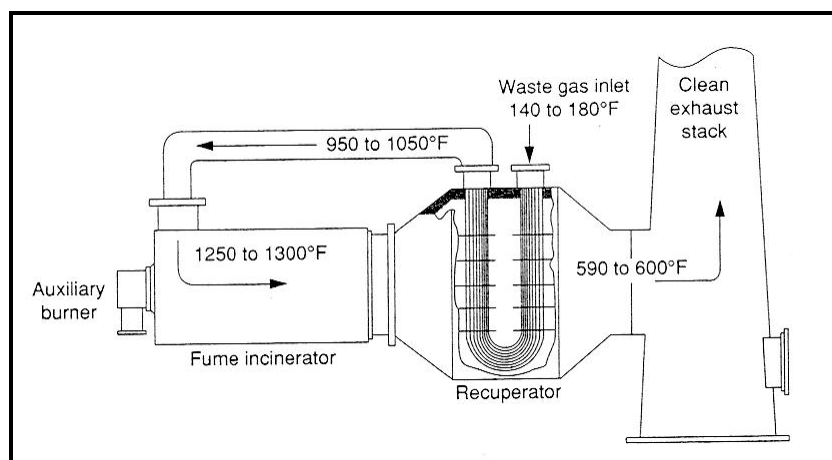


Figure 6.3 A typical thermal VOC incinerator with recuperative heat recovery. (150EF=66EC, 600EF=316EC, 1000EF=538EC, 1300EF=704EC) (picture from LaGrega *et al.*, 1994)

depending on the flexibility that is required and the VOC-containing gas, are either a regenerative or a recuperative recovery system. The thermal efficiencies of these are ~ 95% and ~ 70%, respectively (Ruddy and Carroll, 1993). An example of a recuperative thermal VOC incinerator is given in Figure 6.3.

Catalytic oxidation with *e.g.* Pt or Pd on a Al₂O₃ honeycomb support may give DRE levels up to ~ 95% at somewhat smaller sizes than thermal oxidation units. A serious drawback of these units are the costs related to replacing the catalyst which, in waste-processing gas streams is easily poisoned by *e.g.* chlorine, sulphur, silicon, vanadium, lead, or high molecular weight hydrocarbons. Also temperature excursions reduce catalyst lifetime. Besides this, there is a risk that other gaseous species are converted to hazardous compounds that need further processing downstream. For heat recovery a recuperative system can be used. Catalytic VOC oxidisers are most suitable for the processing of gas streams with constant VOC composition and process conditions. A standard catalyst for VOC control will operate at 350-500EC, whilst a special catalyst formulation may do the job at 200-300EC. Depending on the kinetics of VOC oxidation and the presence of non-VOC pollutants either a monolith, basically a cluster of parallel tubes (for fast kinetics), or a beads/pellets (for slower kinetics, less sensitive to fouling or poisoning) configuration can be selected (Parvesse, 2000).

Thermal and catalytic VOC oxidisers suffer often from incomplete CO burnout. Oxidation of CO will be briefly addressed below (L section 6.8).

A third method is VOC condensation by cooling and/or pressurising. This option is most suitable for relatively high VOC concentrations, ~ 5000 ppmv of gases with

boiling points above, say, 40°C - for lower boiling point VOCs cooling/pressurising costs may become excessive. An advantage here is that the VOC species can be recovered and that gases with VOC concentrations above 25% LFL can be processed: the concentration may even be above the UFL level as well. Typical capacities are 0.05-10 m³/s (Ruddy and Carroll, 1993).

A fourth option is physical absorption on a bed of activated carbon, as illustrated by Figure 6.4. Typical capacities are 0.05-30 m³/s at VOC concentrations of 20-5000 ppm. Removal efficiencies are of the order 90-98%. Similar to condensation processes there is less sensitivity to the LFL and UFL values for the gas although risks for fires are somewhat higher. Activated carbon can be produced from a char or coke material by oxidation with air at 500-600°C or by oxidation with boiling nitric acid.

After a certain period the carbon bed will become saturated, reaching the “break point” at which the concentration in the

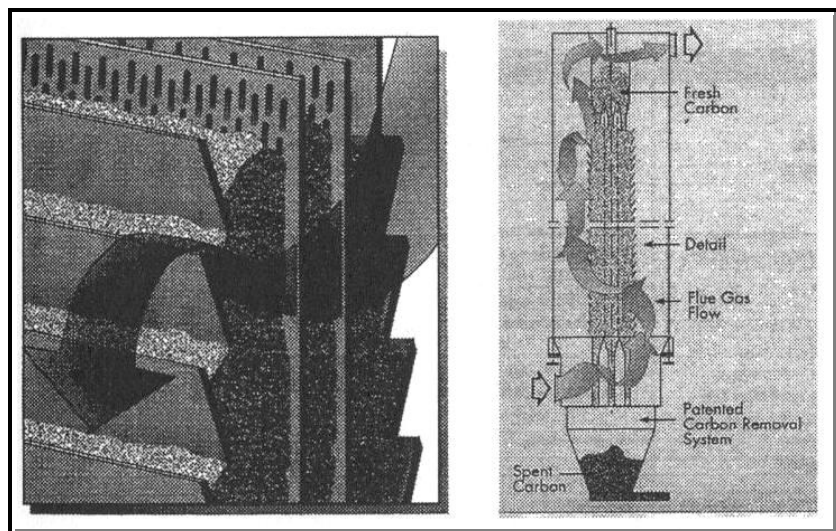


Figure 6.4 Activated carbon bed filter: the STEAG a/c/t™ process (picture from Brüggendick and Gilgen, 1996)

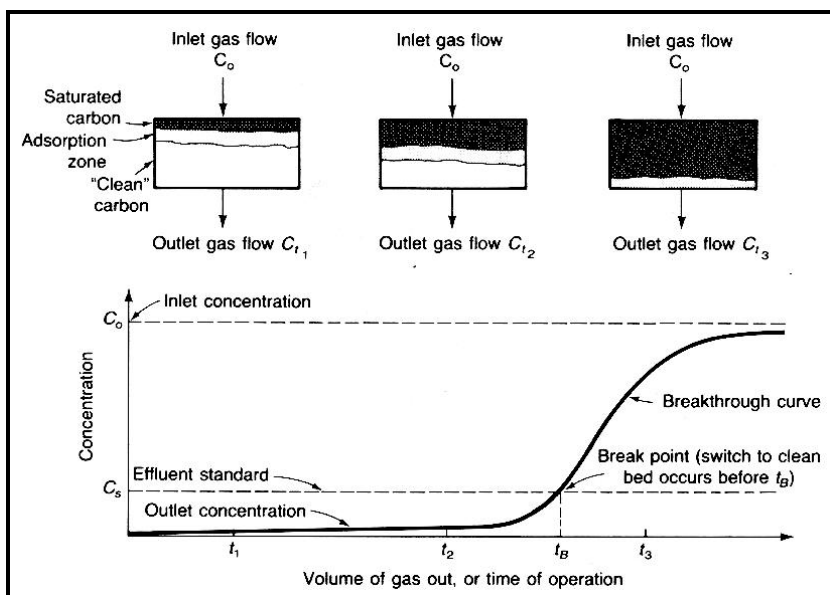


Figure 6.5 Typical break-through curve of an activated carbon adsorption bed (picture from Cooper and Alley, 1994)

exit gas exceeds the target value and quickly rises to the inlet concentration, as shown in Figure 6.5. At this point regeneration is needed which can be done with steam, hot

air or hot nitrogen at 400-1000°C depending on the situation. This may either oxidise the collected VOCs or release them in a more concentrated form for further processing. Alternatively, the bed is replaced, for example if it is classified as hazardous waste. As shown in Figure 6.4, multiple beds can be used for VOCs, dioxins/furans and trace elements (L chapter 7 and 8).

Repeated loading and regeneration will inevitably give some bed deactivation. It also may become deactivated by other species such as halogenated organic compounds and trace elements. Also high moisture contents (relative humidity > 50%) reduce the performance of the carbon bed. For ketones (such as acetone) carbon bed adsorption is less suitable since exothermic polymerisation reactions deactivate the bed and may even result in fires.

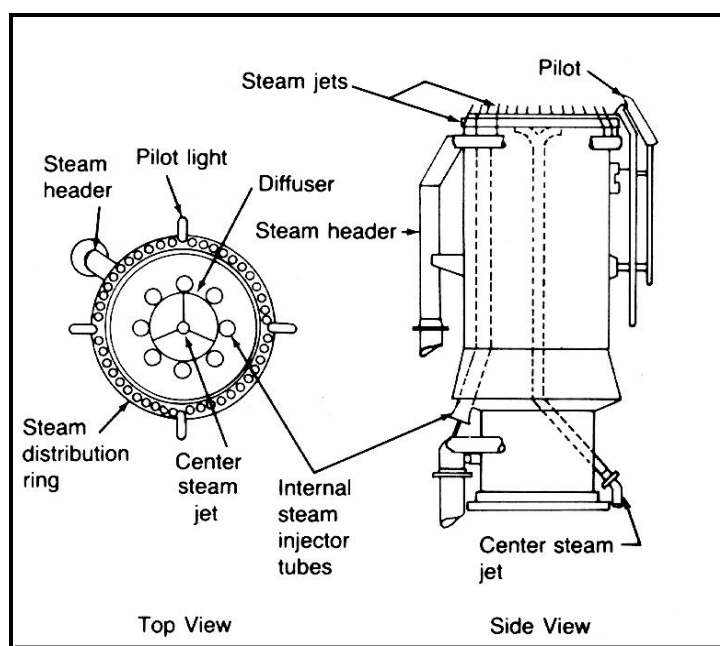


Figure 6.6 A flare tip combustor (picture from Cooper and Alley, 1994)

A fifth and last method discussed here is absorption with a liquid solvent, in packed bed or spray scrubbing devices (see also chapters 3 and 5), the choice for which depends on the presence of particulates in the gas. This option is very suitable for humid gas streams ($RH > 50\%$) with 500-5000 ppm VOC, at capacities of 1 - 50 m³/s.

For gases with VOC concentrations above the UFL level, combustion in a flare located at a stack outlet is possible, as shown in Figure 6.6.

Combustion is achieved by addition of steam and air which brings the VOC concentration between the LFL and UFL concentrations and removes the VOCs by combustion. Without steam only few waste gases burn without problems. A well-known exception is by-product (natural) gas combustion in flares at oil fields. Flare systems are generally part of process emergency control systems, used for heat recovery at other times.

VOC control options, including a cost comparison, are summarised in Table 6.6.

Table 6.6 Selection chart for VOC control technologies
(after Ruddy and Carroll, 1993)

Note : 1 cfm = 1 cubic feet / min, $1 \text{ m}^3_{STP} / \text{min} = 35.3 \text{ scfm}$

| Control Device | VOC Content (ppmv) | Flow Rate (scfm) | Capital Cost 1993 | Annual Cost 1993 | Removal Efficiency | Advantages | Disadvantages |
|-----------------------|--------------------|------------------|-------------------|------------------|------------------------|---|--|
| Thermal Incinerator | 100-2000* | 1000 to 500,000 | \$10 to 450/cfm | \$15 to 150/cfm | 95-99+% | Up to 95% energy recovery | Halogenated compounds may require additional control |
| Catalytic Incinerator | 100-2000* | 1000 to 100,000 | \$20 to 250/cfm | \$10 to 90/cfm | 90-95% | Up to 70% energy recovery | Catalyst poisoning |
| Flare | | <2,000,000 | | | >98% Steam-assisted | VOC destruction of variable emission conditions | Low heating value VOC requires auxiliary fuel |
| Boiler | | Steady | | | >98% | Supplement fuel | Variations may affect process |
| Carbon Adsorber | 20-5000* | 100 to 60,000 | \$15 to 120/cfm | \$10 to 35/cfm | 90-98% | Vapor recovery, Pre-Concentrator | High RH may lower capacity, Pore fouling |
| Absorber | 500-5000 | 2000 to 100,000 | \$15 to 70/cfm | \$25 to 120/cfm | 95-98% | Vapor recovery | Scale build-up, Liquid waste |
| Condenser | >5000 | 100 to 20,000 | \$10 to 80/cfm | \$20 to 120/cfm | 50-90% | Vapor recovery | Scale build-up, Liquid waste |

* <25% of lower explosion limit; RH is relative humidity

VOC emissions from engines are mainly unburned fuel, *i.e.* hydrocarbons (HCs) such as paraffins and light aromatics, and some partially oxidised species such as aldehydes and peroxides. These are successfully oxidised in a catalytic converter using Pt, Pd or Rh, noting that Pd is more sensitive to poisoning by lead and sulphur. This is integrated in a three-way catalyst with CO oxidation and NO_x reduction (7 section 4.16) - see also Koltsakis and Stamatelos (1997). Thermal oxidation reactors for engine flue gases (Heywood, 1988) are a more complicated option that suffers from low gas temperatures and the (too) low concentration of the VOC for combustion. Besides this, only VOCs, HCs and CO emissions are reduced whilst NO_x is unchanged.

6.5 Control of polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic compounds (PAHs) are hydrocarbon compounds composed of several aromatic rings. Some carbon atoms may be substituted by *e.g.* nitrogen or sulphur, giving heterocyclic PAHs. Typical PAHs found in flue gases or in pyrolysis or gasification product gases

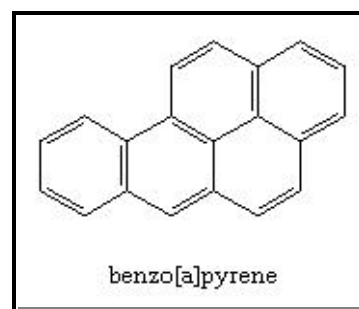
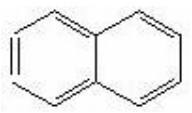
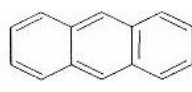
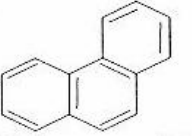
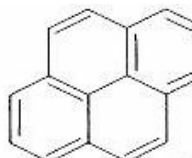
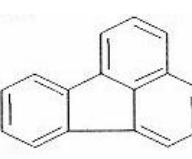
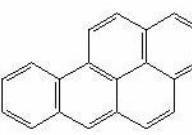


Figure 6.7 Benzo(a)pyrene

are those composed of 2 to 7 aromatic rings. In 1775 already, a physician in London suspected PAHs with 4 or 5 rings to be carcinogenic, for benzo(a)pyrene, or BaP, (see Figure 6.7) this is now a proven fact. As a result of that BaP is the most widely studied PAH compound. Nowadays, more than 25 PAHs and many more heterocyclic PAHs are known or suspected to be carcinogenic. PAHs with more than 4 or 5 aromatic rings are non-volatile and are found as deposited on or absorbed by particles. The simplest PAH, naphthalene, with two aromatic rings ($C_{10}H_8$) has a boiling point of 218°C. Some data on PAHs are given in Table 6.7 (e.g. Huotari and Vesterinen, 1995).

Table 6.7 Properties of some PAH compounds

| | Molecular formula | Molar mass (g/mol) | Boiling point (°C) | Structure |
|--------------------|-------------------|--------------------|--------------------|---|
| Naphthalene | $C_{10}H_8$ | 128 | 218 |  |
| Anthracene | $C_{14}H_{10}$ | 178 | 342 |  |
| Fluoranthene | $C_{14}H_{10}$ | 178 | 340 |  |
| Pyrene | $C_{16}H_{10}$ | 202 | 393 |  |
| Benzo(a)anthracene | $C_{16}H_{10}$ | 202 | 375 |  |
| Benzo(a)pyrene | $C_{20}H_{12}$ | 252 | 493 |  |

Major sources for PAHs are: domestic wood or coal heating, open fires for refuse or after-crop combustion or forest fires, coke and anode production, aluminum production (Söderberg process) and wood preservation works (UN, 1998).

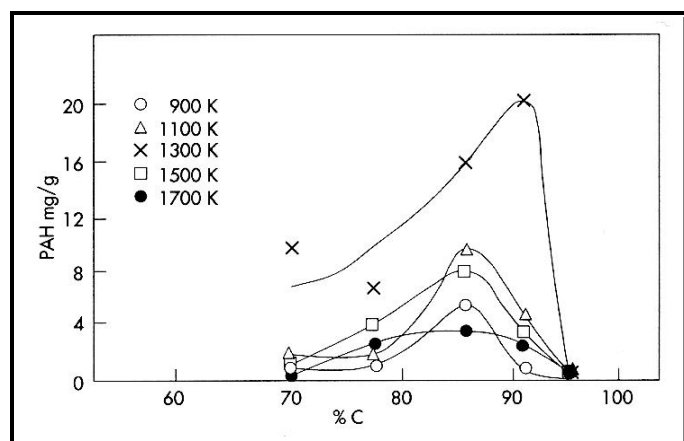


Figure 6.8 PAH formation (mg PAH carbon/g fuel carbon) during coal pyrolysis at various temperatures, 0.3 s (picture from Huotari and Vesterinen, 1995)

Significant amounts of PAHs are produced during pyrolysis and coking processes. For coal pyrolysis in nitrogen, the effect of coal type and temperature is shown in Figure 6.8; maximum PAH formation occurs at ~ 1000EC, with high and medium-volatile bituminous coals producing most PAHs. At higher temperatures, thermal cracking reactions become more important.

During combustion of hydrocarbon-containing fuels, PAHs are produced at 500-800EC, of which the major part is later burnt at higher temperatures. PAHs from combustion facilities are mainly the result of bad fuel/oxygen mixing and cold spots. The smaller the unit, the larger the influence of low temperature zones and the higher the PAH emissions, as illustrated by Table 6.8 for total PAH and BaP. Besides furnace size also furnace type, maximum temperature and especially the air factor (or stoichiometry) are important.

Table 6.8 *Typical PAH and BaP emissions from various furnace types (data from Huotari and Vesterinen, 1995)*

| | Small wood stove | Small solid fuel furnace | Small residential furnace | Heating furnace 1-5 MW | Heat and power units > 5 MW |
|--|------------------|--|---------------------------|---|--|
| PAHs ($\mu\text{g}/\text{MJ}$) | 100-1000 | 1000-3000 (batch) < 1000 (continuous) | < 1000 | 2-10 (solid fuel) < 5 (oil, gas) | < 10 (5 -50 MW) < 5 (> 50 MW) |
| BaP ($\mu\text{g}/\text{MJ}$) | | < 20 | | < 0.1 | < 0.01 (> 50 MW) |

A comparison between a pyrolysis process, a grate firing combustor and a pulverised coal combustion unit shows a very much lower PAH emissions for the last. For FBC of coal, maximum PAH emissions occur at values for the air factor of 1.8 - 2 (Mastral and Callén, 2000). Some PAH emission data are cited in Table 6.9.

Table 6.9 *Effect of fuel type and process type on PAH production (data taken from Huotari and Vesterinen, 1995)*

| | Methyl anthracene and/or fenantrene ($\mu\text{g}/\text{MJ}$) | Fluoranthene ($\mu\text{g}/\text{MJ}$) | Pyrene ($\mu\text{g}/\text{MJ}$) | Fenantrene and/or anthracene ($\mu\text{g}/\text{MJ}$) |
|----------------------------|---|--|------------------------------------|--|
| Pyrolysis | | | | |
| - Montana lignite | | 1720 | 2710 | 10950 |
| - High vol. bit. coal | 5890 | 6320 | 11680 | 1900 |
| Grate firing 200 kW | | | | |
| - High vol. bit. coal | 3160 | 3120 | 2120 | 5160 |
| - Sub-bit. coal | 370 | 96 | 132 | 720 |
| Pulverised coal combustion | 0.005 | 0.0007 | 0.004 | 0.076 |

Depending on the gas phase, temperature and the ash content of the fuel, the PAH compounds are partitioned between the gas phase and the particulate phase. For wood and peat firing units the distribution of PAH compounds between gas phase and particulate phase was given by Huotari and Vesterinen (1995), as in Table 6.10:

Table 6.10 *Gas phase and particulate phase PAH from wood and peat firing (from Huotari and Vesterinen, 1995)*

| | Particulate-bound PAH ($\mu\text{g}/\text{mg}$ solid) | Particulate-bound PAH ($\mu\text{g}/\text{m}^3_{\text{STP}}$) | Gas phase PAH ($\mu\text{g}/\text{kg}$ gas) | Gas phase PAH ($\mu\text{g}/\text{m}^3_{\text{STP}}$) | Particulate concentration ($\mu\text{g}/\text{m}^3_{\text{STP}}$) |
|-------------------------|--|---|--|---|---|
| 10 MW saw waste, grate | 0.002-0.004 | 0.45-13.1 | 4.5-7.4 | 5.8-9.6 | 188-316 |
| 7 MW peat, grate | 0.0001-0.00015 | 0.09-0.15 | 1-2 | 1.3-2.6 | 600-1467 |
| 5 MW peat, gasification | 0.13-1.9 | 16-90 | 0.85-32 | 1.1-41.5 | 28-144 |
| 65 MW peat, FBC | 0.009-0.15 | 0.31-3.2 | 19.5-140.7 | 25.3-183 | 7.6-52 |
| 25 MW peat, Stoker | 0.4-4.5 | 15.7-359 | 267-707 | 316-919 | 40-80 |
| 25 MW wood, batch | 4.3-11.5 | 518-923 | 5044-9003 | 6557-11704 | 80-120 |

PAHs are also emitted in significant amounts from engines. An analysis on emissions from traffic in the San Francisco Bay Area addressed the emission on PAHs and “black carbon” particulates from light duty gasoline and heavy duty diesel vehicles (Miguel *et al.*, 1998). It was found that heavy duty diesel engines (mainly trucks) emit ~ 1440 mg/kg fuel carbonaceous particles with sizes up to 2 µm and ~ 1300 µg/km lighter PAHs (pyrene, fluoranthene). Gasoline-fueled cars emit ~ 30 g/kg fuel carbonaceous particles with sizes up to 0.12 µm and ~ 100 µg/km of both light and the more hazardous heavier PAHs (benzo(a)pyrene, dibenz(a,h)anthracene). Kado *et al.* (2000) measured PAHs from outboard marine engines and found mostly the lighter PAHs pyrene and fluoranthene. Two-stroke engines emitted 25-50 times more than four-stroke engines.

For PAH emission control, one option is to optimise the process (primary measures) as to reduce the formation of these compounds. Higher gas temperatures, sufficient excess air (for combustion processes) and scale-up can be considered. For engines, fuel injection systems have already showed to reduce the unburned fuel, VOC, PAH and soot emissions as a result of finer spraying and more controlled fuel feeding.

For gas cleanup purposes, thermal or catalytic oxidation is an option, although catalysts may be easily deactivated by these heavy hydrocarbons. Very well suitable for PAHs are activated carbon bed absorbers (7 section 6.4, Brüggendick and Gilgen, 1996). If only purely hydrocarbon PAHs are adsorbed, a saturated or end-of-life carbon filter may eventually be incinerated, thereby destroying the PAHs.

6.6 Soot

Soot can be defined as agglomerates of carbonaceous particles of 10-80 nm, forming “clusters” that can be larger than 10 µm, composed of thousands of particles. They are mainly composed of carbon, with some absorbed hydrocarbons, sulphur and nitrogen compounds and trace elements. A TEM (transmission electron microscope) image of a diesel engine soot is shown in Figure 6.9, containing 55-80%-wt elemental carbon + organic carbon, but only 0.02-0.04 %-wt PAHs (Shi *et al.*, 2000).

An extensive analysis on soot formation was given by Haynes and Wagner already twenty years ago (Haynes and Wagner, 1981). Flagan and Seinfeld (1988) describe soot as “Carbonaceous particles (...) produced in the combustion of gaseous fuels and from the volatilised components of liquid and solid fuels”. In short, two routes may lead to the formation of soot, depending on the type of fuel.

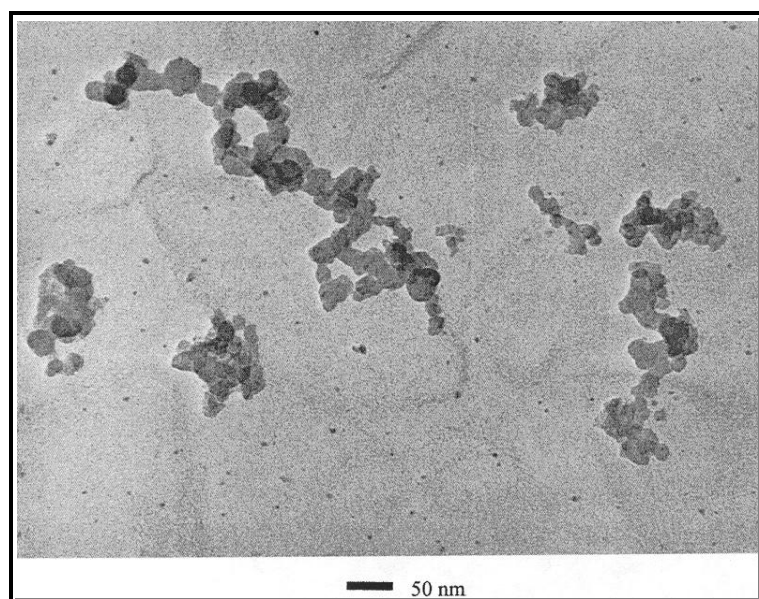


Figure 6.9 Soot particles from a diesel engine (picture from Shi *et al.*, 2000)

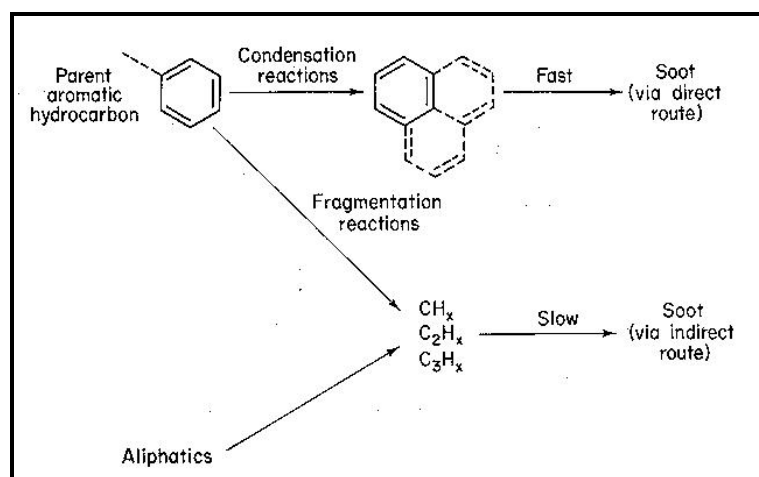


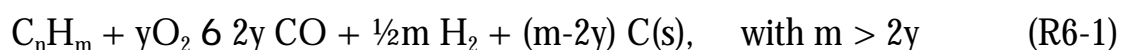
Figure 6.10 Simplified scheme for soot formation (picture from Flagan and Seinfeld, 1988)

For gaseous or light fuel oils containing mainly aliphatics, high temperatures may result in the formation of acetylene (ethyne, C_2H_2) which can “polymerise” via poly acetylenes to form soot. This route is also possible for kiln combustion processes where high temperatures, up to 1600EC may occur locally.

Heavier fuels such as coal and heavy fuel oil contain more aromatics and will form soot by condensation reactions and other processes that have the aromatics as the starting point. Tars (see next section) can be a reaction intermediate here as well. (Flagan and Seinfeld, 1988, Brown, 1997).

A simplified reaction scheme for soot formation is shown in Figure 6.10.

In short, the chemistry of soot formation during sub-stoichiometric stages of combustion can be written as



Soot formation can be prevented by controlled turbulent mixing, and by additives such as iron, nickel, manganese or cobalt, that promote (*i.e.* catalyse) soot oxidation. These soot-reducing fuel additives may, however, increase the soot production as well (Feitelberg *et al.*, 1993).

Soot is a very important species for a combustion process: it plays an important role in radiative heat transfer. It should, however, be oxidised before leaving a furnace or boiler. Still, much is unknown about the formation and oxidative destruction of soot.

For diesel engines, soot formation is closely linked to fuel type, fuel/air mixing and cylinder wall temperature. Other factors are the conditions and mixing during the ignition delay, *i.e.* the time between fuel injection and ignition (Kamimoto and Kobayashi, 1991).

Soot is also formed from polymers/plastics, typically 1 ~ 100 mg/kg polymer depending on temperature and air factor. Polystyrene gives much more soot than polymers like polyethene, polypropene or polymethyl methacrylate. Very small amounts of soot are generated from PVC, which may be due to the release of HCl acting as a flame retardant, *i.e.* delaying the ignition (Shemwell and Levendis, 2000).

Options for the control of soot are basically the same as for PAHs: thermal or catalytic oxidation or removal by a carbon filter. Also a particulate control system will collect soot up to some extent, where it will then present itself as carbon in fly ash.

For gasoline fired engines soot emissions are negligible, whilst for diesel engines it is a serious problem. Recent studies indicate that the soot generated by bio-diesel fueled diesel, resulting from incomplete burnout of PAHs and tars, is carcinogenic as well.

A very powerful solution to this is the so-called CRT (Continuously Regenerating Trap) system shown in Figure 6.11. Hydrocarbon and CO are oxidised by 80-90%, “carbon” (*i.e.* soot) particles are removed by more than 90%. It is based on the principle that carbonaceous particles are collected on a particle filter, where they are oxidised at ~ 250EC by NO₂. This NO₂ is produced by oxidising part of the exhaust gas NO in the catalyst system just upstream of the filter (CRT, 2000).

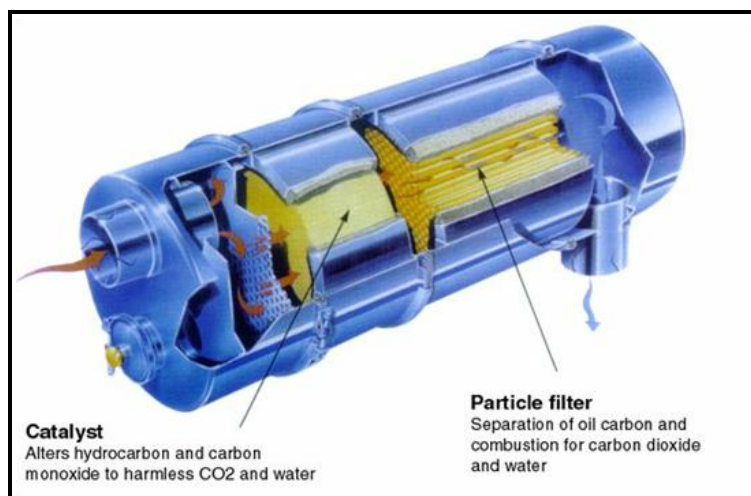


Figure 6.11 CRT filter for diesel vehicles (picture from CRT, 2000)

6.7 Tar

Tar can be defined as condensable organic compounds, which requires the temperature to be further specified for a given application or situation. One method for separating tar from soot is to analyse a solid/condensate sample obtained from a sub-micron filter followed by a dichloromethane (CH_2Cl_2) trap, both operated at 0EC. “Tar” can be taken as the part that is soluble in the CH_2Cl_2 , and “soot” as the part that is not (e.g. Feitelberg *et al.*, 1993).

As was mentioned above, “tar” is a mixture of mainly aromatics such as benzene, toluene, phenol, pyridines, thiophenes and 2-4 ring PAHs such as naphthalene and anthracene. These are formed during pyrolysis or gasification of solid fuels. Depending on the fuel and the process conditions (temperature and gas phase) and reactor type the amounts of phenolic compounds *versus* hydrocarbon aromatics and PAHs can vary widely. For example, Simell (1997) distinguishes “low temperature tar” which is formed at temperatures below 650EC and consists mainly of the primary decomposition products of the fuel, and “high temperature tar”, mainly mono- and polycyclic aromatic compounds, formed by secondary reactions between primary pyrolysis products. Considering then different gasification reactors (7 chapter 2), low temperature tar is obtained from updraft gasifiers, whilst high temperature tar is produced in downdraft, fluidised bed and entrained flow gasifiers.

Currently, tar is receiving a lot of attention in connection with gasification systems for biomass fuels, using air-blown or sometimes steam/oxygen blown fluidised bed gasifiers. Typically these produce fuel gases with several $\text{g}/\text{m}^3_{\text{STP}}$ tar, for wood being an order of magnitude higher than for peat or coal - see Figure 6.12.

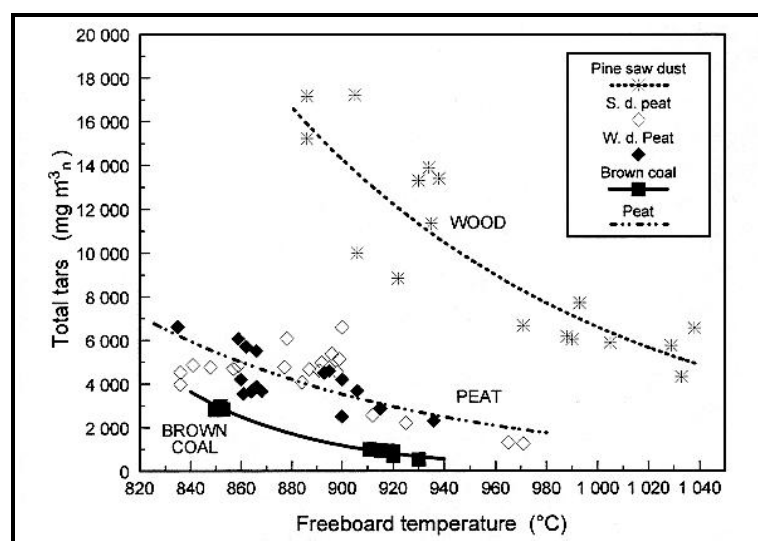


Figure 6.12 Tar production in an air-blown FB gasifier (picture from Simell, 1997)

Some more detail as to what these tars consist of is given in Figure 6.13. For coal and peat, benzene and naphthalene are the major species, for tar from wood and biomass the higher oxygen content gives more phenolic species.

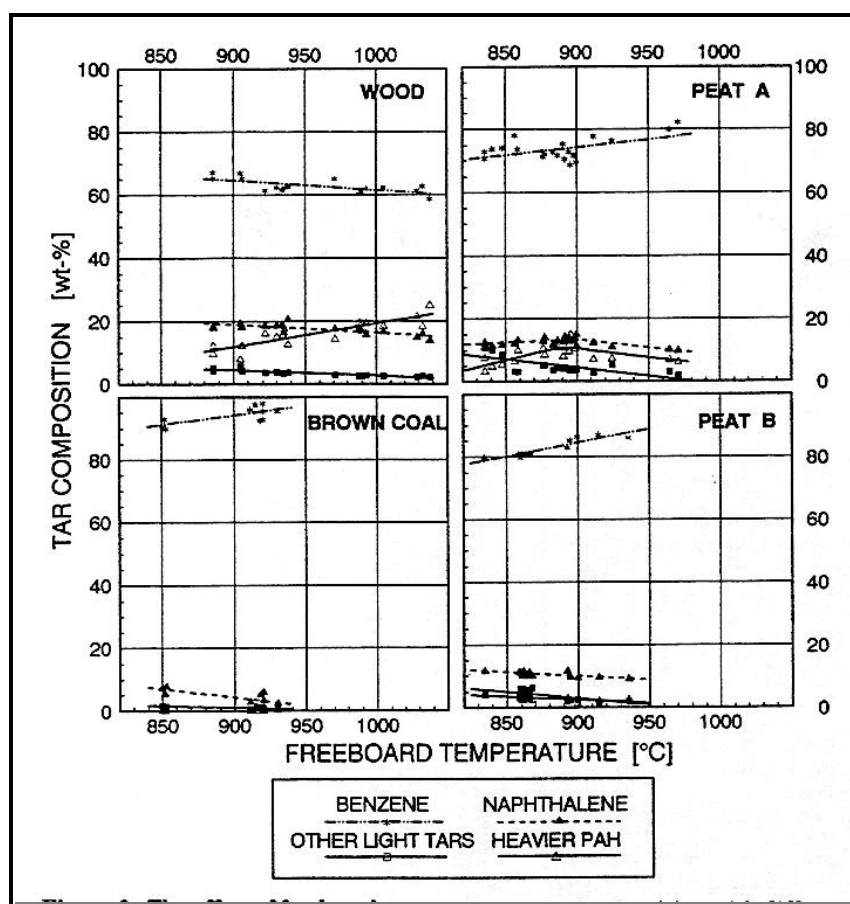
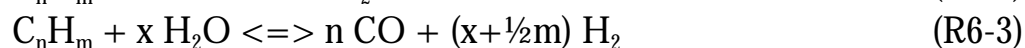


Figure 6.13 Effect of FB gasifier freeboard temperature on tar composition for various fuels (picture from Simell *et al.*, 1992)

The amount of tar in the gas depends very much on the air factor (stoichiometry) during gasification. For FB gasification of biomass the optimal range of operation is roughly from air factor ~ 0.18 until ~ 0.45 : operating below ~ 0.18 gives pyrolysis instead of gasification, and operating above ~ 0.45 results in a low quality (low calorific) fuel gas.

At relatively low temperatures (say, below 850EC) an FB biomass gasifier should be operated at

air factors 0.3 \sim 0.4 to compensate for high tar yields, while operating at ~ 900 EC allows for air factors below ~ 0.25 (Narváez *et al.*, 1996). At increased temperatures, tar cracking and steam reforming reactions become more important:



There are several reasons for removing tar from biomass gasifier product gas, depending on the application. Firing the raw gas in an engine or gas turbine is not possible at these high tar loads, which may result in excessive soot formation, fouling and NO_x formation (from the pyridines and other nitrogen species in the tar). Catalytically active materials for tar cracking have been tested which can be present in the gasifier fluidised bed, or in a separate reactor downstream. As argued by Corella *et al.*, (1999b) this doesn't give much different results (when using a dolomite as tar cracking agent), both for gasification in air or with steam/oxygen mixtures.

A comparison between catalyst for tar removal from a typical biomass FB air gasification gas is shown in Figure 6.14.

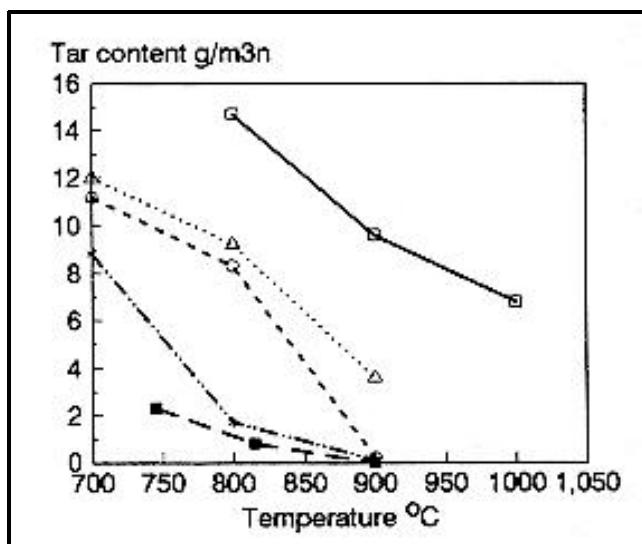


Figure 6.14 Tar cracking efficiency of different catalysts based on 42 g/m³ tar inlet concentration. □ = SiC, △ = Fe sinter, ○ = limestone, • = Fe-dolomite, ■ = Ni-1301. (picture from Leppälähti *et al.*, 1991)

Currently two materials are considered suitable catalysts for this purpose, being dolomites or Ni-based catalysts. The latter show a somewhat better performance. When steam/water gasification is applied the tar cracking efficiency of a dolomite can be ~ 97-99%, and can be below 95% for air gasification due to a different chemical composition of the tar. (Orio *et al.*, 1997). For high temperature gasification (~ 900°C) better performance will be possible with dolomites. Corella *et al.* (1999a) and Caballero *et al.* (2000) claim that better results may be obtained with commercial nickel-based catalysts that are

widely used for steam reforming of heavier hydrocarbons and naphtha. For these catalyst there is a risk of fouling by the tar when its inlet concentration is higher than ~ 2 g/m³_{STP}.

A side-issue in relation to this is the sampling and analysis of tars; progress made by international cooperation can be found on the internet (TarWeb).

6.8 CO

The oxidation of CO occurs mainly via the reaction



which may be relatively slow as a result of mixing limitations, *i.e.* the “unmixedness” that affects non-first order reactions. CO can be more rapidly oxidised to CO₂ by using a Pd or Pt containing catalyst of a monolith type, similar to VOC catalytic

oxidation. An example is CO oxidation in a three-way catalyst for gasoline-fuelled engines. Also methods based on (catalytic) oxidation with ozone (O₃) have been developed.

Alternatively, CO may be converted by the CO/water shift reaction:



which has its equilibrium to the right-hand product side (*i.e.* $\Delta G < 0$) for temperatures below $\sim 820^\circ\text{C}$. Combining this with removal of CO₂ (L chapter 9) gives a method of separating H₂, to be used for electricity generation in a fuel cell (7 chapter 2) from CO in a gasifier product gas.

6.9 References

- Acid News (1999) Swedish NGO secretariat on acid rain, Gothenburg, Sweden, Vol 3/Oct. 1999
- Acid News (2001) Swedish NGO secretariat on acid rain, Gothenburg, Sweden, Vol 1/Mar. 2001
- Alvarez Cuenca, M., Anthony, E.J. (1995) "Pressurised fluidised bed combustion", Blackie Academic & Professional, Glasgow, UK
- Borman, G.L., Ragland, K.W. (1998) "Combustion engineering", McGraw-Hill, New York
- Brown, A.L. (1997) "Modelling soot in pulverised coal flames" MSc thesis Brigham Young University, Utah
- Brüggendick, H., Gilgen, R. (1996) "Adsorption technology brings waste incinerators into compliance - STEAG's /a/c/t™ process in European facilities" ACS Division of Fuel chemistry, Vol. 41 No. 1 (211th ACS National Meeting, New Orleans (LA), March 1996) pp. 399-403
- Caballero, M.A., Corella, J., Aznar, M.-P., Gil, J. (2000) "Biomass gasification with air in a fluidised bed. Hot gas cleanup with selected commercial and full-size nickel based catalysts" *Ind. & Eng. Chem. Res.* **39** 1143-1154
- Chagger, H.K., Jones, J.M. Pourkashanian, M., Williams, A. (2000) "The formation of VOC, PAH and dioxins during incineration", *Trans IChemE* **78(B)** 53-59
- Cooper, C.D., Alley, F.C. (1994) "Air pollution control", 2nd Ed. Waveland Press, Illinois, Chapters 11 & 12
- Corella, J., Orio, A., Toledo, J.-M. (1999a) "Biomass gasification with air in a fluidised bed: exhaustive tar elimination with commercial steam reforming catalysts" *Energy & Fuels* **13** 702-709
- Corella, J., Aznar, M.-P., Gil, J., Caballero, M.A. (1999b) "Biomass gasification in fluidised bed: where to locate the dolomite to improve gasification?" *Energy & Fuels* **13** 1122-1127
- CRT (2000?) "CRT filter for diesel vehicles" from <http://www.kjeldsentransport.dk>
- Feitelberg, A.S., Longwell, J.P., Sarofim, A.F. (1993) "Metal enhanced soot and PAH formation" *Comb. & Flame* **92** 241-253

- Finland (1994) Government decision 626/1994 (1.8.1994)
- Flagan, R.C, Seinfeld, J.H. (1988) "Fundamentals of air pollution control engineering", Prentice-Hill, New Jersey, Chapter 7
- Foster Wheeler (1997) Heat Engineering, Spring 1997
- Haynes, B.S., Wagner, H. Gg. (1981) "Soot formation" *Progr. Energy Comb. Sci.* 7 229-273
- Heywood, J.B. (1988) "Internal combustion engine fundamentals" McGraw-Hill, New York
- Huotari, J., Vesterninen, R. (1995) "Muut polton päästöt", Chapter 11 in: "Poltto ja palaminen", R. Raiko, *et al.*, (Eds.), IFRF Finland, Gummerus, Jyväskylä, Finland
- Kado, N.Y., Okamoto, R.A., Karim, J., Kuzmicky, P.A. (2000) "Airborne particle emissions from 2- and 4-stroke outboard marine engines: polycyclic aromatic hydrocarbon and bioassay analyses" *Environm. Sci. Technol.* 34 2714-2720
- Kamimoto, T., Kobayashi, H. (1991) "Combustion processes in diesel engines" *Progr. Energy Combust. Sci.* 17 163-189
- Koltsakis, G.C., Stamatelos, A.M. (1997) "Catalytic automotive exhaust aftertreatment" *Progr. Energy Combust. Sci.* 23 1-39
- LaGrega, M.D., Buckingham, P.L., Evans, J. (1994) "Hazardous Waste Management", McGraw-Hill, Chapter 12 : "Thermal treatment"
- Leppälahti, J., Simell, P., Kurkela, E. (1991) "Catalytic conversion of nitrogen compounds in gasification gas" *Fuel Proc. Technol.* 29 43-56
- Mastral, A.M., Callén, M.S. (2000) "A review on polycyclic aromatic hydrocarbon (PAH) emissions from energy generation" *Environm. Sci. Technol.* 34(15) 3051-3057
- McConville, A. (1997) "Emission standards handbook 1996: air pollutant standards for coal-fired plants" IEA Coal Research, report IEACR/96, London, UK
- Migule, A.H., Kirchstretter, T.W., Harley, R.A., Hering, S.V (1998) "On-road emissions of particulate polycyclic aromatic hydrocarbons and black carbon from gasoline and diesel vehicles" *Environm. Sci. Technol.* 32 450-455
- Narváez, I., Orio, A., Aznar, M.P., Corella, J. (1996) "Biomass gasification with air in an atmospheric bubbling fluidised bed. Effect of six operational variables on the quality of the produced raw gas" *Ind. & Eng. Chem. Res.* 35 2110-2120
- Orio, A., Corella, J., Narváez, I. (1997) "Performance of different dolomites on hot raw gas cleaning from biomass gasification with air" *Ind. & Eng. Chem. Res.* 36 3800-3808
- Parvesse, T. (2000) "What are the options to control VOC emissions?", *Hydrocarb. Proc.* 79(8) August 2000
- Ruddy, E.N., Carroll, L.A. (1993) "Select the best VOC control strategy", *Chem. Eng. Proc.*, July 1993, 28-35
- Saracco, G. (1999) "Coupling catalysis and high temperature resistant filters", in: "High temperature gas cleaning", Vol. II, 1999, A. Dittler, G. Hemmler, G. Kasper (Eds.), University of Karlsruhe, Germany, pp. 627-640
- Shemwell, B.E., Levendis, Y.A. (2000) "Particles generated from combustion of polymers", *J. Air & Waste Assoc.* 50 94-102
- Shi, J.P., Mark, D., Harrison, R.M. (2000) "Characterisation of particles from a current technology heavy-duty diesel engine" *Environm. Sci. Technol.* 34(5) 748-755
- Simell, P. (1997) "Catalytic hot gas cleaning of gasification gas" PhD thesis, VTT Technical Research Centre of Finland, VTT Publications 330, Espoo, Finland

- Simell, P., Kurkela, E., Ståhlberg, P. (1992) "Formation and catalytic decomposition of tars from fluidisedbed gasification" in: Bridgwater, A.V.(ed.) Proc. of the conf. Advances in Thermochemical Biomass Conbersion, Interlaken, Switzerland, May 1992. Vol 1. Blackie Academic & Professional, Glasgow, UK, pp. 265-279
- TarWeb <http://www.tarweb.net>
- UN (1998) "Draft protocol to the convention of longe-range transboundary air pollution on persistent organic pollutants" United Nations, Economic and social council, report EB.AIR/1998/2, Århus, Denmark, June 24, 1998
- Werther, J. (1999) "Legal requirements on gaseous emissions from waste combustion and are these fulfilled?" lecture at 1999 Finnish Waste-to-Energy course, Part 2, Turku, Finland, Oct. 1999
- WHO (1996) "Updating and revision of the air quality guidelines for Europe"; World Health Organisation, Regional office for Europe, Copenhagen, Denmark, Report EUR/ICP/EHAZ 94 05/MT12
- Wilén, C. (1999) "Production of refuse-derived fuels" lecture at 1999 Finnish Waste-to-Energy course, Part 1, Espoo, Finland, Oct. 1999
- Ågren, C., Elvingsom, P. "Still with us - the acidification of the environment is still going on", The Swedish NGO Sectretariat on Acid Rain, Gothenburg, Sweden (1997)

