VOCs, PAHs, soot, tar, CO

- Definitions
- Volatile organic compounds (VOCs) and ground-level ozone
- Control of VOCs
- Formation and control of polycyclic aromatic compounds (PAHs)
- Formation and control of soot
- Formation and control of tar (from biomass gasification)
- CO

see: www.hut.fi/~rzevenho/gasbook

Definitions of VOCs, PAHs, tar, soot, *etc.*

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	**condensible 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 *et al.*, 1994)

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	

VOCs of interest for thermal power industry

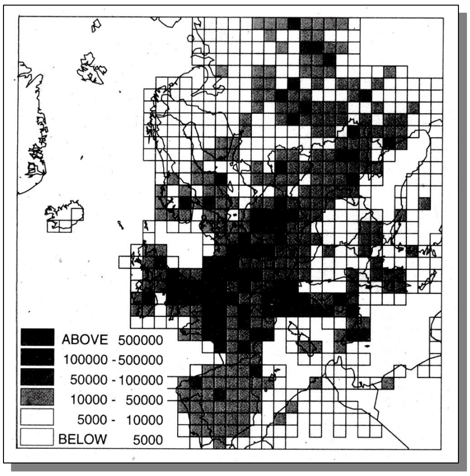
(based on 1990 US Clean Air Act)

Emission standards: CO and THC, TOC

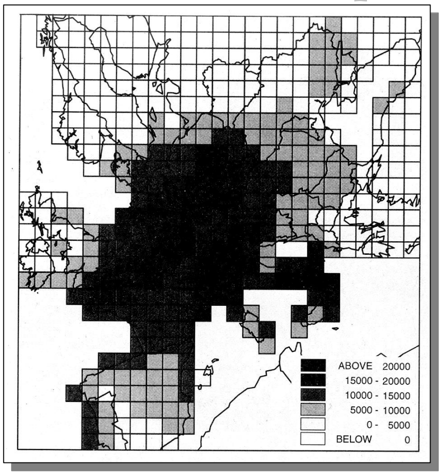
	Power plant Finland (1990+)	MSW incinerator Finland (1994)	MSW incinerator EU (2000)	Power plant Germany (1999)	MSW incinerator Germany (1999)	Hazardous waste incinerator EU (1996)	Waste incinerator USA (1995)
CO	no limit	50	50	250	50	50	76.31
THC	no limit	10	10	20	10	10	no limit

(mg/m$^3_{STP}$ @ 11 % O_2, dry)

VOCs and ground-level ozone in Europe



VOC emissions (incl. methane) in Europe, 1994 (tonnes)



Ground-level ozone in Europe, 1994 (ppb-h above 40 ppb)

VOC emissions from waste incineration plants,

in mg/m³ at 10% CO_2

	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

Lower and upper flammability limits (LFL & UFL) for organic gaseous compounds

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
Benzlyl 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 *m- or p-*	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

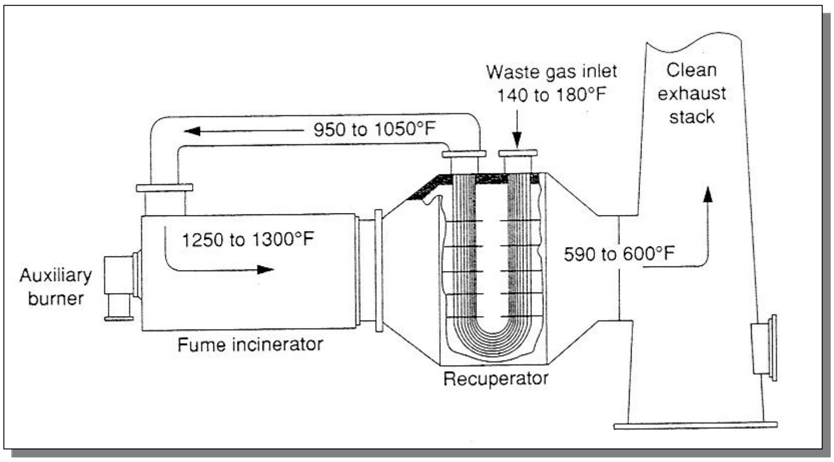
Options for VOC control, and comparison

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

1 cfm = 1 cubic feet / min, 1 m_{STP}^3/min = 35.3 scfm

Thermal VOC incinerator with heat recuperation



150EF=66EC, 600EF=316EC, 1000EF =538EC, 1300EF=704EC

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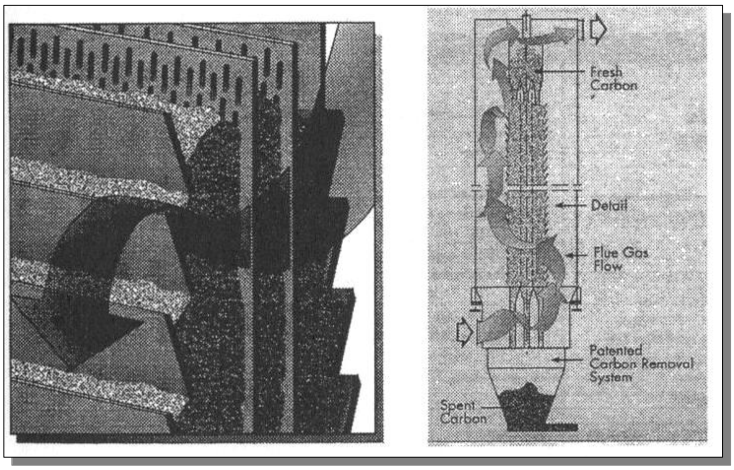
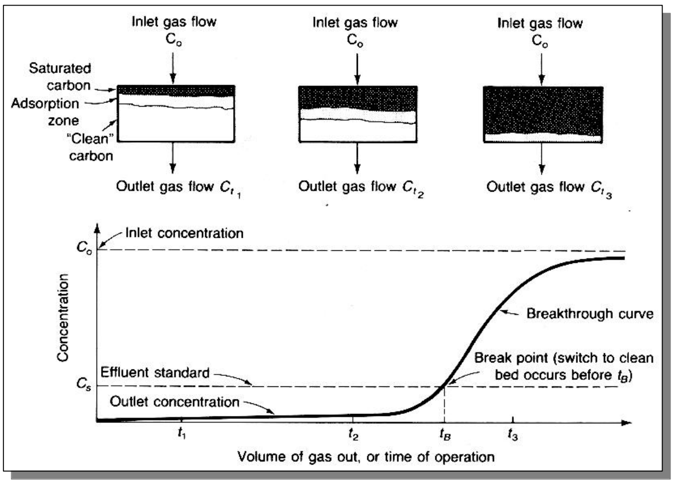
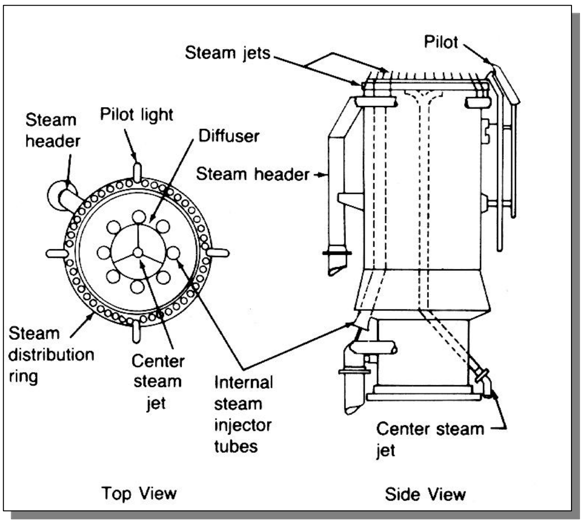
VOCs removal by active carbon beds #1 STEAG a/c/t™ system



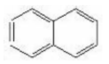
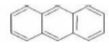
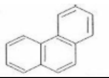
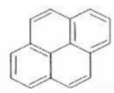
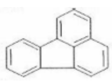
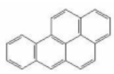
VOCs removal by active carbon beds #2 : breakthrough curve



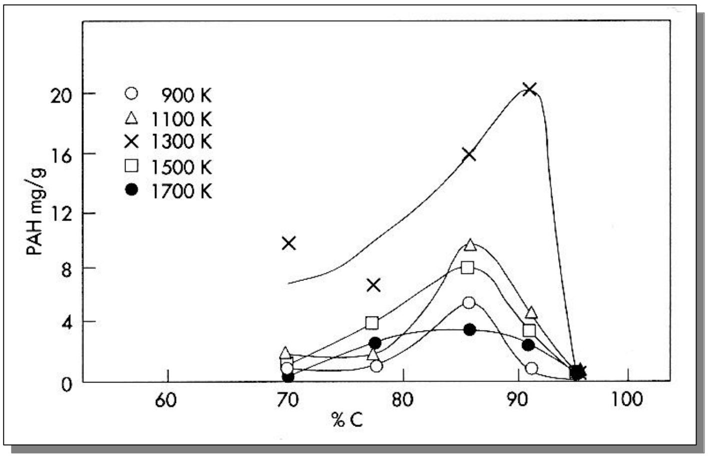


Flare tip combustor for concentrated VOCs

Polycyclic aromatic hydrocarbons (PAHs)

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

PAH formation during coal pyrolysis



coal pyrolysis in nitrogen, 0.3 sec.

PAH and BaP emissions from various furnaces: larger furnaces give less PAHs

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

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Effect of fuel type and furnace type on PAH emissions

	Methyl anthracene and/or fenanthrene (µg/MJ)	Fluoranthene (µg/MJ)	Pyrene (µg/MJ)	Fenanthrene and/or anthracene (µg/MJ)
Pyrolysis - Montana lignite - High vol. bit. coal	 5890	 1720 6320	 2710 11680	 10950 1900
Grate firing 200 kW - High vol. bit. coal - Sub-bit. coal	 3160 370	 3120 96	 2120 132	 5160 720
Pulverised coal combustion	0.005	0.0007	0.004	0.076

Gas phase and particulate phase PAH from wood and peat firing

	Particulate-bound PAH (µg/mg solid)	Particulate-bound PAH (µg/m³STP)	Gas phase PAH (µg/kg gas)	Gas phase PAH (µg/m³STP)	Particulate concentration (µg/m³STP)
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

PAH emissions control

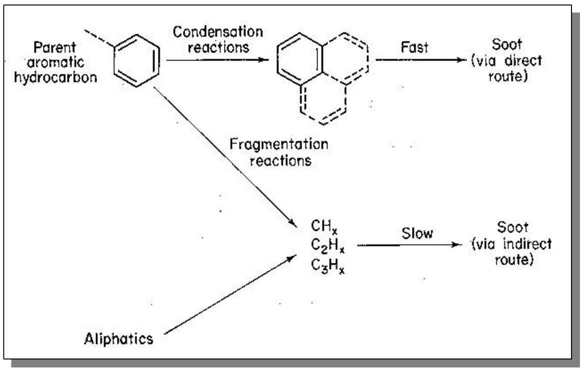
- Thermal oxidation
  (problem : low concentration)
- Catalytic oxidation
  (problem : low concentration, catalyst fouling)
- Catalytic cracking
  (problem : catalyst fouling)
- Adsorption on activated carbon bed
  (the saturated/spent bed can be incinerated !!)

Soot

$C_nH_m + yO_2$ ®

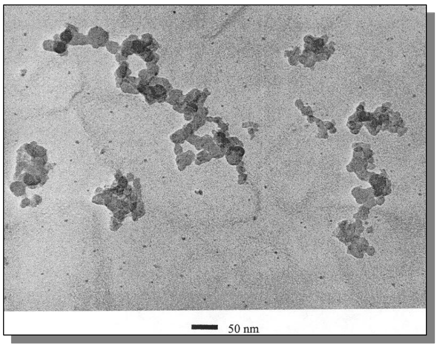
$2y\,CO + ½m\,H_2 + (m-2y)\,C(s)$

with $m > 2y$



- Routes for soot formation

Diesel engine exhaust soot ®



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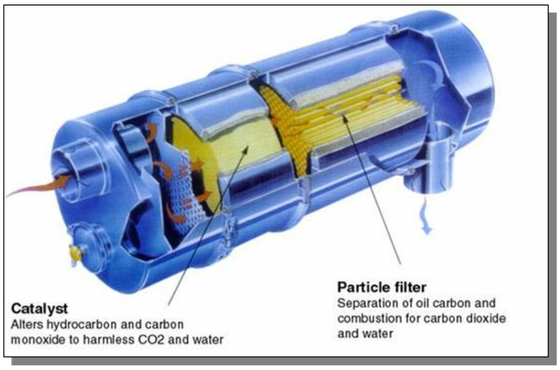
Soot emissions control

See PAHs : thermal or catalytic oxidation, catalytic cracking, adsorption on activated carbon bed, soot-reducing agents (Fe, Ni, Co, Mn)

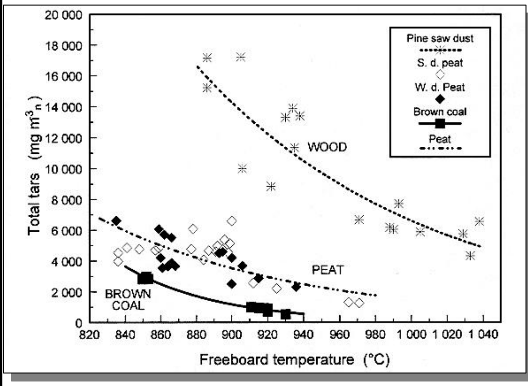
Diesel exhaust gas Continuously Regenerating Trap (CRT) :

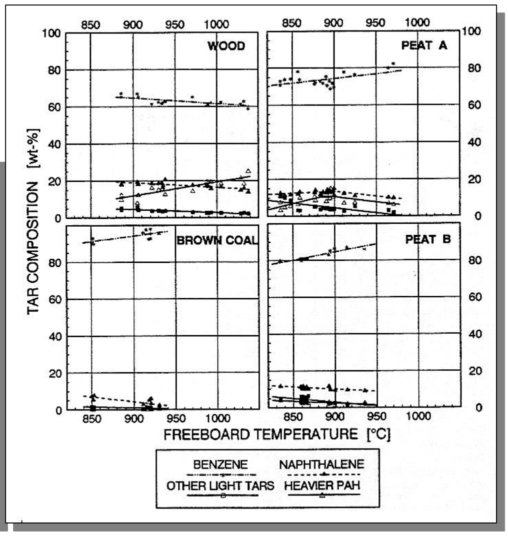
$NO + ½O_2$ ® NO_2

$NO_2 + C(s)$ ® $½N_2 + CO_2$

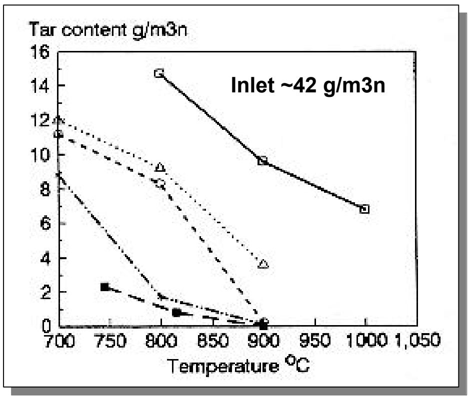


TAR from FB gasification





Cracking of tar from FB biomass gasification



ð = SiC, • = Fe-dolomite, Δ = Fe-sinter,
O = limestone, ■ = Ni-1301

Thermal cracking

C_nH_m <=> nC+ ½m H_2

Steam reforming

C_nH_m + x H_2O <=>
n CO + (x+½m) H_2

CO oxidation

- CO emissions result of low temperature zones ("frozen" CO oxidation), sub-stoichiometry, or bad mixing (sensitive to "unmixedness" due to non-first order kinetics)
- Note: CO is oxidised via $CO + OH \rightarrow CO_2 + H$
- thermal oxidation (if concentration allows),or catalytic oxidation (Pt, Pd, Rh)
- $H_2O + CO \Leftrightarrow CO_2 + H_2$ (*e.g.* for fuel cells)