

# Chapter 7

## Real Fuel Combustion and Air Emissions

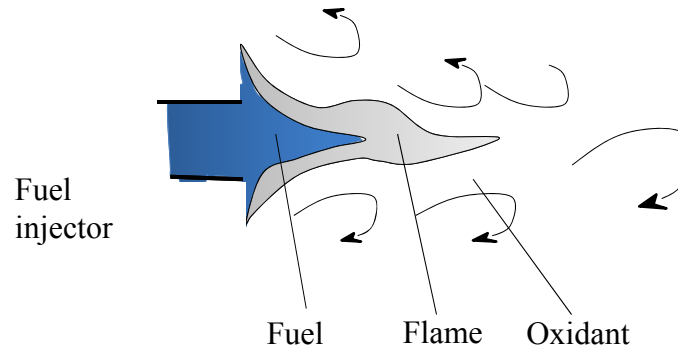
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## Fuels

- Gaseous Fuels
  - Natural gas
  - Biogas
  - Hydrogen
- Solid Fuels
  - Coals
  - Biomass / Wood Pellets
- Liquid Fuels
  - Liquid fossil fuels: Diesel, gasoline, etc.
  - Liquid biofuels: Biodiesel, bioethanol, etc.

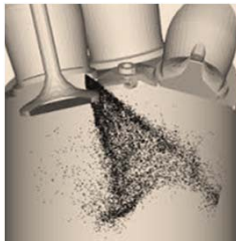
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## Gaseous fuel flame



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## Liquid Droplet Combustion



### 3 Steps

1. Liquid spray (atomization)
2. Droplet vaporization
3. Vapor combustion

- **Droplet vaporization**

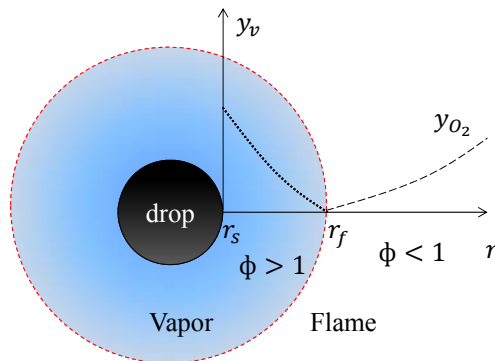
$$q' = c_p(T_v - T_0) + h_{fg}$$

- $c_p$  is the specific heat of the fuel
- $T_v$  is the vaporization temperature for the liquid fuel(K)
- $T_0$  is the initial temperature when the droplets are sprayed into the combustion system
- $h_{fg}$  is the latent heat of vaporization of the fuel (J/mole).

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## Droplet vaporization

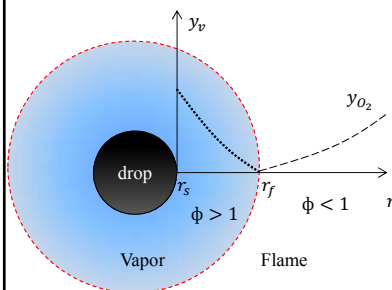
$$\dot{m}_v = \rho_v u 4\pi r^2 = \rho_v u_s 4\pi r_s^2$$



- $\dot{m}_v$  is the vaporization rate (kg/s); it is also the loss rate with respect to the liquid droplet.
- $\rho_v$  is vapor density,
- $u_s$  is the vapor speed leaving the surface and
- $r_s$  is the radius of the droplet.
- $4\pi r_s^2$  is the surface area of the droplet sphere.

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## Droplet vaporization



$$\dot{m}_v = \rho_v u 4\pi r^2 = \rho_v u_s 4\pi r_s^2$$

Assuming that only conductive heat transfer dominates and that the radial profiles of temperature and compositions are quasi-steady, the change of the droplet diameter can be related to the heat transfer from the surrounding to the droplet surface with. Conservation energy for the droplet leads to

$$\dot{m}_v c_p (T - T_v) + \dot{m}_v h_{fg} = 4\pi r^2 k \frac{dT}{dr}$$

$T$  is the temperature at  $r$ ,  $k$  is the thermal conductivity of the liquid droplet at the surface. LHS is the energy for liquid evaporation and RHS is for the heat transfer by conduction

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$$\dot{m}_v(1 - f_v) = -4\pi r^2 \rho_v D \frac{df_v}{dr}$$

$$\frac{1}{2}(r_{s0}^2 - r_s^2) = \frac{tk}{\rho_l c_p} \ln \left[ 1 + \frac{c_p(T_\infty - T_s)}{h_{fg}} \right]$$

$$t_e = \frac{r_{s0}^2}{\frac{2k}{\rho_l c_p} \cdot \ln \left[ 1 + \frac{c_p(T_\infty - T_s)}{h_{fg}} \right]}$$

- The lifetime of the droplets increases with their sizes, and it is in the order of millisecond.
- The life time  $t_e$  is important to characterize the combustion efficiency of atomized liquid fuel droplet and the consequent air emissions.
- If  $t_e$  is longer than the residence time of the combustion system, the droplets will not be burned completely because of incomplete vaporization. As a result, liquid fuel droplets exist in the flue gas (or exhaust). They may be part of the particulate emissions. Meanwhile residual fuel evaporation continues but these extra vapors are not burned at low temperature; this result in extra volatile organic compound (VOC) emissions.
- It is imperative that fine spary droplets favor combustion efficiency and lower the air emissions. However, the upper limit of the droplet size depends on the design of nozzles employed.

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## Solid Fuel Combustion

Properties of typical solid fuels are determined by proximate analysis and ultimate analysis.

- **Proximate Analysis** determines moisture, volatile matter, ash and (in coals and cokes) to rank the fuels by comparing the ratio of combustible to incombustible constituents.
- **Ultimate Analysis**  
Elemental analysis so the simplified chemical formula can be obtained for stoichiometry analysis. ASTM International Standard (MNL 11271 M, Proximate Analysis) specifies how to conduct the proximate analysis of coal. The result separates the products into four groups:  
(1) moisture, (2) volatile matter, (3) fixed carbon, the nonvolatile fraction of coal, and (4) ash, the inorganic residue remaining after combustion.

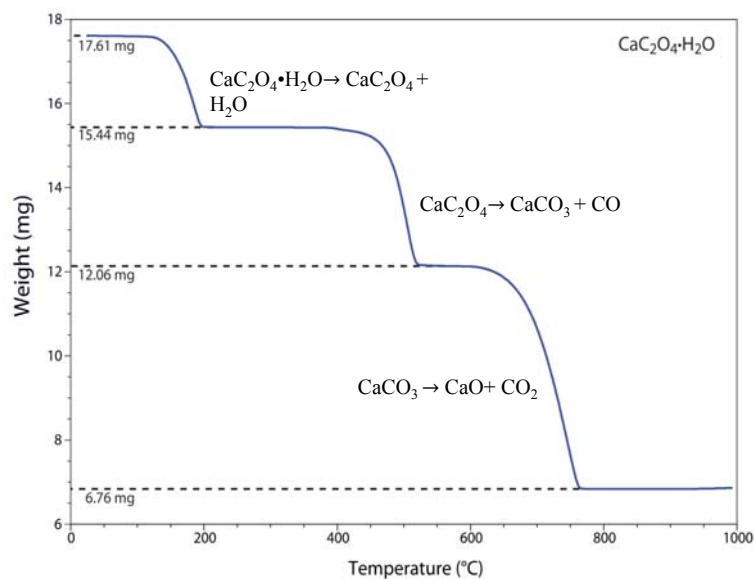
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Coal Rank	Proximate Analysis (wt% as received)			
	Fixed carbon	Volatile matter	Moisture	Ash
Anthracite	81.1	7.7	4.5	6.0
Bituminous	54.9	35.6	5.3	4.2
Subbituminous	43.6	34.7	110.5	11.2
Lignite	27.8	24.9	36.9	10.4

Coal Rank	Ultimate Analysis (wt % moisture and ash free)					Net Heating Value (moisture and ash free) (MJ/kg)
	C	H	O	N	S	
Anthracite	91.8	3.6	2.5	1.4	0.7	36.2
Bituminous	82.8	5.1	10.1	1.4	0.6	36.1
Subbituminous	76.4	5.6	14.9	1.7	1.4	31.8
Lignite	71.0	4.3	23.2	1.1	0.4	26.7

## Thermogravimetric Analysis (TGA)



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	<b>Fuel</b>	<b>Sulphur content, % -wt, dry</b>
Fossil fuels	Coal	0.2-5
	Oil	1-4
	Natural gas	0-10
	Light fuel oil	<0.5
	Heavy fuel oil	<5
	Peat	<1
	Petroleum coke	~5
Biomass	Wood	<0.1
	Straw	~0.2
	Bark	<2

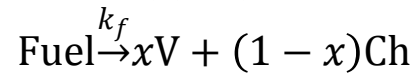
## Coal classification

- Peat
- Lignite coal
- Sub-bituminous coal
- Bituminous coal, and
- Anthracite coal

## Solid Fuel Combustion

The combustion process of these solid particles are modeled by

- devolatilization or pyrolysis,



- volatile combustion, and
- char combustion.

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## Devolatilization or pyrolysis

- $\text{Fuel} \xrightarrow{k_f} xV + (1 - x)Ch$

- $\text{Fuel} \xrightarrow{k_{f1}} x_1V_1 + (1 - x_1)Ch_1$
- $\text{Fuel} \xrightarrow{k_{f2}} x_2V_2 + (1 - x_2)Ch_2$

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## Formation of Air Pollutants

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### Volatile organic compounds (VOCs)

- VOCs are a family of organic compounds that are volatile in nature.
- The organic compounds that are not involved in the formation of smog such as methane, CO, and halogenated organics like 1,1,1- trichloroethane and CFCs are not considered as VOCs.
- Sometimes, polycyclic aromatic hydrocarbon (PAH) naphthalene (boiling point 218 °C) is also referred to as a VOC.

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## Polycyclic Aromatic Hydrocarbon (PAH)

- *“Polycyclic Aromatic Hydrocarbons (PAHs) are a group of semi-volatile organic compounds (SVOCs) that are present in crude oil that has spent time in the ocean and eventually reaches shore and can be formed when oil is burned.” – US EPA definition*
- PAHs mix more easily with oil than water, and less prone to evaporate.
- **Health Impact:** Some compounds are carcinogenic, mutagenic, and teratogenic.

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## PAH as an Air Pollutant

- As an air pollutant, they are mainly adsorbed in particulate matter.
  - In environment, mainly in soil
  - Not much in water or air
- The US EPA has designated 32 PAH compounds as priority pollutants

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## PAHs from Fuel Combustion

- PAHs are produced during combustion when temperature is about 500 to 800 °C, and they are oxidized further above 800°C.
- PAHs are mainly present in the low temperature zone of the flame or a combustion facility due to the poor fuel/oxygen mixing.
- Heavy duty diesel engines mainly found in trucks emit approximately 1300 µg/km of lighter PAHs such as pyrene, fluoranthene, etc.
- Gasoline-fueled cars emit about 100 µg/km of more hazardous heavier PAHs such as benzo(a)pyrene, dibenz(a,h)anthracene, etc.

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## By the way

- High levels of PAHs are found, for example, in grilled or barbecued meat and in **smoked** fish



- *Did you know? The life expectancy in the USA is the shortest in developed nations?*

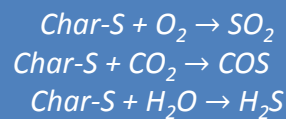
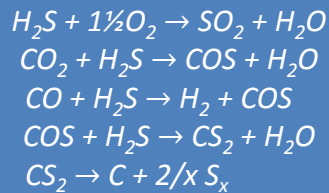
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$\text{SO}_2$  is mainly formed from fuel sulfur

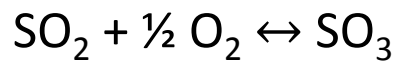
- **Solid fuel Devolatilization**



- **Oxidation**



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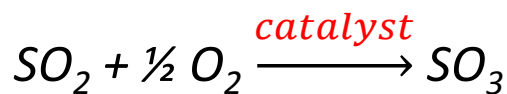


- $\text{SO}_2$  can be oxidized to  $\text{SO}_3$  by
- The van't Hoff equation of the chemical equilibrium constant is

$$K_p = 1.53 \times 10^{-5} \exp\left(\frac{11,760}{T}\right) \quad \text{atm}^{-1/2}$$

- This expression indicates that the concentration of  $\text{SO}_3$  increases with the decreasing combustion temperature. When the temperature is below 900 K,  $\text{SO}_3$  would have been the dominant air pollutant at equilibrium.
- However in a typical flue gas or engine exhaust,  $\text{SO}_2$  is still the dominating air pollutant rather than  $\text{SO}_3$ .
- One of the reasons is that the conversion from  $\text{SO}_2$  to  $\text{SO}_3$  is too slow to reach an equilibrium state. In a typical engineering practice, about 3% of  $\text{SO}_2$  is converted into  $\text{SO}_3$ .

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- Catalysts expedite the reactions, for example,
  - For stationary combustion sources like a coal-fired power plant, there are also various metals in the fuel, and some of them may serve as catalysts for the oxidation of  $SO_2$ .
  - Sulphur in the liquid fuels supplied to automobiles is oxidized to  $SO_2$  in the engine.
  - But in the exhaust  $SO_3$  is present due to the presence of various catalytic metals in the fuel, engine housing, and/or the exhaust treatment systems.

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## NOx

Formula	Name	Properties
$N_2O$	nitrous oxide	colorless gas water soluble
<b>NO</b> $N_2O_2$	nitric oxide dinitrogen dioxide	colorless gas slightly water soluble
$N_2O_3$	dinitrogen trioxide	black solid water soluble, decomposes in water
<b>NO<sub>2</sub></b> $N_2O_4$	nitrogen dioxide dinitrogen tetroxide	red-brown gas very water soluble, decomposes in water
$N_2O_5$	dinitrogen pentoxide	white solid very water soluble, decomposes in water

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## Dominating NO<sub>x</sub>

- Nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>)
- In a typical flue gas, 95% or more of the NO<sub>x</sub> is NO, and the fraction of NO<sub>2</sub> is less than 5%.
- The formation and decomposition of NO is significantly dependent on the combustion process and temperature.

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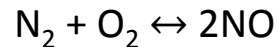
## NO

1. Thermal NO
2. Prompt NO
3. Formation via N<sub>2</sub>O, and
4. Fuel NO

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## Thermal NO

- Thermal NO is formed through the oxidation of  $N_2$  in the air through the following chemical reaction,



- The formation of thermal NO is very sensitive to the combustion temperature,
  - Its formation is negligible when the temperature is 1400 °C or lower.
  - is significant and increases exponentially when the temperature is over 1600 °C.

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## Thermal NO

Reaction	Rate constant
$k_{f1}$ $N_2+O \leftrightarrow NO+N$ $k_{b1}$	$k_{f1} = 1.8 \times 10^8 \exp\left(-\frac{38,370}{T}\right)$
	$k_{b1} = 3.8 \times 10^7 \exp\left(-\frac{425}{T}\right)$
$k_{f2}$ $N+O_2 \leftrightarrow NO+O$ $k_{b2}$	$k_{f2} = 1.8 \times 10^4 T \times \exp\left(-\frac{4,680}{T}\right)$
	$k_{b2} = 3.8 \times 10^3 T \times \exp\left(-\frac{-20,820}{T}\right)$
$k_{f3}$ $N + OH \leftrightarrow NO + H$ $k_{b3}$	$k_{f3} = 7.1 \times 10^7 \times \exp\left(-\frac{450}{T}\right)$
	$k_{b3} = 1.7 \times 10^8 \times \exp\left(-\frac{24,560}{T}\right)$

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## Prompt NO

- Prompt NO is formed only in the combustion zone of the flame where the combustion is incomplete and the hydrocarbon radicals are present.
- The formation of prompt NO does not depend on temperature as significantly as the thermal NO.
- The prompt NO is formed mainly under lower temperature stoichiometric conditions during a short residence time.

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## Fuel NO

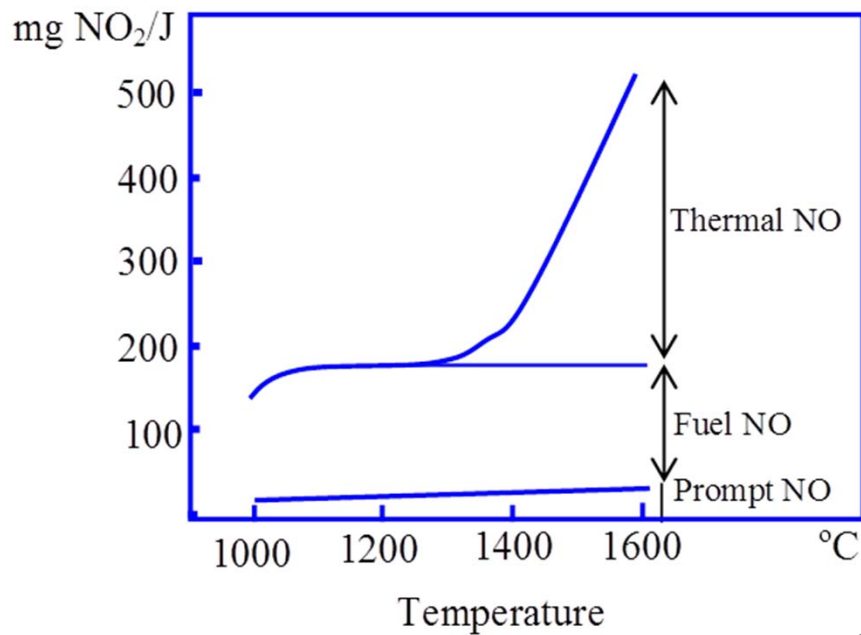
- Approximately 80% of the NO in the flue gas of a coal-firing furnace is produced from fuel nitrogen.
- Fuel NO is sensitive to stoichiometry rather than the temperature because it forms readily at quite low temperatures.

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## Nitrogen in Fuels $\leftrightarrow$ Fuel NO

Fuel	N Content, % -wt, Dry
Coal	0.5-3
Oil	<1
Natural gas	0.5-20
Light fuel oil	~0.2
Heavy fuel oil	~0.5
Peat (young coal)	1-2
Petroleum coke	~3
Wood	0.1-0.5
Straw	0.5-1
Bark	~0.5

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## **N<sub>2</sub>O (Laughing gas)**

- N<sub>2</sub>O is formed through various mechanisms, including oxidation of hydrogen cyanide (HCN) and oxidation of char residue;
- The reaction stops when the temperature is above 950 °C, and the NCO radicals are converted to **NO**

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## **NO<sub>2</sub>**

- NO<sub>2</sub> is formed from NO mainly through the reaction with hydrogen peroxide radical (HO<sub>2</sub>).
- Hydrogen peroxide radical is formed when a hydrogen atom and oxygen reacts in the presence of a third component (M).
- 5% of NO<sub>x</sub> is NO<sub>2</sub>

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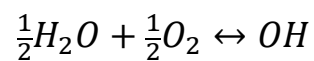
### Carbon monoxide (CO) and Hydrogen Carbon (HC)

- Formation of carbon monoxide and hydrogen carbon is driven by local fuel rich combustion in the flame and imperfect mixing between fuel and oxygen.

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### Carbon dioxide

- CO is converted to CO<sub>2</sub> primarily by
$$CO + OH \leftrightarrow CO_2 + H$$
- and the formation of OH at equilibrium is by



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## Particulate Matter

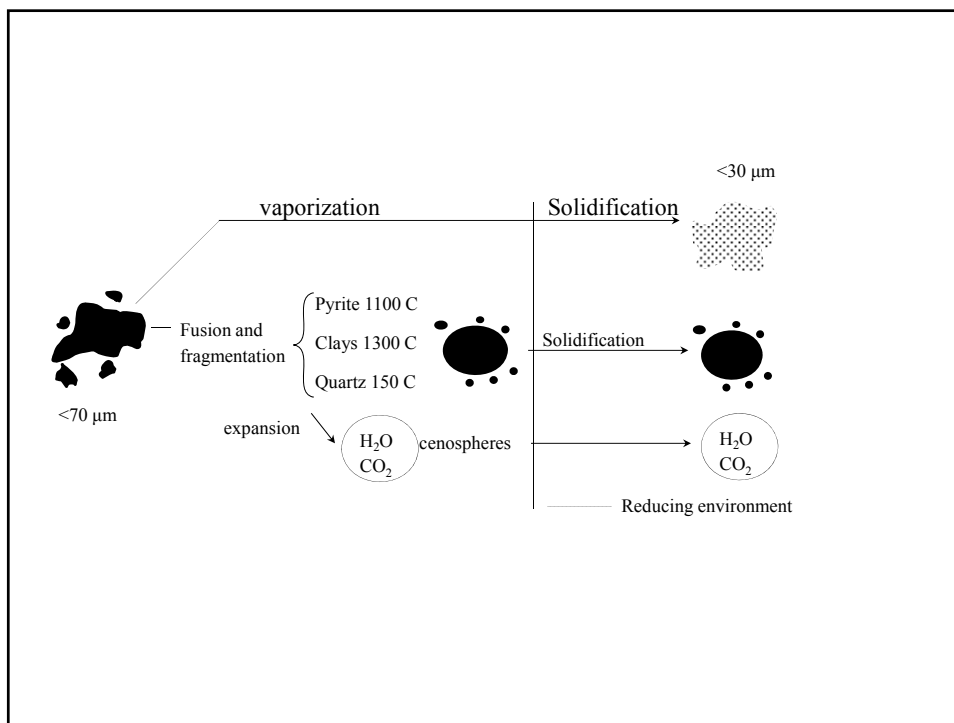
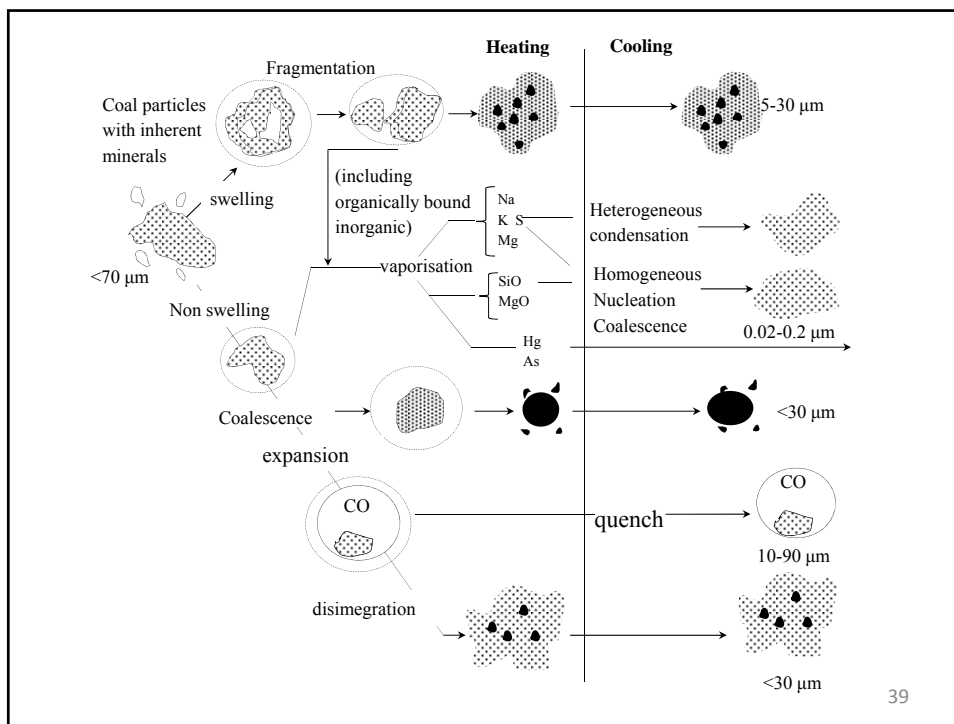
- Particulate matter (PM) is the solid particles or liquid droplets suspended in the air.
- PM<sub>x</sub> – particles with diameter less than x μm
  - e.g. PM<sub>10</sub>; PM<sub>2.5</sub>
- During combustion inorganic minerals in fuel are converted into solid, liquid, and vapors.

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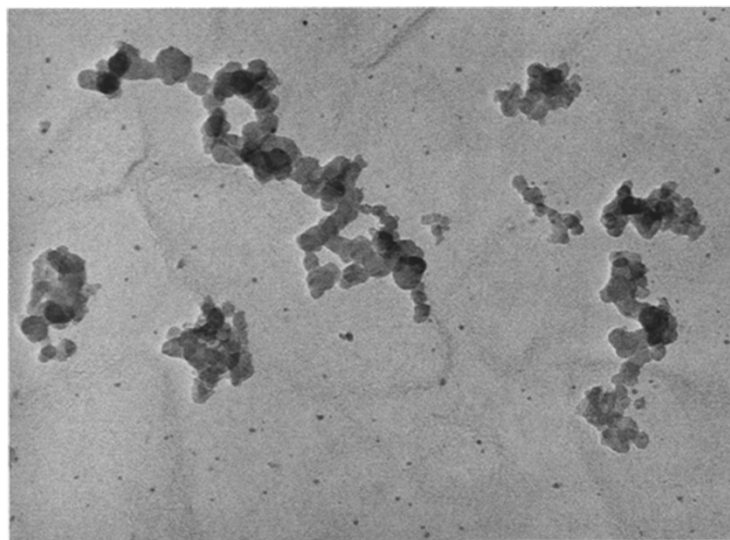
## PM

- The solid and liquid formed in combustion contribute directly to the particulate matter
  - The composition of the ashes depends strongly on the fuel,
    - SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and CaO are usually the primary components.
  - Ash from oils contain vanadium (V), nickel (Ni), plus magnesium (Mg); which is added to the fuel as a corrosion inhibitor.
- The vapors could condense, solidify and form secondary particulate matter before and after the emission.

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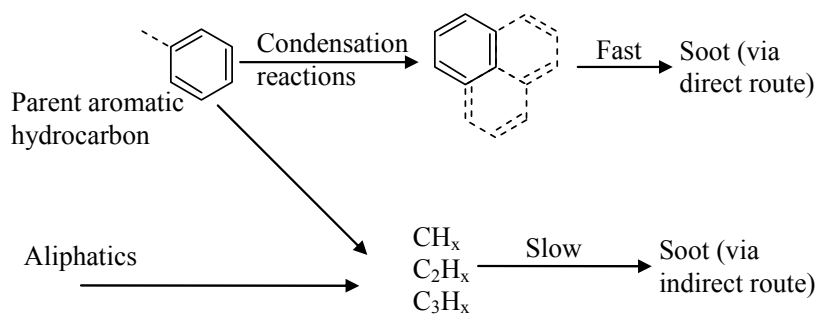
## Soot



50 nm

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- **Soot particles** are mainly composed of carbon, sulphur and nitrogen compounds and trace elements
- Carbonaceous particles (10-80 nm) in the combustion system can agglomerate and form larger particles



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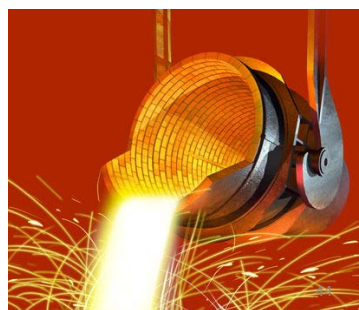
## Heavy Metals

- In Europe, 13 elements of concern are arsenic, cadmium, cobalt, chromium, copper, mercury, manganese, nickel, lead, tin, Sb, Sn, and thallium
- Some of these elements are actually necessary for humans in minute amounts (cobalt, copper, chromium, manganese, nickel)
- Others are carcinogenic or toxic, affecting, among others, the central nervous system (manganese, mercury, lead, arsenic), the kidneys or liver (mercury, lead, cadmium, copper) or skin, bones, or teeth (nickel, cadmium, copper, chromium).
- In Europe, heavy metal emissions are regulated in waste incinerators.

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## Sources of heavy metal emissions

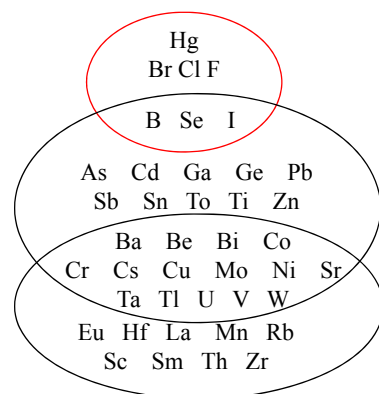
- The emissions of which are regulated in waste incinerators and smelting
- Fossil fuels like coal and heavy oil contain trace elements in the form of organic salts and inorganic minerals, for example,
  - pyrites and other sulphides, (alumino-) silicates and carbonates.
- In typical coals, the concentrations of Pb, B, Cr, Ni and V are high.
- Ni and V are also found in oils.



## Classification of Heavy Metals

- **Class I** – these elements do not volatilize during combustion, and they end up being captured with the bottom and fly ashes. The presence of sorbent (calcium) will expedite this process.
- **Class II** – these elements are vaporized during combustion and are eventually captured by particulates through condensation and nucleation mechanisms when the temperature drops along the duct of flue gases.
- **Class III** – these elements are vaporized but cannot be captured by the particulates in the flue gas.

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### Class III

Volatilised and emitted fully in the vapour-phase – not enriched on the fly ash

### Class II

Enriched in the fly ash and depleted in the bottom ash.

### Class I

Equally distributed between bottom ash and fly ash.

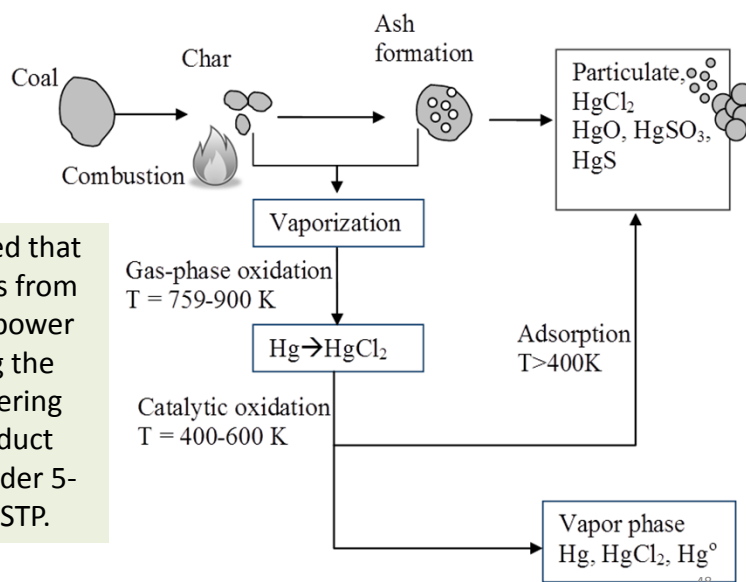
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## Mercury

- **Mercury, a Class III trace element**, is very problematic due to its toxicity and volatility (boiling point 357 °C).
- During combustion typically more than 90% of the incoming Hg penetrates through the flue gas cleaning system and is discharged into the atmosphere as vapor.
- Due to its high volatility, Hg is released from fossil fuels at about 150 °C, mainly as Hg (E), HgCl<sub>2</sub>, Hg<sub>2</sub>Cl<sub>2</sub> and HgS.
- The release of Hg from the fuel will be complete at 500 – 600 °C. Under oxidizing conditions, in the presence of HCl and Cl<sub>2</sub>; Hg (E) is oxidized to HgCl<sub>2</sub> at 300 – 400 °C.

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### Most probable mercury-species transformations in- and post- pulverized coal combustion



It is estimated that Hg emissions from a coal-fired power plant leaving the furnace, entering the flue gas duct are of the order 5-50 µg/m<sup>3</sup> at STP.

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## Greenhouse Gases

- By the end of the 20th century it was widely accepted that CO<sub>2</sub>, CH<sub>4</sub>, nitrous oxide (N<sub>2</sub>O), and water contributed significantly to global warming.
- Water vapour is the most abundant greenhouse gas in the atmosphere and it contributes to 2/3 of the greenhouse effects.
- The remaining effects are caused by other GHGs and referred to as the “enhanced greenhouse effect”, or the “anthropogenic greenhouse effect”.
  - CO<sub>2</sub> alone is contributing nearly 3/4 of the enhanced greenhouse effect.

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## CO<sub>2</sub>

- The major source for CO<sub>2</sub> emissions is the combustion of hydrocarbon fossil fuel.
- CO<sub>2</sub> concentrations in flue gases from natural gas-fired combined cycles power plants are about 4% by volume, however it is increased to 9-14% from coal fired plants.
- These amounts of CO<sub>2</sub> were emitted to the atmosphere without control.

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