Methods of pollution control and waste management

Lecture 8

The Earth's atmosphere and air pollution

Part 4

Sulfur dioxide (SO_2) one of criteria atmospheric pollutants

- A colorless, toxic, corrosive, acidic gas with a sharp odor that is readily soluble in water, primary pollutant, has anthropogenic and natural sources.
- Sulfur dioxide is derived from the combustion of sulfur-containing fossil fuels and is a major air pollutant in many parts of the world.
- One of the major components of the so-called London smog.
- SO_2 and sulfates are the principal chemical species that cause acid precipitation.
- In recent years the use of high-sulfur coal has declined in many countries.

Effects of SO_2 on human health and plants

- In the atmosphere has its primary effect upon the respiratory tract producing irritation and increasing airway resistance, causes death in human at 500 ppm.
- SO_2 is adsorbed onto the surface of particulates and penetrate deeply into the respiratory tract in this way.
- SO_2 is harmful to plants, causing leaf tissue damage and destruction of chlorophyll .

Sulfur dioxide sources

- Any H_2S that does get into the atmosphere is converted rapidly to SO_2

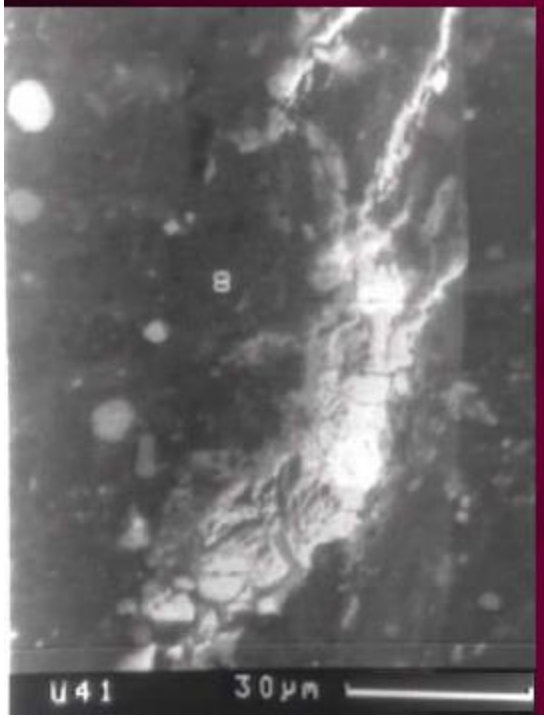
$$H_2S + 3/2\ O_2 \longrightarrow SO_2 + H_2O$$

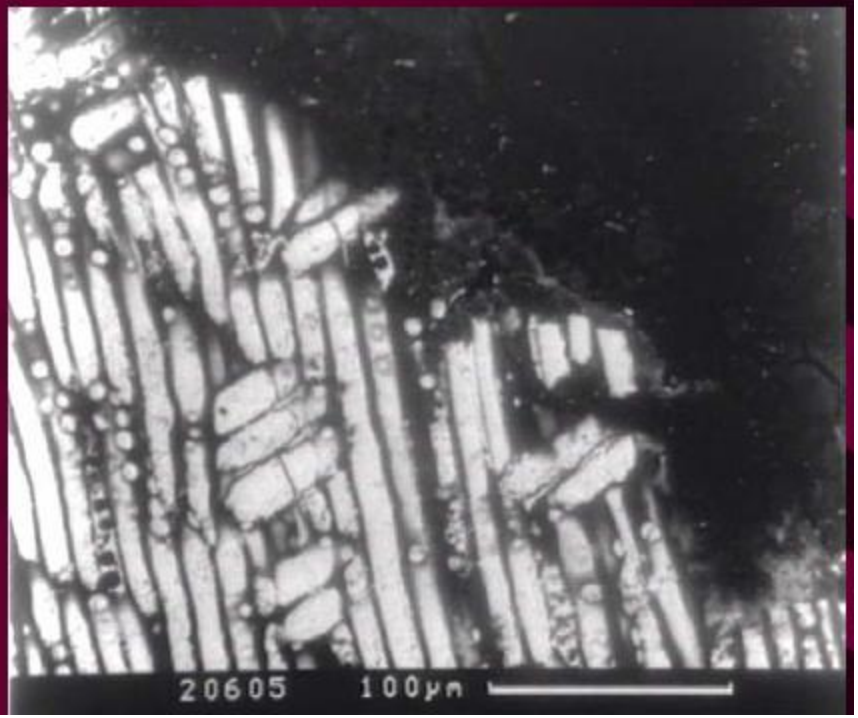
- The primary source of anthropogenic sulfur dioxide is combustion of coal contains high levels of sulfur (~ 50% as pyrite and ~ 50% as organic sulfur)

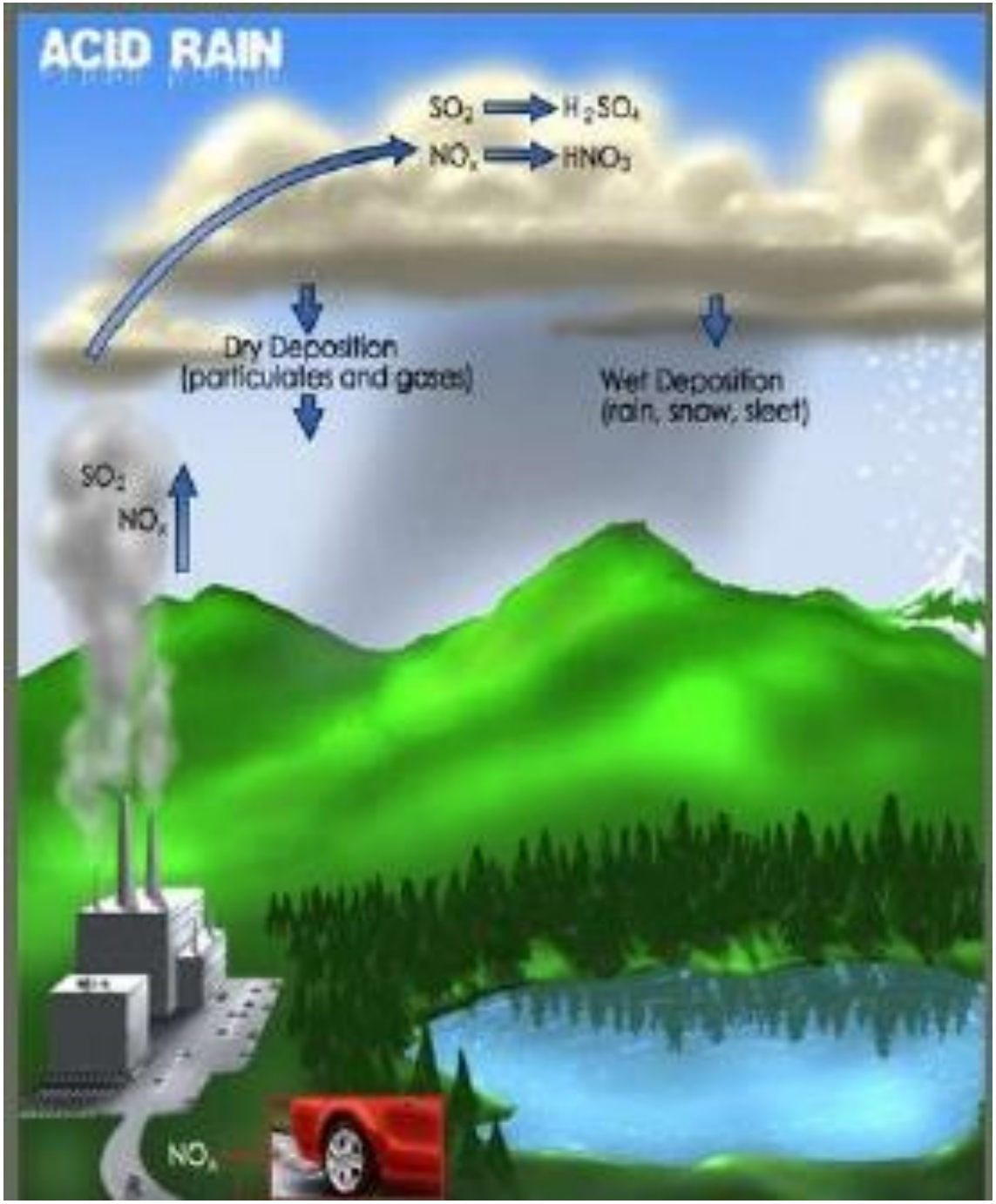
$$4FeS_2 + 11\ O_2 \longrightarrow 2\ Fe_2O_3 + 8\ SO_2$$

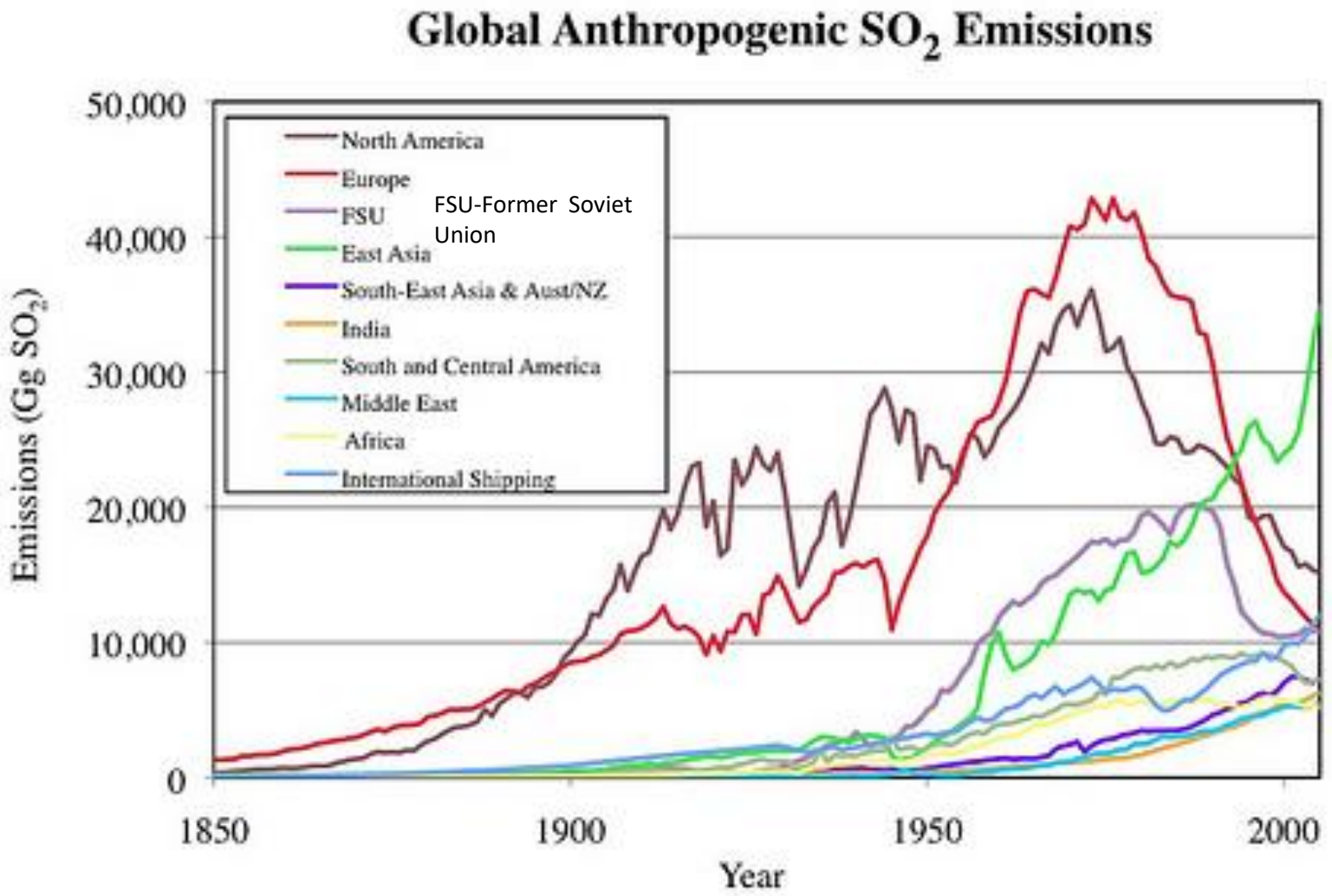
- All of the sulfur is converted to SO_2 with only 1 or 2% leaving the stack as SO_3

Iron disulfide forms






ACID RAIN
$SO_2 \rightarrow H_2SO_4$
$NO_x \rightarrow HNO_3$
Dry Deposition
(particulates and gases)
Wet Deposition
(rain, snow, sleet)
SO_2
NO_x
NO_x



Source: Pacific Northwest National Laboratory

Manmade sulfur dioxide yearly emissions by country show a decline by the historically large emitters - Europe and the US - but increases in growing economies up to 2005.

The methods to control SO_2 emissions

1. Desulfurization of fuel (beneficiation) prior to combustion (physical, chemical, thermal, biological)

2. The removal of SO_2 during the combustion

3. The removal of SO_2 after the combustion (FGD)

4. Conversion of coal to clean fuel by gasification

Sulfur dioxide removal during the combustion

Clean Coal Technologies (CCT)

- **Fluidized bed combustion (FBC)**

  A lime or dolomite bed in the combustion chamber absorbs the sulfur oxides that are generated.

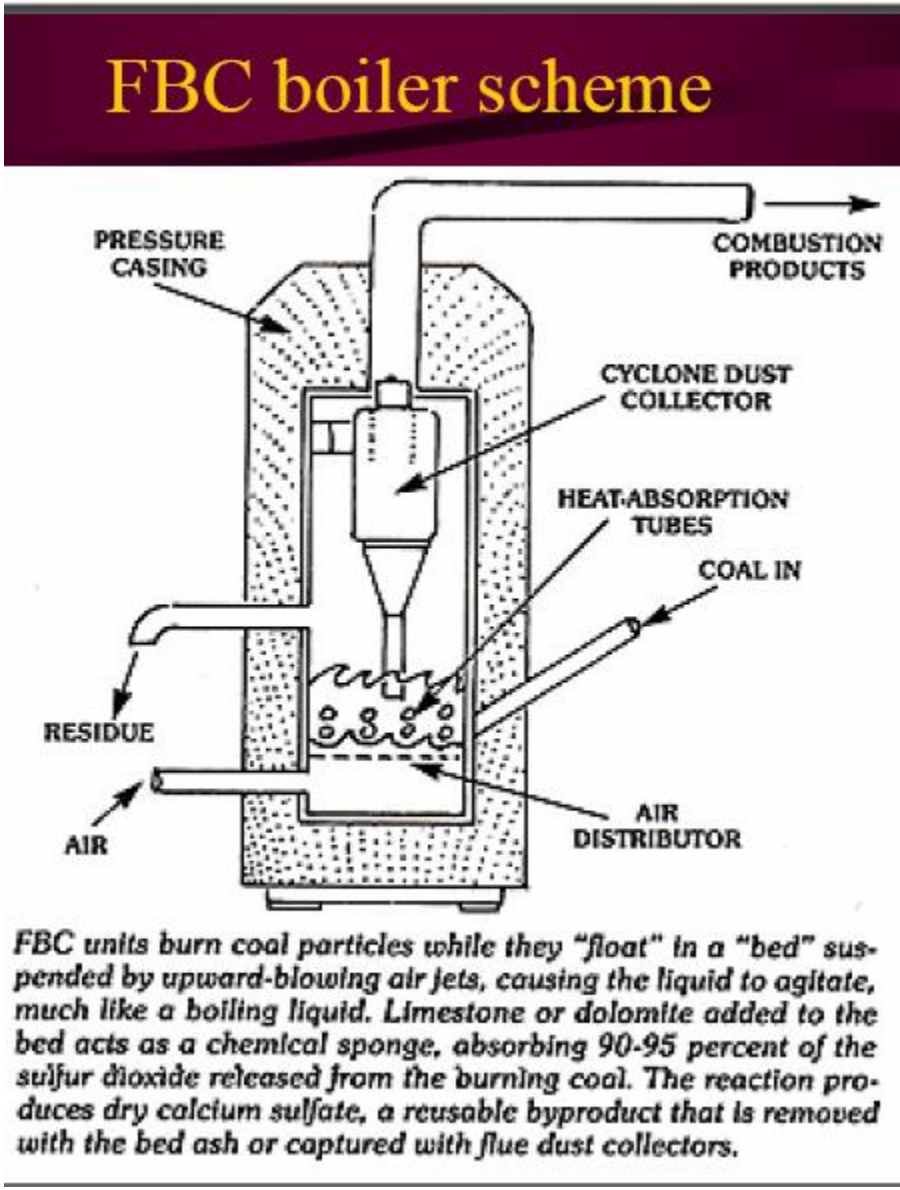
$$CaCO_3 \longrightarrow CaO + CO_2$$

$$CaO + SO_2 + \tfrac{1}{2} O_2 \longrightarrow CaSO_4$$

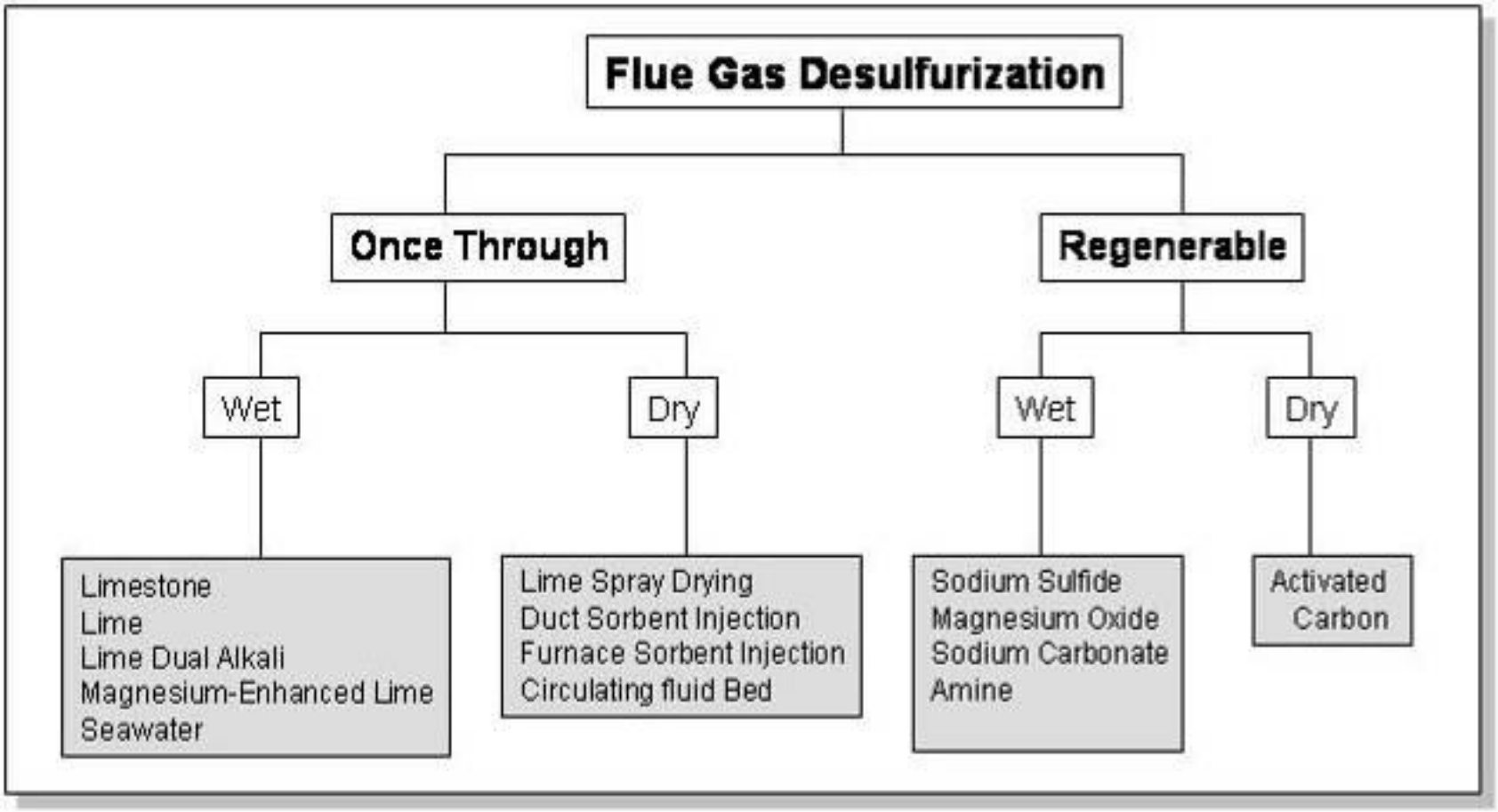
Fluidized Bed Combustion

Fine particle mix of fly ash and lime

- Burned at 750-850^{0}C
- Furnace retention time 20 minutes
- No slag production
- Reduces SO_2 emissions by 95%
- Less volatilisation



Flue gases desulfurization (FGD)



Major stack-gas scrubbing systems

Limestone slurry scrubbing

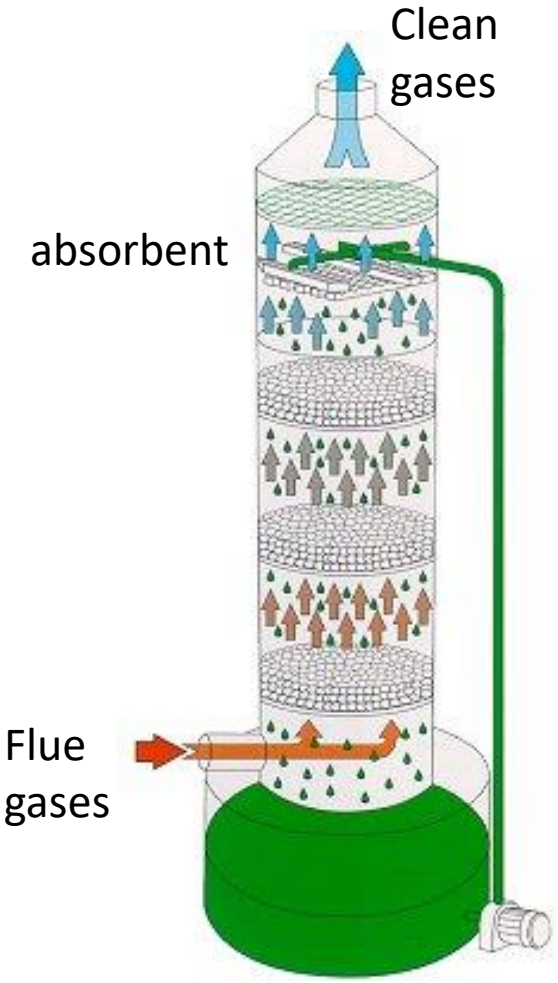
$$CaCO_3 + SO_2 \longrightarrow CaSO_3 + CO_2$$

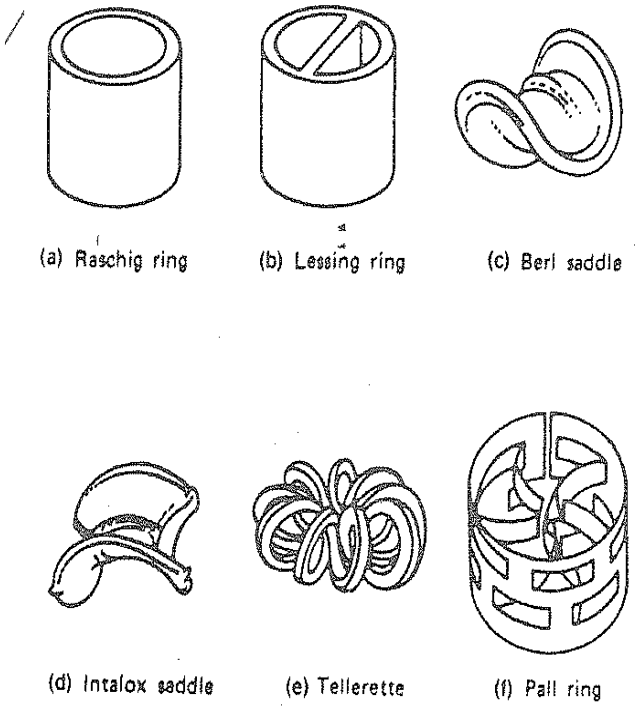
These processes have been also adapted to produce a gypsum product by oxidation of $CaSO_3$ in the spent scrubber medium

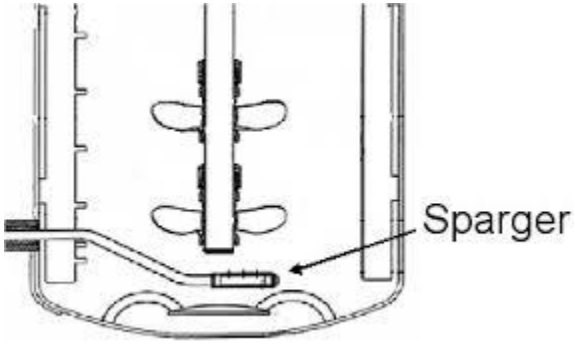
$$CaSO_3 + \tfrac{1}{2} O_2 + 2\ H_2O \longrightarrow CaSO_4 \bullet 2\ H_2O$$

Gypsum has commercial value such as in manufacture of plasterboard and therefore waste products are not generated

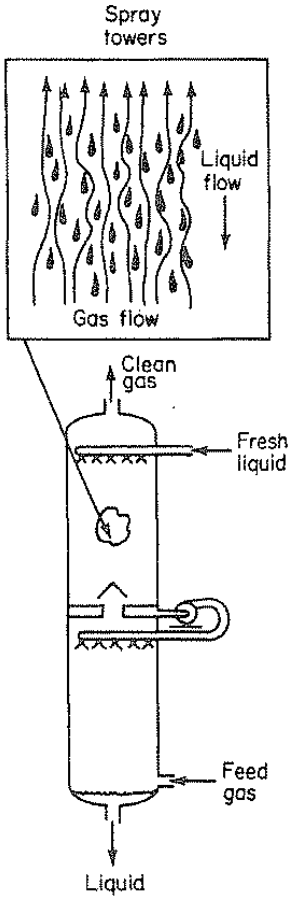
PACKED COLUMN as absorber

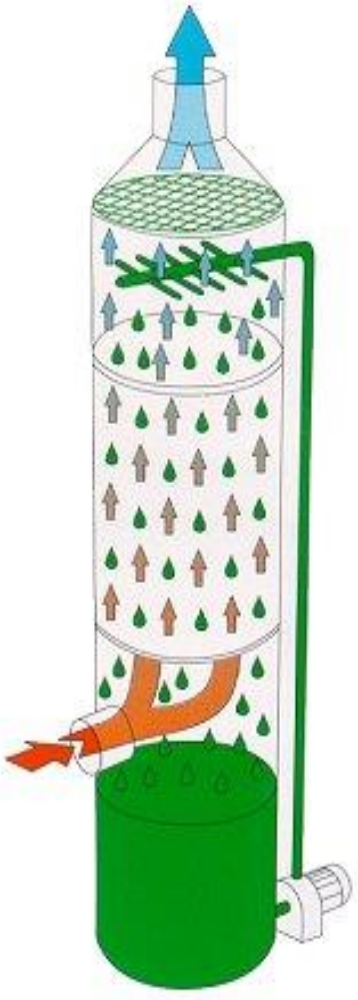






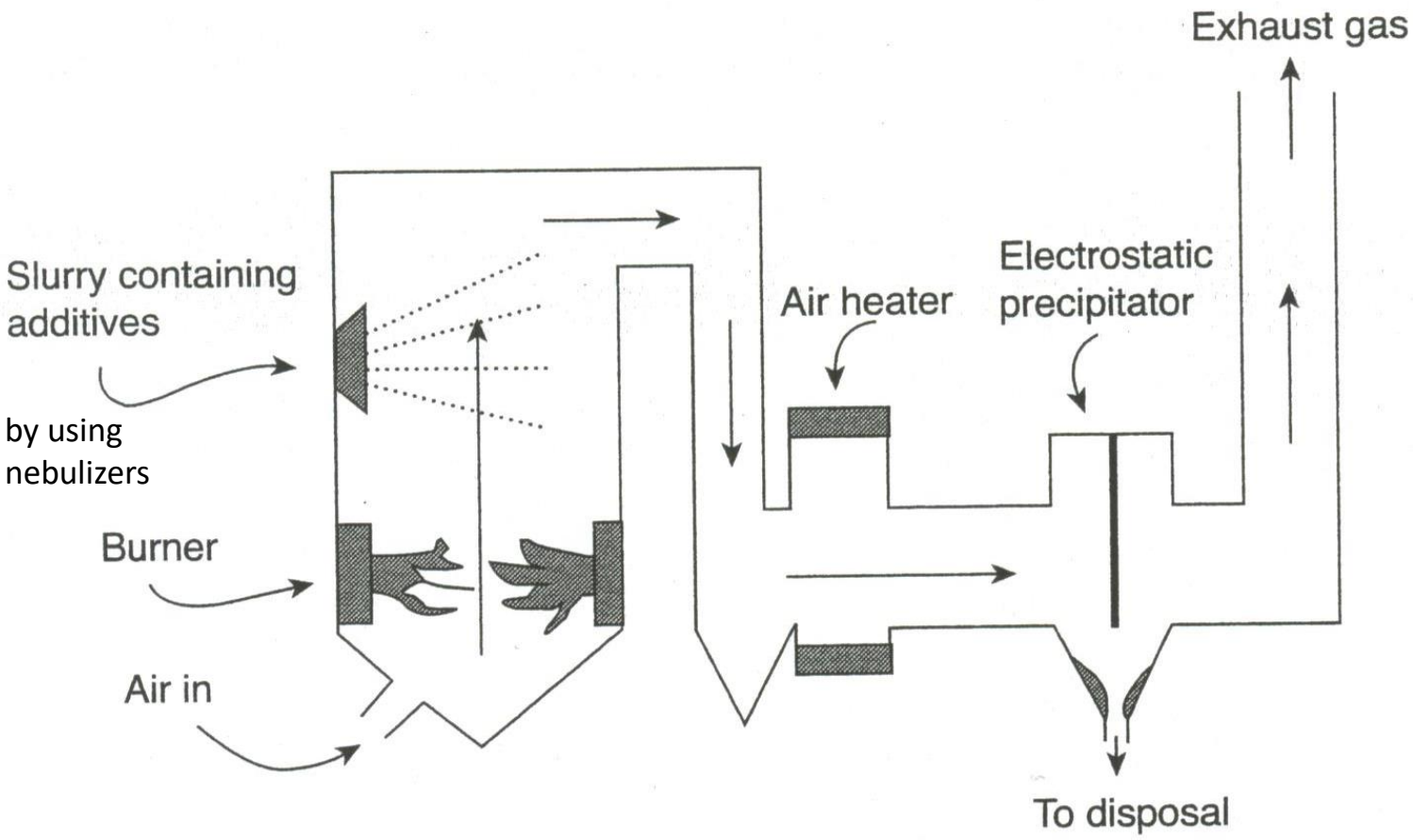
SPRAY COLUMN





The wet FDG system, also called a wet scrubber, is cammonly based on low-cost lime-limestone in the form of an aqeous slurry. This slurry, brought into contact with the flue gas by various technique, absorbs the SO_2 in it.

SONOX process for removal NO_x and SO_2



This system involves in furnace injection of an aqueous slurry of calcium based sorbent and nitrogen-containing additive usually urea

G. W. vanLoon&S. J. Duffy „Environmental Chemistry a global perspective, Oxford University Press, 2011

SONOX process for removal NO_x and SO_2

$$CaCO_3\,(s) \xrightarrow{\text{heat}} CaO\,(s) + CO_2\,(g)$$

$$CaO\,(s) + SO_2\,(g) + \tfrac{1}{2}O_2\,(g) \rightarrow CaSO_4\,(s)$$

$$NH_2CONH_2\,(s) + 2NO\,(g) + \tfrac{1}{2}O_2\,(g) \rightarrow 2N_2\,(g) + CO_2\,(g) + 2H_2O$$

- Furnace temperature ~ 1150 ^{0}C
- Concurrent injection
- Mean droplet diameter ~ 6.6 μm

Coal Gasification

$$C_xH_y + x/2\ O_2 \longrightarrow x\ CO + y/2\ H_2$$

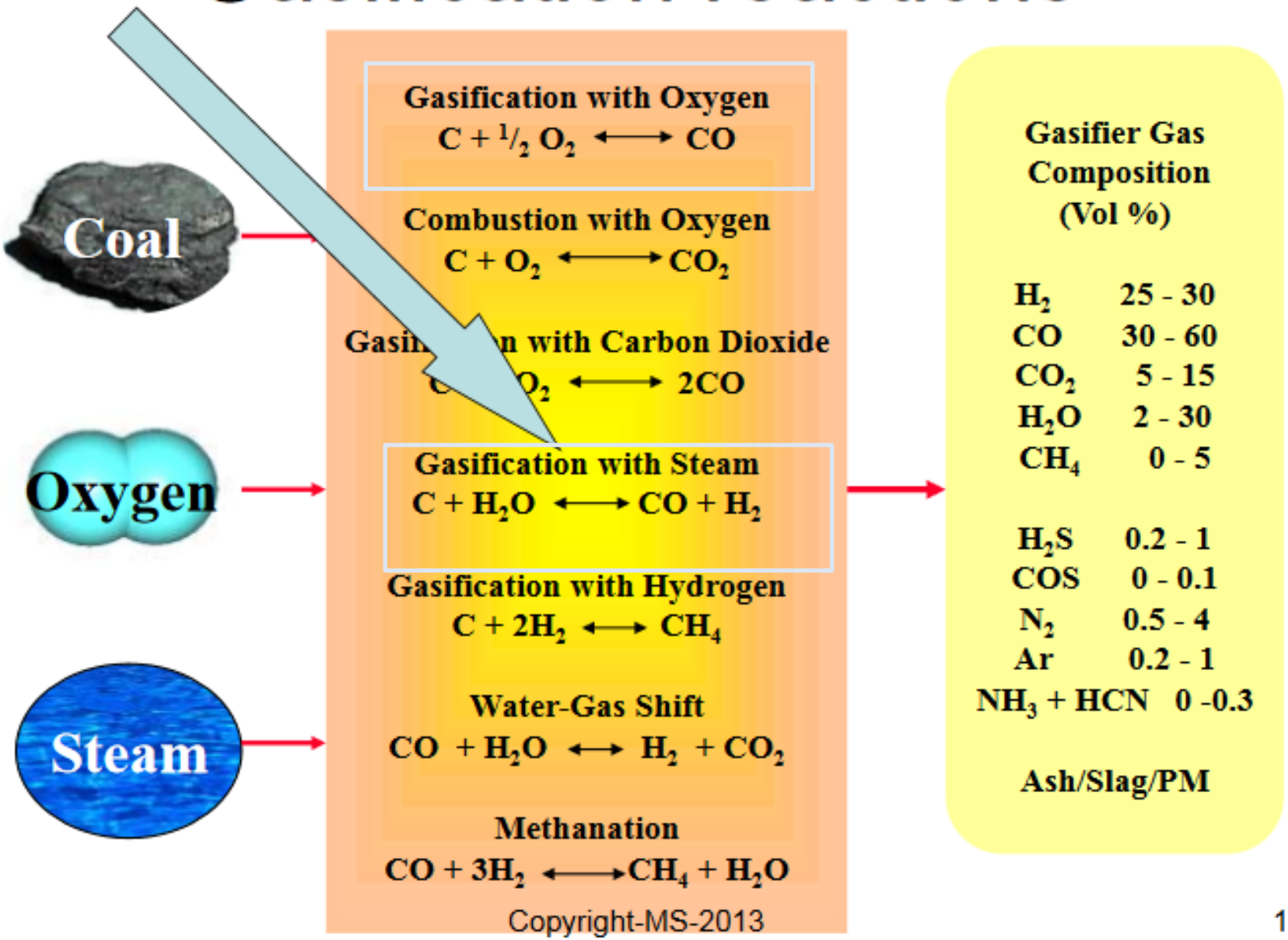
$$C + CO_2 \rightleftharpoons 2\ CO$$

$$C + H_2O \rightleftharpoons CO + H_2$$

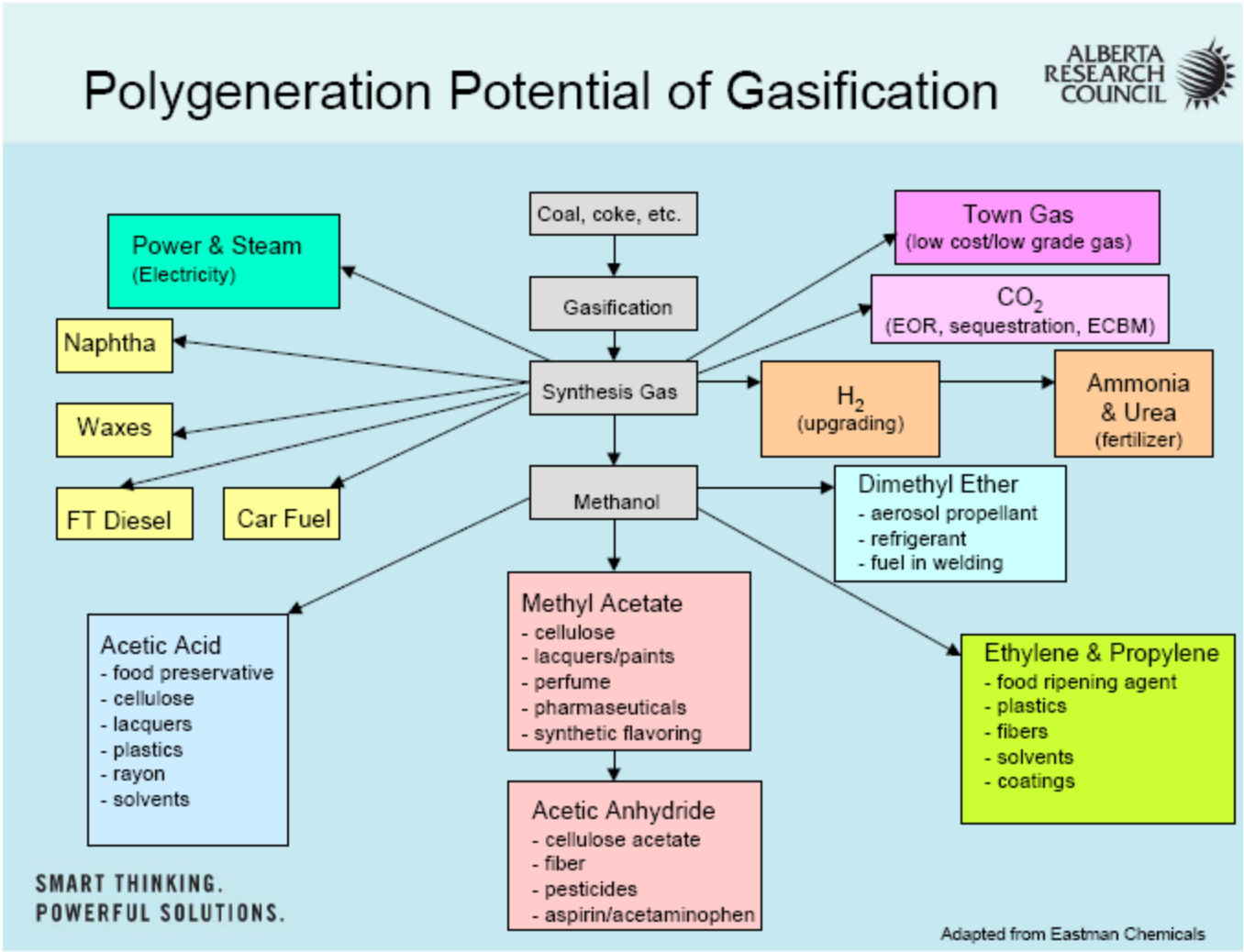
A *partial* oxidation process that can convert carbon or hydrocarbon to hydrogen and carbon monoxide (synthesis gas or syngas).

Coal Gasification

Gasification reactions

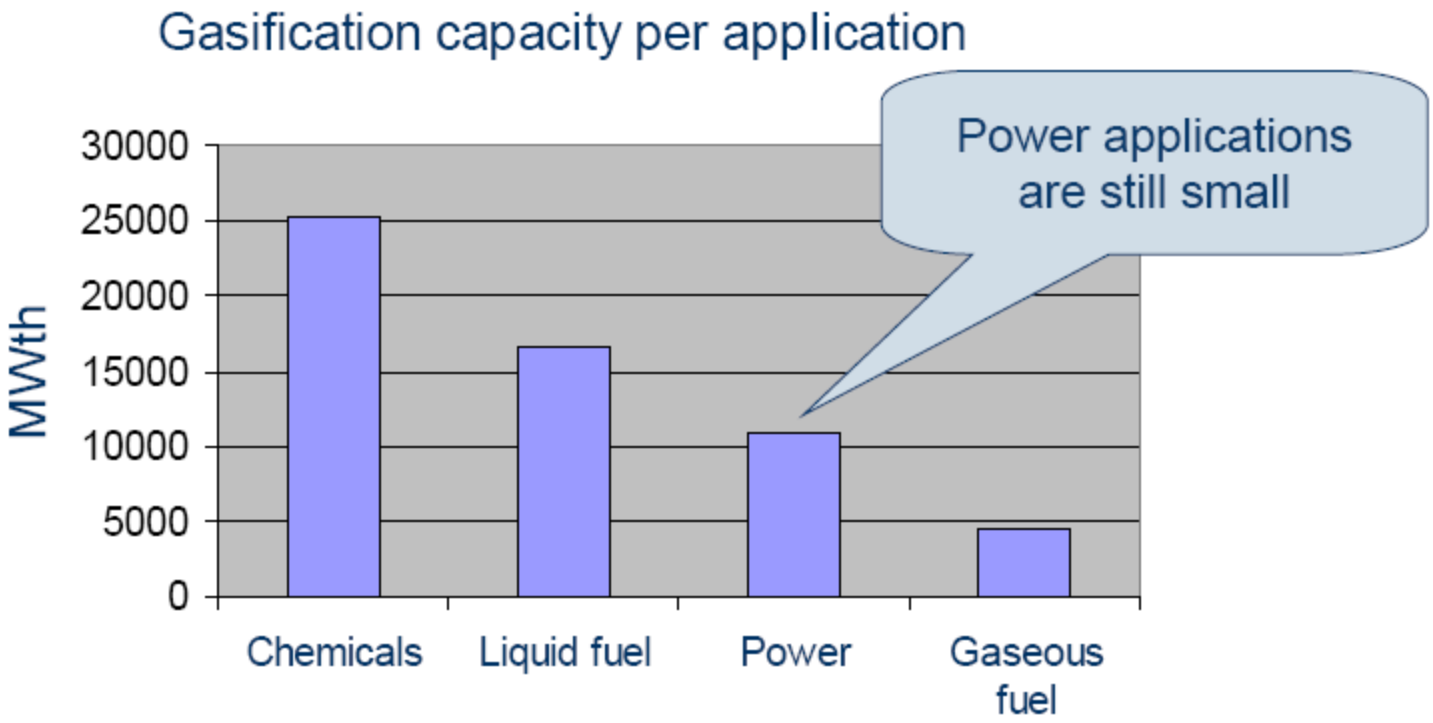


Polygeneration Potential of Gasification



http://www.gasification.org

Commercial status Gasification in 2007



www.gasification.org

Volatile Organic Compounds (VOCs)

Large group of organic chemicals that have high vapour pressure (<133 Pa at room temperature) results from a low boiling point (< 250 ^{0}C measured at standard atmospheric pressure) most of them with less than about 12 carbon atoms.

- Hydrocarbons
- Halogenated hydrocarbons
- Monomers
- Alkohols
- Aldehydes

Volatile Organic Compounds (VOCs)

VOCs are recognized as major contributors to air pollution, due to their toxic nature and as precursors of ozone and photochemical smog. Some VOCs (e.g., benzene) are toxic and carcinogenic, and are regulated individually as hazardous pollutants.

Sources of emission of VOCs

- **Outdoor**

Chemical plants
Petroleum refineries
Pharmaceutical plants
Automobile and airplane manufactures
Food industries
Textile manufactures
Electronic component plants

- **Indoor**

Office supplies
Printers
Insulating materials
Solvents and cleaning products
Painting facilities
Restaurant and domestic cooking
Wood stoves

VOCs treatment methods

- Adsorption
- Condensation
- Thermal combustion
- Catalytic combustion
- Biological treatment
- Membrane methods

Most VOCs are valuable fuels or solvents. For large VOC-containing gas streams recovery is often economical, but not for small streams.

VOCs treatment methods- adsorption

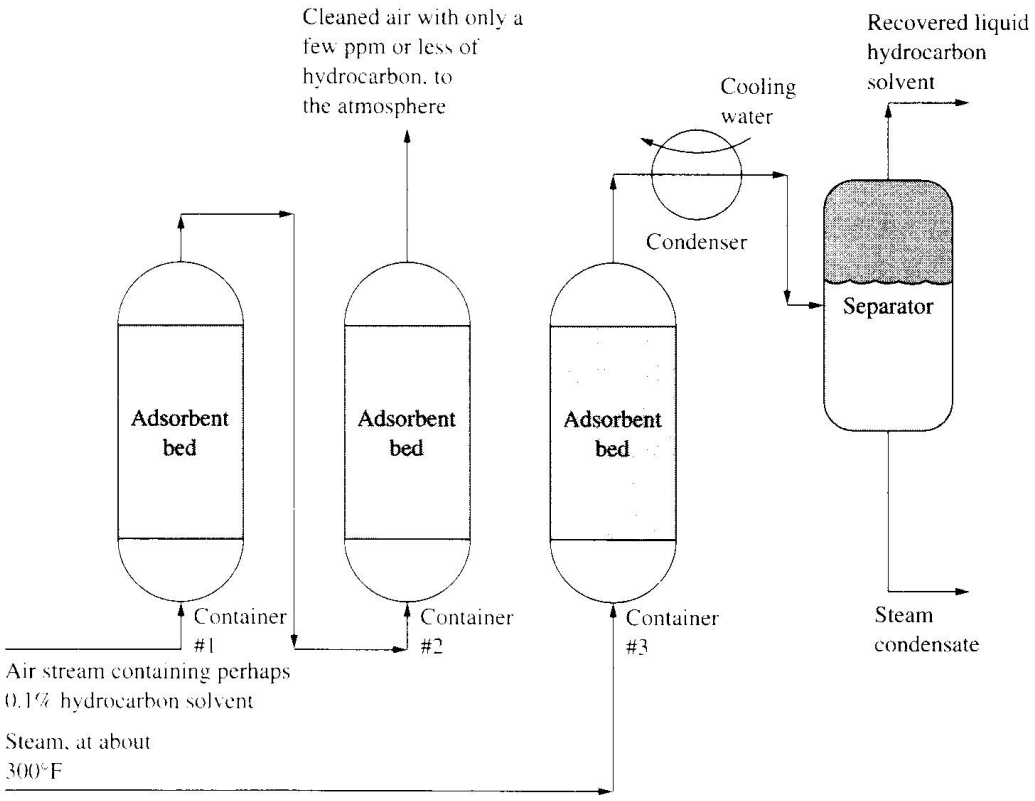


FIGURE 10.10
The typical arrangement for adsorption of a VOC from a gas stream, using three adsorbent beds; automatic switching valves; and steam desorption, condensation, and gravity separation.

Adsorbents:
activated carbon
silica gel
aluminosilicate

Adsorption rate is limited by slowest stage - diffusion (gas stream turbulence and adsorbent surface enlargement to increase rate of adsorption)

VOCs treatment methods- absorption

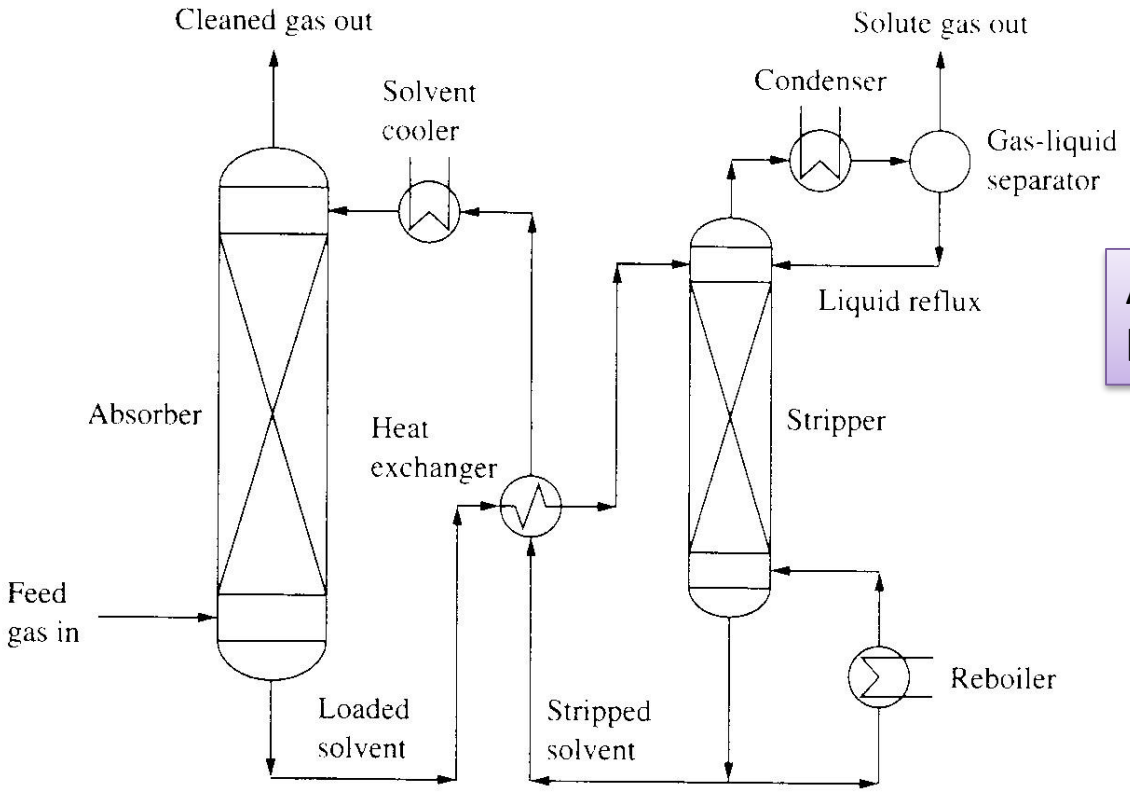


FIGURE 10.15
The flow diagram for the most common method for removing one component from a gas stream.

Absorption in the high boiling organic solvents.

Absorption rate increases with increasing the **interfacial surface and the diffusion rate.**

VOCs treatment methods
Direct flame incineration

Direct flame incineration is used when waste gases are combustible and does not need additional fuel or air (temperature > 1200^0C)

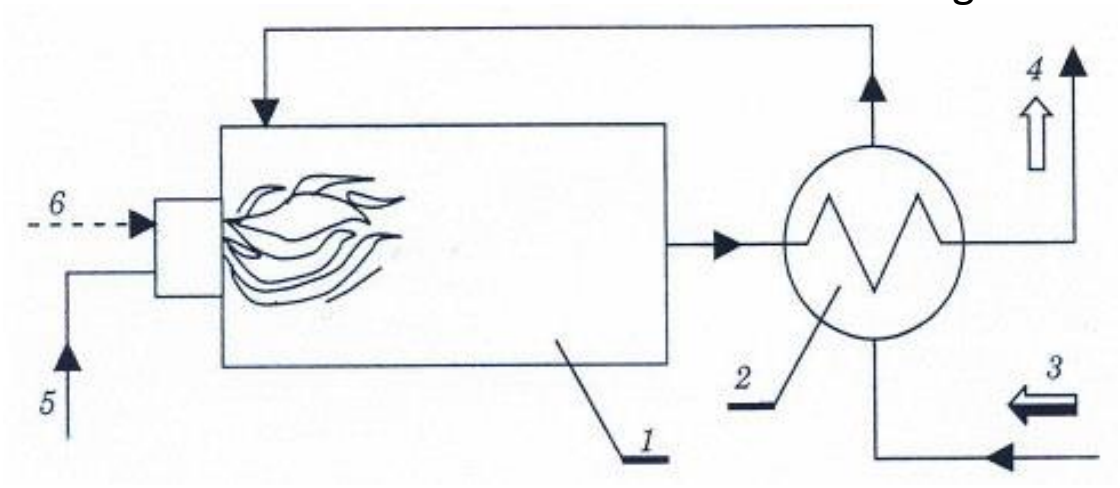
The outlet of a refinery's relief valves are piped to a flare, which is an elevated pipe with pilot lights to ignite any released VOCs.

VOCs treatment methods
Direct flame incineration

Many flares have steam jets running constantly to mix air into the gas being released.

Large, bright orange, smoky flame from the flare indicates a significant release of unburned or partly burned VOCs.

VOCs treatment methods - thermal incineration

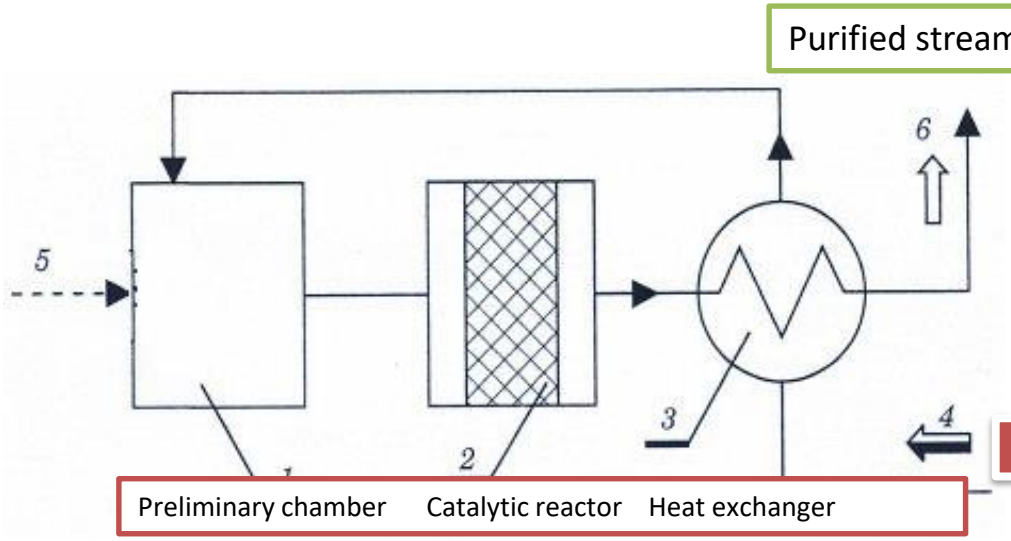


Temperature
600 – 1100^0 C

The contaminated air preheated by fumes in the heat exchanger is introduced to the oxidizing chamber.

In the chamber the contaminants undergo the oxidation to CO_2 and water.

Catalytic combustion



More versatile and economically favorable for low concentrations of organic emissions (< 5000 ppm)

This method operates at relatively low-temperatures (150-350 ^{0}C) with consequent limited emissions of dioxins and NOx

Catalytic combustion

- **Halogenated VOCs**

  Catalytic oxidation of chlorinated HC involves production of HCl and requires the addition of corrosion-resistant materials such as Cr_2O_3, V_2O_5, WO_3 to overcome the activity loss.

$$C_xH_yCl + (2x+z)\,O_2 \longrightarrow x \cdot CO_2 + z\,H_2O + HCl$$

Biological methods in VOCs removal

- Biodegradation by microorganisms (aerobic bacteria). The bacteria oxidize volatile organic compounds to carbon dioxide and water.

$$[CH_2O] + O_2 \longrightarrow CO_2 + H_2O + \Delta H$$

- The typical biofilter (better called a highly porous biochemical reactor) consists of the equivalent of a swimming pool, with a set of gas distributor pipes at the bottom, covered with several feet of soil or compost or loam in which the microorganisms live.

Next lecture 9th January 2019