Chemical Engineering 522

Combustion Processes

Pollutants

Outline

- Measurements
  - Emissions index
  - Basis
  - Corrected Concentrations
- CO/unburnt hydrocarbons
- SO_x
- Particles

Concentrations

- Emissions index
  - Many units for measurement (g/miles, lb/MMBtu, ppm).
  - Which to use?
  - Problems/confusion?
  - How to deal with dilution?
  - Emissions index is most straightforward.
- EI = $m_{i,emit}$ / $m_{f,burned}$
  - Pollution / mass of fuel
  - Independent of dilution
  - Process dependent

$$EI = \frac{x_i}{x_{CO} + x_{CO2}} \cdot \frac{n_c}{n_f} \cdot \frac{M_i}{M_f}$$

$$EI(=) \frac{\text{moles i}}{\text{moles c}} \cdot \frac{\text{moles c}}{\text{moles f}} \cdot \frac{M_i}{M_f}$$

Dry/Wet basis, Corrected Conc.

- Measurements are often made on a dry basis (water interferes).
- Conversion (Turns 15.7):

$$x_{i,\,dry} = \frac{x_{i,\,wet}}{1 - x_{H2O}} = x_{i,\,wet} \cdot \frac{N_{mix,\,wet}}{N_{mix,\,dry}}$$

  - True for rich or lean
- Corrected concentrations
  - If express emissions as concentrations, need to specify the basis, or else one could reduce “emissions” by diluting the effluent!
  - Correct to 3% O_2 on a wet or dry basis.
    - Consistent for different (A/F) of a Given fuel, but not among different fuels (e.g. compared to the EI).
  - $N_{i,1} = N_{i,2}$ (N_i is the same for both bases)
  - $x_{i1}N_1 = x_{i2}N_2$
  - $x_{i1} = x_{i2}N_2/N_2$
  - (Where N_2 is the total moles in basis 2 (not nitrogen ☺)).
  - SEE EQUATIONS 15.9 in Turns

Example

- (15.3 in Turns)
- Engine: iso-octane
  - 76 ppm dry NO
  - Exhaust → 2.3% dry O_2.
  - CORRECT to 5% dry O_2.
- $(x_{NO})_{5\%} = (x_{NO})_{2.3\%} * (N)_{2.3\%} / (N)_{5\%}$

$$N_{wet} = 4.76 \left[\frac{x + (1 + \chi_{O2,\,wet}) y/4}{1 - 4.76 \chi_{O2,\,wet}} \right] + y/4$$

$$N_{dry} = 4.76 \left[\frac{x + (1 - \chi_{O2,\,dry}) y/4}{1 - 4.76 \chi_{O2,\,dry}} \right] - y/4$$

$$N_{2.3\%} = 4.76 \left[\frac{x + (1 - 0.023) y/4}{1 - 4.76 * 0.023} \right] - y/4 = 61.76 \text{ with x=8, y=18}$$

$$N_{5\%} = 4.76 \left[\frac{x + (1 - 0.05) y/4}{1 - 4.76 * 0.05} \right] - y/4 = 72.18$$

- $(x_{NO})_{5\%} = 65$ ppm

SO_x

Fuel wt. %	Range %
Coal	≤10
Heavy residual oil	0.5–4
Blended residuals and crudes	0.2–3
Diesel fuel (No. 2)	0.1–0.8
Unleaded gasoline	0.015–0.06

- Due to Sulfur in fuel
  - Coal, Diesel, (Gasoline)
- S → SO_2 or SO_3.
  - All is converted (unlike NOx).
  - Makes it easier to predict!
  - Equilib → y_{SO2}/y_{SO3} = 3570, but SO_3 usually > equilib (a few % of SO_2)
- Utah coal = $C_{64}H_{32}N_{0.67}S_{0.3}O_{2.5}$. (or 1% S by mass)
  - Combustion → 822 ppmv SO_2.
- SO_2 → SO_3 via OH in gas phase, or via H_2O absorption
  - → H_2SO_4 via H_2O → acid rain

Acid Rain

1908

1968

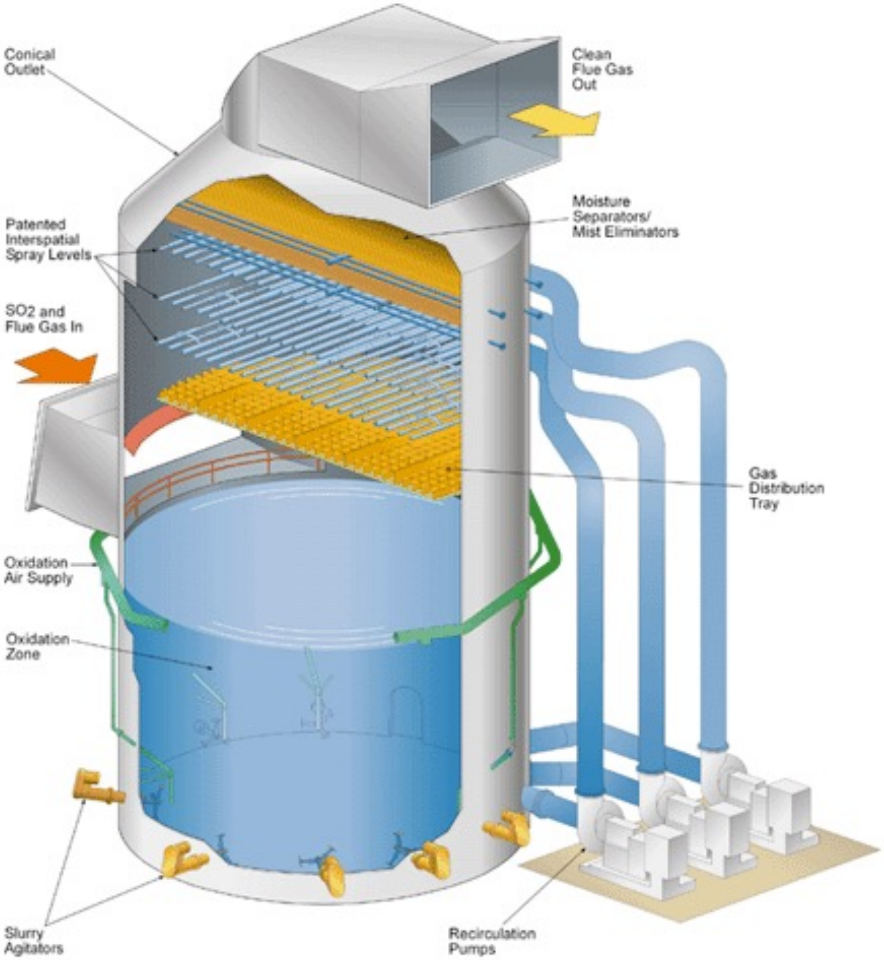
From a castle in Westphalia, Germany

Acid Rain

Control

- Control:
  - Remove S from fuel
    - No S in gasoline → why?
  - Remove SO_x from effluent.
- Reduce SO_2 with limestone or lime:
  - $CaCO_3 + SO_2 + 2H_2O \rightarrow CaSO_3{*}2H_2O + CO_2$.
  - $CaO + SO_2 + 2H_2O \rightarrow CaSO_3{*}2H_2O$
  - Wet or dry: spray an aqueous slurry in a tower.

Flue Gas Desulfurization

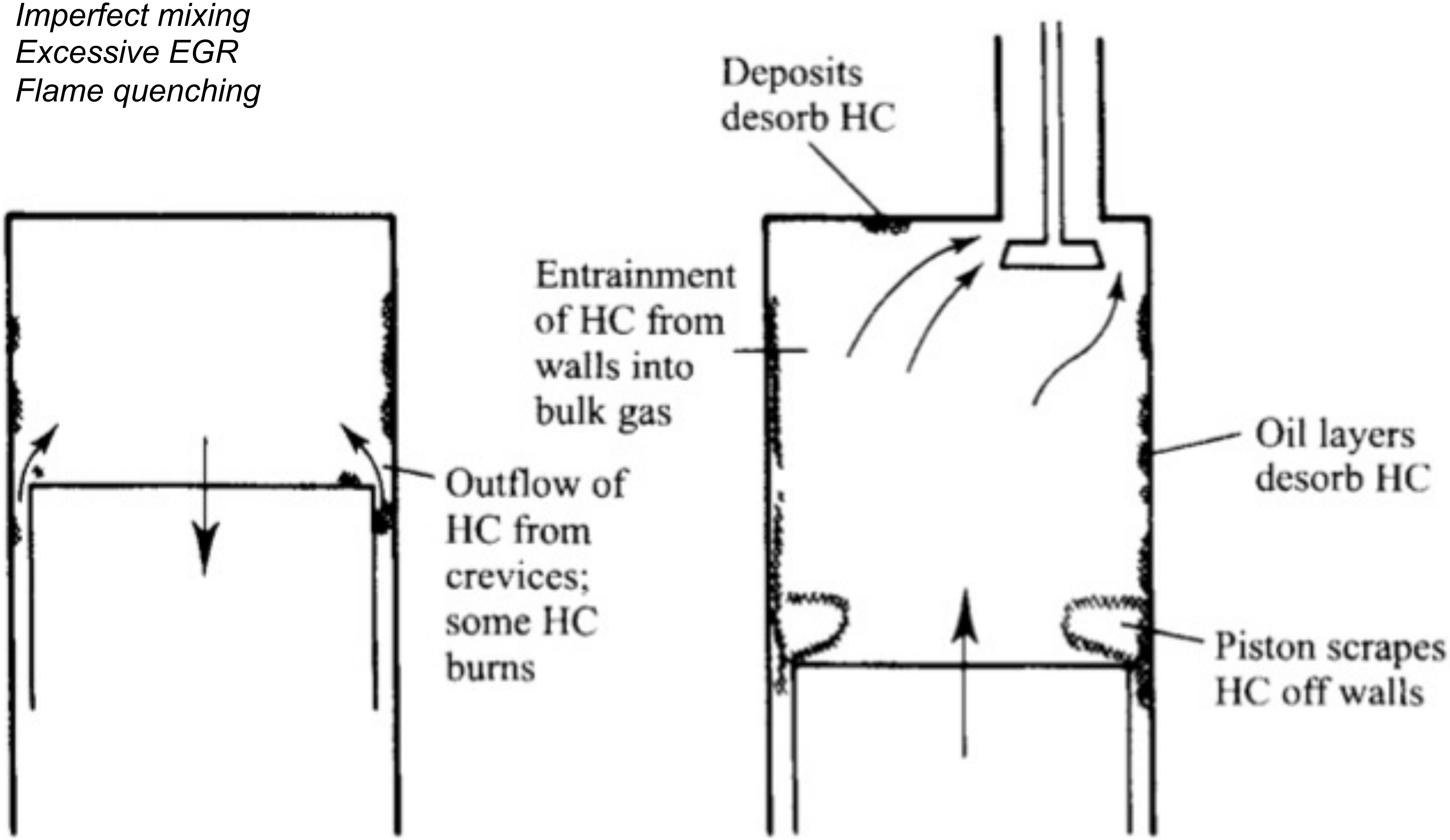


Unburnt HC/CO

- Rich operation (vehicles) under high load or cold startup
- Run lean
  - Stoichiometric works, but incomplete mixing → rich zones
  - So, run lean.
    - Can still get imperfect mixing → some emissions.
    - Can run lean enough that combustion can become weak and incomplete
      - Or, the burning hits even leaner regions outside the flammability limits (discussed later).
- Wall quenching in engines
  - Crevices
  - Oil absorption
- Control with stoichiometry, mixing, or post-combustion oxidation.
  - Three-way catalyst (catalytic converter) → NO, CO, HC.
- Nonpremixed flames always have rich and lean zones.
  - Always produce soot, which may be considered an incomplete combustion product as well as a particulate emission. More on soot later.

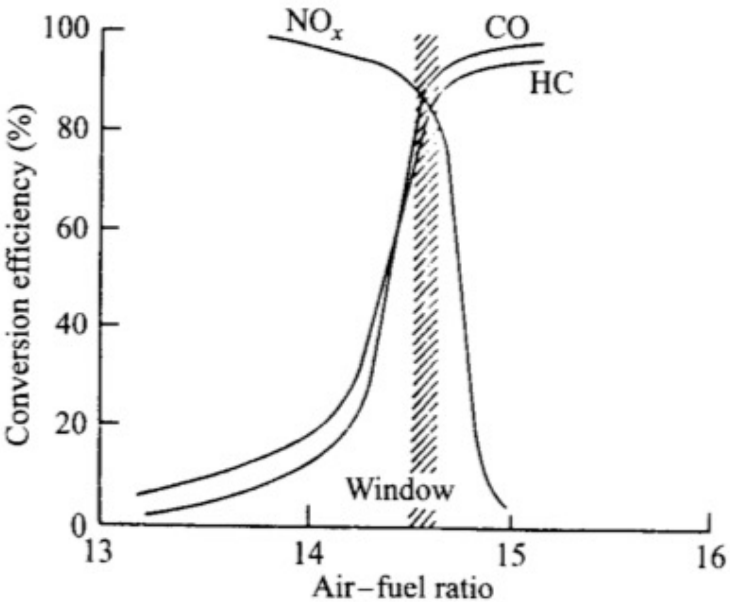
Wall Quenching

- *Imperfect mixing*
- *Excessive EGR*
- *Flame quenching*



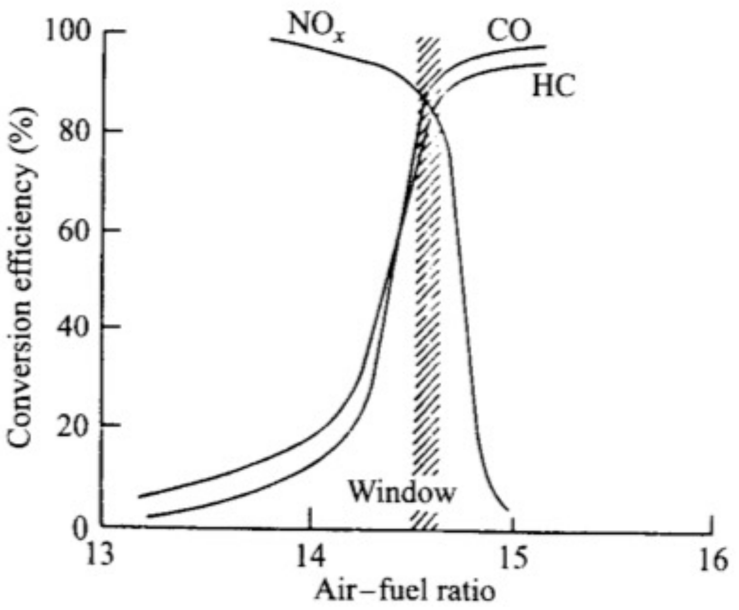
(a) **Expansion** (b) **Exhaust**

Catalytic Converter



Catalytic Converter

- Introduced in 1976
- Noble metal catalysts
  - Platinum (oxid/red), palladium (oxid), rhodium (red)
  - Deposites on a ceramic substrate
- Reduce NO, while oxidizing CO, HC
- Narrow range near stoichiometric
  - Oxygen control
  - Oxygen sensors
- Tetraethyllead poisons (also sulfur)
- Light off temperature: ~500 ^oF
  - Most emissions during first 5 minutes of startup before hot.



John Mooney

Particulates

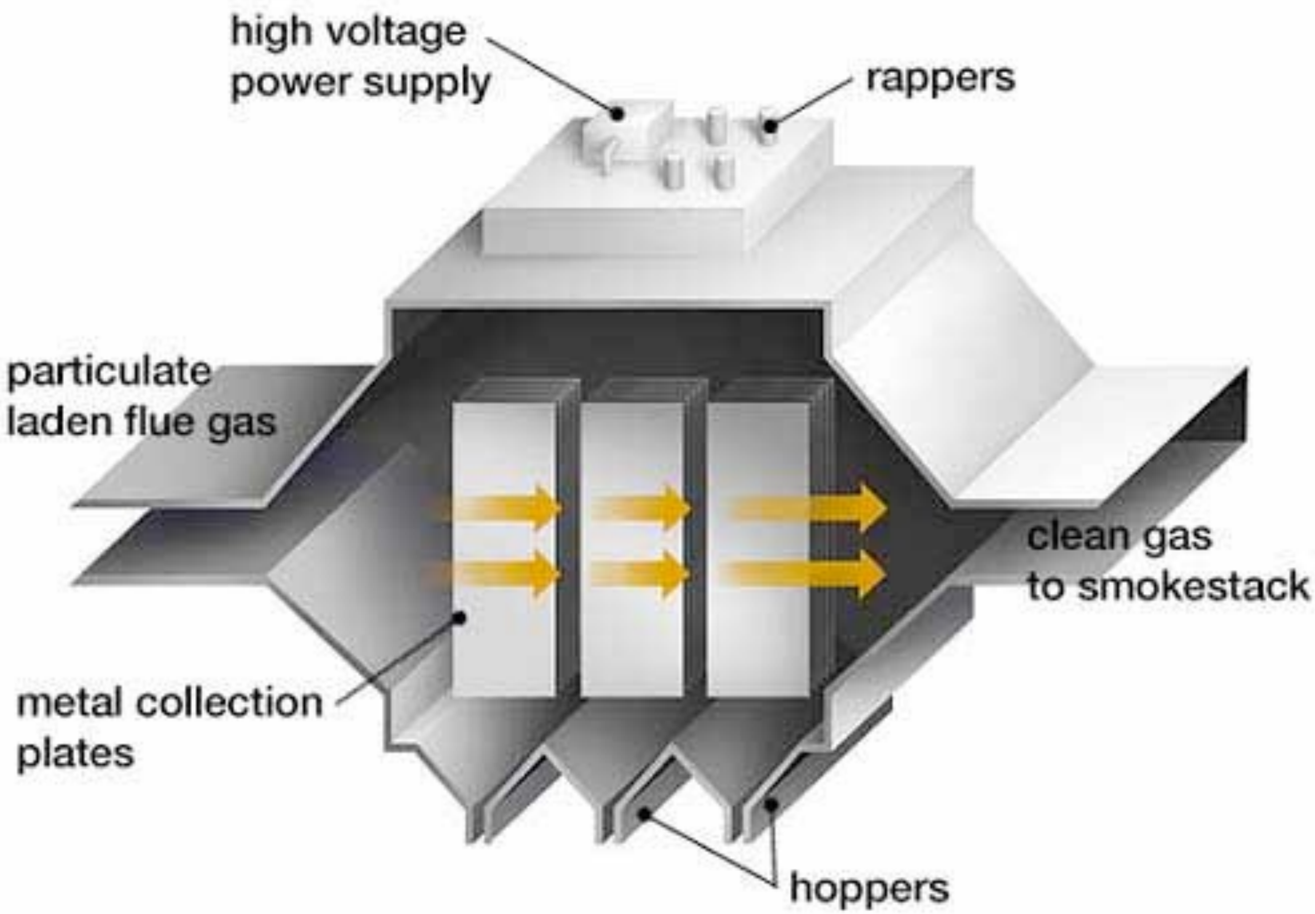
- Soot
- Fly ash
- Fine particulates cause
  - Haze
  - Health hazard: asthma, bronchitis, decreased lung function, shortness of breath
    - Fine soot can penetrate deeply in lungs, carcinogenic
    - See the EPA’s 2004 “Air Quality Criteria for Particulate matter”

Particulates

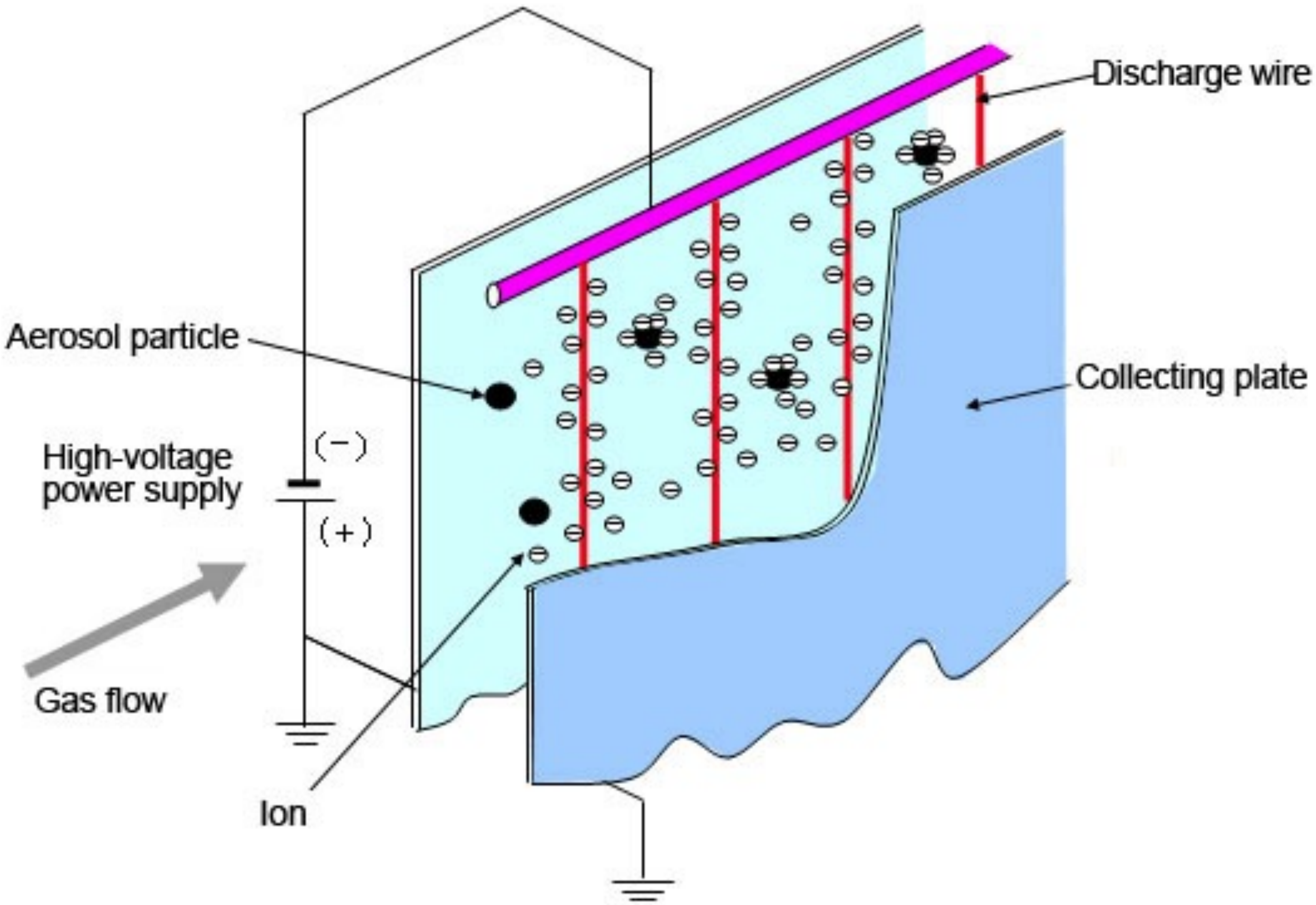
- Nonpremixed (Diesel)
  - Soot
- Premixed (auto)
  - Condensed unburned HC
- Coal
  - Ash, Soot
- Control
  - Soot reduction
  - Collection
- Baghouse

Baghouse

ESP


high voltage
power supply
rappers
particulate
laden flue gas
clean gas
to smokestack
metal collection
plates
hoppers

ESP


Discharge wire
Aerosol particle
Collecting plate
High-voltage
power supply
(−)
(+)
Gas flow
Ion