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PackAlliance:
European alliance for innovation training
& collaboration towards future packaging

Linking **Academy** to **Industry**.
Filters separators

**Training program SPECIALIST IN THE CIRCULAR ECONOMY OF
PLASTIC PACKAGING: modules**

- Eco-design & novel manufacturing processing
 - New materials and biomaterials
 - Citizen and Consumer Engagement
 - **Residue management and valorisation**



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Residue management and valorisation

- Logistic and Sorting
- **Recycling Systems & novel business models for the second life of residues**
- Economic, environmental and legislative aspects of plastic waste



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Recycling Systems & novel business models for the second life of residues

- Optimization of plastics recycling
- Mechanical recycling of packaging waste
- Secondary plastics products. Examples and market trends
- **Chemical routes for recycling. Dissolving, catalytic, and thermochemical technologies**



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Linking **Academy** to **Industry**.

- **ThermoChemical Recycling**
 - Energy Recovery



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Thermochemical Recycling

Process	Reaction conditions	Products
Gasification	15-30 MPa, 800-1600°C	Synthesis Gas (CO and H ₂) end energy
Hydrogenation	20 MPa, 500 °C	Syncrude, Bitumen
Pyrolysis	400-900°C	Wax, oil, gas, energy
Reduction in a blast furnace	2000 °C	Pig iron, furnace gas



Thermochemical Recycling

Interesting technologies for plastic waste feeds that are difficult to depolymerize and are currently not (mechanically) recycled but incinerated or landfilled such as mixed PE/PP/PS, multilayer packaging, fibre-reinforced composites...

Thermochemical Recycling

Gasification

Can be defined as the partial oxidation of hydrocarbons in the presence of lower oxygen levels than are required for complete stoichiometric combustion.

It's a well-developed industrial process for the gasification of coal and heavy oil fractions, which can be modified for use with plastic waste.

Main product: Synthesis gas.



Thermochemical Recycling

Gasification

Synthesis gas: CO and H₂ used to methanol and natural gas synthesis.

Temperatures 800°C-1600°C,
Pressures 15-30 Mpa

Air, oxygen, steam, flue gas, CO₂, H₂
can be used as gasifying agents.

Synthesis gas
CO + hydrogen
(syngas)

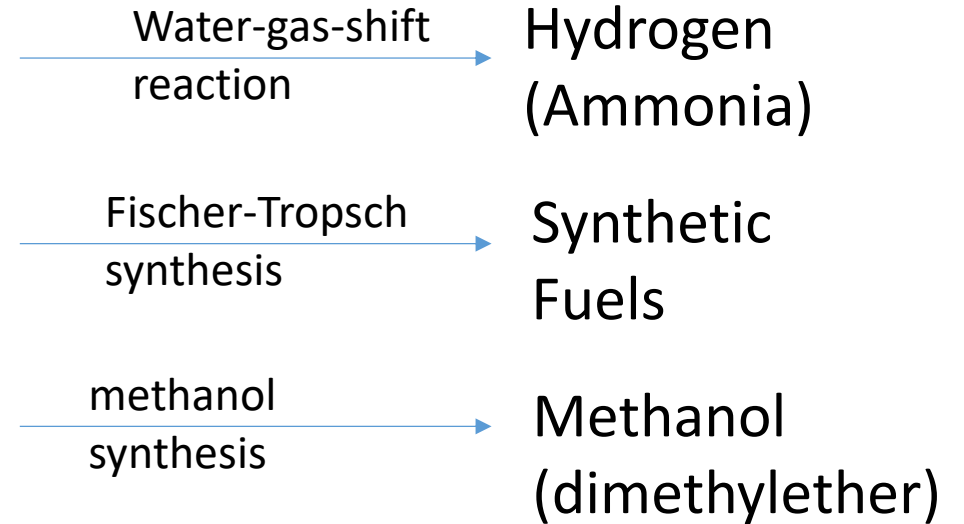


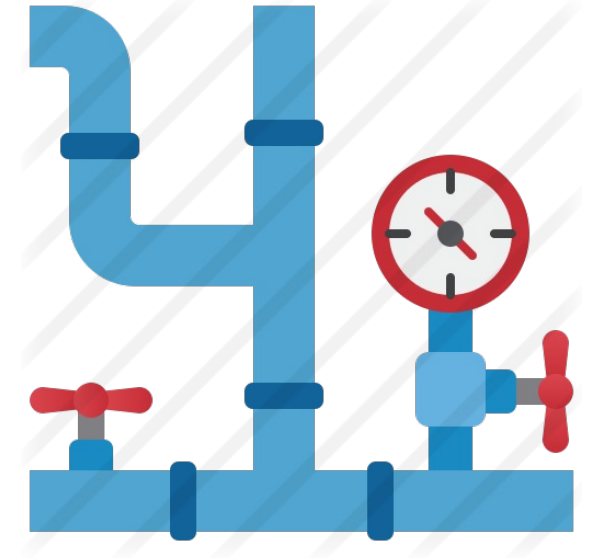
Figure - Syngas uses

Chemical Recycling

Gasification

There are two general types of gasification technology:

- Fixed-bed
- Fluidised-bed.



Chemical Recycling

Gasification

Fluidised-bed technology

If a gas is passed upward through a bed of solids with a velocity high enough for the particles to separate and become freely supported in the fluid, the bed is said to be fluidized.

Advantages over fixed-bed:

- More intimate contact between solids and gas
- High rates of heat transfer
- Uniform temperatures within the bed

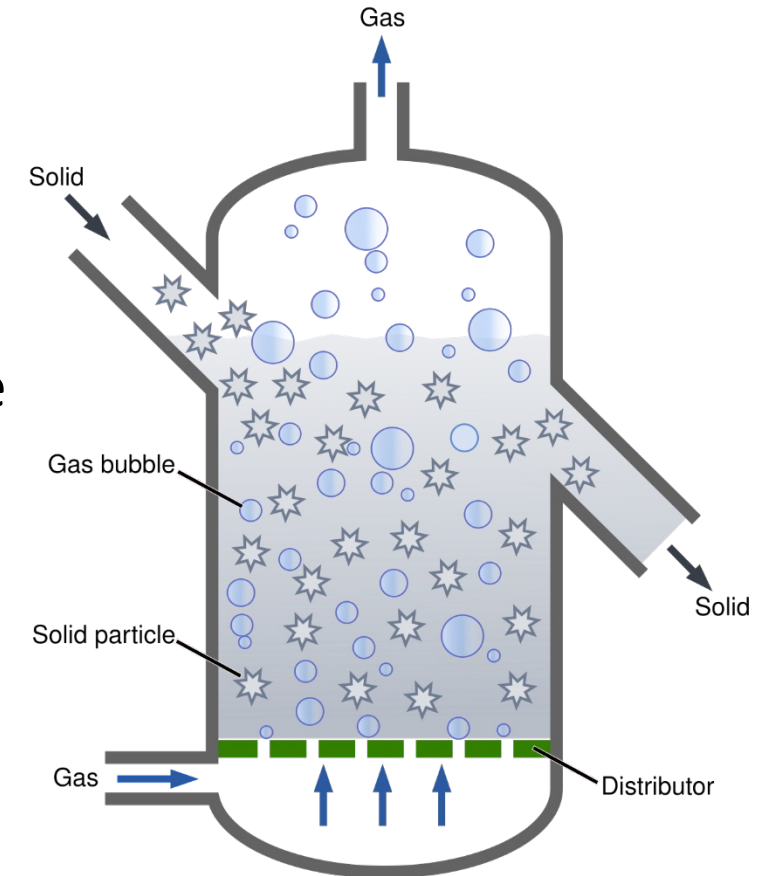


Figure - Gasification reactor.
Source: wikipedia

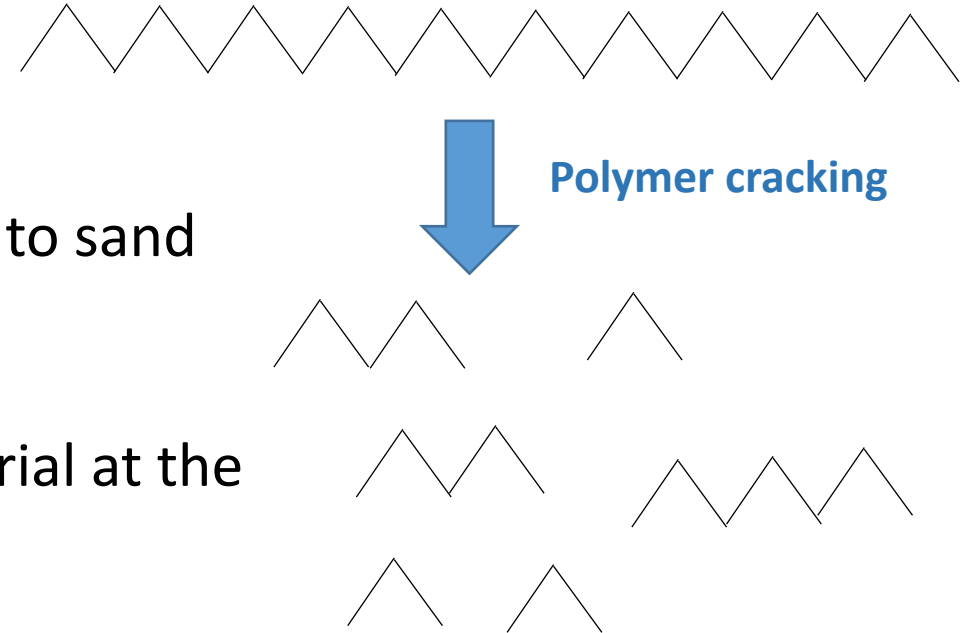
Gasification

Fluidised-bed technology

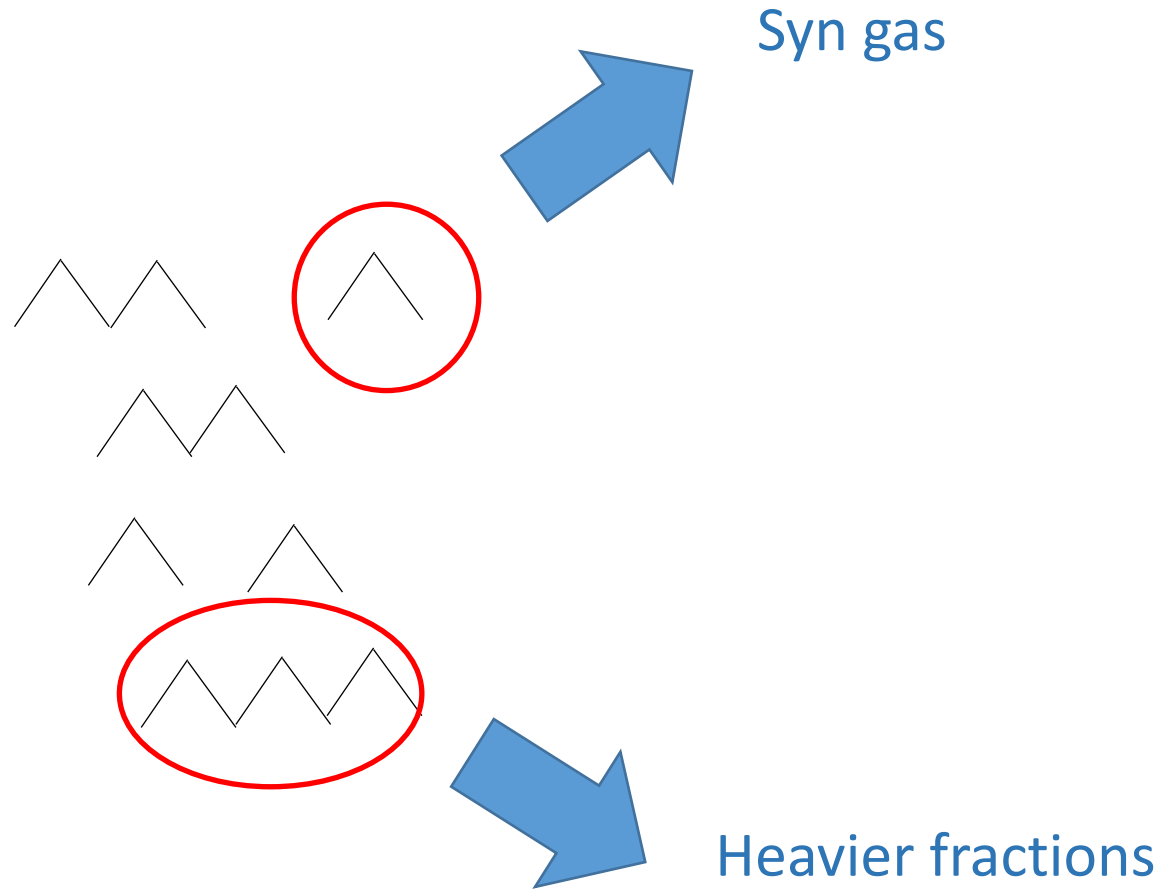
Particles of plastic are rapidly melted and coated on to sand particles.

The polymer cracks to lower molecular weight material at the high temperatures of the bed.

The higher volatility components are transformed onto syngas, leaving heavier, metallic and mineral fractions to be collected at the bottom.



Gasification



Chemical Recycling

Gasification

Fluidised-bed technology

Typically 80-90 % of the waste plastic feed is recovered.

If PVC is gasified, HCl can be generated. It can be removed efficiently and cheaply by introducing calcium oxide into the bed.

This also makes the fluidized-bed more attractive than fixed-bed, where the gas clean-up has to be carried out separately.

Gasification

Fixed-bed technology

The Purox System

- Oxygen as gasifying agent.
- Reactor temperatures 1700°C
- Flue gas is generated: CO, CO₂, H₂, and water vapor.
- Gases contain 80 % of the energy of plastic waste but have to be cleaned.
- The cleaning and the pure oxygen make the system expensive

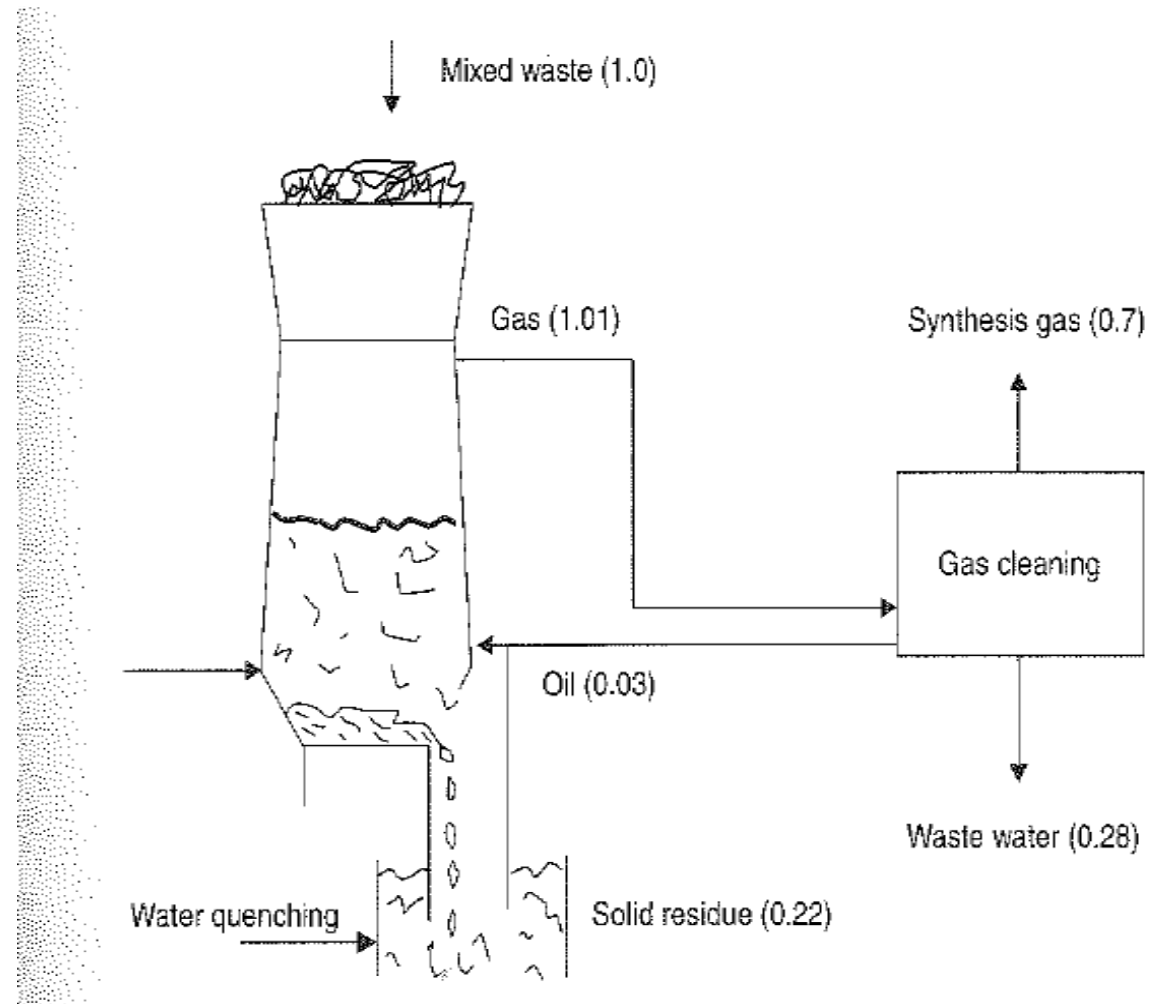
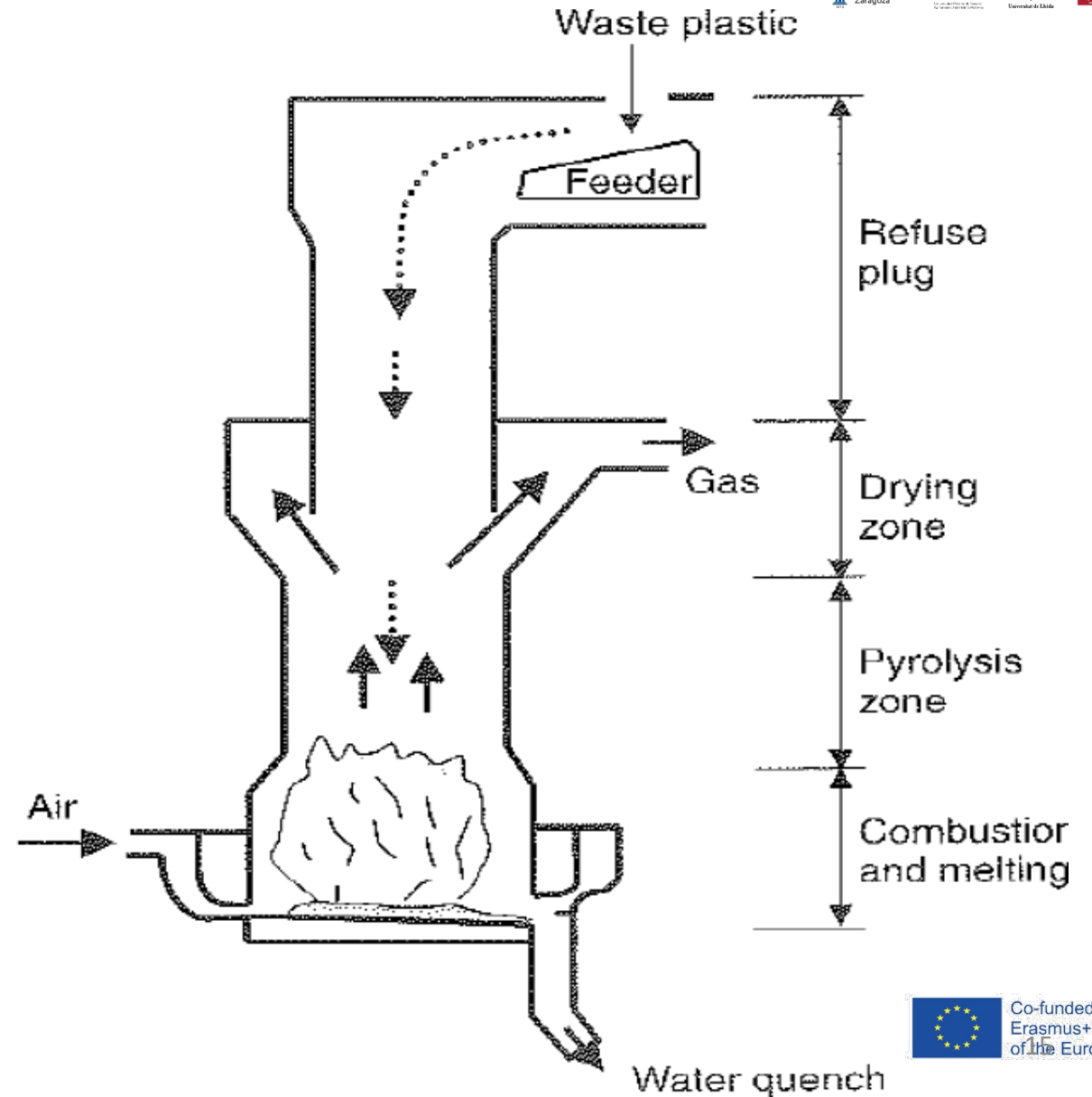


Figure 5- Gasification reactor

The Andco-Torrax System

- Waste polymer is fed into the top of the vertical reactor.
- Air as gasifying agent.
- Gases are clean but with lower calorific value. Exit temperature 400-500°C. Gases are ideal for producing hot water and steam.



Chemical Recycling

Gasification

In summary:

- Synthesis gas is better than flue gas as gases production.
- Gasification has a number of advantages compared to other chemical recycling processes (low capital cost and high product value), but it needs pretreatment processes to separate out waste plastics, which increases the running costs.



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Hydrogenation

Hydrogenation is a chemical reaction between molecular hydrogen (H_2) and another compound or element, usually in the presence of a catalyst such as nickel.

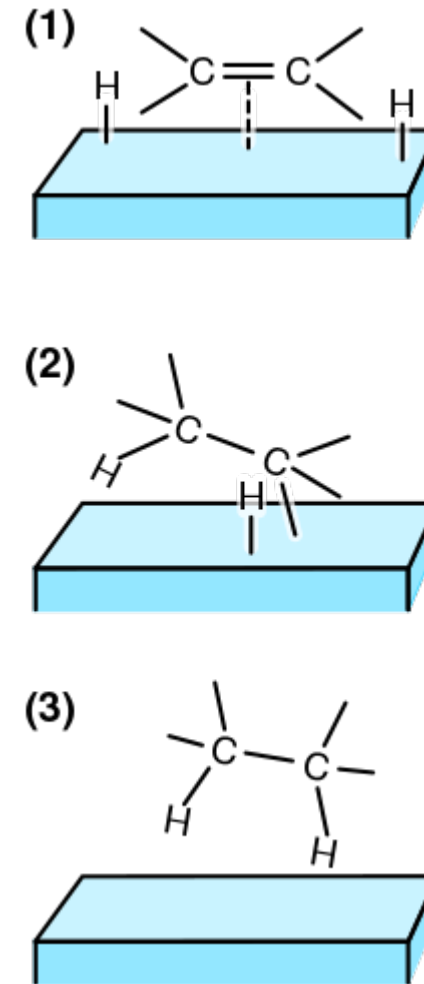


Figure – Hydrogenation steps

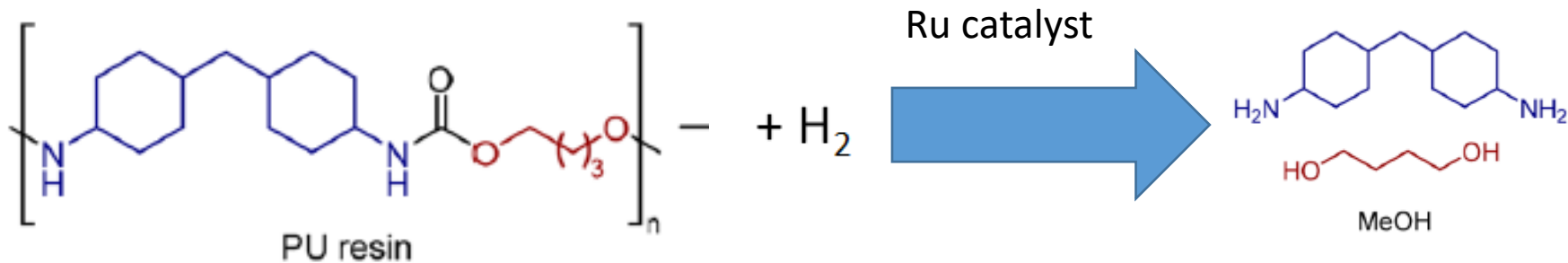
Source: wikipedia

Hydrogenation

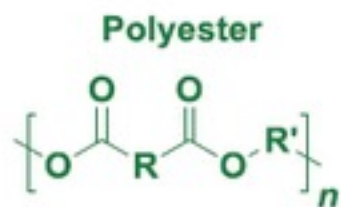
Waste polymer + Hydrogen + Heat + Catalyst → Synthetic oil

Examples of scientific research of hydrogenation of waste polymers (PU)

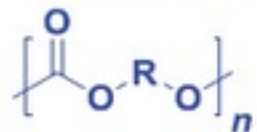
Hydrogenation of Polyurethane:



Examples of scientific research of hydrogenation of waste polymers (polyester and polycarbonate)



Polycarbonates



H₂

Molecular Ru-catalyst

Diols



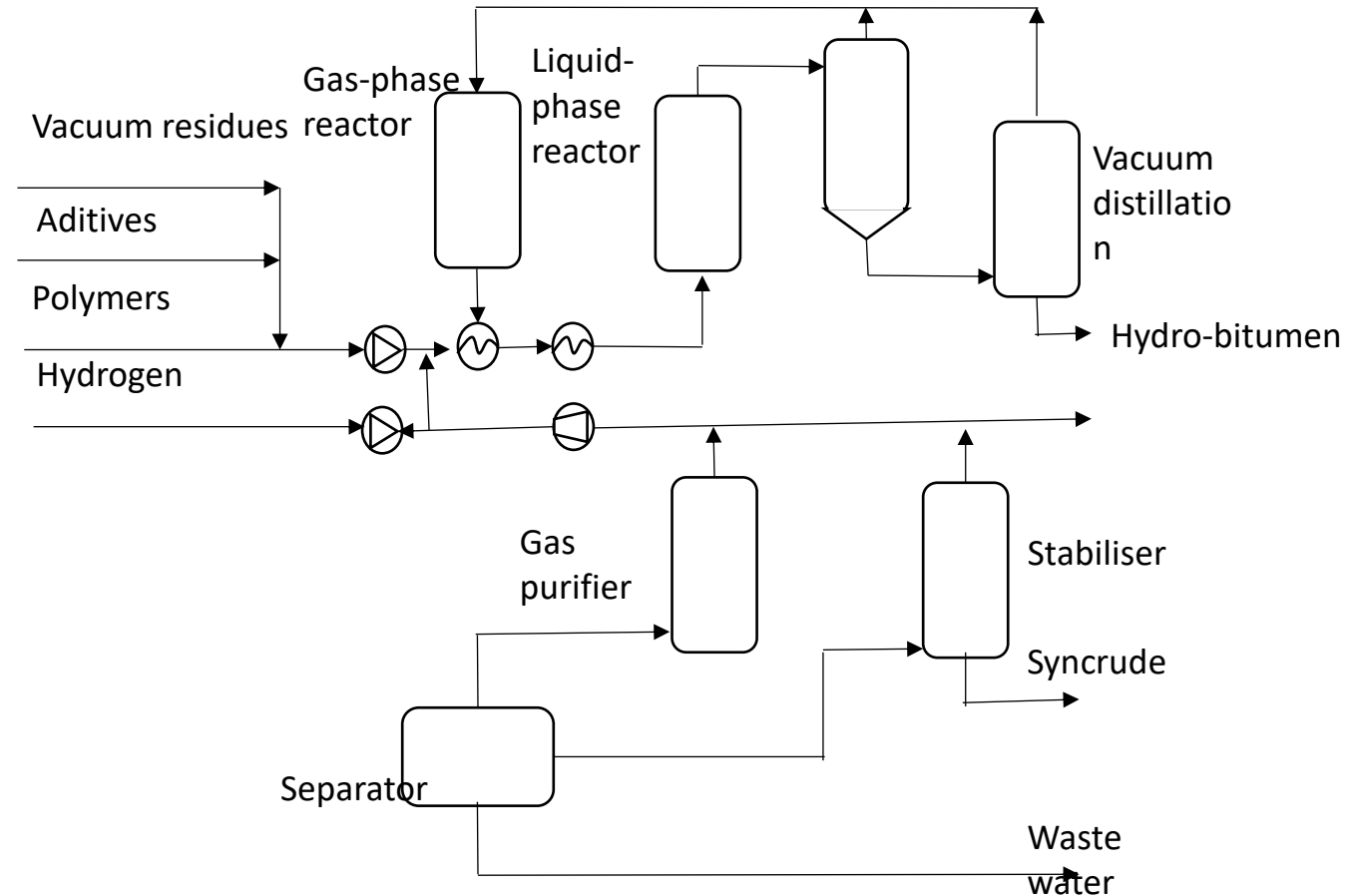
Diol and methanol



Hydrogenation

Bottrop Process

- Depolymerization occurs at 420 °C
- Hydrocracking process takes place in a bubble-column reactor in hydrogen at 480 °C and 20 Mpa.
- The main gaseous products are hydrocarbons and ammonia.
- Solid products are bitumen and syncrude.
- The process is sensitive to the presence of heteroatoms (e.g. S, Cl, N,...) in the polymer.



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Chemical Recycling

Blast Furnace Reduction

Iron ore is reduced in a blast furnace using reducing agents such as carbon, carbon monoxide or hydrogen. Polymer waste can be used as a substitute for heavy oil.

Polymeric material is blown into the bottom of the blast furnace at a temperature of 2000 °C.

Chemical Recycling

Blast Furnace Reduction

Polymeric material pyrolyses to form reducing gases and, at the same time, provides a source of heat.

Polymer substitutes heavy oil as a source of energy and almost 80 % of the gases generated are used through a long blast furnace moving bed.

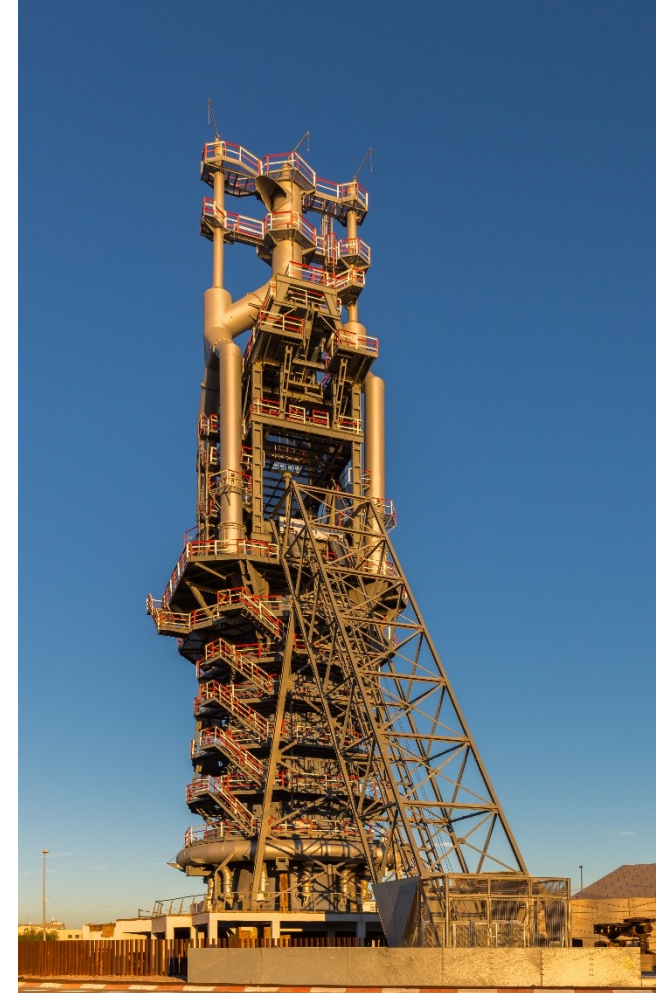


Figure – Blast furnace .
Source: wikipedia



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Pyrolysis

Is thermal decomposition at temperatures from 350-700°C in the absence of oxygen and other gasifying agents.

The polymers decompose to their monomers, oligomers and other organic substances that can be collected separately and used as a feedstock of for energy generation.

High PVC contents limit the application

Waste polymer + Heat → liquid + gaseous + solid hydrocarbons

Chemical Recycling

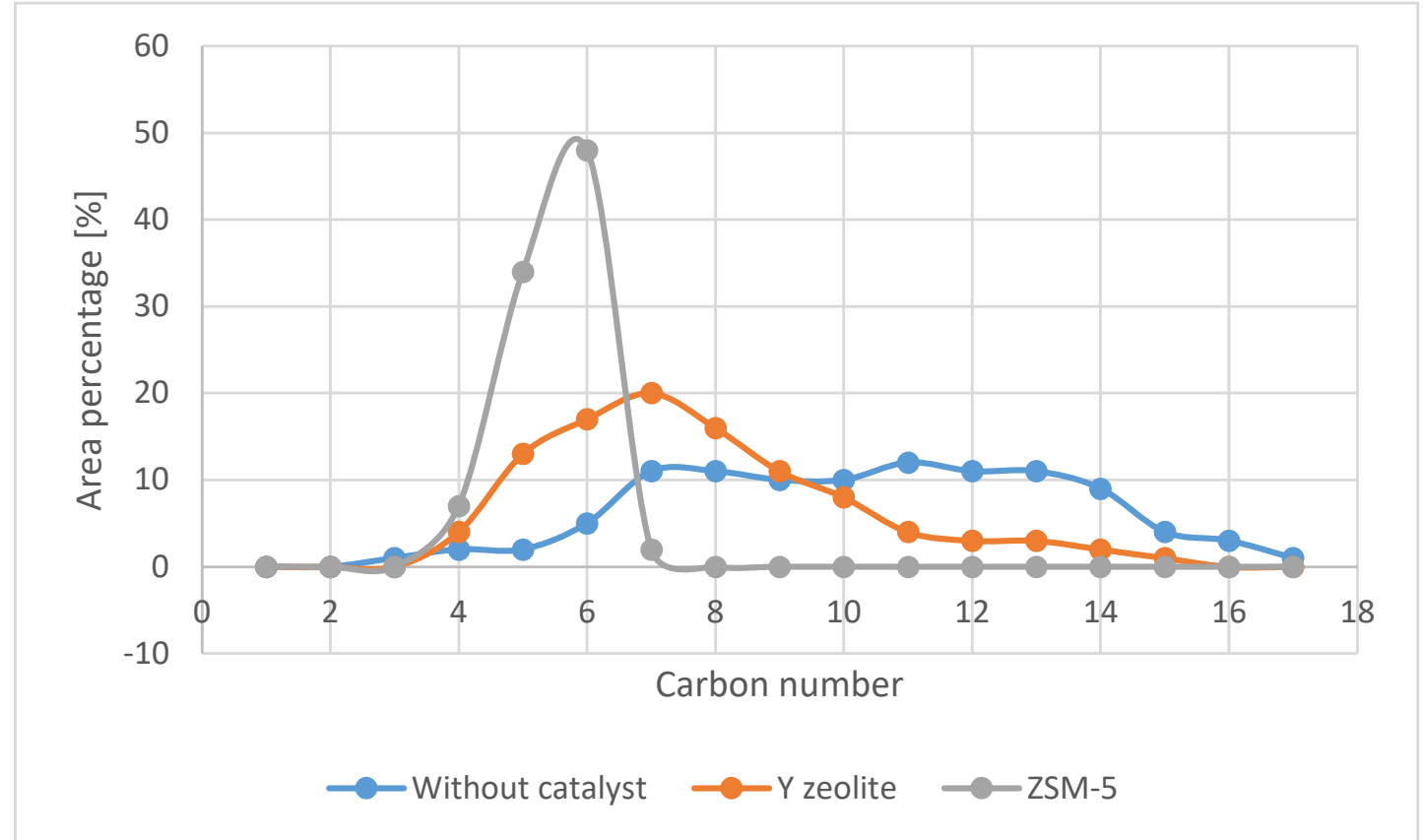
Pyrolysis

It's divided into two main types:

- Thermal (without the presence of catalyst): produces liquids with low octane value and gases require upgrading to be used as fuel.
- Catalytic pyrolysis: reduced temperature and increases value of liquid and gaseous products.

Pyrolysis

- The product spectra is narrowed with catalysis
- Temperatures are reduced (300-350°C)
- Main drawbacks: catalyst contamination



Products distribution of the liquid products of the pyrolysis

Pyrolysis

Reactions that take place on pyrolysis reactor:

- Decompositions into monomers
- Fragmentation of the principal chains into organic components
- Simultaneous decomposition and fragmentation to monomers/oligomers
- Elimination of simple organic components
- Elimination of side chains, producing complex, cross-linked polymer structures.

Plastic Energy Co. has a patented thermal anaerobic conversion technology aimed at converting PSW into feedstock for plastics production or alternative low-carbon fuels. The company has two recycling plants in Seville and Almeria (Spain) which have been in operation since 2014 and 2017, respectively. For every tonne of end-of-life PSW processed, 850 litres of chemical pyrolysis oil (TACOIL) is produced. The company aims to process 200,000 tonnes of plastic by 2020

Enval Ltd. focuses on microwave induced pyrolysis to process plastic aluminium laminates. Recycling aluminium through the Enval process leads to energy savings of up to 75%. With a purity exceeding 98% and a minimum metal yield of 80%, it can be directly reintroduced to the resmelting process.

A typical Enval plant produces 200–400 tonnes of aluminium a year. The generated pyrolytic oils can be used as chemical feedstock or for energy generation. The Enval process can be controlled to adjust yield of the gases and oils according to the operator's requirements. Enval plants can operate at a feed rate of up to 350 kg per hour, which equates to a nominal capacity of 2000 tonnes per year



Pyrolysis

ETIA group

<https://etia-group.com/operations-for-thermal-processing/pyrolysis/>

ETIA Ecotechnologies has developed an innovative patented pyrolysis process Biogreen® that is operating since 2003.



Pyrolysis

Recycling Technologies

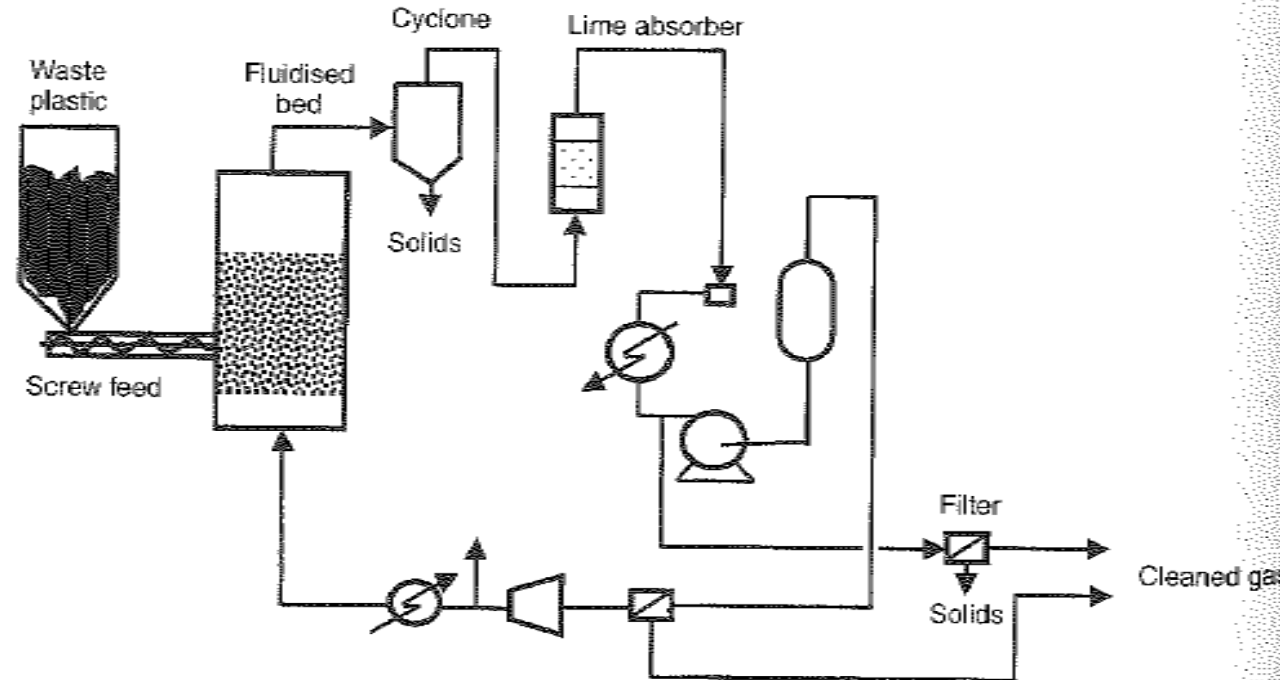
<https://recyclingtechnologies.co.uk/>

Recycling Technologies have developed a process methodology for plastic recycling via converting the plastic waste to fuel and its capacity reaching up to 9000 tpa. They have also commercialised four special ultra-low sulfur oils (reaching less than 0.1% sulfur content) derived from recycled plastics—called Plaxx—which can be used as a fuel substitutes or feedstocks to produce plastics or wax

Pyrolysis

BP Chemicals Pyrolysis Process

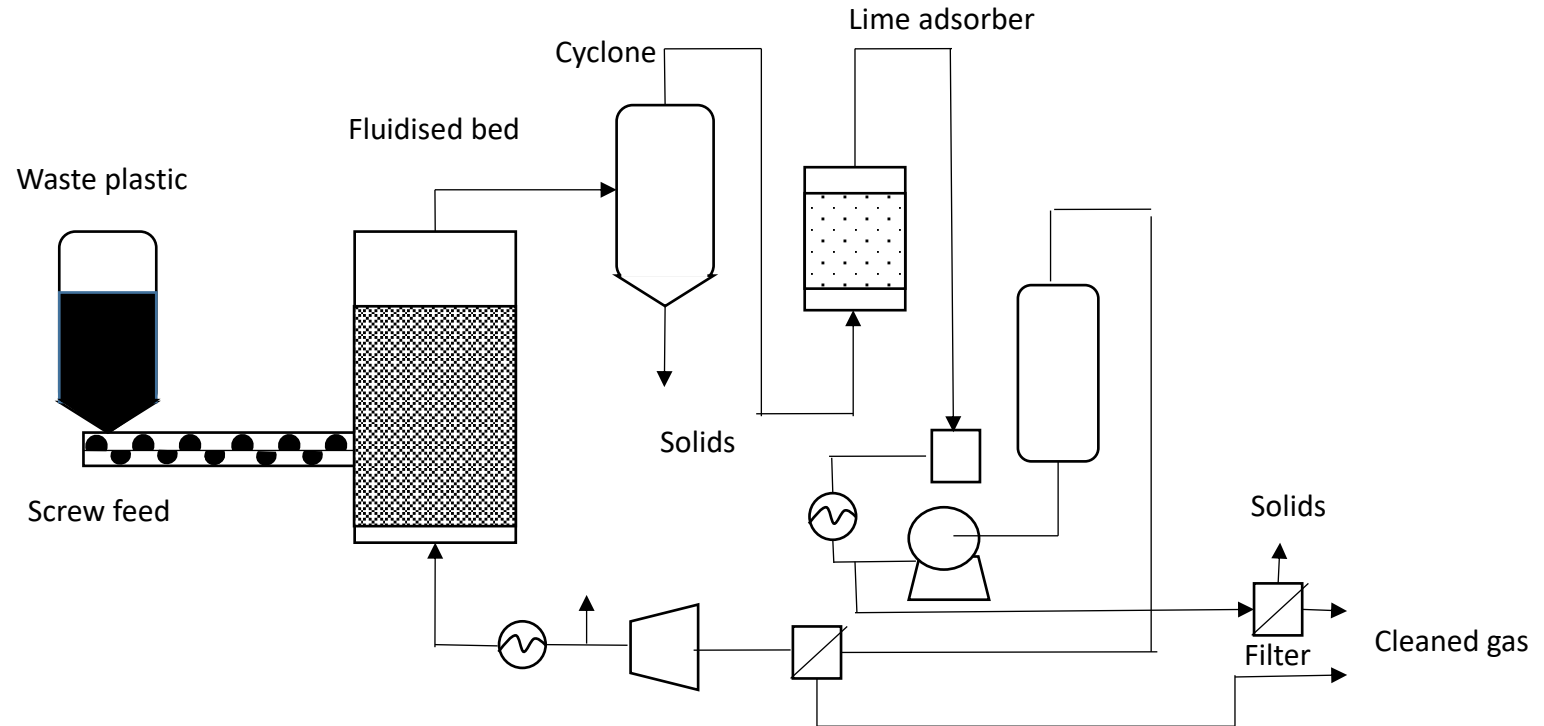
- Fluidised-bed reactor that operates at 500°C in absence of oxygen.
- Hydrocarbons are produced that leave the bed with the fluidising gas.



Pyrolysis

BP Chemicals Pyrolysis Process

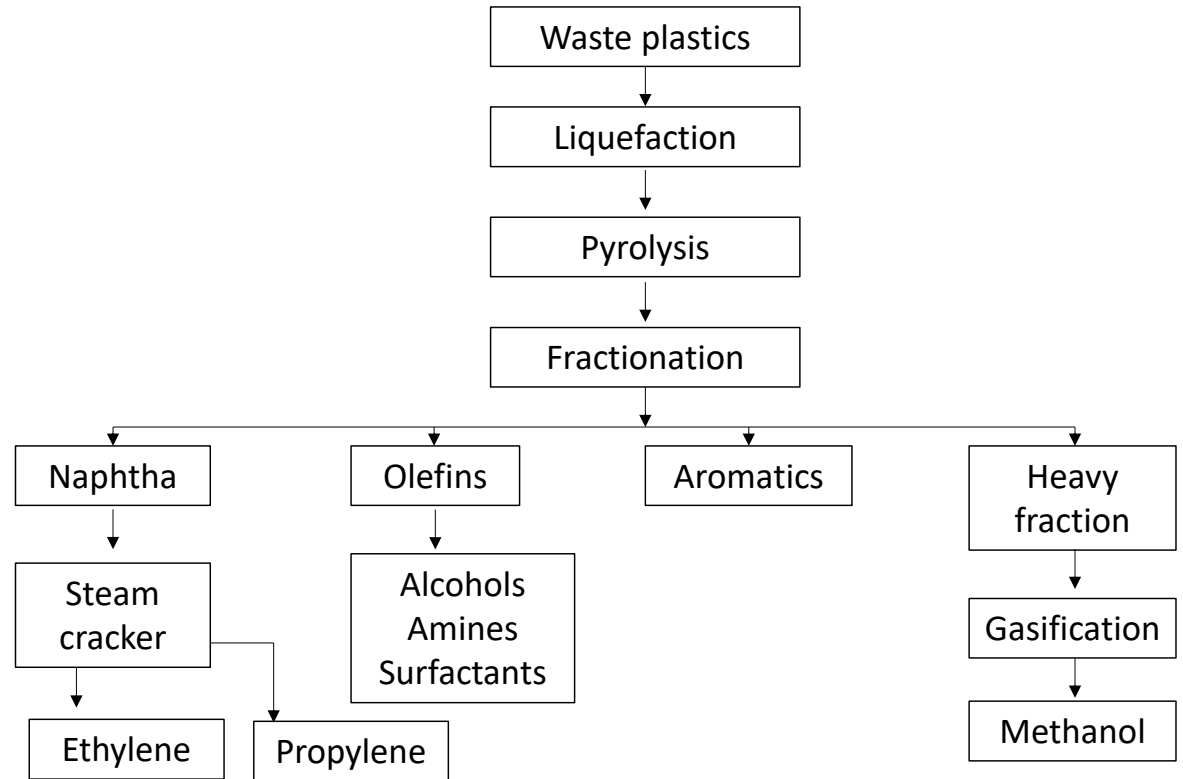
- Purified gas is cooled to condense out the heavier hydrocarbons that can be used to produce liquefied petroleum gas (LPG) and gasoline.
- The remaining lighter hydrocarbons can be re-used as fluidizing gas or as a fuel.



Pyrolysis

BASF Thermolysis Process

- 15000 tonnes/year of plastic polymer can be processed
- The first step is liquefaction at 300-350°C in a cascade of stirred-tank reactors.
- Pyrolysis takes place in a tubular reactor at 400-450°C, followed by two step cooling fractionation, first at 330-380°C and then at 110°C

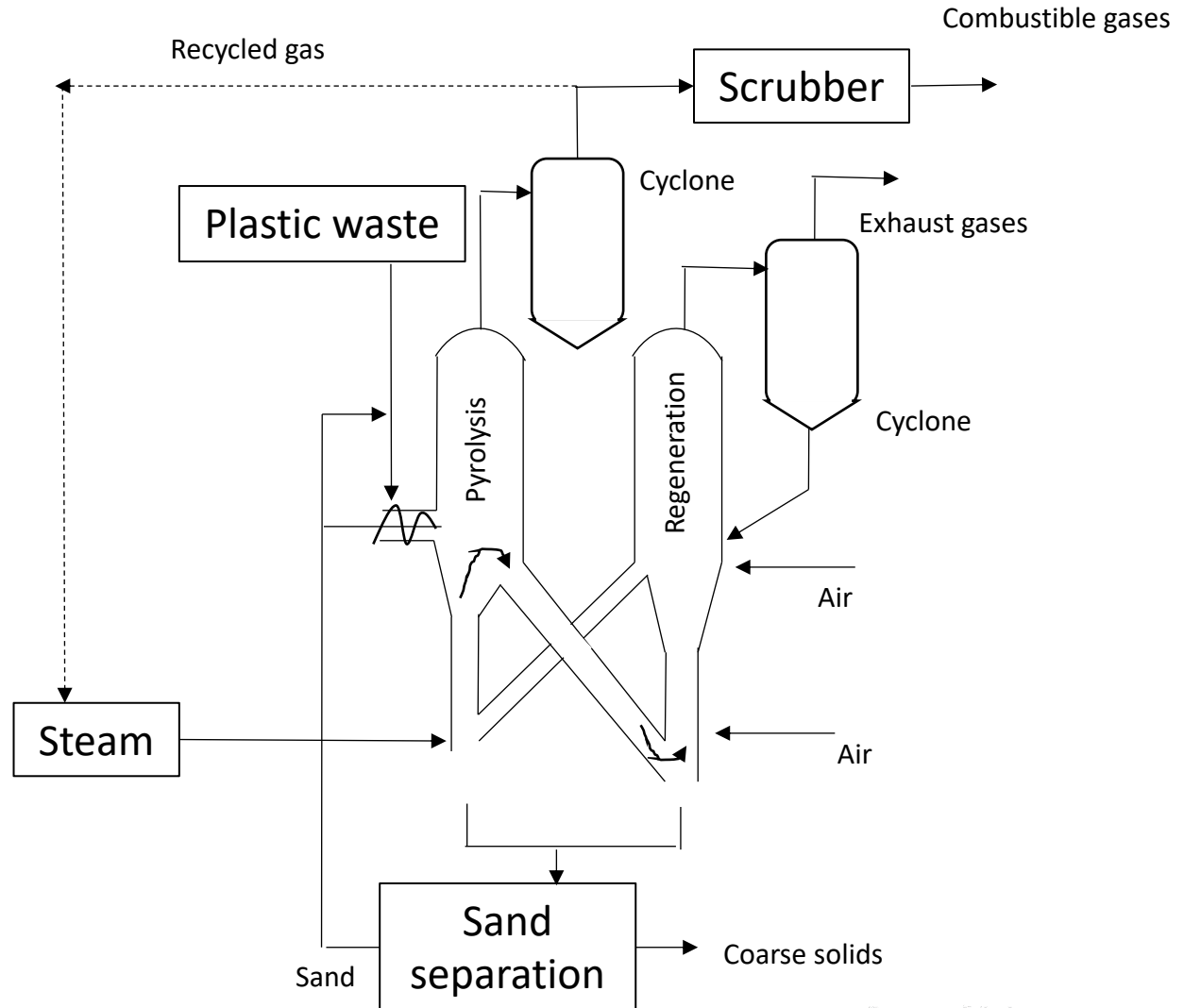


Chemical Recycling

Pyrolysis

Circulating Fluidised-Bed Pyrolysis System

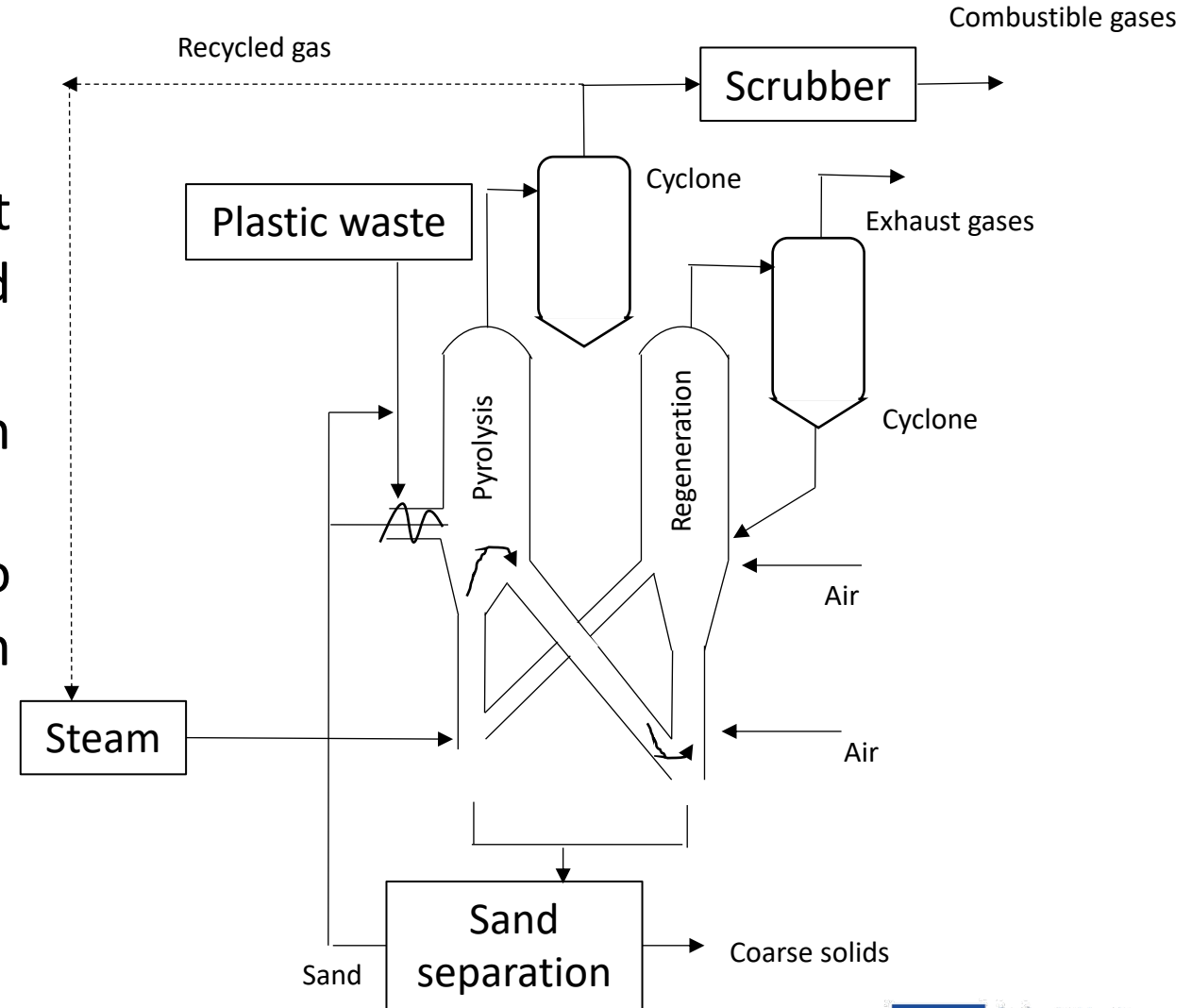
- A mixture of CO, CO₂, H₂, and water vapor is produced.
- Two circulating fluidized beds are used with sand as the fluidizing and heat transfer medium.



Pyrolysis

Circulating Fluidised-Bed Pyrolysis System

- One bed is used for pyrolysis at temperatures between 800-850 °C, and one for regeneration at 950 °C
- Steam is used as fluidizing agent in pyrolysis reactor.
- Solids separated from gases are used to generate steam and some are burned in the regeneration bed to generate heat.





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- Chemical Recycling
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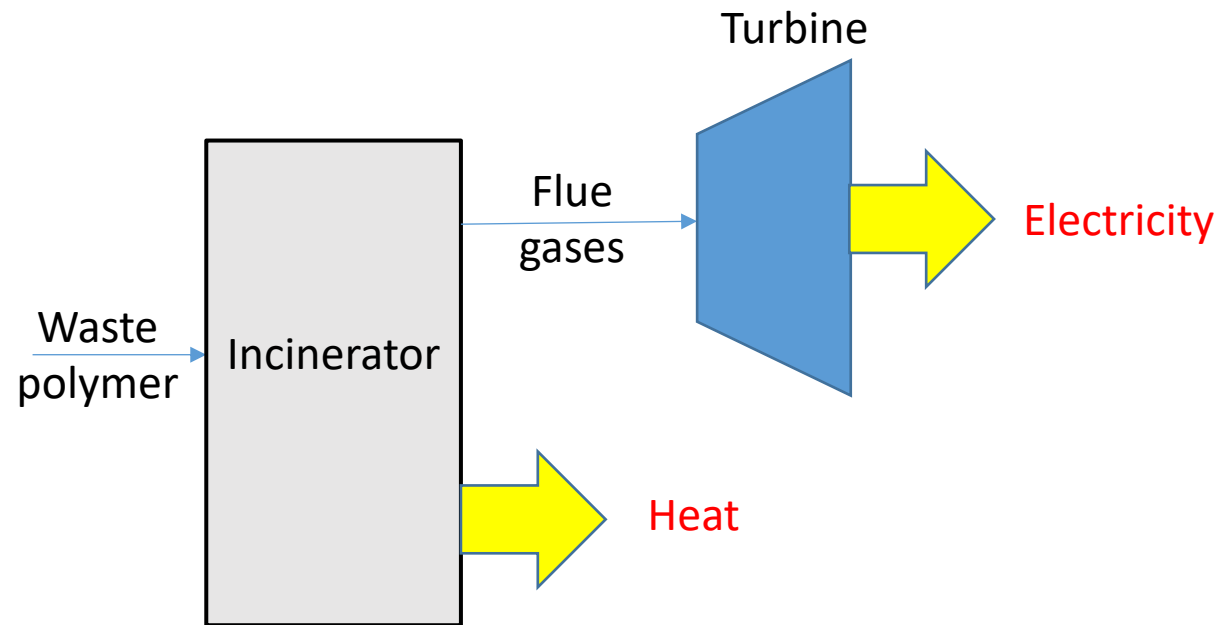
Energy recovery

If mechanical or chemical recycling are not possible, then energy can be recovered from plastic waste as it has a high calorific value.

Energy recovery could take place:

- Burning in a municipal waste incinerator with plastics together with other waste material
- Co-combustion or mono-combustion with plastics and another fuel are burned to generate heat.

Energy recovery



Energy recovery

The main types of incinerator currently in use can be categorized as:

- Mechanical stoker
- Rotary kiln
- Fluidised-bed

Energy recovery

Mechanical-Stoker Incinerator

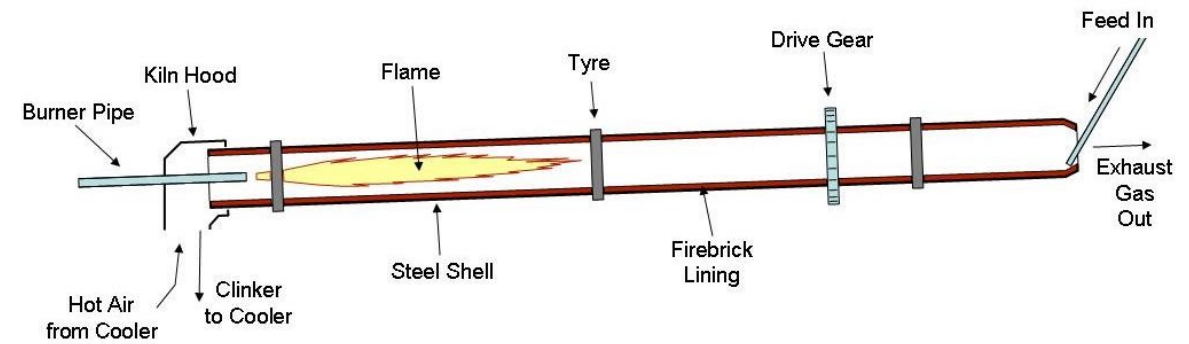
- This is the main type of incinerator for municipal solid waste.
- Waste is fed into the combustion zone by the operation stoke gates or by a simple screw feed.
- Heat is recovered using a exhaust heat boiler or as electrical power by utilizing steam turbines.



Energy recovery

Rotary Kiln Incinerator

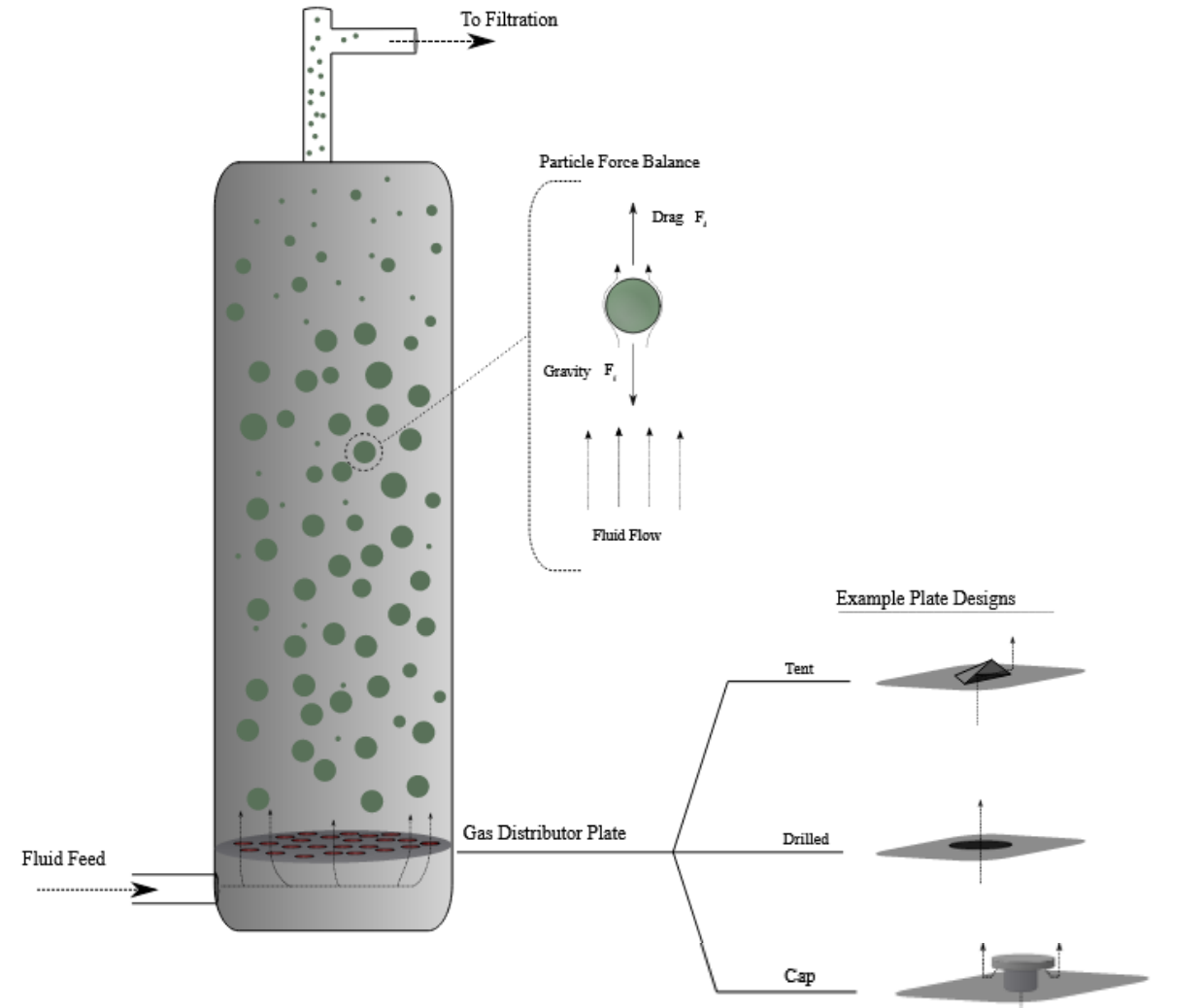
- Similar to the Mechanical-Stoker except that combustion occurs in an inclined, rotating cylinder.
- Waste plastic is introduced into the kiln at $T > 1000 \text{ }^\circ\text{C}$
- Material unburned $\approx 3 \%$
- Expensive technology only applied in cement industry



Energy recovery

Fluidised-bed Incinerators

- Modern incinerators
- Simplicity of operation. No problems associated with residual unburned fractions of waste.
- Used also for MSW and rubber and tyres.
- Sand is used in fluidised reactor.
- Advantages of this reactor:
 - The combustion is easy to control
 - The exhaust gas treatment is not complicated
 - High waste volume reduction



Energy recovery

Fluidised-bed Incinerators

- Energy is recovered in the form of hot water, steam or electricity. Electricity is economic for larger plants.
- Wide temperature and pressure ranges. T 370-540°C, pressure 2.5-10 Mpa
- Lower temperatures mean lower thermal efficiency but prevent corrosion by chlorine.

Incinerator emissions

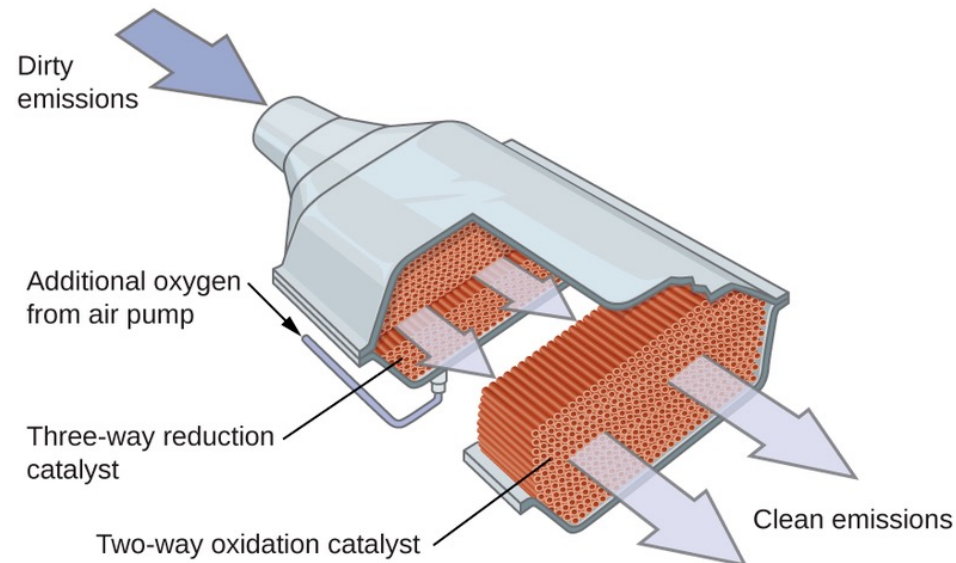
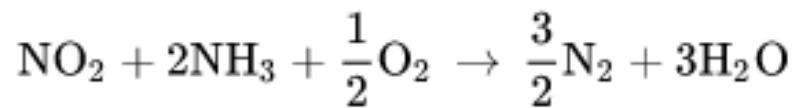
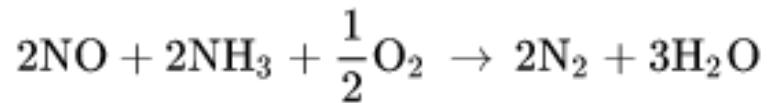
CO, HCl, SO₂, NO_x, particles, heavy metals, dioxins and furans are usual emissions

Energy recovery- Incineration emissions

NO_x can be reduced with a control system for the supply of air and with selective catalytic reduction.

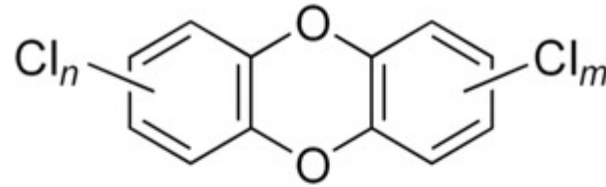
NO_x selective catalytic reduction:

The **NO_x reduction** reaction takes place as the gases pass through the catalyst chamber. Before entering the catalyst chamber ammonia, or other reductant (such as urea), is injected and mixed with the gases.

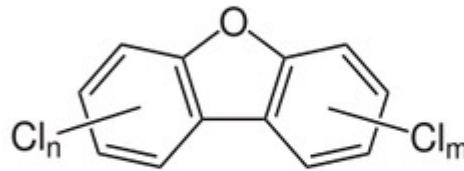


Energy recovery- Incineration emissions

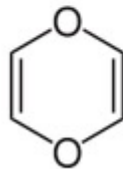
Dioxins can be reduced by a control system for the supply of air, and control of temperature and residence time. Selective catalytic reduction also can avoid dioxins emissions. Dioxins are highly toxic and they are persistent pollutants. Some relevant dioxins.



Polychlorinated dibenzo-*p*-dioxins



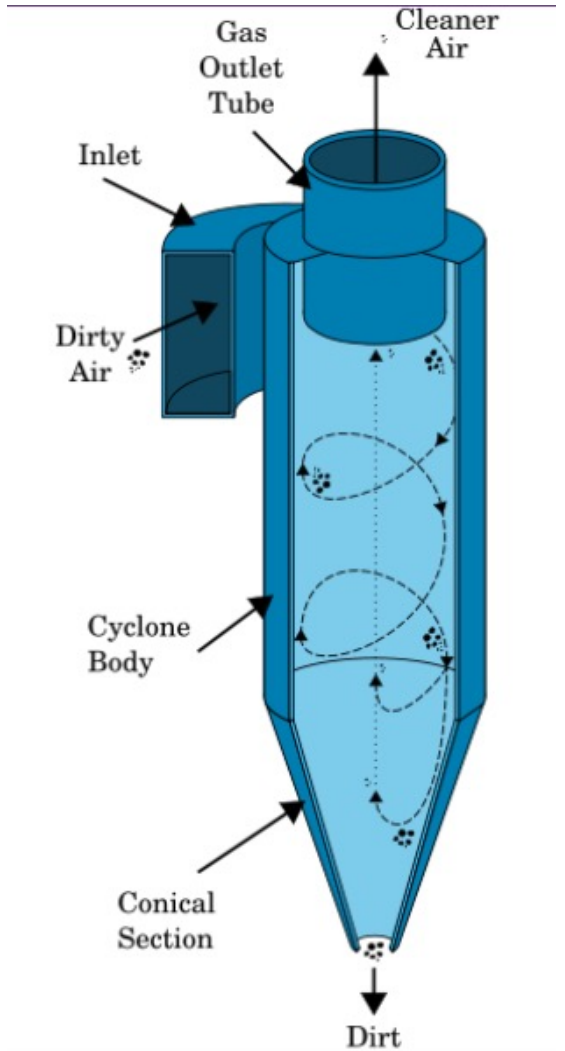
Polychlorinated dibenzofurans



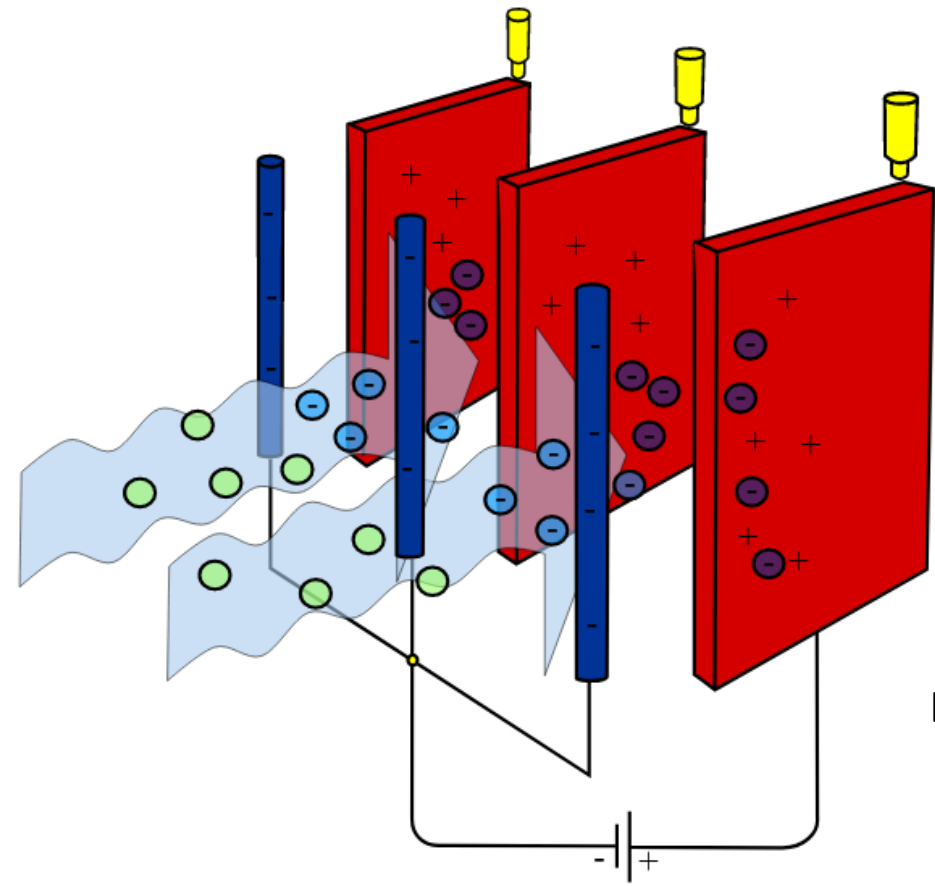
1,4-dioxin

Energy recovery- Incineration emissions

Systems for particles removing



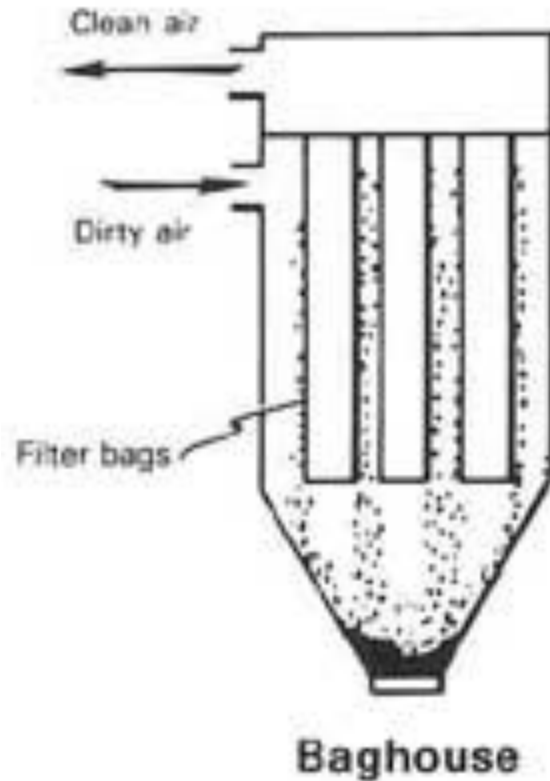
Cyclone



Electrostatic separators

Energy recovery- Incineration emissions

Systems for particles removing

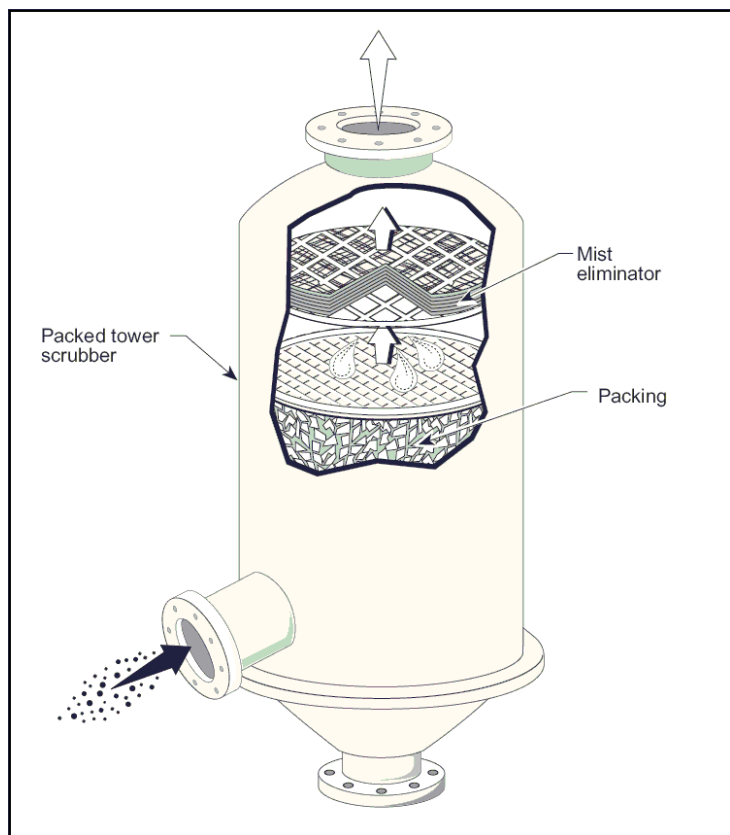


Filters separators

Energy recovery- Incineration emissions

Systems for particles removing

Scrubbers to remove HCl, HF and SO₂



Activated carbon for heavy metals removing



Wet scrubbers



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Linking Academy to Industry.



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Co-funded by the
Erasmus+ Programme
of the European Union

This project has been funded with support from the European Commission.

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