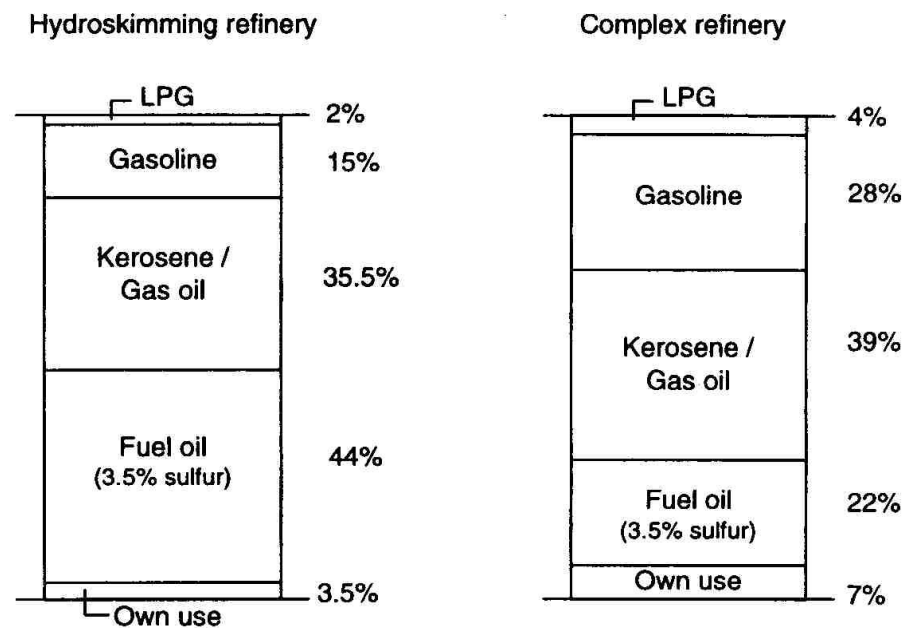


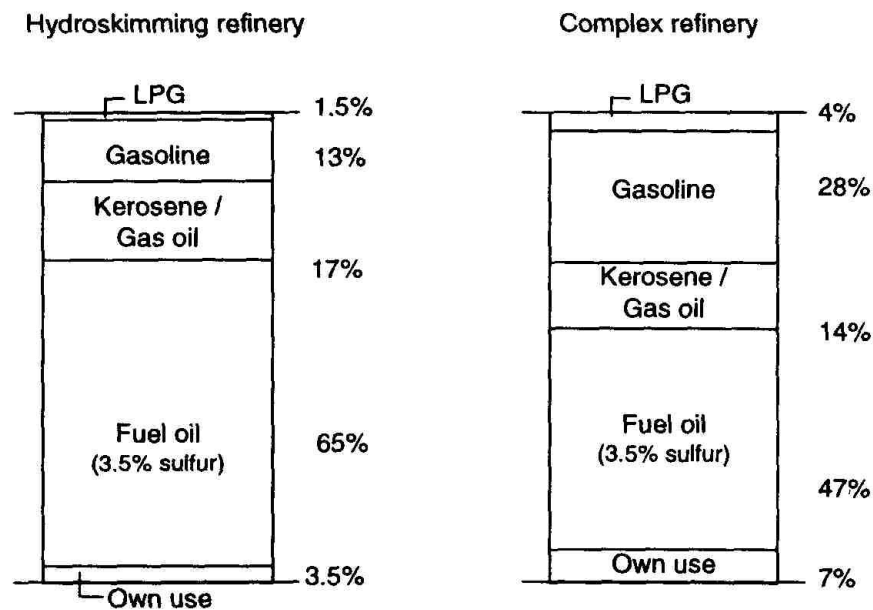
CONVERSION OF HEAVY RESIDUES

- Processing of **light crude**, even in a complex refinery with FCC, hydrocracking *etc.* does not yield a satisfactory **product distribution**. The amounts of fuel oil are too high.



CONVERSION OF HEAVY RESIDUES

- For **heavy oil** the situation is even worse with ~ 50% fuel oil being produced even in a complex refinery.
- Fuel oil is worth < original crude. The value of the **products** decreases in the order: gasoline > kerosene/gas oil > crude oil > fuel oil.



CONVERSION OF HEAVY RESIDUES

There are several reasons for an increased incentive to convert fuel oil into lighter products:

1. The demand for light products such as gasoline and automotive diesel fuels continues to increase while market for heavy fuel oil is declining.
2. Environmental restrictions become more important. Fuel oil contains high amounts of S, N, and metals, so measures must be taken to lower emissions.
3. With the exception of Western Europe, the quality of crude oil shows a worsening trend. It becomes heavier with higher amounts of hetero-atoms, so more extensive processing is required to obtain the same amount and quality of products.

CONVERSION OF HEAVY RESIDUES

In principle there are two solutions for upgrading residual oils and for obtaining a better product distribution. These are *carbon out* and *hydrogen in* processes.

1. Examples of carbon rejection processes are the Flexicoking process (Exxon) and the FCC process discussed earlier.
2. Examples of hydrogen addition processes are the LC-finishing process (Lummus) and the HYCON process (Shell).

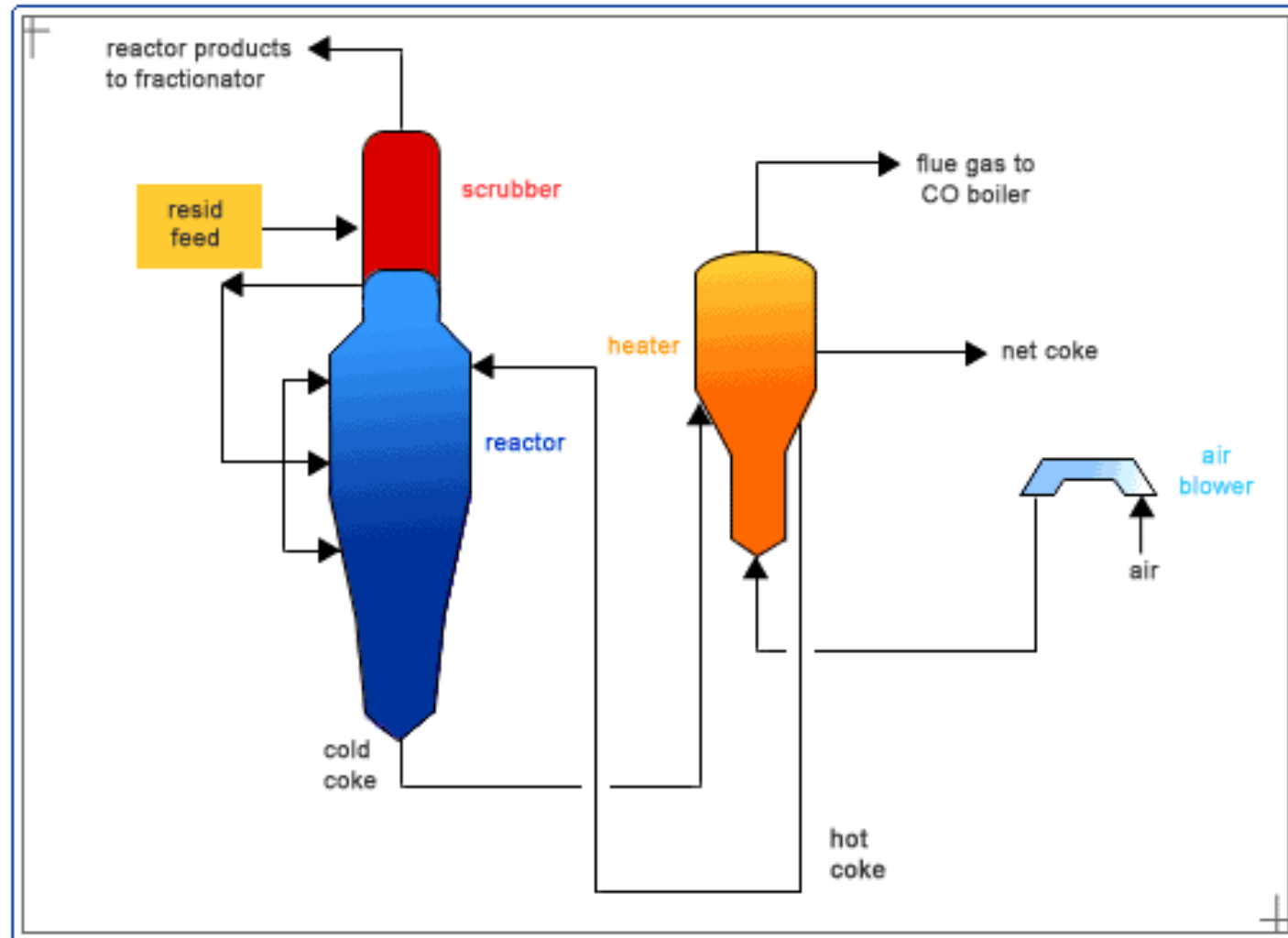
Fluid Coking and Flexicoking

- Both FLUID COKING™ and FLEXICOKING™ use fluid bed technology to thermally convert heavy oils such as vacuum residue, atmospheric residue, tar sands bitumen, heavy whole crudes, deasphalter bottoms or cat plant bottoms.
- FLEXICOKING goes one step further than FLUID COKING: in addition to generating clean liquids, FLEXICOKING also produces a low-BTU gas in one integrated processing step that can virtually eliminate petroleum coke production.
- The advantages are: flexibility to handle a variety of feed types; high reliability with the average service factor between 90 -95%; large single train capacity provides an economy of scale that lowers investment cost; able to process 65 kB/SD of 20 wt% Conradson Carbon resid in a single reactor; time between turnarounds routinely approaches two years; able to process very heavy feed stocks such as deasphalter bottoms at high feed rates.
- Additional FLEXICOKING benefit: Integrated gasification of up to 97% of gross coke production

The Fluid Coking Process

- The fluid coking residuum conversion process uses non-catalytic, thermal chemistry to achieve high conversion levels with even the heaviest refinery feedstocks.
- Since most of the sulfur, nitrogen, metals, and Conradson Carbon Residue feed contaminants are rejected with the coke, the full-range of lighter products can be feed for an FCC unit.
- Use as a single train reduces manpower requirements and avoids process load swings and frequent thermal cycles that are typical of batch processes such as delayed coking.
- The configurations available with fluid coking are: extinction recycle, once-through, and once-through with hydroclones.

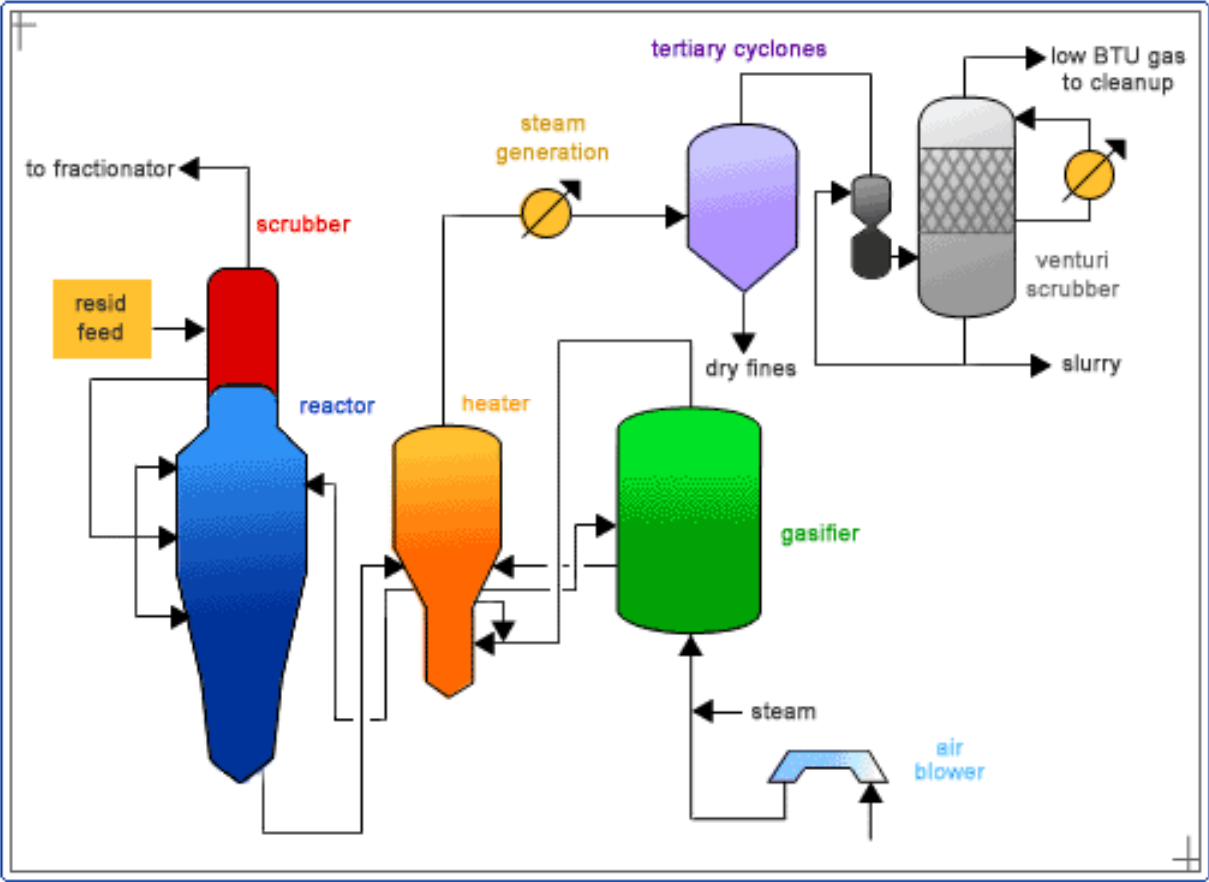
Simplified FLUID COKING Flowplan



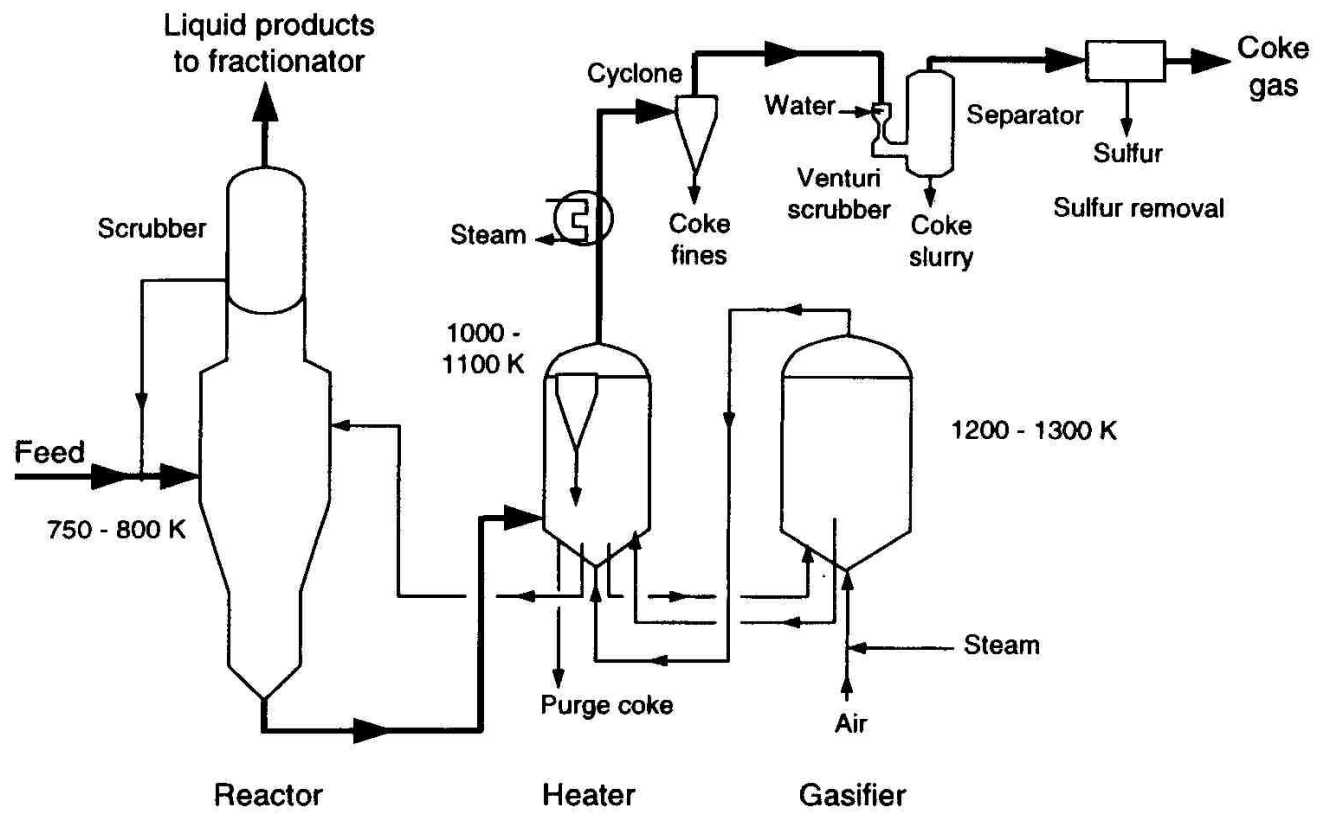
The Flexicoking Process

- Flexicoking is a thermal technology for converting heavy feedstocks to higher margin liquids and producing, a low BTU (*i.e.* a low energy content) gas, instead of coke.
- The conversion of coke to clean fuel gas maximizes refinery yield of hydrocarbons.
- The carbon rejection process results in lower hydrogen consumption than alternative hydrogen-addition systems.
- The low BTU gas is typically fed to a CO boiler for heat recovery but can also be used in modified furnaces/boilers; atmospheric or vacuum pipestill furnaces; reboilers; waste heat boilers; power plants and steel mills; or as hydrogen plant fuel, which can significantly reduce or eliminate purchases of expensive natural gas.
- The small residual coke produced can be sold as boiler fuel for generating electricity and steam or as burner fuel for cement plants.

Simplified FLEXICOKING Flowplan



The Flexicoking Process

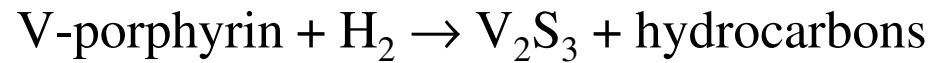
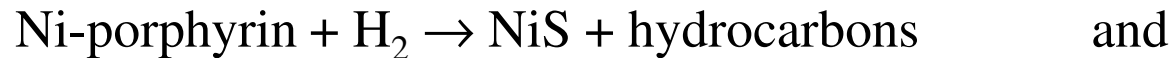


Catalytic hydrogenation of residues

- This is a “hydrogen-in” route.
- It serves two purposes: removal of Sulphur, Nitrogen and metal compounds, and the production of light products.
- Reactions are similar to those occurring in hydrotreating and hydrocracking of gas oils, **but** there are two important differences.
- (1) Residues contain much higher amounts of sulphur, nitrogen and polycyclic aromatic compounds; and
- (2) removal of metals, which are concentrated in the residual fraction of the crude, means that operating conditions are more severe and hydrogen consumption greater than for hydroprocessing of gas oils.

Catalyst deactivation

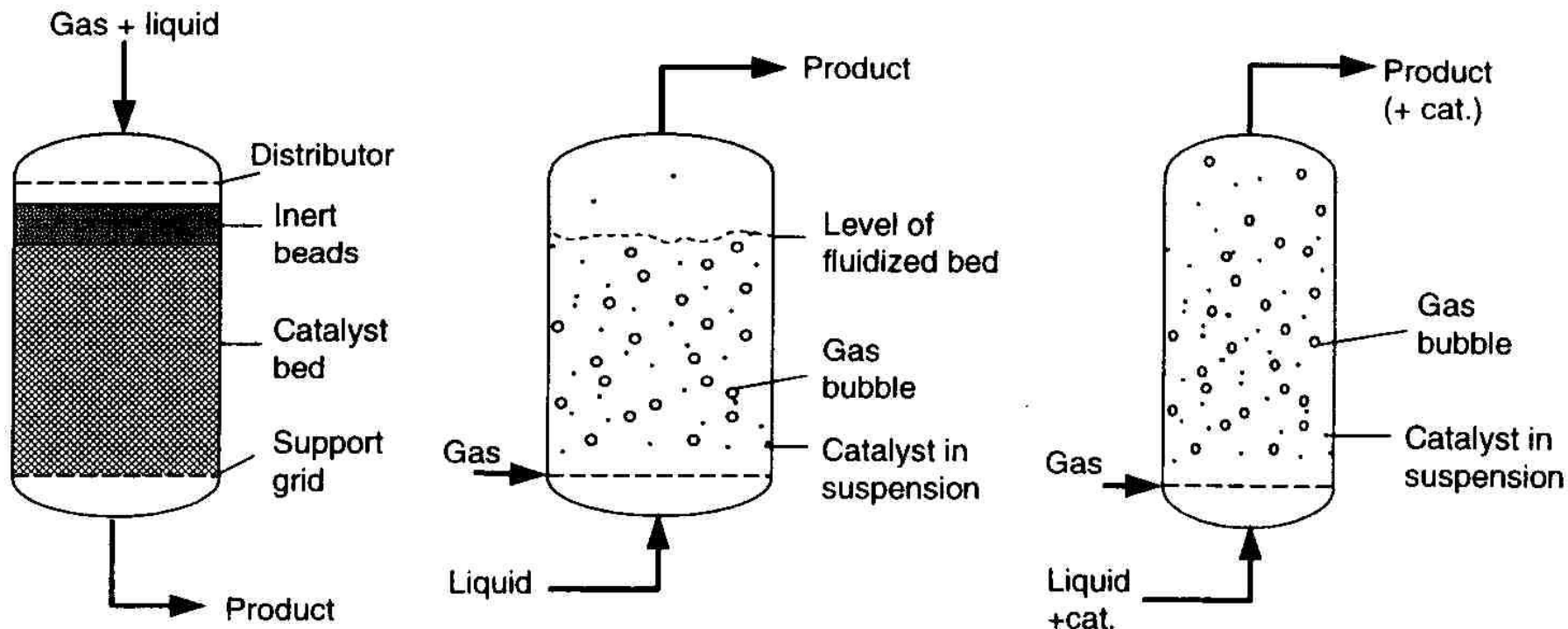
- Deposition of metals causes catalyst deactivation.
- Basically all metals in the periodic table are present in crude oil with the major ones being Ni and V.
- At the reaction conditions H_2S is present, hence metal sulphides are formed.
- The reaction scheme is complex but may be represented simply as:



- The catalyst is poisoned by this process because most of the deposition occurs on the outer shell of the catalyst particles, initially poisoning the active sites then causing pore plugging.

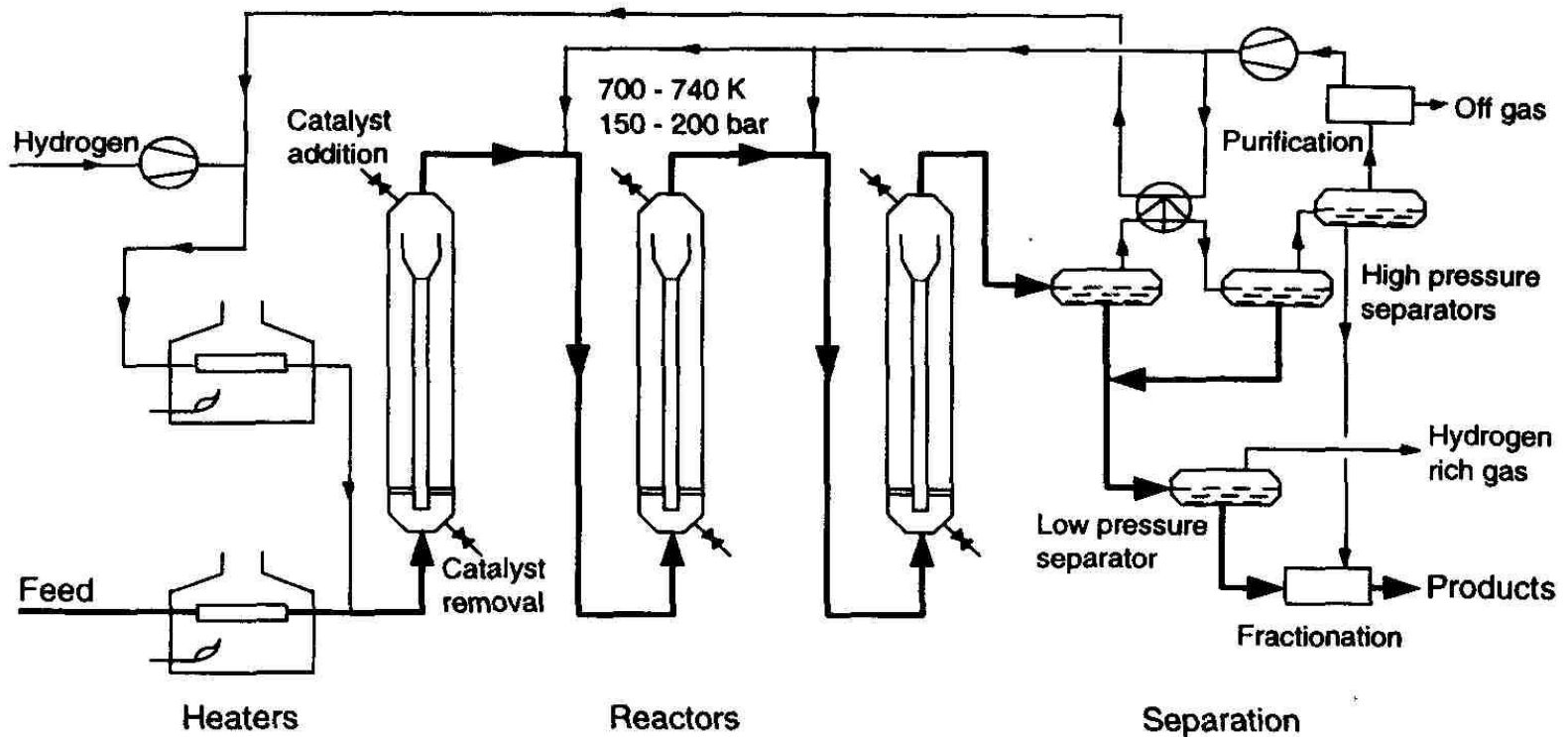
Reactors used for catalytic hydrogenation

- Three types of reactor are used: (1) fixed-bed reactors; (2) fluidized-bed reactors (also called ebulliated-bed reactors); and (3) slurry reactors.



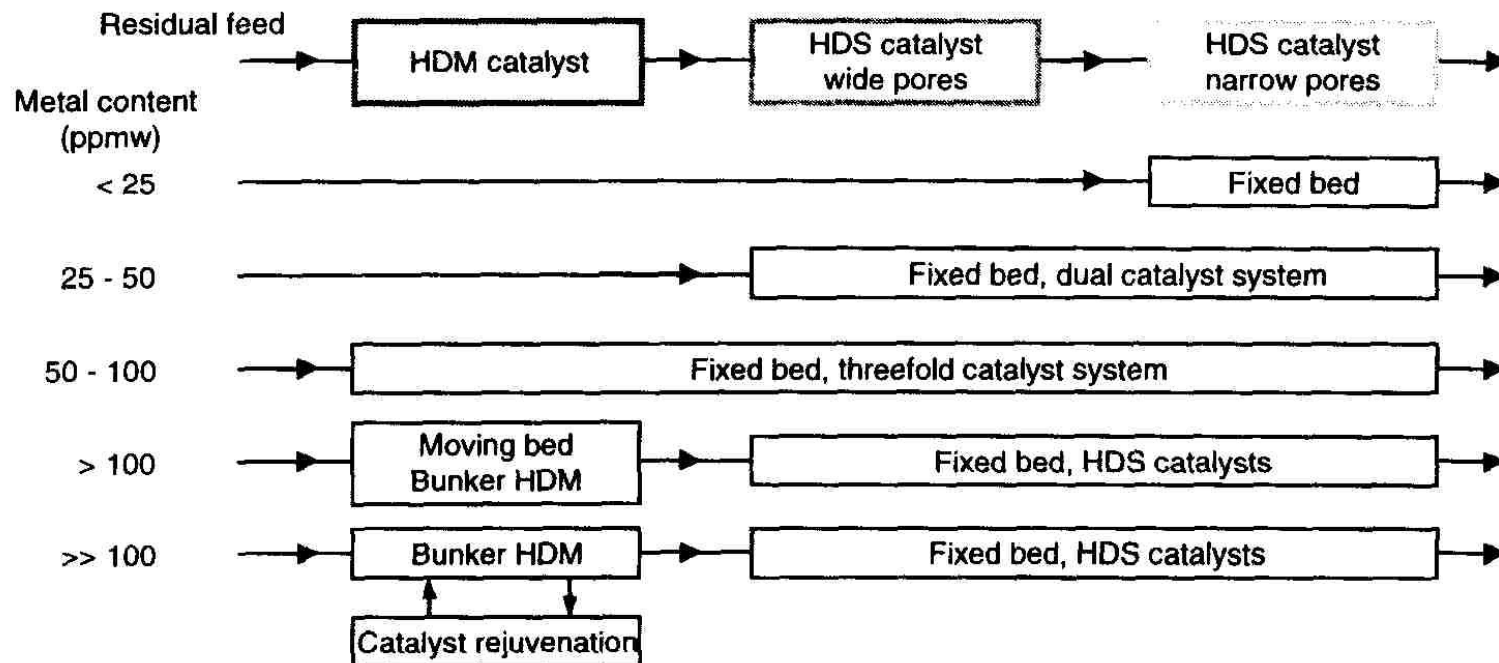
The LC-finishing process

- Developed by Lummus.
- Uses fluidized-bed reactors.

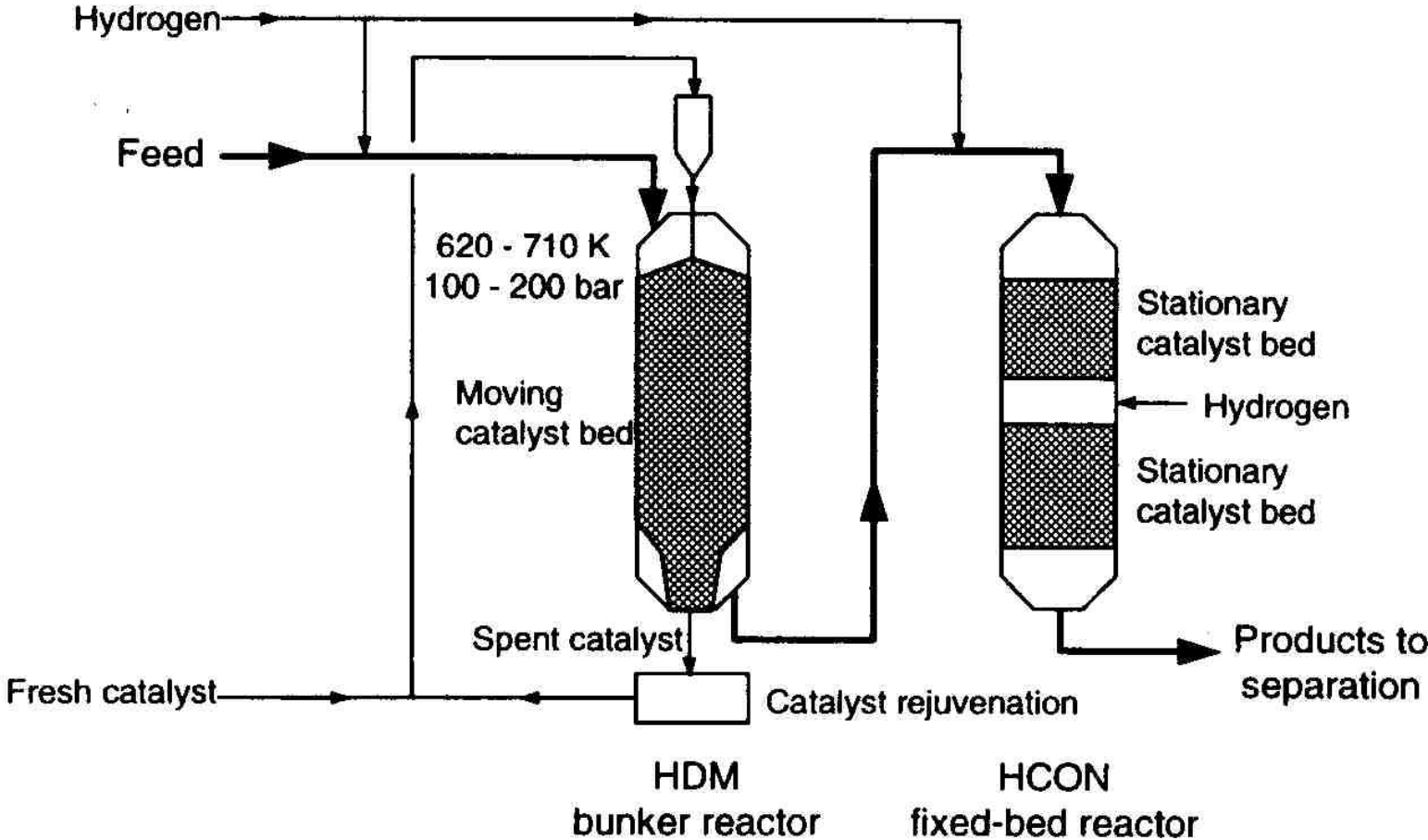


Processes with fixed-bed reactors

- Replacement of deactivated catalyst in a conventional fixed-bed reactor is not possible during operation.
- Depending on the metal content of the feedstock various combinations can be applied.

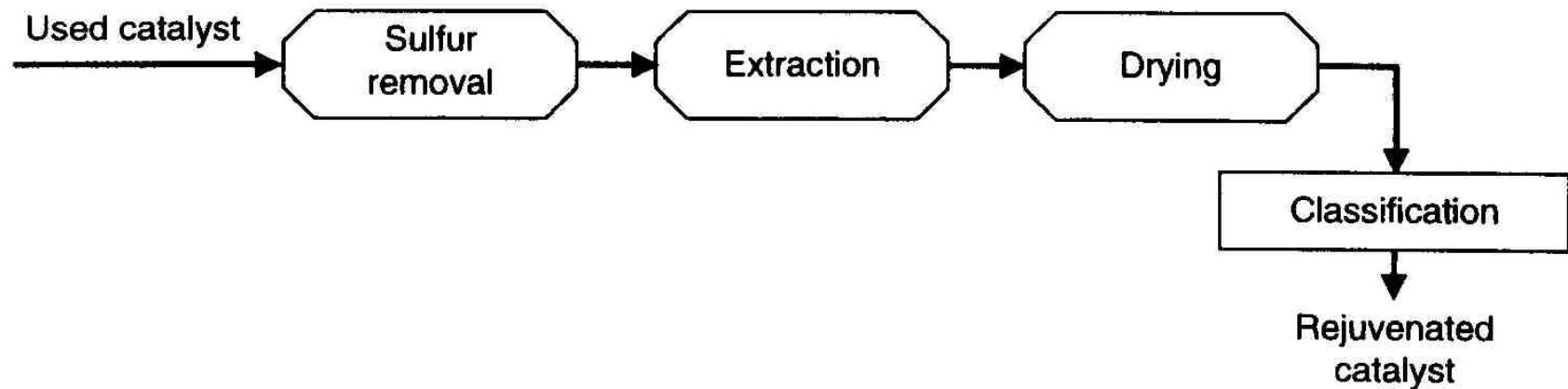


HYCON process



Catalyst rejuvenation

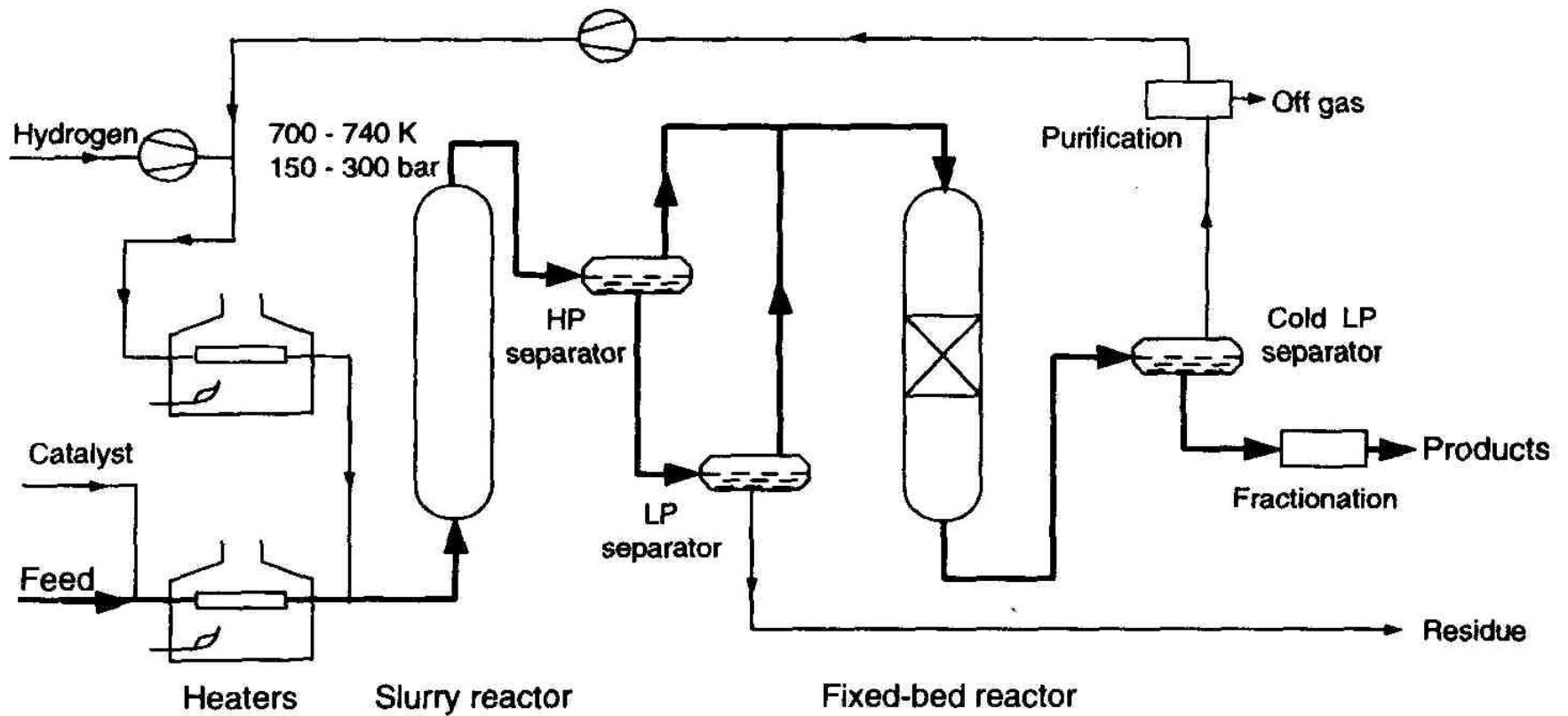
- Catalyst rejuvenation is achieved by removal of metal sulphides and carbonaceous deposits (essentially by oxidation), and by extraction of the metals.



Processes with slurry reactors

- Slurry processes for residue processing are normally designed with the objective of maximizing residue conversion.
- Downstream reactors are then used to treat the liquid products for S and N removal.
- Examples of the slurry process are the Veba Combi-Cracking and CANMET process.
- Conversion of residual feed takes place in the liquid phase in a slurry reactor.
- After separation the residue from the products they are further hydro-treated in a fixed-bed reactor containing an HDS catalyst.
- A cheap, once-through catalyst is used which ends up in the residue.

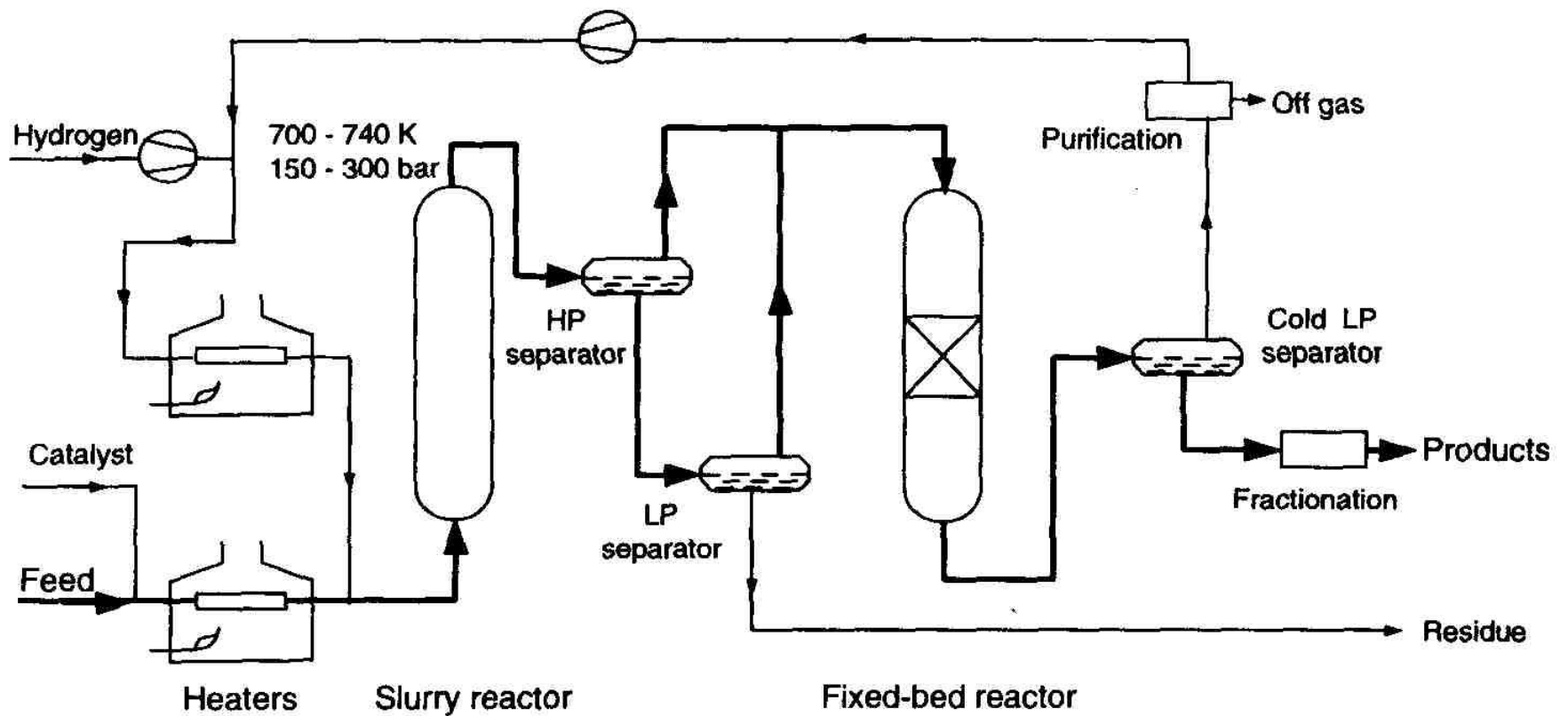
Veba Combi-Cracking process



TREATMENT OF REFINERY GASES

- Removal of H₂S from gases is usually performed by absorption in the liquid phase.
- The concentrated H₂S is frequently converted to elemental sulphur by the “Claus” process (partial oxidation of H₂S)
- In the Claus process 95-97% of the H₂S is converted.
- H₂S is often removed with solvents that can be regenerated, usually **alkanolamines**: *e.g.* CH₂(OH)CH₂NH₂ MEA (mono-ethanolamine).
- These amines are highly water soluble with low volatility and their interaction with H₂S is much faster than with CO₂ so that the amount of absorbed CO₂ can be limited by selecting appropriate conditions.

Flow scheme for H₂S removal by amine absorption



Flow scheme of a typical Claus process

