

partial oxidation of Hydrocarbon's

There are two commercial processes for producing Hydrogen and hydrogen containing synthesis gases by the non catalytic partial oxidation of hydrocarbons under pressure.

These are:

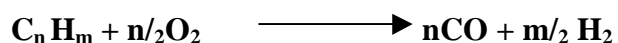
1. Texaco process (1954)
2. Shell gasification process (1956).

Both processes carry out the partial oxidation by burning hydrocarbon with oxygen or oxygen-rich mixtures to produce gas that contains hydrogen and carbon monoxide small quantities of carbon dioxide, water vapor and methane.

The principal advantage of the pressure no catalytic partial oxidation process over steam reforming is that they can operate on any hydrocarbon feed. No desulfurization is required prior to the partial oxidation step. The principal disadvantage is the necessity for providing a supply of 95 – 95% pure oxygen. Which increases plant investment and operating costs.

Chemistry of partial oxidation:

The process is carried out by injecting preheated hydrocarbon, preheated and steam through a specially designed burner into a closed combustion vessel. Where partial oxidation occurs at 1290 – 1400⁰ C, with less than stoichiometric oxygen for complete combustion reaction is given by



The processes is divided into three steps

1. Heating and cracking phase
2. Reaction phase
3. Soaking phase

Equipment required:

Partial oxidation equipment consist essentially of

1. The gasification reactor
2. The waste heat exchanger for heat recovery from the hot reactor gas.
3. The economizer heat exchanger for further heat recovery.
4. The carbon removal system for separating carbon from the reactor product gas.
5. The carbon recovery systems for recycle of carbon.

Hydrogen from coal:

The Texaco coal gasification system of those used for raw gas generation. A similar processing sequence would be needed and similar results would be obtained using other high temperature gasifiers such as shell krupp. Under higher temperature conditions, methane formation is minimized and no tars and oils are produced. High-pressure gasification results in significant power savings from elimination of raw-gas compression. A low temperature gasification process such as the lurgi gasifier or BGC/ Lurgi slugging gasifier requires a more complex processing sequence.

All coal gasification processes can be used to manufacture hydrogen. The highest yield in the primary gasification step however is achieved if pulverized coal is gasified with oxygen at high temperatures. This done in entrained bed gasification reactor, commercialized especially in the koppers – totzek and the Texaco process.

Coal gasification on an industrial scale produces:

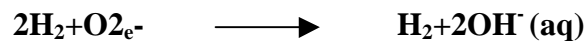
1. Synthetic gases, rich in CO and hydrogen
E.g. gas for Fisher-Tropsch synthesis of gasoline
2. Synthetic gas for the production of acetic anhydride
3. Ammonia Synthesis gas
4. Substitute natural gas
5. Pure Hydrogen from a side stream of a synthesis gas unit

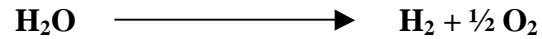
Hydrogen production by electrolysis:

Electrolysis has been used for approximately 100 years for hydrogen production. The first installation was by Norsk Hydro in 1927 in Norway. The election of large electrolysis plant generally depends on the availability of cheap electricity from hydro power station. A total of 5% of the world hydrogen production is by means of electrolysis

Principal

When a direct electrical current is passed through water solution of an electrolyte, hydrogen is evolved on one electrode and oxygen on the other electrolysis is the reverse of Hydrogen combustion. The following reaction occurs at the electrodes

1) Cathode**2) Anode**

3) Cell reaction:

Pure water is not suitable as an electrolyte because of its very low conductivity. Therefore aq. Solution of potassium or sodium hydroxides etc are used.

Types of electrolysis Plants:

1. Normal pressure electrolysis units.
2. Pressure electrolysis.
3. Advanced conventional electrolysis.
4. Water vapor electrolysis.

Electrolysis plant:

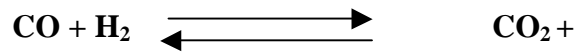
A part from the electrolysis unit electrolysis plant consists of number of different Installations. Such as electricity supply water treatment, electrolyte from product gases. Gas purification and the instrument and the control system dedicated thermal electric plants for the production of hydrogen may build in the future.

Steam reforming Plant:

In this process, hydrocarbon feeds are converted to synthesis gases is usually operated at 650 – 1000⁰C at 0.79 –4.93 Mpa, using catalysts that we originally Pt group metals but are now generally Ni- based different stages in steam reforming are.

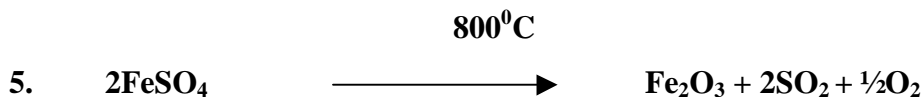
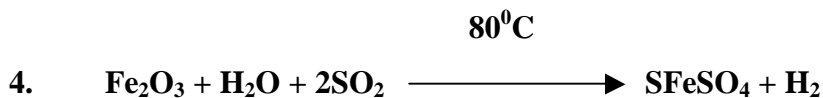
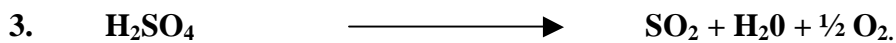
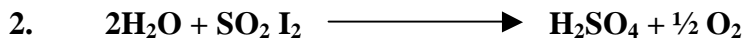
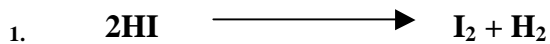
1. Desulphurization.
2. Steam reforming.
3. Co conversion.
4. Gas purification.

1. **Desulphurization:** Because hydrogen feed for steam reforming should be free of sulfur, feed Desulphurization is required. This is done by using Co –Mo catalyst in the presence of H₂
2. **Steam reforming:** In this desulphurized gas is introduced in the primary reformer. This reformer is a direct-fired chamber containing multiple high nickel alloy tubes. The gas leaving the primary reformer is about 76% H₂ 12% co. 10% CO₂ and 13% CH₄.
3. **Co-conversion:** Water gas shifts or co-conversion of exit gases from the secondary reformer is carried out in this section.



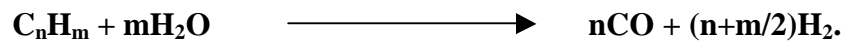
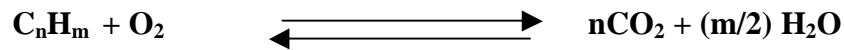
Other process-using Hydrocarbon feeds:

By thermo chemical

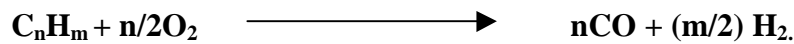


Partial oxidation of heavy oils shell and Texaco processes:

Partial oxidization of heavy oils (shell and Texaco processes) for production of synthesis gas. Shell and Texaco processes permit controlled oxidation by burning hydrocarbons with oxygen, which then provides heat and steam to support the thermal steam hydrocarbon reactions.



Net reaction



Controlled amount of oxygen, steam and CO_2 are added to attain desired ration CO/H_2 in the synthesis gas. The advantage of both processes lie in the tolerance to sulphur in the feed and the capability of utilizing any hydrocarbon as feed reaction converts CO to CO_2 in two stages.

1. High temperature shift.
2. Low temperature shift.

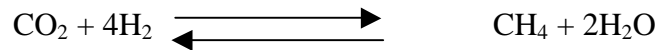
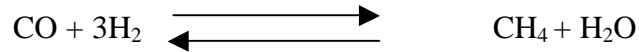
The catalysts are quite susceptible to sulfur and chloride poisoning therefore a ZNO guard is provided if impurities are suspected about 20% of the top of the LTS reactors is replaced every year to extend the catalyst life to 5 years.

Carbon Dioxide Removal:

The gases from LTS discharge contain about 22% CO_2 which is removed in this section. The carbon dioxide is removed by scrubbing with water under pressure a 15 – 20% MEA. The CO_2 absorbed is stripped and recovered and the absorbing solution is recycled.

Methanation:

Methanation of trace impurities of CO and CO₂ removal is often preferred to physical or chemical absorption. Removal of carbon dioxide to the SPPM level in the methanator is essential to prevent poisoning of the catalyst used for ammonia synthesis.



The above reactions are exothermic

Purification by pressure swing absorption (PSA):

The synthesis gas at any point after the secondary reformer is purified by PSA to deliver hydrogen at the go to 99.99% level by removing N₂, CO, CO₂, and CH₄. A poly bed PSA plant uses three to absorbance packed with a molecular sieve absorbent.

Process selection for design of Hydrogen plant

1. **Process selection:** shell gasification.
2. **Application:** Gasification of a wide range of hydrocarbon feed stocks by controlled partial oxidation with oxygen and steam. The product, principally hydrogen and carbon monoxide, may be used after further processing for: hydrogen, methanol and ammonia-synthesis gas, oxo-synthesis gas, fuel gas and reducing gas for direct reduction of ferrous and non ferrous ores.
3. **Feed stocks:** Range from natural gas to heavy asphalt.
4. **Commercial Installations:** 140 commercial installation (1979). With a total capacity of 3 billion SCFD of $H_2 + CO$ are in operation throughout the world.
5. **Licensors:** Shell international petroleum maatschappij. B. V. and shell development coordinator through Lurgi GmbH. W. Germany or **Lurgi corp. USA.**

The principal advantage of the partial oxidation process over Steam reforming is that they can operate on any hydrocarbon feedstock that can be compressed or pumped, from natural gas to oil, residual oils or asphalt .No desulfurization is required prior to the partial oxidation step. Their principal disadvantage is the necessity for providing a supply of 95-99% pure oxygen.

General consideration, which was done before selecting the process

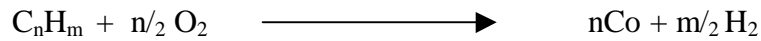
1. Feed stock (raw material)
2. No desulphurization unit is required
3. Gasification of feed with oxygen and steam.
4. Recovery of heat through generation of high pressure steam.
5. Removal of carbon.
6. Removal of H₂S and sulfur recovery.
7. Water gas shift reactions to allow the required H₂/CO ration.
8. Removal of CO₂.
9. Methanation (depends on % purity)

In the shell process the feed enters the homogenizer where carbon agglomerates from soot recovery are broken and dispersed. The Discharge from the homonizer then follows to reactor. In the reactor the feed after first mixing with preheated steam, is cracked to carbon, methane and hydrocarbon radicals during react with oxygen to form carbon dioxide, steam and exothermic heat which in turn is used for the hydrocarbon hydrogen steam endothermic reactions. Finally the product gases reach equilibrium composition of the water gas Shift reaction. The synthesis gases thus produce contains hydrogen sulfide and carbonyl sulfide, which are removed prior to HTS processing.

Manufacturing of Hydrogen by shell gasification process

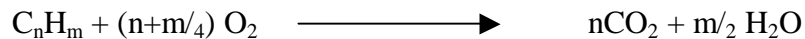
Chemistry of partial oxidation:

The process is carried out by injecting preheated hydrogen, preheated oxygen and steam through a specially designed burner into a closed combustion vessel, where the partial oxidation occurs at 1290 – 1400⁰C, with less than stoichiometric oxygen for complete combustion. The overall reaction is represented by

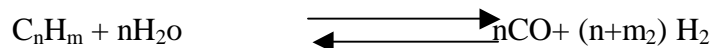


The overall process can be divided into three phases.

1. Heating cracking phase: Preheated hydrocarbons leaving the atomizer are intimately contacted with steam-preheated oxygen mixture. The atomized hydrogen is heated and vaporized by back radiation from the flame front and the reactor walls some cracking to carbon, methane and hydrocarbons radicals occurs during this brief phase.
2. Reaction phase: Hydrocarbons react with oxygen according to highly exothermic combustion reaction partially all of the available oxygen is consumed in this phase.



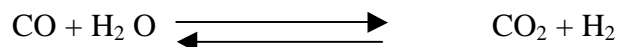
The remaining un oxidization hydrogen reacts endothermically with steam and the combustion products from the primary reaction. The main endothermic reaction is the reforming of hydrogen by water vapor



The complex reactor's results in thermal equilibrium at 1300 – 1400⁰C

3. Soaked phase: The final phase takes place in the rest of the reactor where the gas is at higher temperature. A portion of the carbon disappears by reaction with CO₂ and steam. Some carbon is present in the product gas

The final composition of the reactor product gas is established by the water gas shift equilibrium at the reactor outlet-waste heat exchanger inlet where rapid cooling begins.



Equipment: partial oxidation equipment consists essentially of

1. Gasification reactor.
2. Waste heat exchanger.
3. Economizer heat exchanger.
4. Carbon removal system.
5. CO conversation unit.
6. CO₂ absorber unit.

The process:

Natural gas feed stock is delivered into the suction metering pump which feed it via a steam preheater into the combustor of a refractory line flame reactor. The feed stock must be heated to 210⁰ c in the preheater to ensure efficient atomization in the combustor. A mixture of oxygen and being preheated in a separate steam preheated to 210⁰C before being mind with reactant steam.

The crude gas, which will contain some carbon particles, leaves the reactor at approximately 1300⁰C and passes immediately into a waste heat boiler's where steam at 600 Psg (4140 kN/m²) is produced. The crude gas leaves the waste heat boiler at 250⁰C and further cooled to 50⁰C by direct quenching with water, which also serves to remove the carbon as suspension. The analysis of the quenched crude gas is follows

Gas composition	vol%
CO ₂	4.36
CO	46.93
H ₂	47.54
CH ₄	0.60
N ₂	0.57

H₂S

0.81

For primary flame reaction steam and oxygen feed are fed to the reactor at the following rates

Steam = 0.75 kg/kg of feed st.

Oxygen = 1,16 kg/kg of feed st.

The carbon produced in the flame reaction and which is subsequently removed as carbon suspension in water: amounts to 1.5% by weight of fuel oil feed stock some H₂S present in the crude gas is removed by contact with, the quench water.

The quenched gas passes to an H₂S removal stage where it may be assumed that H₂S is selectively scrubbed down to 15 parts permillion. With substantially nil removal of CO₂. The scrubbed gas at 25⁰C and saturated, has then to undergo CO conversion, final H₂S removal and CO₂ removal to allow to meet the product specifications.

CO conversion is carried out over chromium promoted iron oxide catalyst employing two stages of catalytic conversion; the plate also incorporates a saturator and desaturator operating with a hot water circuit.

Incoming gas is introduced into a saturator where it is contacted with hot water pumped from the base of desaturated, this process serves to preheat the gas and to introduce into it some of water vapor required as reactant. The gas then passes to two-heat exchange in series. In the first, the unconverted gas is heated against the converted gas from the first stage of catalytic conversion; the second heat exchanger the unconverted gas from the stage of catalytic conversion. The remaining water required as reactant is then introduced into the unconverted gas at steam at 600Psig saturated and then gas/ steam mixture passes to the catalyst vessel at a temperature 370⁰C. The catalyst vessel is a single with a dividing plate separating two-catalyst bed. Which constitute two stage of reaction. The converted gas from each stage passes to the heat exchanger previously described and

then to the destaurator, which is further packed column the converted gas is contact counter current with out hot water pumped from the saturated base the temperature of the gas is reduced and the deposited in the hot water circuit an air cooled H.E. then reduces the temperature of the converted gas to 25⁰C for H₂S removal gas leaving this section of plate contains less than 1ppm H₂S and passes to the CO₂ removal stage at a temperature of 25⁰C. The carbon dioxide, which is removed in this section, is removed by scrubbing with water under pressure, a 15-20% MEA solution in water MEA with UCAR amine guard are most economical. Thus final a product of 95% of Hydrogen is produced.