



Process Description

Steam reforming refers to catalytic conversion of light hydrocarbon streams and is currently the most common and least expensive process for “on-purpose” high purity hydrogen production. Possible feedstocks include natural gas, non-olefinic refinery offgases, propane, butane and light naphtha. The process essentially comprises 4 main processing steps; feed purification, reforming reaction, shift reaction and product purification. Reforming reactions are highly endothermic (absorb heat) while shift reactions are moderately exothermic (liberate heat).

Feed gas and recycled hydrogen are mixed, preheated and passed to the feed purification (desulphuriser) section which comprises a reactor containing cobalt-molybdenum oxide (CoMo) catalyst and a pair of drums containing zinc oxide (ZnO) adsorbent. The reactor hydrogenates olefins and converts organic sulphur (mercaptans) and chloride to hydrogen sulphide (H₂S) and hydrogen chloride (HCl), respectively. The absorber removes the H₂S and HCl by chemisorption. The purified feed is then mixed with high pressure (HP) steam and superheated in the convection section of a top-fired or side-fired reforming furnace containing a series of vertical tubular reactors (furnace tubes) filled with nickel-impregnated catalyst. The catalyst-filled tubes are connected to inlet and outlet manifolds by smaller diameter, more flexible tubes (“pigtailed”) to accommodate thermal expansion and contraction of the furnace tubes. The superheated feed enters the tubes and forms an equilibrium mixture comprising mainly hydrogen (H₂), carbon monoxide (CO) and steam (H₂O) with some carbon dioxide (CO₂) and unreacted hydrocarbons (“syngas”). The syngas is cooled by heat exchange with HP boiler feedwater and flows to one or more shift converters where the water-gas shift reaction converts steam and CO and H₂O to more H₂ and CO₂. Typical reforming furnace operating conditions are 800 - 900 °C (1472 - 1652 °F) and 10 - 25 barg (145 – 363 psig). The shifted gas is cooled and flows to a knockout pot for condensate removal and then to the product purification section. The 2 most common purification processes are 1) CO₂ scrubbing (eg. Benfield, Catacarb, Sulfinol) followed by methanation and 2) pressure swing adsorption (PSA). PSA is typically preferred as it is simpler, more efficient and produces higher purity hydrogen (>99% vs 96%). Also, PSA adsorbents can remove residual CO so no low temperature (LT) shift converter and methanator are required.

Key Variables

The key independent variables affecting steam reformer performance are process gas exit temperature, steam:carbon ratio and pressure. The goal is to maximise high purity hydrogen production with minimum energy consumption. Process gas exit temperature and steam:carbon ratio should be maximised while pressure should be minimised.

Safety Issues

The single biggest safety issue for steam reformers is fire/explosion risk in case of a loss of primary containment (LOPC) due to the wide-ranging explosive concentration limits and the low ignition energy for hydrogen and operation above the autoignition temperature for hydrocarbons. Exposure to hydrogen sulphide in the desulphuriser section (normal operation) and nickel carbonyl in the reforming section (during shutdown) and risk of asphyxiation during inert entry to the hydrogenator, absorbers or shift converters (catalyst changeout) are also potentially lethal hazards.

Availability Issues

The hydrogenator and shift converter vessels may be susceptible to high temperature hydrogen attack (HTHA). Reforming furnace pigtailed may fail due to thermal fatigue and dissimilar metal weld cracking while furnace tubes may fail due to overheating caused by direct flame impingement (burner tip fouling or damage) or reforming catalyst degradation (physical damage or catalyst fouling/poisoning). Physical damage can be caused by thermal cycling (resulting in catalyst crushing and flow maldistribution) or by liquid wetting by steam or hydrocarbon condensate after a trip (rapid vapourisation during restart can cause catastrophic catalyst failure). Catalyst fouling can be caused by coking or carryover of boiler solids. Catalyst poisoning can be caused by contaminant breakthrough from the feed purification section. Sulphur and chlorides are particularly severe poisons to steam reforming and shift catalysts.