Hydrogen Production and Management for Petroleum Processing

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Abstract

As refinery product specifications become more stringent to meet environmental requirements, refinery demand for hydrogen has continually increased to supply the required hydroprocessing units. Additional improvements in burning qualities, like cetane, also require more hydrogen. This chapter addresses the processes used to make and/or recover hydrogen for petroleum processing applications. The processes described here include naphtha catalytic reforming, steam-methane reforming, hydrogen recovery, partial oxidation, gasification, olefins cracking, and electrolysis as they relate to hydrogen. Some basic methods for overall refinery hydrogen optimization and management are also described.

Keywords
Refinery • Hydrogen • Reforming • Steam methane reforming • SMR • POX • PSA • Membranes

Introduction and Scope of Discussion

Introduction

As refinery product specifications become more stringent to meet environmental requirements, refinery demand for hydrogen has continually increased to supply the required hydroprocessing units. Additional improvements in burning qualities, like cetane, also require more hydrogen.

For many refineries, the by-product hydrogen produced by naphtha reforming has been able to supply sufficient hydrogen. The drive toward ultralow sulfur diesel and near-zero gasoline sulfur has exceeded the availability of hydrogen from reforming in most cases.

Full-conversion and cracking refineries today generally need incremental hydrogen that is produced "on purpose." A refinery with a hydrocracker will almost always need incremental hydrogen. This chapter explores the alternative methods for hydrogen production, with a focus on the most commonly applied hydrogen plant technologies.

Many refineries obtain the additional hydrogen supply "over the fence" from a second party. Several gas suppliers, like Praxair, Air Liquide, and Air Products, offer these services. They are especially common where the hydrogen can be used by several different facilities in an area. The plants used to make the hydrogen still follow the same processes discussed below. The main difference in over-the-fence supply is that the refiner is not directly responsible for the hydrogen plant operation.

Production Processes

The first source for hydrogen in a refinery is always catalytic naphtha reforming. This process is discussed in detail elsewhere in this book. We will only touch on reformer hydrogen qualities and issues in this section.

Incremental hydrogen will be our primary focus here. In order of importance to refineries, the key processes for making or recovering incremental hydrogen are:

- Steam-methane reforming
- Refinery gas recovery
- Partial oxidation/gasification
- Olefins cracking by-product recovery
- Electrolytic hydrogen
- Other processes

We will look at each of these processes in turn and provide references for additional information.

Recovery Processes

The recovery processes for hydrogen can apply to several of the production technologies. We will discuss the three most common recovery processes employed in refineries:

- Pressure swing adsorption
- Membranes
- Cryogenic recovery

Management

All the incremental hydrogen in the world is not helpful if it is poorly managed. Poorly managed hydrogen ultimately ends up getting burned in most refineries, and this is a waste. We will discuss some approaches to ensure that hydrogen is not wasted to fuel or flare.

Catalytic Reforming of Naphtha

Discussion

Production of hydrogen as a by-product of catalytic naphtha reforming is very common. This provides a large piece of the hydrogen supply in a refinery.

Semi-regenerative reformers can typically make about 1,000 scf of hydrogen per barrel of reformer charge, while continuous reformers can make around 1,700 scf of hydrogen per barrel charge. Cyclic reformers operate between.

Process details for naphtha reforming are in the chapter entitled "▶ Catalytic Reforming in Petroleum Processing" of this handbook. We will focus here on the hydrogen quality produced by the naphtha reformer and its implications in hydroprocessing.

Reformer Hydrogen Properties

Reformer hydrogen composition can vary widely as shown in Table 1. Hydrogen from a continuous reformer (CCR) will have a relatively constant composition, while hydrogen from a semi-regen unit will vary from start of run (just after regeneration) to end of run (just before regeneration). A cyclic reformer's hydrogen

Table 1 Some typical catalytic naphtha reformer hydrogen products

Type of reformer	Semi-regen	Cyclic	CCR
Hydrogen yield, scf/b charge	1,000–1,300	1,100–1,500	1,600–1,800
Typical hydrogen quality, v%			
Hydrogen	75–89	83–87	85–90
Methane	3–6	3–4	2–3
Ethane	2–5	3–4	2–3
Propane	1–5	3–4	1–2
i-Butane	0.2–2	1–2	1–2
n-Butane	0.2–2	1–2	1–2
C5-Plus	3–5	1–2	3
Chloride (as HCl)	(1–3 vppm)	(1–3 vppm)	(1–3 vppm)

composition will vary over an intermediate range, because the individual reactors are regenerated one at a time and swung back on line.

When viewing these hydrogen compositions from a user's standpoint, two items are of note:

- Methane, ethane, and propane will build up in the recycle gas system of any unit that uses the hydrogen, depressing the effective hydrogen partial pressure.
  - In many cases, the reformer hydrogen is sent initially through the naphtha hydrotreater (NHT or pretreater), sometimes once through, ahead of the naphtha reformer. The naphtha hydrotreater acts as a sponge to remove almost all the heavier impurities and some of the lighter hydrocarbons. The NHT is effectively improving the hydrogen purity before it goes to other units. There is also a benefit in recovering the yield represented by the heavier hydrocarbons.
  - Some refineries send the reformer hydrogen through a pressure swing adsorption (PSA) unit, a membrane unit, or a steam-methane reformer (SMR) to improve the purity. The impurities are rejected to fuel gas or, in the case of the SMR, used to make more hydrogen. The higher-purity product maintains high hydrogen partial pressures in the hydrogen users.
  - If the hydrogen is routed directly to a user, the impurities in the gas appear in the products from the user. When looking at net yields in a user, this needs to be factored into the balance.
- The residual chloride in reformer hydrogen presents a problem for users.
  - The chloride would normally be coming from the reforming process, but poor desalting of the crude, poor water-chloride balance control in the reformer, or organic chlorides in the crude may greatly increase the reformer hydrogen chloride contents.
  - In hydroprocessing units, the chloride, starting out as HCl, will end up forming ammonium chloride deposits in the effluent train and increasing corrosion rates.

  - Sometimes, the chloride content is tolerable, especially if the reformer hydrogen is only a minor portion of the makeup to the user.
  - See the discussion of effluent salts in the chapters on hydrocracking and hydrotreating.
- Frequently, reformer net hydrogen is sent through a low-temperature chloride absorber to remove the chloride compounds.
  - These absorbers use granular solid sorbents, like alumina, to remove the chloride to about 0.1 vppm as HCl.
  - The sorbent must be monitored and periodically changed out.
  - These beds often have issues with channeling unless the reformer hydrogen stream is kept free of liquid (Do not let it cool).
  - If there are substantial olefins in the reformer hydrogen (e.g., from running a reformer past EOR), there are significant aromatics in the gas, and/or the sorbent surface is acidic (which can be due to the being nearly spent or from presence of excessive water vapor), a chloride absorber will make “green oil.” These are polymeric, chlorinated hydrocarbons. They will drop out in low spots, foul compressor valves, and move chloride into the process units. These can somewhat defeat the purpose of the absorber. Absorbents are available to reduce green oil formation through the absorbent used or alkaline additives to reduce acidification of the surface.

Further Information on Reformer Hydrogen

Please refer to the chapter on naphtha reforming for additional detail on hydrogen production from catalytic reforming.

Steam-Methane Reforming

Introduction

Steam-methane reforming (SMR) is the main process used in refineries to produce hydrogen. It should not be confused with catalytic naphtha reforming. The technology is offered by several companies on a proprietary basis, including Haldor Topsoe, Foster Wheeler, CB&I/HoweBaker, Lurgi, and KTI.

In the SMR reactions, methane is reacted with steam at very high temperatures and relatively low pressures to make hydrogen and a mixture of CO/CO_2. The process is used extensively by all industries requiring hydrogen. The largest hydrogen plants are used in the manufacture of ammonia. These are usually several times larger than the plants we use in refineries.

When a facility decides to purchase hydrogen over the fence from a gas supplier, that supplier is normally making the hydrogen using SMR.

Advantages of the SMR process are:

- High yields and efficiency – low cost of hydrogen
- High-purity hydrogen product (93–100 %)
- Feedstock flexibility (natural gas, refinery gases, refinery liquids – anything with carbon)
- Relatively easy to operate (governed by equilibrium)
- Relatively easy to monitor (you cannot ignore an SMR, however)
- Scalable – smallest units less than 1 MMscfd to more than 800 MMscfd
- Open art technology, although some equipment and design methods are proprietary
- Many design, equipment, catalyst, and sorbent suppliers, who will help train your personnel and monitor plant
- Well-established safety and support organizations (e.g., AIChE Annual Safety in Ammonia Plants and Related Facilities Symposia)

The disadvantages of the SMR process are largely manageable:

- Severe operating conditions push materials limits
- Cleanup of feedstock and products can be complex
- SMR plants work best at high loads – they do not operate well below 50 % rate
- They like stable production rates – rate changes require a lot of adjustments that are not automatic
- The plants produce CO/CO_2, NO_x, trace organic oxygenates (like methanol), and trace ammonia – all of which must be reported and managed within environmental limits
- An absolutely stable supply of boiler feedwater is required – loss of boiler feedwater for a few minutes (or sometimes seconds) can have drastic consequences

Now, we will walk through the process step by step. The process will focus primarily on making hydrogen from natural gas or refinery gases, with appropriate touches on SMR of refinery liquids.

SMR Processes: Step by Step

The steam-methane reforming process, in its most common form, can be divided into several distinct process sections, as shown in the block flow diagram of Fig. 1:

- Feed gas compression – may be required for low pressure gas feeds
- Feed liquid vaporization – required for liquid feeds
- Feedstock purification – removes all impurities to prepare the feedstock for the SMR; recycle hydrogen is needed if feed contains insufficient hydrogen

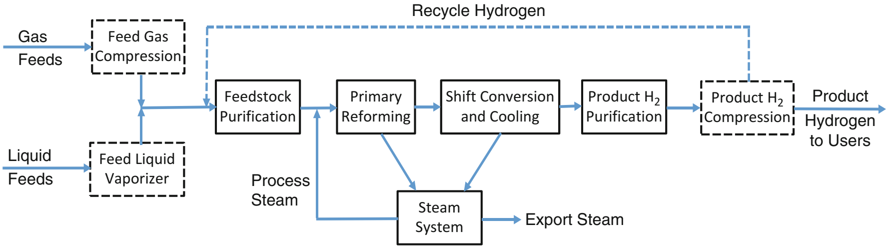


Fig. 1 Block flow diagram of typical steam-methane reforming hydrogen plant

- Primary reforming – reaction of the feedstock with steam to make hydrogen
- Shift conversion and cooling – further reaction of residual CO to make more hydrogen and cooling of raw hydrogen
- Product hydrogen purification – removing impurities from the raw hydrogen to make the high-purity hydrogen product
- Product hydrogen compression – needed at users or inside the SMR hydrogen plant, supplies any recycle hydrogen needs
- Steam system – generates steam from waste heat to supply the process steam requirements; surplus steam is exported to the refinery

We will consider the major process steps in order as the feedstock flows through the plant.

Feedstock Purification

Any feed to the primary reforming section of the plant must be very clean and must only be gaseous. It cannot have any sulfur, halides, olefins, liquids, or other less common contaminants. The function of the purification section is to remove all of the contaminants. In the process, the feedstock will be heated up toward the SMR reaction temperature.

The simplified process flow diagram for the final feedstock purification (or pretreat) steps of most SMR plants is shown in Fig. 2.

Ahead of the purification section, the feedstocks require some preparation:

- Gas feeds:
  - All liquids knocked out of the gases
  - Low pressure gases compressed to required pressure, typically around 450–500 psig
- Liquid feeds:
  - Filtered
  - Vaporized, normally in a kettle-style vaporizer

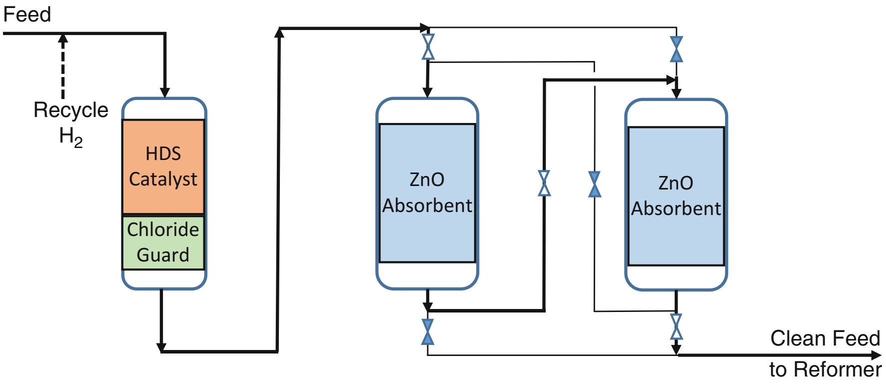


Fig. 2 Typical SMR feedstock final purification system. Note: excludes upstream preparation of feeds, such as amine scrubbing

- All feedstocks:
  - Blended together – preferably in controlled proportions
  - Final trace liquid knocked out

If the blended gas contains very high H_2S levels (more than about 10 vppm), the mixed feed will be routed through an amine scrubber to remove the bulk of the H_2S. The rich amine from the scrubber is sent to regeneration for sulfur recovery, normally out of the SMR plant. A typical reaction in the scrubber, using MEA as an example, is shown in Eq. 1:

$$HOC_2H_4 - N - H_2(aq) + H_2S(g) \longleftrightarrow HOC_2H_4 - N - H_3^+(aq) + SH^-(aq) \quad (1)$$

Depending on residual sulfur after amine scrubbing, very sour gases may also be scrubbed with caustic to remove traces of H_2S down to the sub 10 vppm H_2S range. That caustic reaction is shown in Eq. 2. The spent caustic is routed off plot for disposal:

$$H_2S(g) + NaOH(aq) \rightarrow NaHS(aq) + H_2O(l) \quad (2)$$

The somewhat cleaner feed gas is then mixed with enough hydrogen for hydrotreating and heated to about 600–750 °F. If there are significant olefins present, the preheated temperature may be lower to offset heat of reaction from olefin saturation (see below). The amount of hydrogen required depends on the feedstock but generally falls in the following ranges:

- Natural gas feed: 2–5 v%
- Refinery gases: 2–5+ v%
- Propane and butane: 12 v%
- Naphtha: 25–35 v%

The preheated feed plus hydrogen is now routed to a hydrotreating reactor to convert any residual organic sulfur compounds quantitatively to H_2S and to eliminate olefins. Organic chlorides that may be present are all converted to HCl. Equations for these reactions are below. The reactions are driven almost totally to completion and they are all exothermic:

$$\text{Sulfur} : \mathrm{RS(g)} + \mathrm{H_2(g)} \rightarrow \mathrm{RH(g)} + \mathrm{H_2S(g)} \tag{3}$$

$$\text{Olefins} : \mathrm{R - C = C - R'(g)} + \mathrm{H_2(g)} \rightarrow \mathrm{R - C - C - R'(g)} \tag{4}$$

$$\text{Chlorides} : \mathrm{R - Cl(g)} + \mathrm{H_2(g)} \rightarrow \mathrm{RH(g)} + \mathrm{HCl(g)} \tag{5}$$

Because all the reactions are exothermic, the gas temperature can increase across the hydrotreating reactor. However, since the starting sulfur and chloride contents will be very low in the feeds, the main reaction generating heat is olefin saturation. Olefins can generate 40 °F rise per percent olefin in a gaseous feed, 15 °F per percent olefin in butane feed, and 10 °F per percent olefin in a naphtha feed. These rises place a limit on the amount of olefins in a feedstock. Hydrotreated product can be recycled back through the feed compressors to help moderate the reaction, but this consumes feed gas compressor capacity.

For gaseous feeds, the practical limit is about 5 % olefins in the combined feed (including any recycle). To manage this concentration of olefins, you have to lower the hydrotreater inlet temperature about 200 °F, to about 500–550 °F. If you go lower in temperature, the hydrotreater reactions may not initiate. Higher temperature may result in a hydrocracking runway.

The pretreated gases, now at about 700–750 °F, are passed through a bed of chloride trap and beds of zinc oxide (ZnO). The chloride trap, normally activated alumina ($NaAlO_2$), absorbs the chlorides quantitatively until it is nearly spent. The zinc oxide beds absorb the sulfur quantitatively (<0.01 ppm residual is possible) until the beds are nearly spent. Two ZnO beds are usually used in series with the valves and piping to change out the beds on line and swing the order of the two beds. The essential equations in the sorbent beds are below. These reactions are slightly exothermic, but do not generate significant heat at the low impurity concentrations seen in hydrogen plant feeds:

$$\text{Chlorides} : \mathrm{2HCl(g)} + \mathrm{2NaAlO_2(s)} \rightarrow \mathrm{NaCl(s)} + \mathrm{Al_2O_3(s)} + \mathrm{H_2O(g)} \tag{6}$$

$$\text{Sulfur} : \mathrm{H_2S(g)} + \mathrm{ZnO(s)} \rightarrow \mathrm{ZnS(s)} + \mathrm{H_2O(g)} \tag{7}$$

Some units do not have separate hydrotreaters. This is not unusual where a plant only feeds sweet natural gas. In these cases, combined function hydrotreating/absorbing catalysts may be used. Some of the sweet feed units may also not use a hydrogen recycle, but there is some risk of thiophene sulfur getting through. Activated carbon has also been used instead of ZnO for sulfur sorption, but this is uncommon today because activated carbon has such a low capacity.

The general ranges for key operating conditions in the purification section of an SMR hydrogen plant are:

Hydrotreating	
Temperature	550–750 °F
Pressure	350–500 psig
GHSV	<3,000–4,000 h^{-1}
Catalyst	CoMo, NiMo
Absorbers (chloride and sulfur)	
Temperature	650–750 °F (from hydrotreater)
Pressure	300–500 psig
GHSV	500–3,000 h^{-1}
Catalysts	
Chlorides	Activated alumina
Sulfur	Zinc oxide
Combined function catalyst/sorbents also available	

Now, we have sweet, clean, hot gas feedstock available for the SMR reaction.

Primary Reforming

The simplified process flow diagram for the primary reforming section of most SMR plants is shown in Fig. 3. The preheat and heat recovery arrangements can vary. This is where most of the hydrogen will be made.

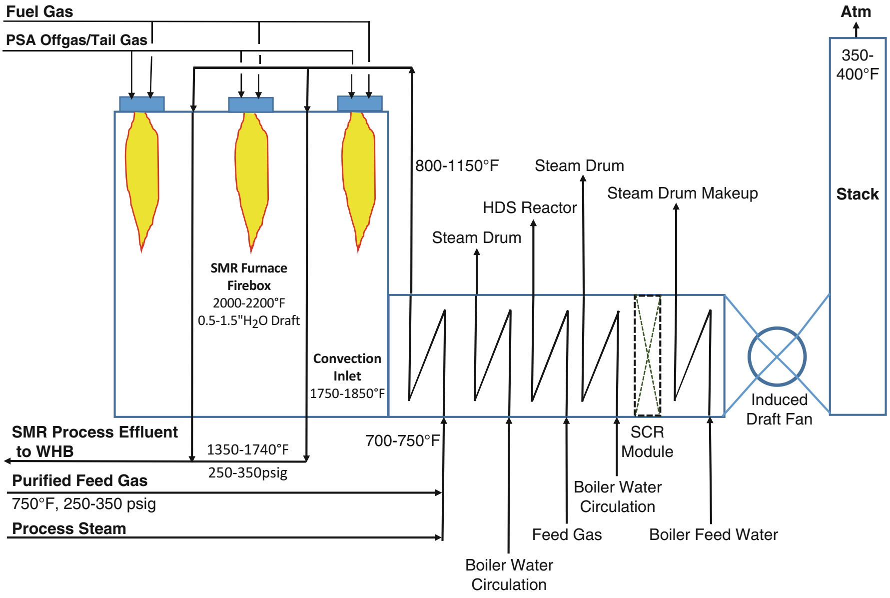


Fig. 3 Typical down-fired primary reformer simplified process flow diagram

In this section of the plant, the hot, pretreated feed is mixed with steam in a precise proportion based on the amount of carbon in the feed. This is the critical steam/carbon ratio and is based on moles of steam per mole of carbon in the feed. Steam/carbon ratio typically ranges from 2.0 to 5.0, depending on the hydrogen plant design. Most new plants in refineries run 2.5–3.0 for gaseous feeds. The ratio is increased for butane and heavier feeds and if additional heat is needed to cool the shift effluent (to be discussed later).

The combined reformer charge is preheated further to 800–1,150 °F by exchange before entering the reforming furnace radiant tubes. It is a large firebox with rows of catalyst-packed tubes surrounded by the burner flames. The SMR reactions occur in the furnace at ~1,350–1,740 °F and ~250–350 psig. There can be hundreds of tubes in a typical furnace.

Flow distribution to the tubes is by pressure drop, so the inlet and outlet header designs and catalyst loading are carefully controlled to ensure exactly the same pressure drop exists through each tube – and hence the same flow. In practice, there are some deviations and an allowable tolerance.

The reactions occurring in this section of the SMR plant are primarily:

Feed gas cracking to methane:

$$C_nH_{2n+2} + n - 1H_2 \rightarrow nCH_4 + \text{Heat} \tag{8}$$

Steam-methane reforming:

$$CH_4 + H_2O + \text{Heat} \longleftrightarrow CO + 3H_2 \tag{9}$$

Water-gas shift:

$$CO + H_2O \longleftrightarrow CO_2 + H_2 + \text{Heat} \tag{10}$$

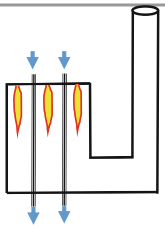
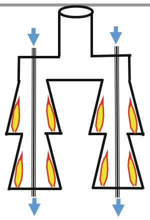
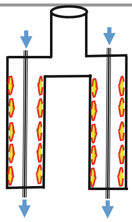
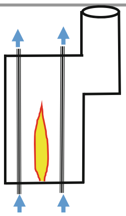
In the first reaction, which normally occurs in the catalyst near each tube inlet, all hydrocarbons coming in are cracked to methane. The catalyst used for this is an SMR catalyst that has an alkali metal component added. The alkali helps scavenge coke that may form on the catalyst from the cracking reactions.

The steam-methane reforming reaction is our primary objective in this section of the plant. Steam reacts with the methane to produce hydrogen and carbon monoxide. This reaction consumes **a lot** of heat. The heat consumed by reforming is why the primary reforming reactions are carried out in tubes within a furnace firebox.

Finally, the carbon monoxide will react further with steam to make additional hydrogen and carbon dioxide. This reaction is favored by lower temperatures, so it only goes part way to completion in the reforming furnace.

All the products are at or near equilibrium at the furnace outlet conditions when the catalyst has good activity. As the catalyst ages, the composition at the furnace outlet drifts away from equilibrium, and the outlet temperature must be raised to maintain production.

Table 2 Comparison of common steam-methane reforming furnace types

Furnace type	Down fired	Terrace-wall fired	Side fired	Bottom fired
Layout				
Advantages	Steam and feed quickly brought to reaction temperature; cheaper furnace box construction; fewer burners	Better control of heat flux; lower tube wall temperatures; moderate firebox cost	Good control of heat flux; lower tube wall temperatures	Relatively low cost; steam and feed quickly brought to reaction temperatures; fewer burners
Disadvantages	High heat flux near top = high tube wall temperatures; ID fan generally required; can have large footprint for convection section	More burners; draft balance and control with multiple cells; convection elevation high or need to use ID fan	Many (hundreds) small burners; high risk of flame impingement; draft balance and control with multiple cells; convection elevation high or need to use ID fan; High cost; Air preheat distribution cramped	Potential high tube wall temperatures near bottom; usually limited to small reformers; draft imbalance potential

The equilibrium can be calculated from the furnace inlet composition and outlet pressure and temperature using published SMR and water-gas shift K values. These data are available, for instance, in *Catalyst Handbook* (by Katalco, Springer-Verlag, NY, 1970) as Tables 2 and 3 of the Appendices to that book. Be sure you look carefully at the form of the K_{SMR} equation to get the right direction for the reaction you are calculating.

For convenience, the charts have been converted to equations relating K_{SMR} and temperatures below:

SMR reaction:

$$K_{SMR} = \left[P_{CO} \times P_{H_2}{}^{3}\right] / \left[P_{CH_4} \times P_{H_2O}\right] \tag{11}$$

where partial pressures are in atmospheres and temperature is °C.

Table 3 Common materials damage mechanisms in SMR hydrogen plants (Reference: API Recommended Practice 571)

	Damage mechanisms																		
Equipment affected	Creep/stress rupture	High temp hydrogen attack	Oxidation	Thermal fatigue	Refractory degradation	Temper embrittlement	Amine cracking	Chloride stress corr. Cracking	Steam blanketing	Thermal shock	Short-term overheading - stress rupture	Sigma-phase/chi embrittlement	Reheat cracking	Dissimilar metal weld cracking	CO_2 corrosion	Amine corrosion	Boiler water/condensate corrosion	Metal dusting	Pressure cycle fatigue
Feed gas hydrotreater		X																	
ZnO drums		X																	
Convection steam gen coils			X								X						X		
SMR furnace tubes/refractory	X		X	X						X	X	X		X				X	
SMR furnace process outlet	X	X			X							X							
Waste heat boiler/steam gen		X			X				X								X		
SMR effluent hot bypass		X	X		X					X				X				X	
HTSC inlet		X																	
HTS converter	X	X				X							X						

HTSC outlet		X																	
LTS converter		X				X							X						
Shift effluent cooling								X							X				
Shift effluent to KO drum								X							X				
Solvent CO_2 removal																			
CO_2 absorber							X								X	X			
Rich solution lines/equipment							X	X							X	X			
CO_2 stripper							X								X	X			
CO_2 stripper reboilers							X	X							X	X			
Lean solution lines/equipment							X	X							X	X			
Methanator preheat exchange		X																	
Methanator reactor		X																	
PSA purification																			
PSA vessels																			X

Correlations are valid within +/−1 °C (1.8 °F) between 200 and 1,200 °C (400–2,200 °F):

$$\begin{aligned}K_{SMR} = \exp(&-4.8858E-14*T^5+2.1457E-10*T^4\\&-3.8682E-07*T^3+3.7620E-04*T^2\\&-2.2251E-01*T+5.8282E+01)\end{aligned} \tag{12}$$

$$\begin{aligned}T,{}^\circ C = &-1.7663E-05*\ln(K_{SMR})^5+1.1690E-03*\ln(K_{SMR})^4\\&-3.5357E-02*\ln(K_{SMR})^3+9.4694E-01*\ln(K_{SMR})^2\\&-2.9272E+01*\ln(K_{SMR})+6.1880E+02\end{aligned} \tag{13}$$

Water-gas shift reaction:

$$K_{WGS} = [P_{H_2} \times P_{CO_2}]/[P_{H_2O} \times P_{CO}] \tag{14}$$

Note that this is the reciprocal of the normal WGS K value.

Partial pressures are in atmospheres absolute and temperature is °C.

$$\begin{aligned}K_{WGS} = \exp(&-7.1865E-15*T^5+3.3071E-11*T^4\\&-6.2984E-08*T^3+6.4760E-05*T^2\\&-3.9276E-02*T+1.1066E+01)\end{aligned} \tag{15}$$

$$\begin{aligned}T,{}^\circ C = &-2.9492E-01*\ln(K_{WGS})^5+4.4116E+00*\ln(K_{WGS})^4\\&-2.6510E+01*\ln(K_{WGS})^3+9.3947E+01*\ln(K_{WGS})^2\\&-2.9167E+02*\ln(K_{WGS})+8.0912E+02\end{aligned} \tag{16}$$

It should be noted that inerts entering the furnace will pass through unreacted and dilute the products. These inerts will affect the equilibrium by reducing the reactant and product partial pressures.

If the feedstock contains CO, CO_2, or O_2 (as some natural gas does), you have to remember to account for this in the equilibrium calculations.

Key operating conditions around the primary reforming furnace are thus:

Process-side conditions	
Steam/carbon molar ratio	2.0–5.0+
Temperatures	
Feed preheat coil inlet	700–750 °F
Preheat coil outlet	800–1,150 °F
Reforming furnace outlet	1,350–1,740 °F
Pressures	
Reforming furnace outlet	250–350 psig

(*continued*)

Tube pressure drop	15–40 psi
Catalyst volume/GHSV	By designer
Firebox-side conditions	
Firebox temperature (firing level)	2,000–2,200 °F
Draft at burners	0.5–1.5 “H_2O
Flue gas exiting firebox (bridgewall)	1,750–1,850 °F

Water-Gas Shift

The outlet from the reforming furnace consists of hydrogen, CO, CO_2, residual CH_4, a lot of steam, plus any inerts. These products are all at or close to equilibrium at the process outlet temperature from the furnace, usually in the 1,350–1,740 °F range. At these temperatures, there will still be 30–70 % of the carbon present as CO. This CO can be “shifted” to CO_2 with incremental production of hydrogen at lower temperatures using the water-gas shift reaction:

$$CO + H_2O \longleftrightarrow CO_2 + H_2 + \text{Heat} \tag{17}$$

The simplified process flow diagram for the water-gas shift section of most SMR plants is shown in Fig. 4. The heat recovery arrangements in this section will vary, depending on the type of purification system used and the shift stages employed.

For the first shift stage, the reformer effluent is cooled, usually in a large steam generator or waste heat boiler, to about 650–700 F and enters a high-temperature shift (HTS) reactor. This fixed-bed reactor is packed with a chrome-promoted, iron oxide shift catalyst. In the reactor, most of the CO is shifted to CO_2, with additional hydrogen production. The temperature in the reactor rises 50–100 °F due to heat released by the reaction, so reactor effluent is around 700–800 °F. Pressure is low. Normally, all plants have HTS reactors. The catalyst is fairly robust and stable, resistant to poisoning.

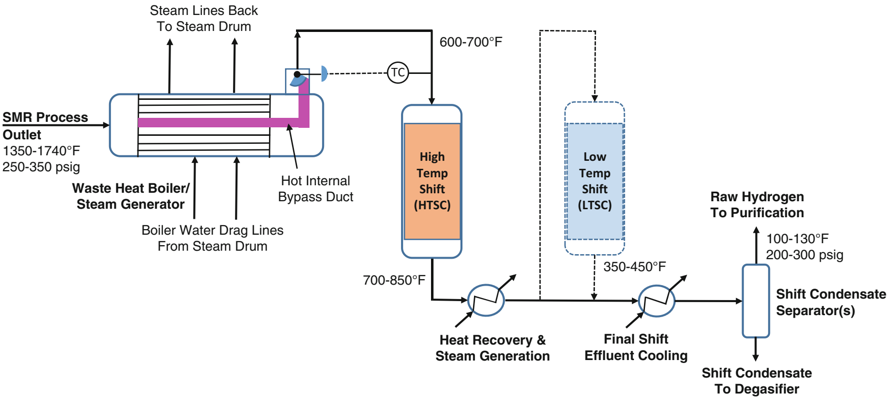


Fig. 4 Typical water-gas shift simplified process flow diagram

The HTS effluent is cooled further. In pressure swing adsorption (PSA)-based plants, the effluent is normally cooled all the way to near-ambient conditions without further shift. In plants employing a wet chemical purification system and in a few PSA plants, there is a low-temperature shift (LTS) reactor to make additional hydrogen and eliminate more CO. Some plants use medium temperature shift (MTS) reactors, but these are less common.

The LTS reactor normally uses a copper-based catalyst to reduce the residual CO to less than ∼0.5 v% (can be as low as 0.1 %). This type of catalyst is not robust, so activation and management of the LTS catalyst requires special procedures. A LTS reactor tends to make methanol and ammonia, which will contribute to emissions later. This issue is exacerbated by very low steam/carbon ratios. Specific, low-methanol catalysts are available to limit these side reactions. For a unit with only HTS, the addition of LTS can increase hydrogen production 5–10 %, provided the purification system can handle the extra load. Purification may need to be debottlenecked.

In the final steps of shift effluent cooling, we condense and recover the unreacted steam (shift condensate) for reuse. The relatively dry raw hydrogen is then sent to final purification.

Shift condensate will be saturated with CO_2 and is quite corrosive. It is handled in stainless steel equipment. Direct reuse of the condensate with the dissolved CO_2 would cause high corrosion rates in the boiler system and introduce excessive amounts of CO_2 into the steam from the hydrogen plant – causing high corrosion rates in condensate systems throughout the refinery. Before reuse, the shift condensate must be "degassed" by steam stripping to remove the CO_2. This can be done separately in a dedicated stripper or degasifier or combined with deaeration of incoming boiler feedwater (BFW). Combining degassing with deaeration is generally less effective.

Because the shift condensate also contains methanol and other trace organic oxygenates plus trace ammonia, disposal of the stripper or degasifier off-gas must be considered. Environmental regulations limit the options in many areas. If a unit only has HTS, degasifier off-gas can often go to atmosphere. In other cases, the degasifier or deaerator off-gas can be routed to the reforming furnace firebox. Some units use high-pressure steam strippers to remove the dissolved gases, with the stripper off-gases routed back to feed as part of the process steam.

Typical key operating conditions in the water-gas shift section of the plant are:

Temperatures	
High-temperature shift reactor	
Inlet	600–700 °F
Outlet	700–850 °F
Low-temperature shift reactor	
Range	350–450 °F
Final shift condensate separator	100–130 °F
Pressure	
Final raw hydrogen to purification	250–350 psig

The raw hydrogen is now ready for purification to the final product.

Purification

There are two general approaches to purification of raw hydrogen which we will consider here:

1. Pressure swing adsorption
2. Wet chemical/solvent with methanation

Pressure Swing Adsorption

In modern hydrogen plants, pressure swing adsorption (PSA) is the most common method of purification. The resulting product is nearly 100 % pure hydrogen, and the off-gas can be used as fuel in the SMR furnace.

Refer to the section "Pressure Swing Adsorption" of this chapter for more detailed discussion of PSAs. The following comments address how a PSA is applied in SMR hydrogen plant service.

A PSA is typically integrated into an SMR hydrogen plant as shown in Fig. 5.

The PSA feeds the cooled, dry (<130 °F) raw hydrogen from the SMR shift effluent. The PSA beds adsorb the impurities from the raw hydrogen at inlet pressure (~250–450 psig normally). Pure, nearly 100 %, hydrogen is produced at near PSA inlet pressure.

Each bed in the PSA is periodically cycled off-line and depressured to release the adsorbed impurities. This cycle occurs a few times per hour, typically. Off-line, the pressure in the PSA bed is decreased in steps to near atmospheric pressure (say 4–6 psig). The adsorbent releases the impurities at the low pressure. The resulting tail gas or off-gas is sent to the SMR furnace as fuel.

There are normally several (4–12) PSA adsorbers that are connected together in a system. The PSA system uses control valves, headers, surge vessels, and a

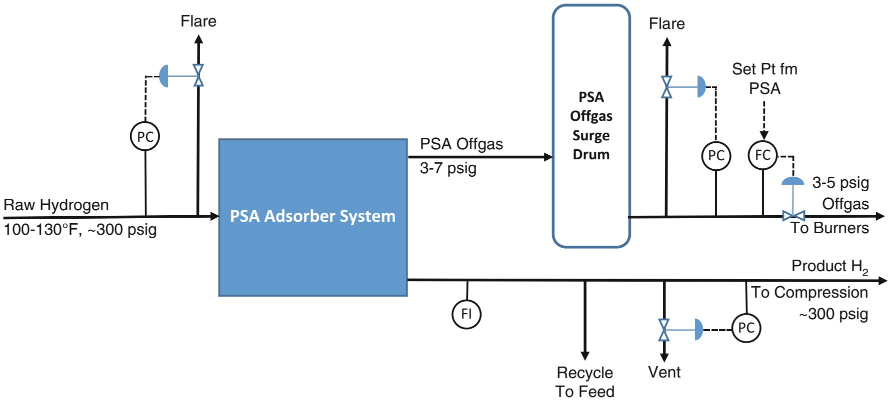


Fig. 5 Typical PSA product hydrogen purification system integration simplified process flow diagram. For details inside PSA adsorber system box, refer to more detailed PSA system process flow diagram in PSA discussion

programmable logic controller to swing each bed through the adsorption-desorption steps in sequence to provide continuous product hydrogen flow. The off-gas is collected in a surge drum to moderate pressure and composition changes before it is sent to the SMR furnace to be burned. The off-gas provides about 50–70 % of the SMR fuel requirement.

Hydrogen recovery in a PSA tied to an SMR unit typically ranges from 80 % to 92 % of the total hydrogen produced in the plant, with a good typical value of about 85 %. The multiple steps in the bed regeneration sequence help optimize hydrogen product recovery. More steps increase recovery, but can require more beds and additional complexity. There may be 50–100 individual steps in the sequence for several beds.

Hydrogen recovery can also be enhanced by online analyzers to monitor product or intermediate-pressure step gases.

One downside of a PSA tied to a continuous process is that it either works or it does not. There are several problems that can cause a PSA to trip. In a trip, your hydrogen product is immediately lost and the hydrogen plant will experience a major upset as the off-gas fuel is lost immediately – causing a major furnace firing disturbance.

The most frequent problems for PSAs are valve failures. These can be expected a few times a year. Sometimes, the PSA logic can work around a problem by removing pairs of beds from service and not interrupting the flow; but often a problem trips the unit. Operators will develop experience to manage the trips with time.

The finished PSA product is nearly 100 % hydrogen, with traces of nitrogen and CO (typically <100 ppm N_2, <10 ppm CO). N_2 and CO are the first gases that will break through a PSA. The PSA operation can be adjusted to allow more or less N_2/CO slip, depending on the hydrogen user limitations. For instance, if the hydrogen is used in an isomerization unit, you would want less than 1 ppm CO. This can be achieved by a PSA, with some loss of recovery. More typically, a CO level of <10 vppm in the product hydrogen is the target. Allowing more CO to slip into the product hydrogen does not significantly increase the amount of hydrogen recovered and, at some point, actually decreases net hydrogen recovery because methanation begins consuming the hydrogen in the users.

Wet Chemical/Solvent with Methanation

Most of the older hydrogen plants used a wet chemical/solvent approach to hydrogen purification. These systems remove nearly all the CO_2, but leave CO in the product hydrogen; hence, plants using wet chemical/solvent purification follow the CO_2 removal with a methanation step to eliminate the CO.

The chemical processes used here generally follow these equations, using DGA as an example solvent:

Absorption/desorption:

$$\mathrm{Solvent(aq)} + \mathrm{CO_2(g)} \longleftrightarrow \mathrm{Solvent.CO_2(aq)} \tag{18}$$

Table 4 Typical SMR hydrogen plant CO_2 removal solvents (Reference: Benamor (2012) Carbon capture and Storage . . ., Gas Processing Center, Qatar University)

Removal system type and technology	Licensor/Supplier
Amine solvent systems	
Monoethanolamine (MEA)	Fluor (Econamine^{SM})
Diglycolamine (DGA)	Fluor (Econamine^{SM})
Methyldiethanolamine (MDEA)	
Jefftreat	Huntsman
Gas/Spec CS-2000	Ineos
BASF aMDEA (MDEA + Accel)	BASF
ADIP-X (MDEA + Accel)	Shell
Ucarsol	Dow
KM CDR (KS-1 hindered amine)	Mitsubishi Hvy Ind
Hot potassium carbonate systems	
Catacarb and LRS-10	Eickmeyer and assoc
Benfield and Benfield ACT-1	UOP
Physical solvents	
Selexol	UOP/Dow
Mixed solvents	

Methanation:

$$CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g) + \text{heat} \tag{19}$$

Table 4 provides a summary of the wet chemical/solvent processes that are available for hydrogen purification, along with a few comparison notes. Some of the processes employ simple chemical solvents. Some use physical solvents. Some use combined chemical and physical solvents. Some of these processes may be patented or involve proprietary information.

Most of these processes offer an option that is not readily available in a PSA system: i.e., food-grade carbon dioxide is a by-product of the process. This CO_2 product can be sold to help offset operating costs. This has some advantage in the current drive to reduce greenhouse gas emissions.

Figure 6 provides a typical flow sheet for a wet chemical/solvent system of hydrogen purification. An amine-type system is used in this example since these are the most common. Individual processes and units may deviate from this flow, but the general principles are the same.

In the wet chemical/solvent approach, cool, raw hydrogen is sent to an absorber where the CO_2 is removed by a circulating solvent. The scrubbed hydrogen, with residual CO and saturated with water, is heated and sent through a fixed-bed methanation reactor (methanator). The catalyst in the reactor is a high nickel oxide material, in a reduced form. The CO is converted almost quantitatively to methane according to Eq. 19 above, consuming some of the hydrogen. Note that methanation is really just undoing the reaction we performed in the SMR furnace, and it will release just as much heat – although from much less reactant.

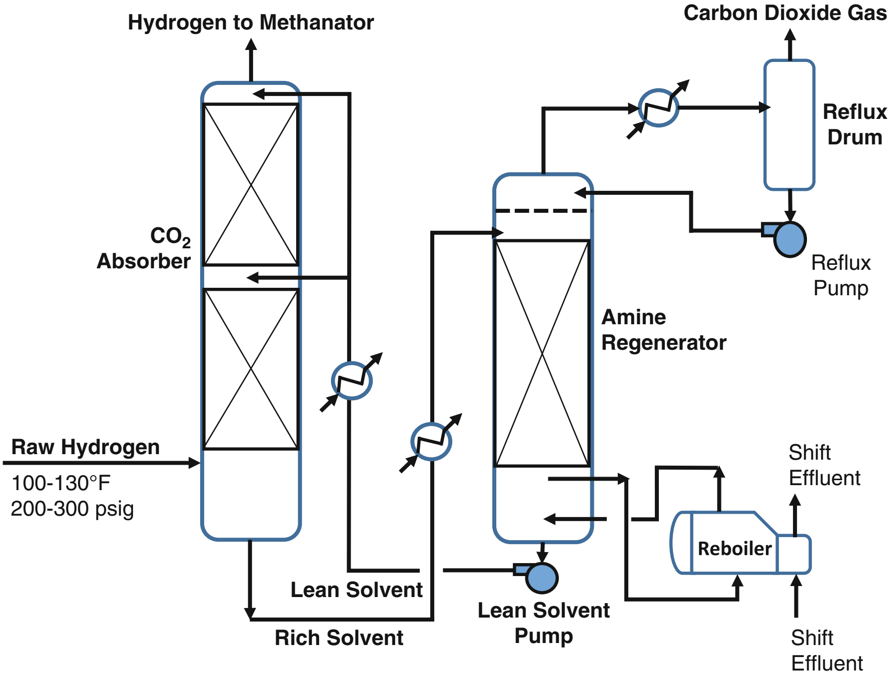


Fig. 6 Typical wet chemical/solvent CO_2 removal system for an SMR hydrogen plant

The outlet temperature of the methanator is controlled by the inlet temperature and the CO slip out of the last shift reactor. The final hydrogen from the methanator is cooled and sent to the users.

Dry hydrogen after the methanator is typically 92–96 % hydrogen, with the balance being methane. There will also normally be <10 vppm $CO+CO_2$ remaining plus some water from saturation of the hydrogen from the absorber and the methanation reaction.

Because the methanator is so highly exothermic, a methanator normally has an automatic emergency shutdown system, which will bypass the reactor and send the hydrogen to flare or vent on high-high temperature to avoid failing the reactor vessel or piping.

Meanwhile, our solvent containing the CO_2 ("rich" or "fat" solvent) is preheated and sent to a reboiled stripper or regenerator. In the stripper, the CO_2 is driven overhead to a condensing system. The water condensed from the overhead is refluxed to the stripper.

The overhead gas, which is nearly pure CO_2, is vented or sold as carbon dioxide product. For a CO_2 liquid product, only minor final cleanup is needed. Sales of CO_2 are typically via an over-the-fence arrangement with a gas supplier who does the final cleanup, liquefies, and ships the product.

The regenerated ("lean") solvent from the bottom of the stripper is cooled and circulated back to the CO_2 absorber for reuse. Small amounts of makeup water or solvent may be needed to cover losses or a small water purge may be necessary to avoid accumulation. Water balance and solvent purity must be controlled within limits.

Key operating conditions for a solvent CO_2 removal system depend on the solvent used, so are not listed here. A methanator will normally operate in the 200–300 psig range with temperatures from 600 to 700 °F inlet and 700–800 °F outlet. The temperature rise in the methanator will be about 130 °F per v% CO in the methanator feed and about 108 °F per v% CO_2 in the methanator feed.

Overall Hydrogen Plant Reaction

For material balance, catalyst activity monitoring, and process control purposes, it is helpful to look at the overall hydrogen plant reaction equation. The overall equation for an SMR hydrogen plant is

$$\begin{aligned} CH_{2\alpha} + XH_2O &\longleftrightarrow aCO + bCO_2 + (1 - a - b)CH_4 \\ &+ (X - a - 2b)H_2O + (3a + 4b + \alpha - 2)H_2 \end{aligned} \tag{20}$$

where

α = factor based on feed C/H molar ratio
X = steam/carbon molar ratio
a, b = coefficients for CO and CO_2 concentrations, respectively, at any point in the process

This equation allows you to calculate the composition of the wet gas at any point in the process from the SMR furnace inlet to the final shift outlet, as well as the composition at the methanator outlet – given a few of the gas analyses in the system. You can assume equilibrium (or some temperature difference from equilibrium) and use the K_p value tables. The calculation will be iterative. There is more about this under "Operations and Monitoring."

Another useful view of steam-methane reforming is presented in Figs. 7, 8, 9, 10, 11, and 12, based on information in *Catalyst Handbook* (by Katalco, Springer-Verlag, NY, 1970). These charts show how the various reactions involved in steam-methane reforming are interrelated to reach the final product. The values from the charts are only approximate, but can be used to help calculate wet gas compositions at the reformer outlet.

There are separate charts for reformer outlet methane, CO, and CO_2 from reforming of both gases (methane) and liquids (naphtha). The methane charts would apply when 2α in Eq. 20 is greater than about 2.5 (butane and lighter). When 2α is less than 2.5 (pentane and heavier), the naphtha charts can be used.

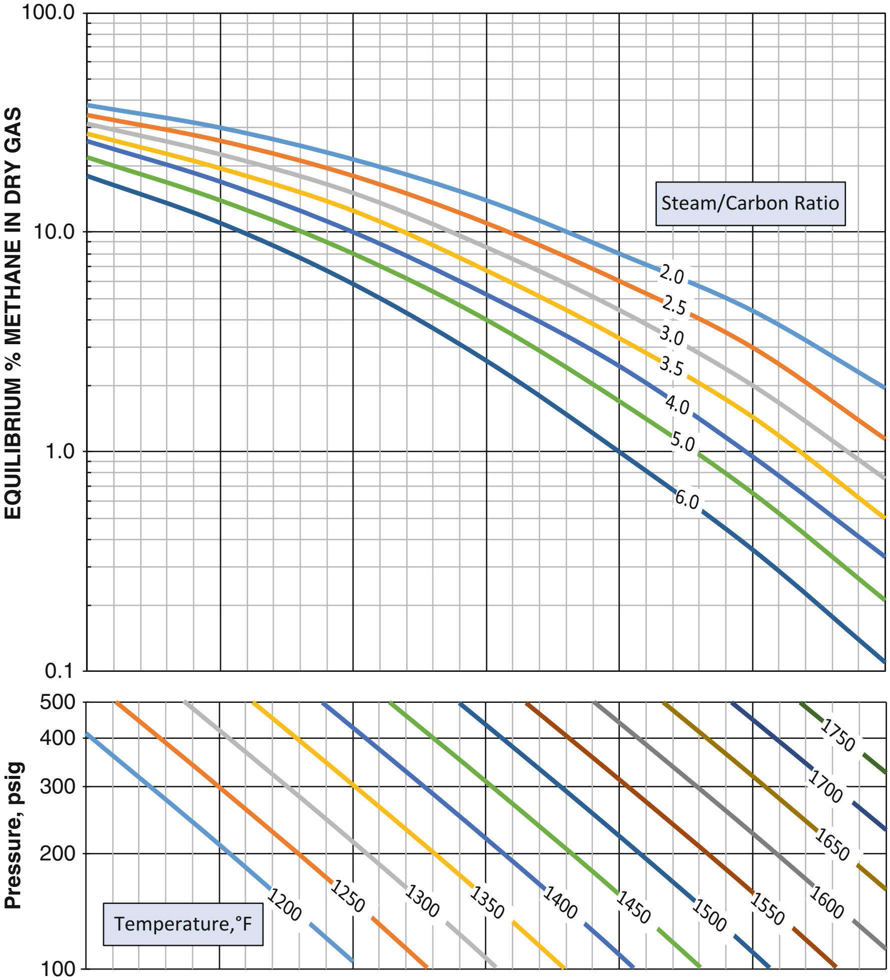


Fig. 7 CH_4 slip equilibrium chart for steam/methane reforming of methane (After: Katalco 1970)

One use of these charts is to estimate the required temperature change for the SMR reformer to target a specific methane slip. For instance, suppose you are operating a unit on natural gas (methane) at 3.0 steam/carbon ratio and 300 psig getting 7.5 % methane slip. On the upper chart for methane slip during methane reforming, find 7.5 % methane slip. Follow the methane slip horizontally to the 3.0 steam/carbon ratio line. Follow the vertical index line straight down to the bottom portion of the chart where the index crosses 300 psig. Your estimated equilibrium temperature is about 1,465 °F (you have to interpolate between the lines). This may or may not be the same as the actual process outlet temperature, but you are only going to use it as a reference in this example.

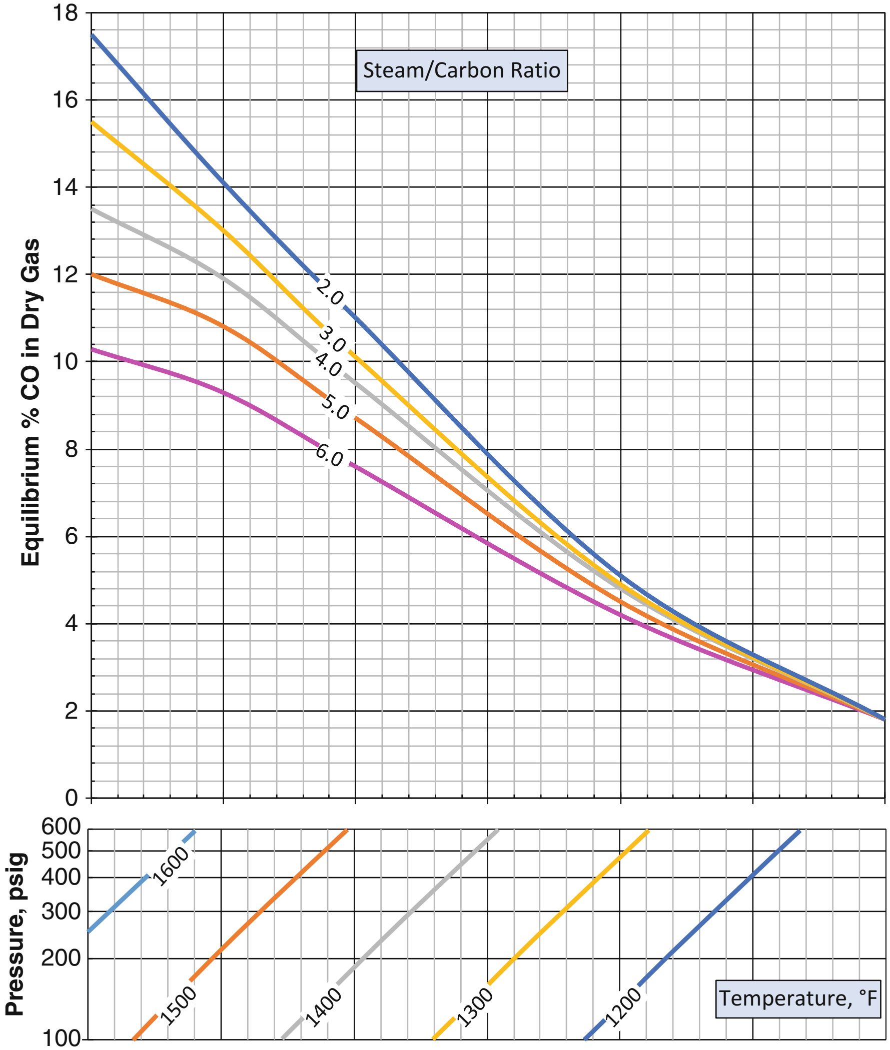


Fig. 8 CO slip equilibrium chart for steam/methane reforming of methane (After: Katalco 1970)

Now, you want to decrease the methane slip to a new target of 6.0 v% methane. You can increase steam/carbon ratio or you can change temperature. Suppose you chose to change temperature. In the upper chart, find where 3.0 steam/carbon crosses the 6.0 % methane slip line. Then, follow the index line vertically down to the 300 psig on the lower chart. The indicated equilibrium temperature is about 1,500 °F. So, increasing the reformer outlet temperature by 1,500 °F−1,465 °F = +35 °F should bring the methane slip to 6.0 v%.

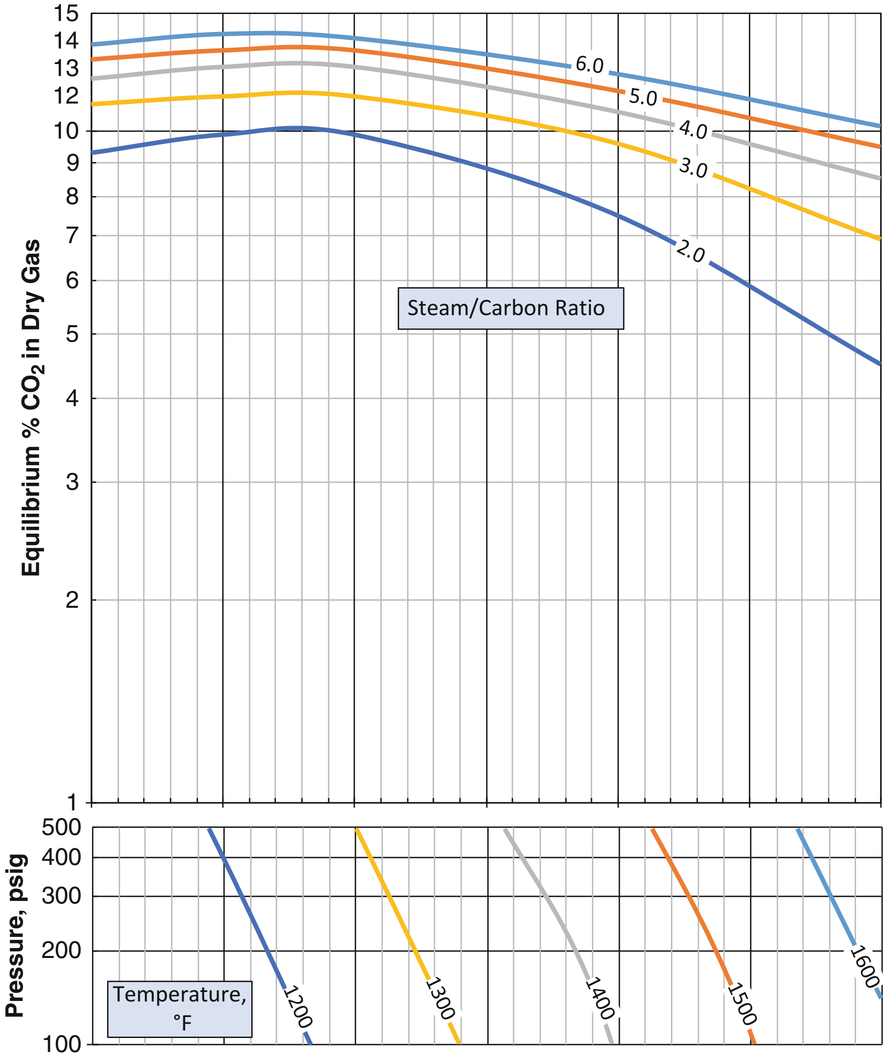


Fig. 9 CO_2 slip equilibrium chart for steam/methane reforming of methane (After: Katalco 1970)

Steam System

Intimately integrated into the SMR process is a steam system which provides process steam as well as removes the large amount of waste heat required to cool the furnace process outlet, shift outlet, and flue. The steam system allows a hydrogen plant to be nearly self-sufficient. Many hydrogen plants generate surplus, high-pressure steam that is exported to the refinery. They can be major steam

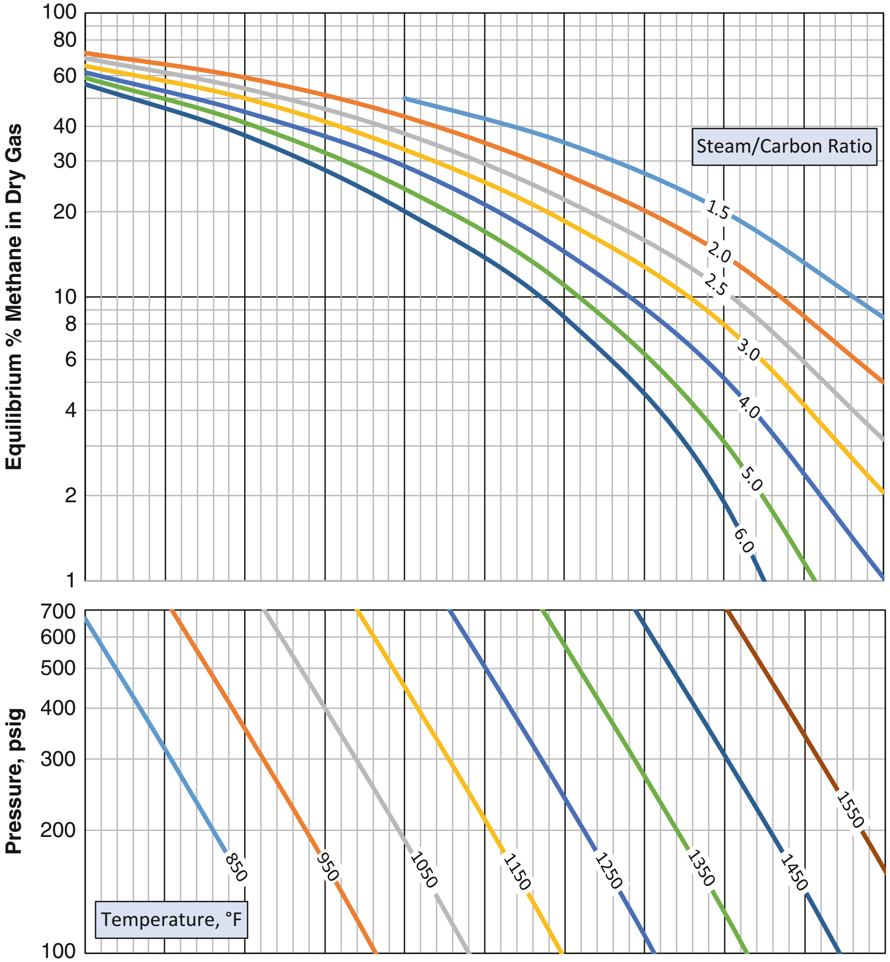


Fig. 10 CH_4 slip equilibrium chart for steam/methane reforming of naphtha (After: Katalco 1970)

generators, replacing boilers. When properly designed and spared, hydrogen plants can supply steam in an emergency, such as the loss of other boilers.

A typical steam system for an SMR hydrogen plant is illustrated in Fig. 13. Many configurations are used for these systems, however.

There are three areas where most steam is generated in a hydrogen plant:

- Reforming furnace process outlet. Here, a steam generator/waste heat boiler (WHB) is installed. The WHB cools the process gases from their exit temperature of 1,350–1,740 °F down to the HTS converter inlet temperature of about 700 °F. The final temperature is controlled by bypassing hot gas around

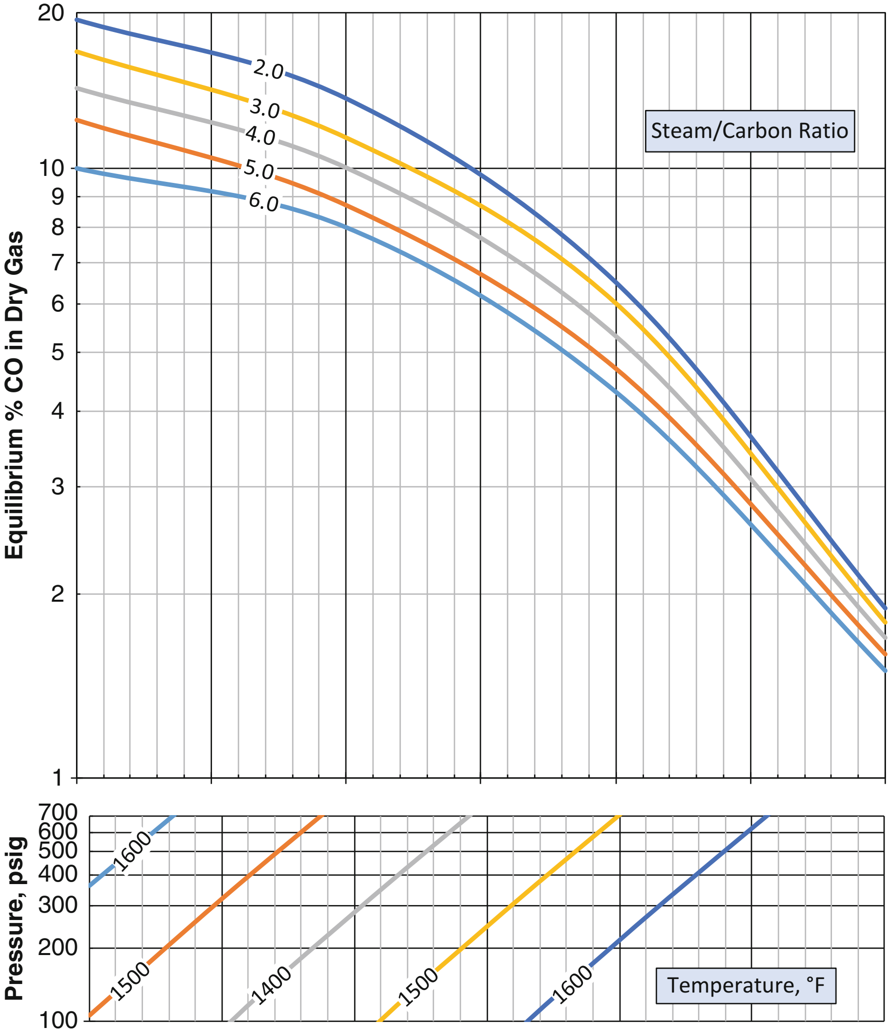


Fig. 11 CO slip equilibrium chart for steam/methane reforming of naphtha (After: Katalco 1970)

(or through) the steam generator using a damper system. Water supply to the WHB is normally by thermosiphon from a steam drum located somewhat above the WHB. Vaporization is typically 10–20 % in the WHB.

- Reforming furnace flue gas. One or more steam generation coils plus an economizer to preheat boiler feedwater are normally included in the flue gas ducting. These are usually thermosiphon or forced circulation steam generators tied to the main steam drum.
- High-temperature shift reactor effluent. Many plants employ a separate steam generator(s), sometimes kettle style, on the shift reactor effluent to recover

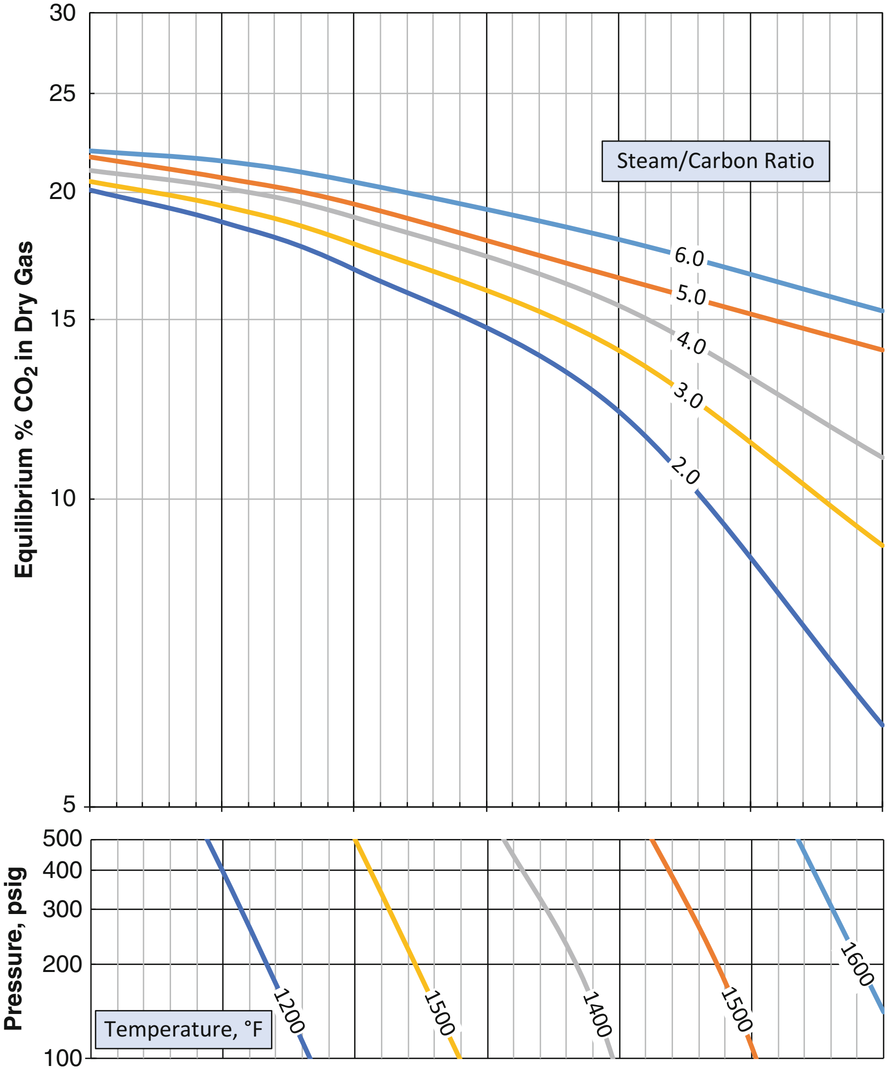


Fig. 12 CO_2 slip equilibrium chart for steam/methane reforming of naphtha (After: Katalco 1970)

additional high-level heat. In plants that use wet chemical/solvent CO_2 recovery, this heat is normally used to drive the solvent system, so the steam generator may be omitted in these plants.

Treatment of the boiler feedwater (BFW) for the steam generator systems and steam from hydrogen plants is critical. Table 5 summarizes the typical BFW treatment requirements.

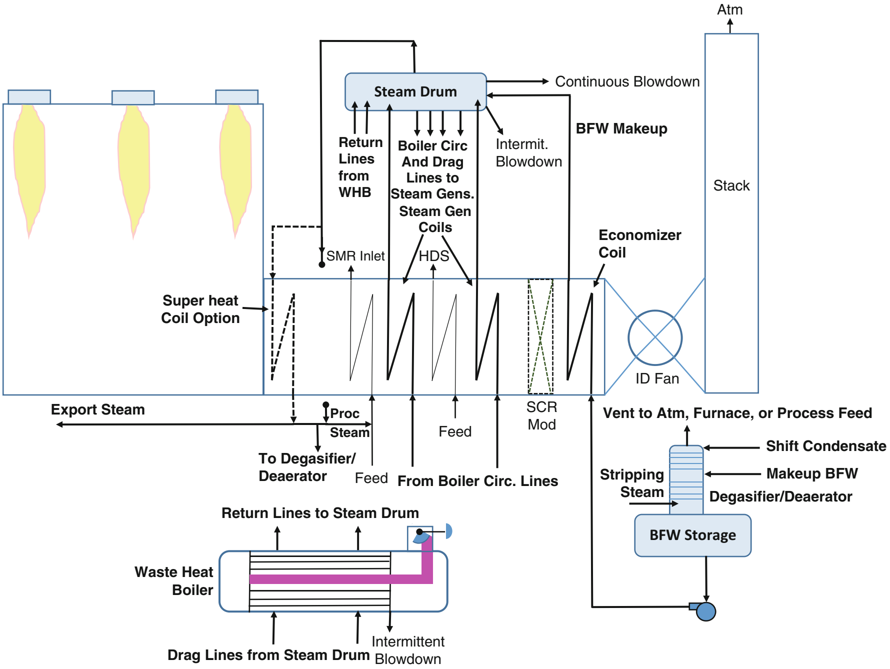


Fig. 13 Typical SMR steam system simplified process flow diagram. Note: This is only one possible configuration presented, for example. Other steam generators may also be installed in the shift effluent

Table 5 Typical SMR hydrogen plant boiler chemical treatment (Reference: Nalco)

Function	Chemical	Feed point	Notes and comments
Oxygen scavenger	Passivating scavenger	Deaerator/degasified storage tank	No sulfur compounds
Boiler pH control	High-purity caustic	BFW to pump suction	Depends on makeup water; avoid ammonia and amines
Boiler internal treatment	Polymer system	BFW to pump suction	Avoid ammonia generation; need iron dispersant capability; analytical capability to track chemicals; maximize cleanliness of boilers
Supplemental iron dispersant	Polymer system	BFW to pump suction	Needed if chelant or phosphate internal treatment is used
Condensate treatment	Mixed amines	Export steam line only	Amine boiling points should match condensate system pressures; H_2 plant condensate system should be stainless steel; amine in H_2 plant will convert to ammonia in process

Hydrogen plant steam systems are highly stressed and require higher treatment levels than normal boilers. In the WHB on the furnace outlet, for instance, the tube walls will be over 1,000 °F. When working with a boiler chemical vendor, you need to be sure the vendor is experienced in hydrogen plant chemical treatment. One specific caution is that BFW for a hydrogen plant should not use sulfite as an oxygen scavenger. The small amount of residual sulfur that ends up in the steam will poison the reforming catalyst.

Recycle of shift condensate can introduce higher levels of CO_2 into the steam generated. The CO_2 becomes a corrosion problem in condensate systems using the steam. Critical factors in preventing this corrosion are:

- Proper stripping of the shift condensate, as noted in the discussion of the water-gas shift section above
- Injection of amine corrosion inhibitors into the export steam that will drop out into the condensate headers at the correct pressures/temperatures

Unique Equipment Design and Metallurgy Considerations

In this section, we will review a few of the unique considerations in hydrogen plant equipment design. Properly addressing these factors is critical to building and operating a hydrogen plant.

SMR Furnace

Here, we will highlight only some of the more important considerations around an SMR furnace. These furnaces are not “run-of-the-mill” units. They require design experience. For very large furnaces, computational fluid dynamics (CFD) may be employed to ensure heat release and flow in the firebox are properly designed.

- *Style of furnace* – The SMR furnaces are generally some of the largest, if not the largest, fired heaters in a refinery. Several furnace types have been used, as shown in Table 2. The table enumerates some of the key advantages and disadvantages of each style of heater. Today, most hydrogen plants are either down fired or terrace-wall fired.
- *Radiant tubes* – Some typical hydrogen plant tube configurations are depicted in Fig. 14.

  The tubes are made of high nickel alloys (HK-40, Manurite, etc.). Tube IDs range from 1.5 to 5.5 in.. The tube design temperature is chosen based on the calculated maximum expected end-of-run wall temperature. The design margin today is about 50 °F higher than the maximum expected wall temperature. This can be very tight. Our ability to monitor tube temperatures is about +/− 100 °F. Monitoring will be discussed later.
- *Burners* – SMR furnaces use large numbers of burners to distribute heat evenly to all the tubes. Because the firebox operates over 2,000 °F, the burners used

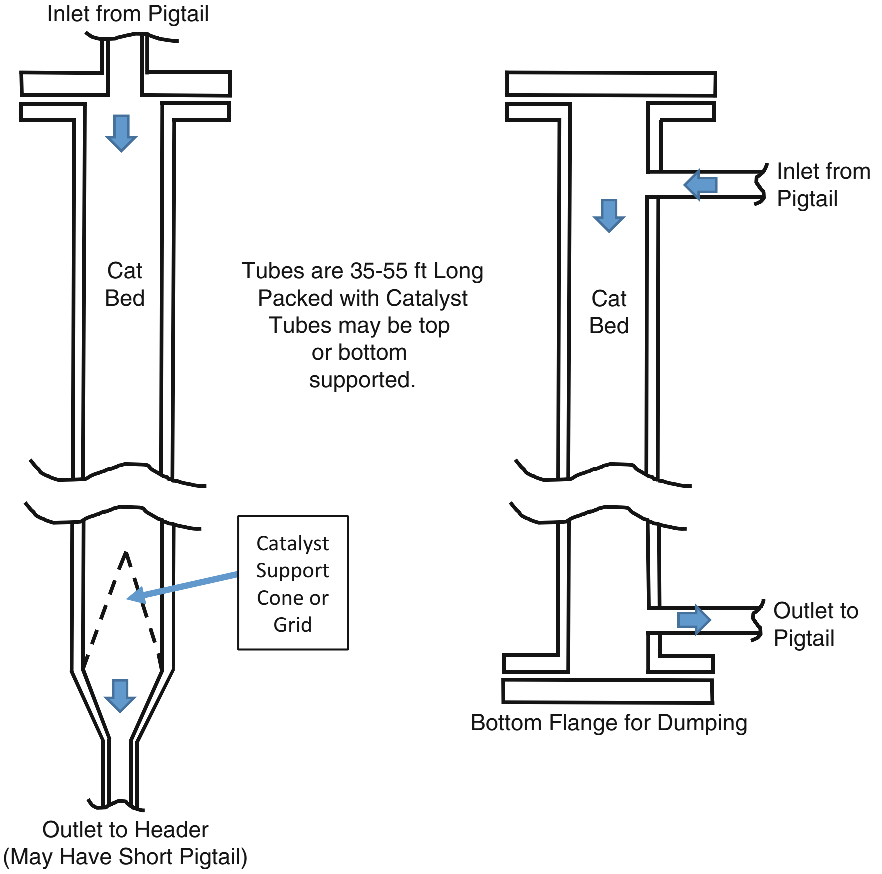


Fig. 14 Some typical SMR tube arrangements. Note: These are examples only. There are many styles in use

today are generally special low-NOx styles. In PSA hydrogen plants, the burners have an extra, low-pressure-drop nozzle for PSA off-gas.

Arrangement or design of the burners must avoid flame impingement on the tubes. All burners may not be the same size, as dictated by the heat input requirements in a given section of the heater.

- *Convection section* – The convection sections of hydrogen plant furnaces generally have a series of services. Typically, you will see coils for:
  – Steam superheat
  – Mixed steam/feed preheat
  – Steam generation (one or more levels)
  – BFW economizer/preheat
  – Combustion air preheat

In some areas, selective catalytic reduction (SCR) units may be installed in the flue to reduce NO_x. These systems employ a catalyst matrix with very low pressure drop (inches of water). Ammonia is injected into the flue ahead of the catalyst through a grid of nozzles. The ammonia is vaporized outside the flue and diluted into hot air to improve distribution. The SCR must be located in an exact temperature range (depending on the catalyst chosen). Sometimes, these are retrofitted to existing hydrogen plants, with the convection coils rearranged to ensure the correct temperature range.

- *Furnace draft control* – SMR furnaces may be natural draft, induced draft, or forced/induced draft. You seldom see forced draft-only furnaces in this service. Older units tend to be natural draft. For down-fired furnaces or where an SCR is required, induced draft is used. If a furnace has air preheat, it will generally have both forced and induced draft fans.

  The burner registers provide additional draft control. The registers must be open enough to allow the control system to work.

  PSA off-gas combustion introduces a swing into the fuel gas controls that will affect draft. The draft will vary slightly every couple of minutes as the PSA cycles. Controls around the PSA attempt to moderate the swing, but generally cannot eliminate it. With careful tuning of controllers, the swing can generally be managed. Keep in mind that swinging draft also means swinging excess oxygen levels.
- *SMR process outlet header* – The high process outlet header temperatures from an SMR furnace give rise to special problems when transferring the effluent to the waste heat boiler. The outlet headers inside the firebox are generally high alloy (e.g., Incoloy). The high alloy is transitioned to a lower alloy header, normally something like 1¼ Cr steel, that is lined with a refractory system. Figure 15 illustrates the types of refractory arrangements normally seen in this service.

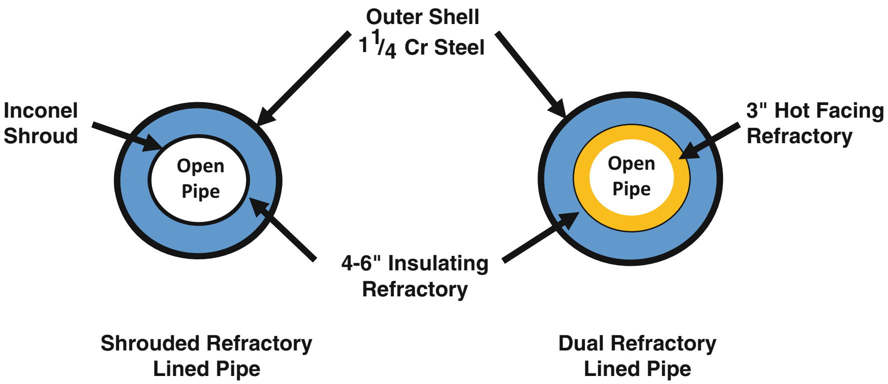


Fig. 15 Typical refractory systems for SMR furnace process outlet

The refractory-lined effluent piping needs to be monitored to ensure that an internal refractory failure does not lead to a pipe wall failure. Even a small crack in the refractory will increase wall temperature. A major refractory loss will rapidly heat the wall above its allowable maximum. To monitor for this, the outside wall of the transfer line is painted with temperature-indicating paint, normally changing color if the pipe wall exceeds about 500 °F. This provides a margin between maximum allowable temperature and actual.

Conversely, it is important that the steel wall of the refractory-lined header be maintained above the water condensation temperature. The SMR effluent, if condensed, will form carbonic acid. That acid will corrode the low-alloy steel. The outside wall of the refractory lined pipe normally runs about 250–350 °F to meet all the requirements.

- *Safety* – Any fired heater needs a safety system, and an SMR furnace is not an exception. The complexity of the SMR means that the safety systems around these units are correspondingly more complex. These systems will not be comprehensively covered, but a few specific considerations in SMR furnaces are highlighted:
  - *Loss of draft control* – Because an SMR fires at such high rates, loss of draft control in the firebox creates a potentially hazardous situation. This can occur with loss of the forced or induced draft fans, damper or register control issues, PSA trips, excessive changes in fuel gas rates, high or low fuel pressures, and many other causes. Safety systems for these furnaces generally trip on high or low draft. These systems are backed up by excess oxygen monitoring at the firebox outlet.
  - *SCR problems* – Where a furnace has an SCR, the SCR may be tripped on high or low flue gas temperature or on loss of ratio control in the vaporizer skid. These trips are intended to avoid potentially explosive mixtures or deposits in the vaporizer and/or flue.
  - *Fuel gas, pilot gas, or PSA off-gas high/low pressures* – Depending on the type of failure, there will generally be trips on several fuel stream pressures because these can cause other issues. Fuels are tripped out of the furnace to avoid accumulating an explosive mixture. Generally, pilot gas is maintained unless draft is lost.
  - *Firing protection* – In modern reformers, the safety systems contain a number of interlocks to ensure the heater is fired safely. Typical interlocks include verifying that all fuels are isolated before allowing a purge, ensuring that a purge is completed, verifying that pilots are lit before allowing main fuel to be admitted, and verifying that the main fuel is on before allowing PSA off-gas. Factory Mutual (FM) cock valves and nitrogen pressurization of fuel headers have both been used to verify fuel isolation before allowing a purge to start.
  - *Process trip* – If the process side of the furnace trips for any reason, the heat load on the furnace is drastically and immediately reduced. The furnace must be cut back very quickly, and this can lead to the furnace tripping on draft or fuel pressure. Generally, however, a process trip does not require a furnace trip if the furnace can be reduced back to pilots with control.

Waste Heat Boiler

- *General design* – The SMR effluent steam generator or waste heat boiler is normally a large, horizontal heat exchanger. See Fig. 16 for a sketch of a typical WHB exchanger.

  The inlet to the process side of the exchanger is connected to the SMR furnace with the refractory-line transition header. The WHB inlet is normally refractory lined also, with high alloy inserts into each of the boiler tubes.

  There is normally a single, larger, lined tube that passes through the boiler to act as a hot gas bypass duct. In some units, this may be an actual bypass around the WHB, rather than through it.

  The hot gas bypass is equipped with a damper to control the final process outlet temperature from the WHB. The damper is generally arranged to act like a three-way valve – restricting the flow through the boiler tubes as it opens to allow hot gas bypassing. Sometimes, the bypass is automatically controlled, but manual control is also used.

  On the water side of the exchanger, the flow is generally by thermosiphon, so water from the overhead steam drum is distributed to the WHB at several points along the bottom of the shell. Mixed steam/BFW returns to the steam drum from outlets distributed along the top of the shell. Intermittent blowdown is taken from the bottom of the shell. The steam side of the WHB is hard to inspect normally.
- *Metal dusting* – The process conditions in the WHB can result in metal dusting. This is where the process gases cause migration of carbon to the grain boundary metals, and the metal crystallites essentially turn to dust. It is promoted by reducing gases (H_2, CO, methane) in the 900–1,500 °F range. While a hydrogen plant normally has an oxidizing atmosphere, the reformer outlet is much closer to reducing conditions. Metal dusting is seen more at low steam/carbon ratios. The metal tubes and the hot gas bypass in a waste heat boiler are especially susceptible to this damage. The inserts on the tube inlets and selection of metallurgy help control this phenomenon.

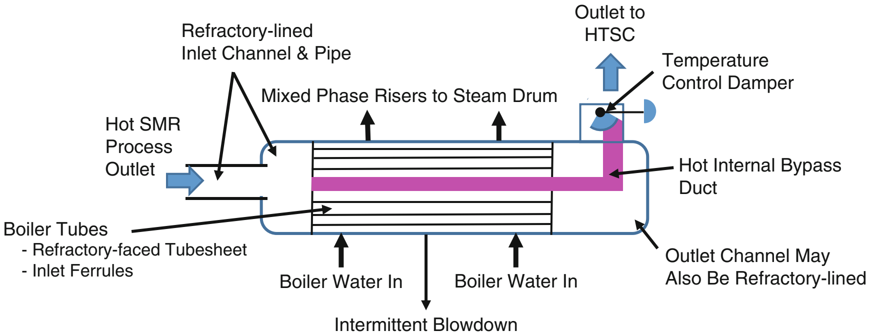


Fig. 16 Sketch of a typical SMR furnace process outlet waste heat boiler or steam generator

PSA Systems

Most modern hydrogen plants use pressure swing adsorption (PSA) systems. Refer to the detailed PSA discussion in the section "Pressure Swing Adsorption" of this chapter for information on critical aspects of PSAs.

Some specific areas to note about PSAs in the discussion are:

- Valves and sequence steps
- PSA adsorbers
- Off-gas/tail-gas drum
- Control system

Wet Chemical/Solvent Systems

Wet chemical or solvent CO_2 removal systems present their own challenges in design. We will focus on amine solvent systems here, since they are most common. Hot carbonate and other systems have some of the same issues, with slightly different flavors.

A couple of the challenges considered here are:

- *Corrosion management*
  As with most acid gas removal systems, metallurgy of the system needs to consider the materials handled. Some specific considerations with hydrogen plant systems are:
  - Amine scrubbing solutions subject equipment to potential amine cracking. Post-weld heat treatment of amine handling systems is advisable.
  - The amine regenerator/CO_2 stripper tower and overhead are subject to carbonic acid attack. Stainless steel piping is needed.
  - Carbonic acid attack is also seen in some unexpected places around the stripper: shell near the reboiler return line and the piping and shell around the stripper inlet line. It is advisable to consider alloying these areas and watching the maximum velocities.
  - In MEA amine systems, arsenic compounds may be used for corrosion inhibitors. These are effective, but introduce an additional hazard during operation and maintenance.
  - Solvents tend to build heat-stable salts. These need to be eliminated to keep the solution healthy. Some systems employ side-stream reclaimers to remove the salts. They can also be removed by ion exchange using an outside service company.
- *Filtration*
  The circulating solvent streams will build up corrosion products and other solids, in spite of corrosion inhibitors. These materials need to be removed from the stream. This is normally accomplished by side-stream filtration of a slipstream off the main circulating flow. The slipstream usually passes through a cartridge filter and may also go through an activated carbon filter to remove potential foaming materials or trace organics that you do not want in the solvent.

Materials Damage Mechanisms

There are a number of mechanisms that can cause damage to materials in a hydrogen plant. Some of these have been alluded to in the above discussion. For a complete review of the damage mechanisms and management practices, please refer to API RP-571. This is an excellent resource for any type of system.

For general reference, the mechanisms highlighted in RP-571 for hydrogen plants are summarized in Table 3.

Operations and Monitoring

Operations

The following discussion will briefly describe the main operating phases of an SMR hydrogen plant from start-up through shutdown. Initial commissioning of a hydrogen plant is beyond the scope of this discussion. For additional detail, consult the references listed at the end of this chapter.

- *Start-up*

  Start-up of a hydrogen plant follows this general outline:
  - Inventory water in the steam system. If the unit has solvent CO_2 purification, the solvents are inventoried in parallel.
  - Air-free the process system with nitrogen.
  - Pressure and circulate the process system with a noncondensable gas.

    This is often nitrogen, but pure hydrogen or natural gas can also be used. Do not use reformer hydrogen.

    It is also possible to heat the furnace to 800 F in the flue without circulation. The downside of this approach is that the high-temperature shift converter is not heated up, so it must be bypassed when steam is introduced and then heated later with process flow.

    If the system uses a LTS converter, this converter should be bypassed. It will be activated later.
  - Fire the reforming furnace and heat to about 800 °F in the *furnace outlet flue gas* (convection inlet) at 50–100 °F per hour.

    When the flue gas reaches the required conditions, the SCR (if applicable) can be started.

    Initially, you would use only a few burners evenly distributed in the furnace. As the furnace heats up, add more burners and ensure they are evenly distributed in the firebox to avoid tube failures from flame impingement. These comments apply throughout the start-up procedure.
  - Slowly start process steam and increase steam rate to at least 50 % of design with continued heating to 1,000 °F in the *process outlet* temperature from the furnace.

    Inert circulation can be discontinued at this point since the main flow is now steam.

  There may be condensation of steam in the HTS converter initially, but the converter will dry out. Do not heat the shift converter too fast to avoid catalyst damage.
  If the initial heat up to 800 °F did not use inert gas flow, then the HTS converter should be bypassed and heated up with steam at a controlled rate once the main flow is stable.
- Continue increasing temperature and steam rate to feed gas inlet conditions at no more than 100 °F per hour – normally about 1,200–1,300 °F on the *process outlet* from the SMR furnace.
- Start clean feed gas.
  If the system has a low-temperature shift converter, the converter is bypassed.
  Adjust the feed gas purification conditions to clean up the feed gas. You should have no detectable H_2S in the reformer feed gas (<0.01 ppm).
- Maintain a high steam/carbon ratio ($>\sim 6.0$) in the reformer as the reforming catalyst and HTS converter catalyst are activated over a few hours.
- Continue heating to 1,350–1,550 °F *process outlet* temperature from the SMR furnace with the high steam/carbon ratio. Adjust the SMR and HTS temperatures to your start-of-run targets.
- If the hydrogen plant uses PSA purification, the PSA can be purged out with nitrogen and then started up, initially taking no product.
  Once the product hydrogen is on spec, the product can be sent to the users.
  The PSA off-gas can be sent to the SMR furnace for firing once the PSA is stable.
- If the hydrogen plant uses wet chemical purification, the absorber system can be started and stabilized.
  The methanator can be heated up before being brought on line at the initial target temperature. Nickel carbonyl formation is a potential concern here. The methanator temperature must be over 400–450 °F before introducing gases containing CO.
  CO_2 production can start when the system is stable.
- Once the main process is stable, the low-temperature shift converter is normally activated and brought on line. This may be a couple of days after the main process.
- Finally, move the steam/carbon ratio to the target level and begin adjusting operating conditions to targets.
  Adjust the SMR furnace to achieve the desired methane slip.
  Adjust the HTS and LTS converters to obtain the target CO slip.
  Adjust the PSA cycle or the solvent system conditions to obtain and maintain targets.
  Export surplus steam.

- *Routine operations*
  There are not a lot of major adjustments required for hydrogen plant operating conditions normally. The rate may be increased or decreased with corresponding adjustments, but certain targets stay the same. Note that hydrogen plants operate

best at a steady, stable rate. They do not respond well to frequent rate changes. Daily rate changes are usually tolerable; hourly changes make operation difficult.

The most common adjustments to operating conditions are listed below. This is, by no means, a comprehensive listing.

– *Feed purification*

Adjust temperatures and/or absorber flows and loadings to maintain non-detectable H_2S in the reformer feed.

– *Reforming furnace*

Maintain steam/carbon ratio at design. Slight changes may be needed, depending on the feedstock.

Pressure is not normally changed.

Reformer process outlet temperature is controlled to maintain the target methane slip.

Firebox-side control of the reforming furnace is similar to other furnaces, with appropriate safety interlocks. The PSA gas may introduce fluctuations that must be managed by the controls.

Adjustments to manage methane slip can be estimated from the figures included in the overall process discussion section. These figures relate methane slip, steam/carbon ratio, temperature and pressure for methane, and naphtha feedstocks. Essentially, they are graphical representations of the SMR equilibrium with parameters in the normal operating ranges.

If the furnace has an SCR, the vaporizer and ammonia flows will be automatically controlled. They just need to be monitored.

– *Shift conversion*

Adjust the shift converter inlet temperature to obtain the target outlet CO slip. For quick estimates relating CO slip, temperature, and steam/carbon ratio, the following equation can be used:

$$\ln(\mathrm{CO}) = 3.5514 * \ln(\mathrm{T}) - 1.6775 * \ln(\mathrm{S/C}) - 20.338 \tag{21}$$

where:

CO = v% CO in dry gas

T = Temperature at reactor outlet, °F

S/C = Initial steam/carbon molar ratio to SMR

Note that, because the reaction does not change the number of moles in the vapor, there is negligible pressure effect in this range.

– *Product purification*

For a PSA system, the time on adsorption for a single bed is adjusted to maintain purity. Sometimes, this is part of the “capacity” factor. The control system makes the other necessary adjustments. Routinely check the PSA valves for leakage around the packings and smooth action.

For a solvent purification system, the absorption and regeneration flows, temperatures, pressures, and solvent loadings need to be kept within the design limits.

  - *Steam systems*

    Adjust blowdown rates to target conductivities. This may be automatic.

    Adjust BFW preheat conditions. This must be coordinated with other conditions.

    The steam system controls will normally handle changes in the plant.

    Stripping conditions in the shift condensate degassing system need some attention to ensure the CO_2 is removed. Use the system design as a guideline to what conditions to expect.

- Shutdown

  Shutdown of a hydrogen plant generally follows the same sequence, regardless of the type of unit. The primary steps are:

  - Cool reforming furnace to 1,200–1,300 °F process outlet temperature.
  - Stop feed, but continue steam. Stop the PSA, if present.
  - Steam the catalysts for 2–6 h at 1,200 °F in the reformer.

    The LTS converter may be bypassed and shut down separately.
  - Cool the reforming furnace with steam flow at no more than 100 °F per hour to about 800 °F at the flue gas outlet from the radiant box.

    During this time, inert gas flow can be reintroduced to the process, if desired. Inert flow will help cool the HTS converter and other equipment.

    If the unit has a methanator, it should be removed from the flowing system and separately purged at least five times with nitrogen before cooling below 400–450 °F to prevent nickel carbonyl formation.
  - Stop steam flow. If using inert flow, continue cooling with the inert gas. The SMR furnace can be shut down when firing reaches minimum.
  - Purge the entire system with nitrogen to eliminate hydrogen and hydrocarbons. Test for CO in the gas. The concern is that nickel carbonyl may form at low temperatures ($<\sim$450 °F). CO must be less than 10 vppm in the system if you are below this temperature. The methanator is especially susceptible to nickel carbonyl and should be managed separately as noted above.

Monitoring

Table 6 provides a list of the key variables to monitor in an SMR hydrogen plant, along with the frequency. The following discussion describes calculation of some of these key variables. Issues around tube wall temperature monitoring in reforming furnaces are also discussed.

Most catalyst suppliers for hydrogen plants will provide a detailed material balance and analysis of your unit's performance if you provide them with operating data. Table 7 indicates the information needed to obtain a detailed performance analysis from a supplier. You should be continually monitoring the unit yourself; but, it is still a good idea to have a third party evaluation periodically (say quarterly). This service is usually provided at no cost.

- *Material balance*

  Successful monitoring of an SMR hydrogen plant process starts with a good material balance for the plant at a point in time. The flow, composition,

Table 6 Typical key SMR hydrogen plant monitoring parameters

Monitored variable	Frequency	Basis
Overall unit		
Feed rate(s)	Daily	Trend meters
Production rate(s)	Daily	Trend meters
Material balance	Weekly/monthly	Detailed calculation
Feed pretreat process		
Hydrogen recycle rate	Daily	Trend meter
Hydrotreater temperatures	Weekly	Review data
Zinc oxide bed outlet H_2S	Weekly	Look for breakthrough
SMR and shift processes		
Steam/carbon ratio	Daily	Trend, verify weekly
Reformer outlet temperature	Daily	Trend
Reformer outlet pressure	Daily	Trend
Reformer tube pressure drop	Weekly	Trend normalized dP – watch for jumps
Reformer max tube wall temp	Weekly	Trend, watch for hot spots
Methane slip	Daily	Trend, adjust
Reformer ATE	Weekly/monthly	Calculate, trend – watch for deactivation
Shift converter outlet temps	Daily	Trend
Shift converter rises	Daily	Trend
CO slip	Daily	Trend, adjust
HTSC ATE	Weekly/monthly	Calculate, trend – watch for deactivation
LTSC temp front location	Weekly/monthly	Calculate, trend – watch for deactivation
Boiler water chemistry	Weekly	pH, conductivity, hardness – adjust
Steam production/ distribution	Weekly	Trend – watch for loss in rates
SCR performance	Weekly/monthly	Watch for increasing NH_3 rqmt => deactivation
Product purification		
Overall purification		
Product purity, % H_2	Weekly	Watch for loss of purity, ethane
Product H_2/unit feed	Weekly	Watch for loss of efficiency, trends
Solvent/wet chemical		
Lean and rich loadings	Weekly	Keep within design limits
Methanator rise	Daily	Trend, watch for increases => CO_2 removal problem
Methanator temp front location	Weekly/monthly	Trend location in bed => deactivation
CO_2 production rate	Daily	Trend
Pressure swing adsorption		
Recovery, v% raw H_2	Weekly	Calculate and trend => efficiency loss, optimization

Table 7 Example of data needed by third party to analyze hydrogen plant performance

Date:	
Unit:	
Location:	

Notes:

1. Provide as much actual data as possible.
2. Use only measured values.
3. Provide process PFD.

SMR Design Data		
Number of tubes		
Tube ID/OD	inches	
Fired/loaded height	feet	
Tube material		
Type of furnace		
Key Flow Rates		
Design feed rate	MMscfd	
Feed rate	MMscfd	
Recycle H2	MMscfd	
Raw H2 to purification	MMscfd	
Total product	MMscfd	
PSA offgas	MMscfd	
Process steam	lbs/hr	

Gas Analyses		**Feed**	**Reformer**	**HTS**	**LTS**	**Meth In**	**Meth Out**
H_2	v%						
N_2	v%						
Ar + He	v%						
CO	v%						
CO_2	v%						
CH_4	v%						
C_2	v%						
C_3	v%						
C_4s	v%						
C_5s	v%						
C_6-Plus	v%						
Sulfur	ppm						

Reactor Data		**Hydrotreater**	**Cl-guard**	**ZnO**	**Reformer**	**HTS**	**LTS**	**Methanator**
Catalyst type								
Bed diameter	feet							
Bed height	feet							
Catalyst volume	cubic feet							
Inlet Pressure	psig							
Outlet pressure	psig							
Inlet temperature	°F							
Outlet temperature	°F							
Other bed temperatures	°F & Location							
					Provide IR Survey			

pressure, and temperature for the process streams at the following points are required for the best results. The minimum data required are indicated by asterisks below:

- Feed gas ahead of pretreat system
  Gas chromatograph (GC) analysis* – note that even natural gas feed will have variable composition
  You especially need the moles of carbon per mole of feed*
  Flow rate*
- Feed pretreat system inlet
  Feed gas analysis from above
  Flow rate of feed and recycle hydrogen
- Reforming furnace inlet
  Composition calculated from pretreat system inlet after reactions plus process steam flow
  Flows for feed gas and steam*

- Reforming furnace outlet/HTS inlet

  Ideally, you want a GC of the reformer outlet gas, but this is a hard sample to take.

  You can back calculate the composition from the methane contents in the raw hydrogen to purification*.

  Total flow will be the same as the reformer inlet.
- LTS inlet (if applicable)

  Need a GC of the HTS converter outlet

  Total flow is normally the same as the HTS outlet.
- Raw hydrogen before purification

  Need a GC of this dry gas going to the purification system*

  Assume the gas is saturated with water

  Need the total gas rate*
- Product hydrogen to methanator (if applicable)

  A GC of this is nice, but it can be estimated from the raw hydrogen by removing the CO_2.

  The stream will be saturated with water at absorber overhead conditions.
- Product hydrogen

  Need a GC of this stream*

  Need flow rate*
- Product CO_2 (if applicable)

  This stream will be mostly CO_2, so it mainly needs the temperature and pressure.

  It will be saturated with water at production conditions.
- PSA off-gas (if applicable)

  GC of the gas*

  Flow rate*
- Shift condensate

  This stream is normally not metered, so the flow must normally be calculated or estimated from the other streams.

  It may be sampled; the CO_2 content can be estimated assuming the water is saturated with CO_2 at production conditions.

  If there are hot and cold shift effluent separators, you need to estimate the flows and CO_2 contents for each separator.

  Using the available data, a component-by-component material balance can be constructed, along with the pressure and temperature for each stream. An example of how to do this is in the Appendix of this chapter.

  Where data are not available (especially GCs), the data can be calculated assuming equilibria and using the overall equation for SMR reforming (Eq. 20). Remember that you want the *wet* compositions at each point because water is a major participant in many of the reactions.

  Usually, this can all be built into a spreadsheet that will reconcile all the data. This takes an initial effort to set up; but once the spreadsheet is built, it greatly improves your ability to analyze the hydrogen plant operation.

  Once you have a reasonable material balance, catalyst activity tracking and other analyses are possible.

- *Steam/carbon ratio*

  The molar ratio of steam to carbon is one of the most critical parameters to monitor in an SMR. To calculate the steam/carbon ratio (sometimes abbreviated S/C):
  - Use the feed detailed analysis to calculate the moles of carbon per mole of feed. Include any CO or CO_2 in the feed as part of the calculation.
  - Calculate the total moles of feed using the feed flow meter, with corrections. Normally, this will be moles per hour of feed.
  - Calculate the molar rate of carbon in the feed from the moles carbon per mole feed times the feed rate. This will normally be moles carbon per hour.
  - From the process steam flow meter, calculate the moles of steam per hour.
  - Divide the moles steam per hour by the moles carbon per hour to get the steam/carbon ratio.

  For liquid feedstocks where composition is not necessarily available, the carbon in the feed can be estimated using C/H ratio correlations from API based on boiling range and specific or API gravity.

  The S/C must be maintained within a specified range. A high ratio will make more hydrogen, but loses some efficiency in the process. A low ratio leads to coking and deactivation of the reforming catalyst, as well as making less hydrogen.

  Note that you do not need the whole material balance to calculate the steam/carbon ratio. Often, the ratio is calculated online with sufficient accuracy using average compositions to allow the direct control of the ratio by the basic process control system.

  See the Appendix for a sample calculation of the corrected steam/carbon ratio.
- *Reforming catalyst approach to equilibrium*

  Using the reformer outlet composition from the material balance and the equilibrium K values, the equivalent reformer outlet temperature that the equilibrium corresponds to can be calculated. This calculated temperature is subtracted from the actual temperature to obtain the “approach to equilibrium” (ATE) temperature. This is a way to track reforming catalyst activity.

  Note that an equation for calculating the equilibrium temperature from the calculated K value is included in the overall reforming process discussion in section “Primary Reforming” of this chapter (Eq. 13).

  The ATE value is normally negative with fresh catalyst. The actual approach is zero, but heat loss from the actual catalyst outlet to the reformer outlet temperature measuring point results in the negative value. This is not really a problem, because you will track catalyst activity by relative changes in the ATE.

  Over time, the reformer ATE trends upward as the furnace eventually cannot reach equilibrium. At some point, you decide to replace the catalyst. Reformer catalyst can typically operate over 5 years, unless it is poisoned or coked. However, even a few minutes with very low or no steam in the feed may dictate an immediate end of run.

The ATE value calculated will bounce around significantly, so you are really looking for a trend. Another hint that the catalyst is spent is if you detect any ethane above ~0.05 v% in the product hydrogen.

See the Appendix for a sample calculation of the reformer approach to equilibrium.

- *HTS catalyst approach to equilibrium*

  Similar to the reforming furnace, you can calculate the approach to equilibrium from HTS using your material balance compositions and the previously provided equilibrium information.

  Note that an equation for calculating the equilibrium temperature from the calculated K value is included in the overall reforming process discussion in section "Primary Reforming" of this chapter (Eq. 16).

  The HTS will not completely reach equilibrium, normally. A plot of the ATE in the HTS will trend upward with catalyst deactivation. You will need to decide at what point you want to replace the HTS catalyst. Usually, this will be determined by the amount of CO slipping and your ability to handle it downstream. The ATE plot does allow early identification of major problems.

  See Appendix for a sample calculation of the HTS converter approach to equilibrium.

- *PSA recovery*

  For units with PSAs, it is important to track the hydrogen recovery in the PSA. Poor recovery may indicate problems with the valves as well as potential adsorbent issues.

  Using the material balance, you can determine the hydrogen recovery in several ways. The most straightforward approach is to determine the percentage of the incoming hydrogen that exits in the product hydrogen stream. Since the product hydrogen is essentially 100 % hydrogen, the recovery is just the product hydrogen flow rate divided by the PSA feed gas % hydrogen times feed gas rate, all times 100 %.

  This recovery should be around 85–87 %. If it is lower, the PSA is not performing and needs to be further investigated. If it is above about 92 %, there is probably a metering or analysis error.

  See the Appendix for a sample calculation of PSA recovery.

- *Reforming furnace tube wall temperature monitoring*

  One of the trickiest aspects of SMR furnace operation seems to be obtaining accurate tube wall temperatures. When you "shoot the tubes" with an infrared thermometer, there are a number of interferences:

  - You are looking through hot combustion gases that have some luminosity.
  - You are getting reflections from the very hot furnace refractory walls.
  - You may be seeing part of the furnace refractory in the background.
  - The emissivity of the tube walls may be different or the tube wall may have a deposit on it.

  To manage some of these interferences, IR thermometers for hydrogen plants look at a relatively narrow frequency of IR radiation that minimizes the gas interference. The measuring zone on an IR thermometer is usually a small spot focused on the tube. A laser sight may be used. Equations are used to correct the reading for background and reflected radiation. Still, the resulting tube wall temperature measurements are probably not accurate to more than +/− 50–100 °F. There are techniques available, such as the "gold cup measurement method," which directly measure tube wall temperature by contact. These can be used to verify other readings or to calibrate readings.

Some refiners routinely take infrared photos of their tubes to monitor issues and trends. This is a good approach for trending, but, from experience, these photos seem to indicate higher temperatures than other methods.

- *Reformer pressure drop*

  Pressure drop in the reformer tubes is one of the best and simplest methods to track catalyst coke buildup and catalyst crushing. The pressure drop needs to be normalized for rate.

  To normalize the pressure drop in a furnace, you can use Eq. 22. The flow factor is usually the volumetric flow of steam plus feed gas. You could refine the factor further, but the simple volumetric flows at STP seem to work fine. The exponent, n, is determined by trial and error to minimize scatter of the normalized dPs. Once set, the same value of n is used consistently for a given plant, and it is usually between 1 and 2:

$$\mathrm{dP_{norm}} = \mathrm{dP_{act}} \times (\mathrm{F_{norm}}/\mathrm{F_{act}})^{\mathrm{n}} \tag{22}$$

  where
  $\mathrm{dP_{norm}}$ = normalized pressure drop
  $\mathrm{dP_{act}}$ = measured pressure drop
  $\mathrm{F_{norm}}$ = flow factor at normalized condition
  $\mathrm{F_{act}}$ = flow factor at measured conditions
  n = scaling exponent, determined by best fit

  The normalized pressure drop is trended with time. When excessive coking incidents or shutdowns occur, you will see step increases in the normalized pressure drop. The maximum allowable pressure drop will normally be set by either (1) the ability to get feed gas into the plant or (2) the ability of the purification system to deliver product at the required pressure. Once the maximum dP is reached, the reformer catalyst has to be replaced.

  See the Appendix for a sample calculation of normalized reformer pressure drop.

- *LTS converter activity*

  Tracking of catalyst activity in a low-temperature shift converter is accomplished by tracking the position of the temperature rise front (as a percentage of the total bed depth) as it moves through the catalyst bed. The catalyst is poisoned slowly in service by both sulfur and chloride in a plug-flow manner. It is much more sensitive to these poisons than reforming or HTS catalysts.

  Replacement of the LTS catalyst should be planned when the deactivated catalyst reaches about 70–80 % of the bed depth. The position of the deactivated catalyst front can be plotted with time to project end of run.

Note that if there is a sulfur slip problem in the feed gas pretreatment system, the LTS catalyst will take a large hit and may need to be replaced immediately. Activity of this catalyst cannot be recovered in service.

- *Methanator activity*
  Similar to a LTS catalyst, methanator catalyst will deactivate in a plug-flow manner. The methanation reaction occurs quickly, producing a sharp temperature rise in the catalyst bed. The position of this sharp rise can be trended using the available temperature points at different elevations in the bed. The bed should be replaced when the rise is about 70–80 % of the way through the bed.
  Fortunately, methanator catalyst is fairly robust, so it does not deactivate quickly.

Catalyst Changeout

Fixed-Bed Reactors

Changeout of the fixed-bed catalysts and sorbents in a hydrogen plant is similar to changeout of fixed beds in any other process units. There are a few specific points highlighted below.

- Methanator and hydrotreating catalysts contain nickel and may generate nickel carbonyl if any CO is present.
  - In the methanator, CO may be left by inadequate purging during shutdown. Refer to comments in the generic shutdown procedure.
  - Hydrotreating catalyst that has coke on it can begin low-level combustion and generate CO. The CO may react with nickel on the catalyst to release nickel carbonyl.
  - In both cases, the reactors should be routinely monitored for CO whenever work is occurring in or around the reactors.
- PSA adsorbents are normally dense loaded using a method specified by the technology provider. The pressure drop through each vessel must be as close as possible to the same value, so care must be taken during the dense loading process.
- PSA adsorbents generate a large amount of heat if they are exposed to water, even atmospheric moisture. Do not let these materials get wet and do not unload or load adsorbents in rain.
- Shift catalysts, both HTS and LTS, will probably be self-heating if they contact air. Monitor the unloading atmosphere to keep them blanketed with inert gas.
- Zinc oxide, carbon adsorbents, and certain other solids used in a hydrogen plant reactor do not hold up well during handling. They will generate a lot of dust. Respiratory protection and dust management practices should be employed by anyone near these materials.
- Because of the high nickel content of methanator catalyst, respiratory protection must be used by anyone handling either fresh or used methanator catalyst.

- Get samples of all your spent materials for postmortem analysis. Your catalyst supplier will generally be willing to provide some analyses of the spent catalysts to identify poisoning mechanisms and other potential issues.

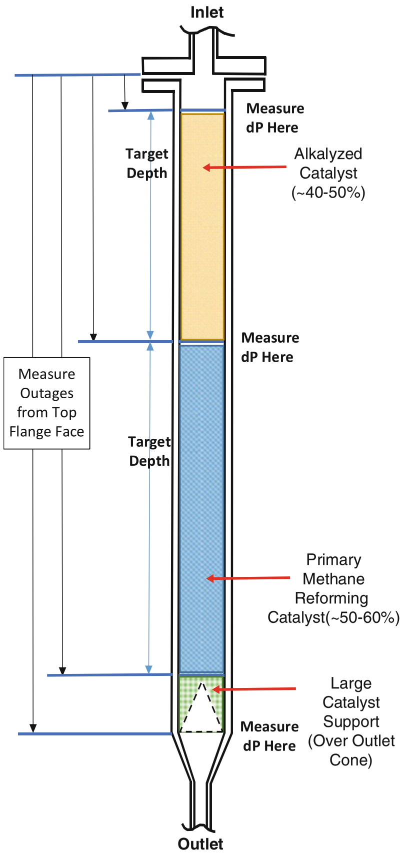
Work with your catalyst and adsorbent suppliers and the catalyst handling personnel to ensure the materials are loaded and unloaded safely and correctly. This will provide the best performance from the fixed-bed reactors and absorbers/adsorbers.

SMR Reformer Tubes

Unloading and loading of reformer tubes presents some special challenges. Each tube is a small, fixed-bed reactor. A few of the critical items are noted below.

- The reforming catalyst contains high levels of nickel, which is a known carcinogen. Anyone handling the catalyst or around catalyst dust should be wearing respiratory protection. Vacuum systems and dust suppression measures should be used.
- Catalyst is unloaded from the reformer furnace tubes by vacuuming. It may be necessary to break the catalyst up to get it out. Contractors experienced in hydrogen plant catalyst replacement are accustomed to the procedures.
- Reloading of catalyst is best accomplished with one of several available dense loading methods (Unidense, Spiraload, Catcade, etc.). Sock loading can be done, but is not as effective (i.e., you will probably have to vacuum out and reload more tubes to meet pressure-drop constraints).
- A typical catalyst tube loading and loading data sheet are shown in Table 8.
- Every tube in the reforming furnace must have as close to the same pressure drop as possible because flow to the tubes is distributed by pressure drop. The dPs of all tubes will be measured (1) empty, (2) after loading each layer of catalyst, and (3) after all the tubes are completely loaded. When measuring the dP on each layer, load all the tubes before taking the measurements and do not load tubes while you are taking measurements. Each dP should be within +/− 10 % of the average dP using a pressure-drop measurement apparatus like that shown in Fig. 17. An experienced hydrogen plant catalyst loading company will have their own pressure-drop apparatus. Dense loading techniques generally are able to achieve +/− 5 %.
- Sample the spent SMR catalyst from each catalyst layer at several points in the furnace. Composite these samples by layer for analysis. Your catalyst supplier will generally provide a postmortem analysis of the catalyst to identify poisoning mechanisms and enable him to advise you on future operations. This is especially important if you experience a rapid, unexpected poisoning event for which you could not identify a cause.
- When loading, make sure you get the right catalysts in the right order in the tubes. This is most easily accomplished by only loading one type of catalyst at a time throughout the entire furnace.

Table 8 Typical SMR furnace tube loading and data record sheet



Loading Date: ☐ **Unit/Equipment:** ☐ **Page** ______ **of** _______

Loading Measurements													
	Bottom Support			**Primary Reforming**			**Alkayzed (Top) Catalyst**			**Video**	**Pressure Drops**		
	Outage	**Volume**	**Weight**	**Outage**	**Volume**	**Weight**	**Outage**	**Volume**	**Weight**	**Check**	psi		
Tube No	ft-in	cft	lbs	ft-in	cft	lbs	ft-in	cft	lbs	Empty	Empty	Middle	Full

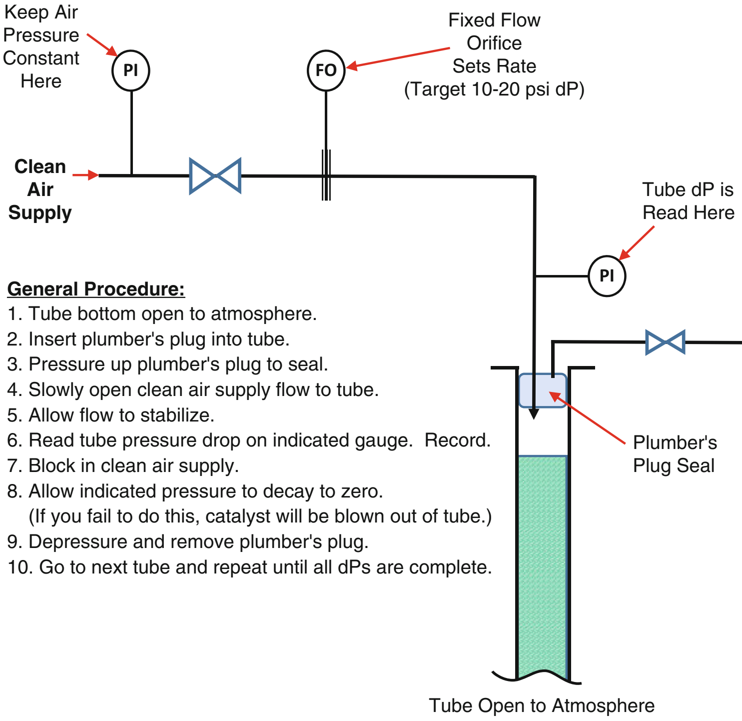


Fig. 17 Procedure for measuring SMR furnace tube pressure drops

- It is a good practice to select a few tubes in different sections of the furnace to load as “test tubes” before beginning to load the entire furnace. Usually, you pick about 1–3 % of the furnace tubes as test tubes. Load this subset of tubes just like you load the rest of the furnace: (1) take empty dPs, (2) load each layer and then measure dPs, and (3) take final dPs after loading. Track the weight of catalyst in each layer of the test “tubes” (and how many buckets or socks are required for each layer). The resulting data will act as a check on loading the balance of the furnace.
- After a tube is loaded, cover the tube opening to ensure nothing gets accidently dropped into the tube before closure.

Loading the SMR furnace sounds more difficult than it is. An experienced hydrogen plant loading contractor will be able to perform the work adequately.

Troubleshooting

As alluded to in the foregoing discussion, there are several things that can result in problems when operating a hydrogen plant. Table 9 provides a matrix of the most common symptoms and related problems in the SMR process, along with potential

Table 9 Common SMR process problems troubleshooting chart

Type of symptom	Observation	Possible problem	Possible remedies
Uneven SMR tube temperatures	Discolored lower half of tubes	Catalyst ≥ 5 years old	
		Settling	Plan catalyst reload
		Crushing	Plan catalyst reload
		Catalyst 2–5 years old	
		Settling	Track, potential reload
		Crushing due to shutdowns	Plan catalyst reload
		Catalyst ≤ 2 years old	
		Poisoning	Steam catalyst, potential reload if not recovered
		Coking	Immediately steam catalyst, potential reload
		Bad load	Reload catalyst if too severe
		Unstable operation	Check feed analysis, instruments, stabilize process
	Discolored upper half of tubes	Whole tube hot	
		Plugged tube	Pinch or cap tube before failure, reload if widespread hot tubes
		Maldistribution	Check steam rate, increase steam/carbon
		Boiler carryover	Check boiler chemistry, level instruments
		Very top of tube hot	
		Crushing (empty tube zone)	Plan catalyst reload if widespread
		Hot middle of tube	
		Flame impingement	Adjust burners and draft
		Wrong catalyst loaded	Reload catalyst if not tolerable
		Sulfur poisoning	Check ZnO slip, potential upstream upsets
		Giraffe-necking (spotty tubes)	
		Isolated poisoning	Look for poisoning source, increase steam/carbon, potential to steam catalyst
		Low steam/carbon	Increase/correct steam/carbon, check feed, check flow
		Random hot spots, stripes	
		Voids in catalyst load	May be able to vibrate tube, otherwise reload is widespread, may cap/pinch individual tubes

(*continued*)

Table 9 (continued)

Type of symptom	Observation	Possible problem	Possible remedies
Increased SMR pressure drop	Gradual increase in dP	Tube color even	
		Slow sulfur or other poisoning	Check ZnO outlet H_2S, check upstream sources
		Tube color uneven	
		Feed too heavy	Check feed analysis, increase steam/carbon
		Boiler carryover	Check boiler chemistry, level instruments
		Low steam/carbon	Check feed analysis, increase steam/carbon
	Rapid increase in dP	After upset	
		Bad sulfur or other poisoning	Steam catalyst, potential reload if not recovered
		Catalyst damage	Probable reload, unknown problem
		Heavy feed during upset	Immediately steam catalyst, run high S/C for extended period,
		Compaction	Reload catalyst
		No upset	
		Bad dP instrument	Check instrument
		Bad metering	Check meters
		Low steam/carbon	Check feed analysis, increase steam/carbon
		Heavier feed than known	Check feed analysis, increase steam/carbon
High methanator temperature	High rise	High Inlet CO2	
		CO2 removal system failure	Correct CO_2 removal system problem, bypass methanator or shutdown to fix
		Low reformer outlet temperature	Check feed, S/C, adjust SMR temperature
		Poor shift converter operation	Check feed, S/C, adjust HTS/LTS temperatures
		Low steam/carbon ratio	Check feed analysis, increase steam/carbon
		High feed carbon content	Check feed analysis, increase steam/carbon
		Sulfur poisoning of reformer or shift	Steam reformer catalyst, replace shift catalyst
PSA system problems	PSA system problems are beyond the scope of this chart. Work with your PSA vendor to troubleshoot PSA problems		

remedies. This table is by no means all-inclusive, but can be used as a starting point for troubleshooting.

SMR Process Flow Sheet Variations

The foregoing section described the most common, and simplest, process flow sheet for carrying out steam-methane reforming with a couple of minor variations in the product hydrogen purification system. There are other process variations in commercial operation. These are less common, but may be encountered or considered for a specific plant. Some variations may be helpful in debottlenecking or production rate increases. The three most common variations are briefly described below.

Pre-reforming

A pre-reformer is a fixed-bed reactor installed upstream of the main SMR reforming furnace. The pre-reformer performs the cracking part of the reactions (Eq. 8) and does some minor reforming. At the pre-reformer outlet, the feedstock has been converted to essentially all methane for the SMR furnace. This enables the furnace tube volume to be devoted to the SMR reaction.

A pre-reformer also acts as a guard bed for the main reforming catalyst; it takes any impacts from poisoning and protects the furnace catalyst. Pre-reformers can often be taken off-line and changed out, while the main process continues, albeit with an easier feed during the changeout. Pre-reformer catalyst is permanently deactivated by sulfur, chlorine, and other poisons. The pre-reformer helps open up the possible feedstocks for a hydrogen plant and levels out feedstock variations.

Heat is supplied to the pre-reformer by replacing one of the convection steam generation coils with a pre-reformer preheat coil. This means less steam generation from the plant, but improves hydrogen production efficiency.

Some process designers like to always include a pre-reformer in their flow sheet. Others offer pre-reforming as an option or for increasing rate. Addition of a pre-reformer to an existing hydrogen plant can enable it to make about 10–20 % more hydrogen and use a lower steam/carbon ratio. The shift cooling and product purification systems still need to have enough capacity to handle the incremental raw hydrogen produced, so some additional debottlenecking may be required.

This technology is offered by Haldor Topsoe, ThyssenKrupp Uhde (Uhde), CB&I/HoweBaker, Technip, Kellogg Brown & Root (KBR), and others.

Exchanger Reforming/Post-Reforming

An exchanger reformer uses waste heat from the SMR furnace to reform additional feed and make more hydrogen. The post-reformer is usually an exchanger with catalyst-packed tubes. Heat is supplied by waste heat in the SMR furnace effluent or convection section at the expense of steam generation.

This type of reformer can also be used in place of a primary reformer with tight heat integration.

Additional feed gas and steam may be introduced ahead of the post-reformer to provide incremental production. About 35–40 % additional hydrogen can be made by post-reforming. As with the pre-reformer, the shift cooling and product purification systems may have to be debottlenecked to take advantage of post-reforming.

This technology is offered by Haldor Topsoe, KBR, Uhde, and others.

Autothermal Reforming

Autothermal reforming (ATR) can be added in parallel to a standard SMR furnace to significantly increase hydrogen production or it can be used in place of the conventional SMR furnace. In autothermal reforming, feed gas is partially burned using pure oxygen. Steam may be injected along with the feed. The CO_2 produced is recycled to moderate the combustion temperatures. The heat from burning is used to drive the reforming reactions in the balance of the feed. You make CO directly in the combustion process and then shift it to hydrogen. No catalyst is required; however, some systems do incorporate reforming catalyst. The ATR effluent joins the main hydrogen plant gases going to the HTS converter and flows through the rest of the plant.

An ATR can also be used in series as a post-reformer. You find ATRs more commonly in ammonia or methanol manufacture than refinery hydrogen production, since ATRs can easily make the necessary synthesis gas.

This approach to reforming is related to gasification, although gasification usually refers to making hydrogen from residuum/pitch or solids by partial oxidation followed by a sour shift reactor and product cleanup.

As with the other variations, if an ATR is added, the cooling and purification system capacities may need to be debottlenecked. This type of reformer also requires availability of pure oxygen, which usually means proximity to an air separation plant.

This technology is offered by several suppliers, including Haldor Topsoe, KBR, Süd Chemie, Lurgi, Imperial Chemical Industries, and Johnson Matthey.

Partial Oxidation

Introduction

Partial oxidation (POX) has been used commercially to produce hydrogen from very heavy liquid feedstocks (resid, asphalt, tar) and solids (coal, petroleum coke). Essentially, this is a gasification process. More commonly, the technology is used to generate synthesis gas for other products, however. Texaco had several POX hydrogen plants at one time, but these have been largely replaced by the more reliable and easier to operate SMR furnace plants. Still you will occasionally find POX plants associated with refineries.

POX is essentially the same as autothermal reforming discussed above. The distinction drawn here is between the types of feedstocks. In autothermal

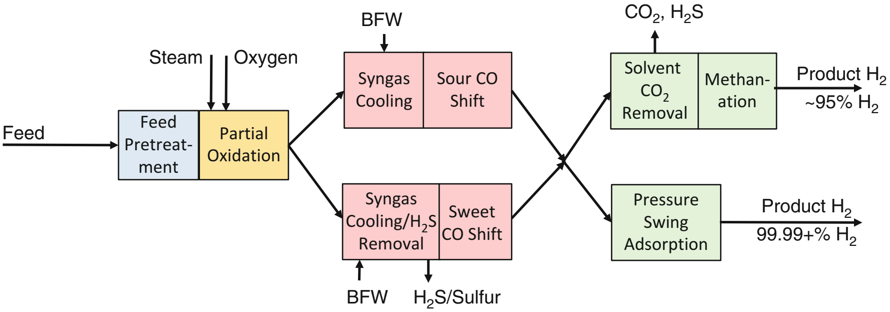


Fig. 18 Block flow diagram of partial oxidation hydrogen plant options

reforming, we have focused on gases through naphtha. There are several of that type of plant in operation. The autothermal reformer feedstock has generally been cleaned to SMR reformer standards, so sulfur in minimal.

For a POX unit, the feedstock generally still contains sulfur, ash, and other contaminants. This has equipment, catalyst, and reliability implications.

Process: Step by Step

A POX hydrogen plant process can be broken into three primary steps, as illustrated in Fig. 18:

- Gasification of the feedstock by partial oxidation
- Shift reaction to increase hydrogen generation
- Product purification and recovery

Along with these sections, there is a major boiler feedwater and steam generation system, much like for an SMR plant.

We will consider each of these systems in turn.

Gasification/Partial Oxidation

The POX process starts with a gasifier or combustor. In the gasifier, the feedstock that has been slurried and/or heated is introduced into a combustor. In the combustor, the feed is burned with pure oxygen, in an oxygen-deficient atmosphere, according to Eqs. 23 through 27. Steam is injected with the feed for reaction and atomization:

$$C_xH_y(l,s) + {}^{x}/_{2}O_2(g) \rightarrow xCO(g) + {}^{y}/_{2}H_2(g) + \text{Heat} \tag{23}$$

$$CO(g) + {}^{1}/_{2}O_2(g) \longleftrightarrow CO_2(g) + \text{Heat} \tag{24}$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) + \text{Heat} \tag{25}$$

$$CH_4(g) + H_2O + \text{Heat} \longleftrightarrow CO(g) + 3H_2(g) \tag{26}$$

$$CO(g) + H_2O(g) \longleftrightarrow CO_2(g) + H_2(g) \tag{27}$$

Because the sulfur and other contaminants have not been removed from the feed, the sulfur will be converted to H_2S and some SOx. Nitrogen compounds will similarly be converted to NH_3 and oxides.

The products equilibrate at the combustor outlet conditions. The products will include CO, CO_2, H_2O, H_2, H_2S, SO_2, NO_x, inerts, etc. These will exit the combustor as gases. Some of the ash, soot, and other solids in the feed will leave the combustor with the gases as fines. The remaining ash, solids, and soot will deposit in the combustor. Some combustors are followed by water quench on the outlet, which collects soot and ash for removal.

Shift Conversion

The products in the combustor effluent are similar to those from an SMR. The gases differ from SMR effluents primarily because they are sour (H_2S present), contain entrained solids, and have different ratios of the shift reactants.

Further, shift conversion is necessary to make a practical amount of hydrogen. The shift reaction itself proceeds via Eq. 28 below:

$$CO(g) + H_2O(g) \longleftrightarrow CO_2(g) + H_2(g) \tag{28}$$

There are two general approaches to shift conversion in POX plants, as illustrated in Fig. 18.

- The H_2S can be removed, along with soot and other solids and the resulting gases sent to conventional shift converters – a process tolerant of impurities is used for this, such as Rectisol (cold methanol).
- The soot and solids can be removed and the product sent to a sour shift converter before final cooling. The availability of sour shift catalysts is fairly recent.

Product Purification and Recovery

The raw hydrogen is finally purified. If the raw hydrogen is sour, the purification system will need to remove both H_2S and CO_2. This would entail a system like a CO_2 Rectisol (cold methanol), which may be followed by PSA. If the sour components have been removed ahead of the shift reactor (or after shifting), then the purification system can be either wet chemical/solvent or PSA.

Equipment Design and Metallurgy

The key to the POX process is the combustor/gasifier design and the quench immediately downstream.

Several combustor system designs have been used. There are many combustor variations offered by Linde, Shell, Lurgi, and others. Because this is a very severe service, more than one combustor is normally installed to permit servicing of the equipment.

These systems will not be discussed in further detail here. The POX system suppliers are the best references.

Concluding Remarks on POX

POX hydrogen plants are not common, but this is a viable option to make hydrogen and it has been used on a commercial scale. The costs are high compared to making hydrogen in an SMR. Still, POX units can feed solids and residual materials that are not feasible to run in an SMR. There are times POX may be favored.

We will not go into further discussion of POX at this time. Several vendors offer this technology, including Linde, Lurgi, and Shell.

Electrolytic Hydrogen

Introduction

Hydrogen can be made by electrolysis of water. There are packaged units available for this service. These are generally limited in size, so they are not commonly used in refineries. They are being considered for renewable energy applications.

The following discussion provides only a broad brush background for this type of unit. Contact the suppliers of these units for additional information.

Process

Electrolytic production of hydrogen occurs in an electrolytic cell. The overall process is simple, as described in Eq. 29:

$$H_2O(l) + \text{power} \rightarrow H_2(g) + {}^1/{}_2O_2(g) \tag{29}$$

The reaction requires an electrolyte. Normally, potassium hydroxide is used, as noted in the flow diagram below.

There are three types of cells available, as summarized in Table 10.

The general flow sheet for an electrolysis hydrogen plant is shown in Fig. 19.

Concluding Remarks on Electrolytic Hydrogen

No further details about electrolytic hydrogen production are offered here, because of the limited opportunities for refinery application at this time. Future renewable

Table 10 Types of electrolytic cells for making hydrogen

Type of technology	Key elements
Solid oxide electrolysis cell (SOEC)	Operate at high temperatures (~800 °C); outside heat sources (waste heat) can reduce electrical requirement, long start-up times, and material differential expansion issues
Polymer electrolyte membrane cell (PEM)	Operate at low temperatures (<100 °C), simple, commercially available, variable voltage input capabilities, no KOH required, high pressures
Alkaline electrolysis cell (AEM)	Operate at intermediate temperatures (~200 °C), high electrolyte (20–30 % KOH or K_2CO_3) concentrations

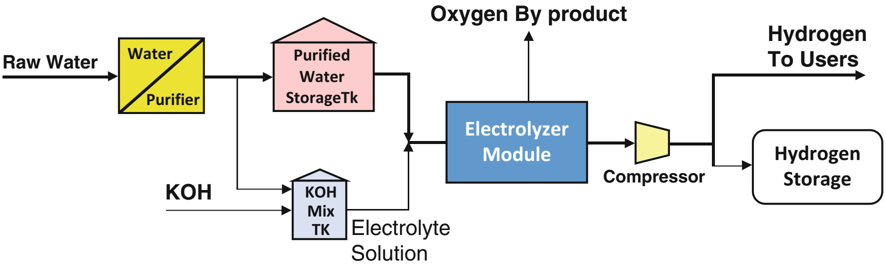


Fig. 19 Simplified typical electrolysis flow sheet for low-pressure electrolyzer (Source: Ivy 2004)

developments may change this picture, but widespread use of electrolytic hydrogen in refineries is not likely in the near future.

Manufacturers of commercially available units include:

- Avalence LLC – high-pressure and ultrahigh-pressure hydrogen, small units; brand name: “Hydrofiller,” focus on hydrogen fueling (www.avalence.com)
- Proton Onsite – fuel hydrogen and renewable focus, backup power systems integrated with fuel cells; brand name: “HOGEN RE” (www.protononsite.com)
- Teledyne Energy Systems – PEM units to 150 Nm^3/h (134,000 scfd); brand name: “TITAN” (www.teledynees.com)
- NEL Hydrogen AS (Norsk Hydro) – atmospheric pressure units, 50–485 NM3/h (45,000–434,000 scfd); brand name: NEL-A (www.NEL-hydrogen.com)
- Hydrogenics – alkaline and PEM cells; brand name: “HySTAT” (www.hydrogenics.com)

Olefin Cracking By-Product Recovery

The furnaces that make olefins from refinery feedstocks like ethane, propane, and naphthas make hydrogen as a by-product according to Eq. 30, using ethane cracking as an example:

$$C_2H_6(g) + \text{Heat} \rightarrow C_2H_4(g) + H_2(g) \tag{30}$$

The hydrogen by-product from this reaction can be recovered as part of ethylene recovery and separation. Recovery of the hydrogen can be accomplished cryogenically or using membranes.

This is a source of hydrogen in some refineries that are tied to chemical plants. The product hydrogen will contain some contaminants (like CO, N_2, CH_4), but will generally be about 90–98 % pure.

Refinery Gas Recovery

Introduction

A lot of hydrogen made in a refinery finds its way into the fuel gas and other systems. Eventually, much of this hydrogen gets into fuel gas, if it is not recovered. Burning the hydrogen can be wasteful. Ideally, you want to prevent the hydrogen from getting into the fuel gas in the first place. That discussion will be covered under hydrogen management.

Many refiners chose to recover hydrogen from the various refinery off-gases for reuse. Membrane and PSA units are normally used for this service. Cryogenic recovery is also feasible, but the increased complexity in operating cryogenic units makes them less desirable, unless recovery of light hydrocarbons (ethane, ethylene) is also desired.

Process Discussion

Membrane Recovery

Membrane technology can be applied to several refinery gases:

- Catalytic reformer off-gas
- Hydrotreater off-gas and purge
- Hydrocracker off-gas and purge
- Fuel gas
- FCC off-gases
- PSA off-gases

Table 11 indicates how membranes can be used to recover the hydrogen from a few of these gases and their effectiveness.

Figure 20 illustrates the key process steps in using membranes for hydrogen recovery in a possible application. The pressures and purities are for illustration only.

Note that the feed gas to a membrane must be clean (no solids, low sulfur, etc.), free of liquids (both aqueous and hydrocarbon), and at elevated pressure

Table 11 Some typical refinery hydrogen recovery membrane applications (Source: Fleming 2006)

	Typical source purity	Membrane product purity	Hydrogen recovery
Refinery gas source	Mole % H_2	Mole % H_2	%
Catalytic naphtha reformer	70–80	90–97	75–95+
FCC off-gas	15–20	80–90	70–80
Hydroprocessing purges and off-gas	60–80	85–95	80–95
PSA off-gas	50–60	80–90	65–85

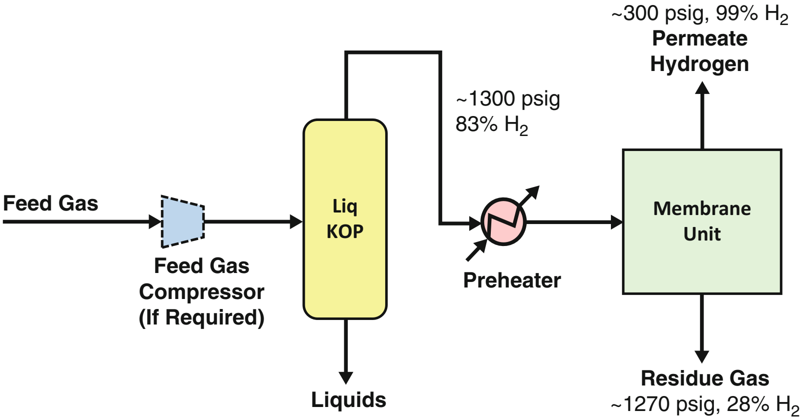


Fig. 20 An example of a hydrogen recovery membrane application (Reference: Fleming 2006)

(prefer >1,000 psig, but can be used at less than 1,000 psig). The final hydrogen from a membrane unit will be at low pressure and the impurities are rejected at high pressure. The product hydrogen must be recompressed for use.

Additional discussion of membranes follows later in this chapter.

Pressure Swing Adsorption Recovery

PSAs can be used to recover hydrogen from refinery gases in essentially the same services as membranes. PSA recovery will be 60–90 % of the contained hydrogen and product purity can be nearly 100 %.

Figure 21 illustrates how a PSA can be integrated into a recovery scheme.

The feed gas for a PSA unit must be of similar quality to that for a membrane unit – clean, no liquids, and high pressure. The pressures used for PSAs can be somewhat lower than for a membrane (~300 psig is alright), with some loss of recovery or increase in size. The product hydrogen from a PSA will be available at essentially feed pressure, but the purge gases containing the impurities are at low pressure.

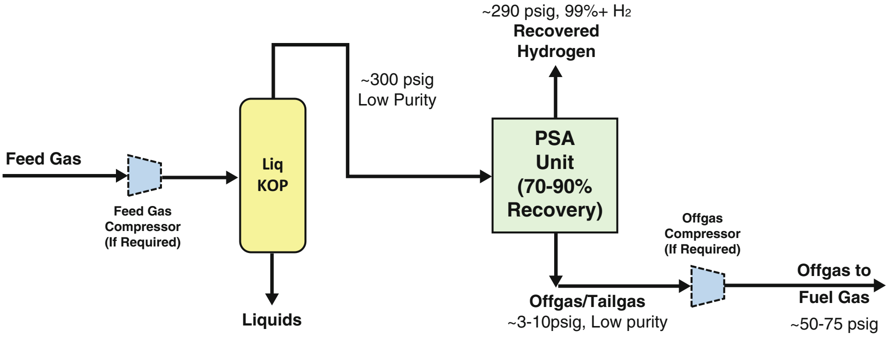


Fig. 21 An example of a hydrogen recovery PSA application

Additional discussion of PSAs follows later in this chapter.

Other Options

Over the Fence

A refiner does not necessarily have to operate his own hydrogen plant, or even hydrogen recovery units. Several industrial gas supply companies will build and operate facilities to make or recover hydrogen for a refinery. This service can be provided onsite or offsite. Here, this arrangement is referred to as “over-the-fence” supply. The supplier will charge for the hydrogen. The charge includes cost of operation, cost of the facilities he needs to build (amortized over time), and a profit margin. There is usually a take-or-pay arrangement for a minimum volume of hydrogen. Handling of emissions impacts can be negotiated.

This type of arrangement is especially advantageous where several facilities in an area need hydrogen. An industrial gas supplier can build a pipeline connecting the facilities, along with one or more hydrogen production or recovery units to supply the pipeline. The supplier may take refinery off-gases to make the hydrogen and return steam as well as hydrogen. The potential for multiple sources of hydrogen producing into the pipeline improves the reliability of hydrogen supply.

Involvement over the fence can also be as simple as the gas supplier installing a membrane unit inside the refinery to recover hydrogen from off-gas from a catalytic reformer, for instance. The supplier operates and maintains the membrane unit for a fee.

Industrial gas companies often are better (i.e., more reliable) at operating hydrogen plants and recovery facilities than a refiner, since this is their main business. The resulting reliable hydrogen supply means fewer production problems in the refinery.

This type of service is well established by companies like Air Products, Air Liquide, Praxair, and others.

Tube Trailers

Sometimes, you need only a small amount of hydrogen of high purity. This is common for semi-regeneration naphtha reformer start-ups. In these cases, hydrogen is often supplied at high pressures in tube trailers. These are available from many industrial gas suppliers. The high pressure eliminates the need for compression by the user.

A typical, large tube trailer from Air Products, for example, holds about 126,000 scf (3,570 Nm^3) of hydrogen at 2,640 psig (83 barg).

Pressure Swing Adsorption

Introduction

Throughout the discussion of hydrogen production, we have referred to pressure swing adsorption (PSA) units. In this section, we will go a little deeper into the design and operation of these units. The discussion will be limited to nonproprietary information and available public literature. There is a great deal of proprietary knowledge needed to design an effective and reliable PSA unit. Detailed design is best accomplished by one of the PSA suppliers – such as UOP, Air Liquide, Linde, Air Products, or CB&I. Industrial gas suppliers will also install and operate recovery PSA systems at a refinery in an over-the-fence arrangement.

Also, note that hydrogen PSAs are not the same as PSAs for other purposes (like instrument air drying or air separation). They require specific knowledge of the hydrogen applications.

Process: Step by Step

A simplified process flow diagram for the business end of a generic 5-bed PSA is illustrated in Fig. 22. To mimic a continuous process, a PSA unit consists of a series of identical vessels filled with adsorbents. There are typically 4–12 beds.

The vessels are connected by several headers that carry the feed gas, product hydrogen, purge and equalization gases, and off-gas or tail gas. The final off-gas passes through a large surge drum that moderates pressure and composition surges for the off-gas and minimizes the pressure swing impacts on the system receiving the off-gas – normally an SMR furnace or fuel gas header/compressor.

Adsorbents in the vessels are selected based on the impurities in the feed gas. For instance, in a typical SMR hydrogen plant, the bottom portion of the PSA bed will contain activated carbon and the upper portion will contain molecular sieve. The activated carbon can easily adsorb methane, CO_2, water vapor, some CO, and other trace compounds. The mole sieve adsorbs nitrogen and the balance of the CO.

It is critical that the feed gas be as dry as possible. If the gas has a high moisture content, water adsorption may reach the molecular sieve where it will permanently attach, reducing adsorption capacity. SMR hydrogen plant raw hydrogen feed is limited to about 130 °F to avoid this problem.

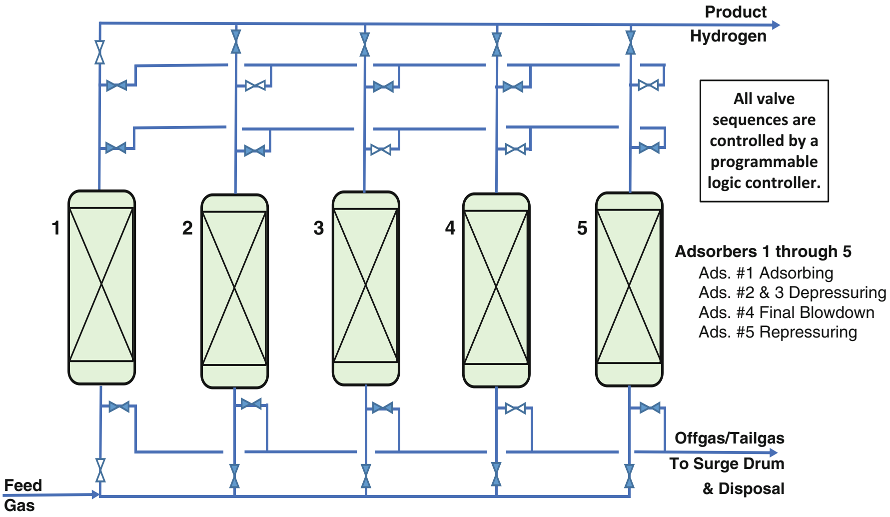
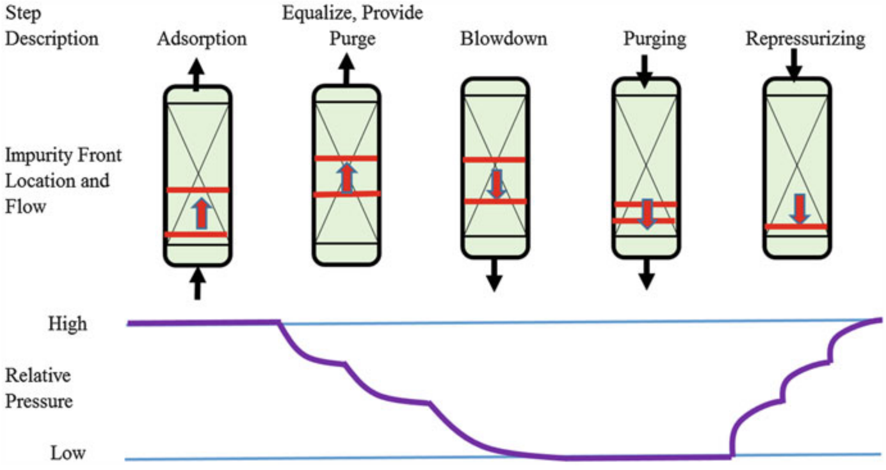


Fig. 22 Simplified process flow diagram of a 5-bed PSA unit

Table 12 Example PSA bed cycle steps



Adsorption releases heat. The temperature of a PSA bed rises slightly (5–20 °F) during the adsorption steps and drops back down as the bed is depressured. If any liquids reach the bed, the adsorption heat rise will be very high, so liquids are strictly excluded.

The steps in a typical PSA cycle applied to one bed are shown in Table 12. There are several sub-steps in the actual control software, but the cycle will generally follow the pattern in the table. The table also illustrates the pressure steps a single adsorption bed progresses through during a cycle.

Let us start with a single target adsorber at full pressure being brought on line and follow the steps:

- *Adsorption* – Raw feed is brought into the pressured vessel, normally in upflow. Impurities in the feed adhere to the adsorbents from the bottom up, with hydrogen adhering the least. Hence, hydrogen passes mostly through the bed and onto production at nearly full pressure. The bed stays on line for a set time, determined by the amount of impurities in the feed and the flow rate. This adsorption time can be fine-tuned based on the product hydrogen purity. Nitrogen and CO will be the first impurities to begin slipping out of the bed – normally setting the maximum adsorption time. During this time, another adsorber bed is being brought up to pressure using a little of the product hydrogen so it can be swung on line when our current bed is taken off-line, without any pressure bumps.
- *First equalization* – At the end of the adsorption time, the feed and product valves are closed on the vessel of interest, and the other vessel that was being pressured up with product hydrogen goes on line. Then, the first equalization valve opens on our target adsorber. This is the first of several depressurization steps. The initially purged gases are fairly pure hydrogen, so flow in this first step is upward and the hydrogen leaving is used to pressure up another adsorber bed that will be brought on line next. There is no gas coming into the vessel. This is called an equalization because at the end of the step, the pressure of our target vessel and the pressure of the vessel it is repressuring are both about equal.
- *Additional equalizations and providing purges* – There are typically two more equalization steps with other PSA vessels. In these steps, gas from our target vessel is dropped in pressure. Flow out of the vessel is still upward. There is no incoming flow. Flow from the current vessel, which is reasonably pure, is used to push the impurities out of other, lower-pressure vessels. During these steps, the actual impurities front in the target bed is continuing to rise.
- *Blowdown* – Now, we begin rejecting the impurities from the bottom of our target vessel using downward flow. The vessel pressure is dropped to the low tail-gas or off-gas drum pressure. This is where the impurities are largely desorbed. Some hydrogen is unfortunately lost in the process. At this point, there is no incoming gas, just depressurization out the bottom of the vessel.
- *Purge* – Now, the vessel is purged to blowdown using gas from one of the other PSA vessels in the "provide purge" step. This is downflow at low pressure. The impurities are reduced to their minimum in the bed.
- *Equalization steps* – The vessel is now repressured using equalization step gases from other vessels that are being depressured. As the pressure is increased, the purity of the repressuring gases increases. Flow is downward to avoid fluffing the bed and there is no outgoing flow at this time.
- *Repressurization* – There is a final repressurization step using product hydrogen in downflow to bring the bed pressure up to the product header pressure and avoid a pressure bump when the vessel comes on line. There is no outflow.

- *Adsorption* – The vessel is brought back on line in upflow to start the next cycle by opening the feed and product valves.

  There are pressure and time criteria for completion of each step before the sequence will advance. If these are failed, the control system can adjust or, if the failure is serious enough, it can shut down the PSA and block in the vessels.

Equipment Design and Metallurgy

Valves

PSA systems depend heavily on control valves to accomplish their function. Each PSA vessel has four to six valves associated with it, depending on the number of steps in the cycle. Each PSA vessel valve will go through around 35,000 cycles per year on average. In addition, there are other valves that control surge pressures and compositions of the off-gas or tail gas.

All of these valves must be routinely and regularly checked and serviced to ensure reliability of the PSA system. Valve failure is the number one problem in low PSA reliability.

PSA designers have specific valves they recommend for their units based on extensive experience. It is wise to take advantage of their expertise. These are not normal control valves. The valves have specific features tailored to the PSA service.

PSA Adsorbers and Cyclic Service

Just as each PSA vessel valve will go through about 35,000 cycles per year, each vessel is pressurized and depressurized about 35,000 times per year. This cyclic stress on a vessel can exacerbate small defects in construction of the vessel, resulting in cracking of vessel.

This cyclic loading has to be recognized in specifying and monitoring the vessels. Normally, there are periodic inspections for cracks growing from the cyclic stresses. Inspection methods continue to develop for this service.

Off-Gas/Tail-Gas Surge Drum

The off-gas or tail-gas surge drum is a large vessel designed to moderate the pressure and composition changes that come from the PSA vessel cycles. This is required to provide a relatively stable fuel supply to the SMR furnace or other fuel gas users.

At one time, there were two surge drums employed – one to moderate the pressure cycles and a second drum to even out the compositions. This two-drum system resulted in very stable off-gas flow and composition.

Recent practice for PSAs uses a single surge drum combined with improved control valve logic and tuning to provide stable off-gas flow. This has not been quite as effective as the two-drum system, but works well enough and significantly reduces capital cost and footprint.

The surge drum is mostly just an empty space, but the inlet lines from the PSA usually terminate inside the surge drum with elbows or distribution headers. These improve mixing and reduce composition variations. Pressure surge may be managed with control valves (in and/or out) of the surge drum.

Control System

The PSA cycles are controlled by a programmable logic controller (PLC). In some cases, this logic has been incorporated into the plant's distributed control system (DCS), but more often the logic is housed in a dedicated PLC, with interfaces to the DCS.

The control system will normally match the capacity of the PSA to the plant rate and handle rate changes. The system can manage some types of valve failures by switching between operation modes (number of beds on line), with minimal upset. Many systems have built-in diagnostics to help analyze problems. The systems can also be combined with online gas analyzers to optimize recoveries.

Operations

Start-Up

From a routine standpoint, the start-up of a PSA is relatively simple:

- The PSA system is air-freed.
- Feed gas is lined up to the unit. Off-gas is lined up to the surge drum and, usually, flare. The vessel block valves are all opened, with the control valves still closed.
- The adsorber pressures are set to the required starting pressure profile for a desired start-up step using available gases. This may also be automatic.
- The PLC is started at the desired step and the PSA valves begin cycling. All the incoming feed gas goes out through the surge drum to flare initially for a few cycles to establish the correct impurity profiles.
- Once the system is operating reliably and smoothly, hydrogen production to users can begin.
- Once the system is stable, the off-gas can be routed to either the SMR or fuel gas.

Shutdown

Shutdown of a PSA unit is accomplished by stopping the PSA cycle. The control logic in the PLC will automatically block in the vessels and freeze the cycle and pressures in the current step. Incoming feed gas will go to flare or its alternative destination. The off-gas/tail gas will stop immediately.

Adjustments will need to be made to downstream, and possibly upstream, units that feed the PSA or use the off-gas.

Routine Operation

Once in service, the PLC controlling the PSA will operate the unit and continuously monitor for problems. The operator may need to adjust the adsorption cycle time periodically to fine-tune the cycle or for major rate changes. Generally, the PSA system will take care of itself.

Table 13 Key routine monitoring parameters for a PSA unit

Parameter	Basis	Frequency	Criteria
Hydrogen recovery	$\%\ \text{Recovery} = (\text{mols or scf } H_2 \text{ in product})/(\text{mols or scf } H_2 \text{in feed gas}) \times 100\%$	Weekly	Trend and watch for loss of recovery with time
Feed and off-gas pressures	Review pressure trends	Daily	Ensure pressures stay within allowable ranges
Feed gas temperature	Review data	Daily	Ensure temperature stays within allowable range
Feed gas composition	Review data	Weekly	Watch for excessive ethane or heavier components
Adsorption time	Review adsorption time for each bed in seconds	Weekly	Trend and watch for increasing requirement at the same feed rate
Product purity	ppm CO in product hydrogen – this will need to be by detector tube or other sensitive means, GC will not be adequate	Weekly	Trend and watch for increases in CO with time. Do not run for extended periods with low purity
Valve packing leakage	Physical inspection	Weekly	Should not be able to feel gases coming from any packings
Cycle diagnostics	Review PLC exception logs or pressure graphs for each vessel	Weekly	Look for anomalies in the cycles like extended repressurization times or changes to patterns

Once a unit is operating, it is worthwhile to have your PSA vendor periodically review the operation and fine-tune it (say, annually). They can help spot potential issues that may not be obvious.

Monitoring

Table 13 provides a summary of the important parameters and equipment to monitor on a PSA during operation. Early detection of problems provides an opportunity to make a controlled switch to an alternate operation without the PSA control system making a radical move on its own and causing an upset.

Troubleshooting PSAs

Table 14 provides a summary of the more common PSA problems and hints at possible causes. This is a starting point. The control software error logs and information will often provide a good starting point for troubleshooting.

Table 14 Some common PSA problem symptoms and possible causes

Symptom	Possible causes/remedies
Repressurization	PLC or other instrument problem
Too long or slow	PLC or other instrument problem
	Repressurization valve/instrumentation problem
	Low product header pressure (look at users)
Too short or fast	PLC or other instrument problem
	Associated control valves or instrument problems
Blowdown	
Too long or slow	PLC or other instrument problem
	Blowdown valve/instrumentation problem
	High blowdown header backpressure (look downstream)
	Valves leaking into header from other vessels
Too short or fast	PLC or other instrument problem
	Blowdown valve/instrumentation problem
Purge	
Too long, slow, incomplete	Associated control valves or instrument problems
	Valve leakage from another vessel
	Low product purity
Too short or fast	PLC or other instrument problem
	Instruments/valves on vessel providing purge gas
Pressure/flow bumps/variations	
Feed/product headers	See repressurization symptoms
Off-gas/tail-gas header	See blowdown or purge symptoms
	Problems with off-gas or purge control system
	Valve leaks or instrument problems in associated valves
	Controls/instrumentation problem around off-gas surge drum
	Tail-gas compressor problem (if applicable)
Feed or product flow fluctuations	See repressurization symptoms
	Feed flow varying (check upstream)
	See purge and blowdown symptoms
Low product purity	PLC or other instrument problem
	Adsorption time set too long
	Adsorbent damage or loss (from another problem)
	See repressurization, blowdown, and purge symptoms
	Wet or hot feed gas – possible carryover
	High feed flow rate
	High off-gas/tail-gas pressure (look for downstream problem)
	Bad analytical data

(*continued*)

Table 14 (continued)

General PSA problems causing shutdown or alarm	Low-low product pressure (causes high feed flow capable of lifting bed)
	High/low feed temperature (instrument or upstream cooling problem)
	Low instrument air pressure (instrument air supply problem)
	Long cycle times (see repressurization, blowdown, and purge symptoms)
	PLC or other instrument problem
Dust in outlet header or other PSA headers on inspection	Excessive feed flow rate causing adsorbent milling/carryover
	PLC cycle sequence or other instrument problem

Detailed discussion on troubleshooting more complex issues is beyond the scope of this book. PSA unit vendors are usually more than happy to help in troubleshooting. As noted above, a periodic (annual) review of the unit operation by the PSA vendor is advisable to identify problems that are not obvious.

Membranes

Advances in technology have made membranes a viable hydrogen recovery option for several types of systems. The discussion of the applications for membranes and the typical process flow in hydrogen recovery service is in the section "Refinery Gas Recovery." Membrane capacities over 60 MMscfd of feed are possible because of the modular nature of the process. These units are, in fact, usually supplied as prefabricated modules.

Reviewing the flow sheet in Fig. 20 above, compressed, high-pressure raw gas (preferably >1,000 psig) passes through a knockout drum or coalescer to eliminate any possible liquids in the feed. The clean raw gas is then fed to a bank of several membranes housed in tubes, all operating in parallel. Hydrogen diffuses through the membranes to the low-pressure side and exits (permeate). The impurities remain on the high-pressure side and exit (residue).

Product hydrogen permeate from a membrane will range from 80 % to 98 % purity, with 65–95 % recovery. Feed hydrogen for a membrane unit can range from 15 % to 80 % hydrogen purity, although purity greater than 70 % is best.

The most common membranes for hydrogen are hollow fibers or wound sheets of thin polyaramide or polyimide on a support material. The membrane selectively allows the smallest molecules to pass; so hydrogen gets through preferentially. The membrane materials are fairly resistant to damage from most chemicals they may encounter, but eventually are damaged to the point of requiring replacement.

Other membrane materials, including inorganics, are in development.

Basic monitoring of a membrane unit would consist of periodically calculating the hydrogen recovery percentage and trending the product hydrogen contaminants. Feed composition and potential carryover should also be tracked routinely. Membrane system vendors would provide additional support for analyzing system performance.

Membrane systems for hydrogen recovery are offered by several suppliers, including Air Liquide (MEDAL™), Air Products (PRIZM™), and UOP (Polysep™). Industrial gas suppliers will also install and operate membrane systems at a refinery in something akin to an over-the-fence arrangement.

Cryogenic Recovery

Hydrogen can be recovered cryogenically from various refinery gases and olefins cracking gases. It is normally a by-product of recovering other, more valuable materials, such as ethylene. Industrial gas suppliers and others will install, own, and operate cryogenic recovery units in an over-the-fence arrangement.

Figure 23 illustrates application of a cryogenic unit to recover hydrogen from refinery fuel gas. The gas must first be compressed to about 200–500 psig and cooled. It is pretreated to remove moisture, CO_2, and other impurities before chilling in a multiservice, plate exchanger from −60 to −120 °F. The fluid is flashed and the vapor sent to a second stage of cooling in a plate exchanger to much lower temperatures followed by separation. The gas from the second stage flash drum is expanded across a valve and provides cooling to the two plate exchangers. Final product hydrogen from the cryogenic system is about 65 % hydrogen starting with a stream at, perhaps, 30 % hydrogen. By-products include

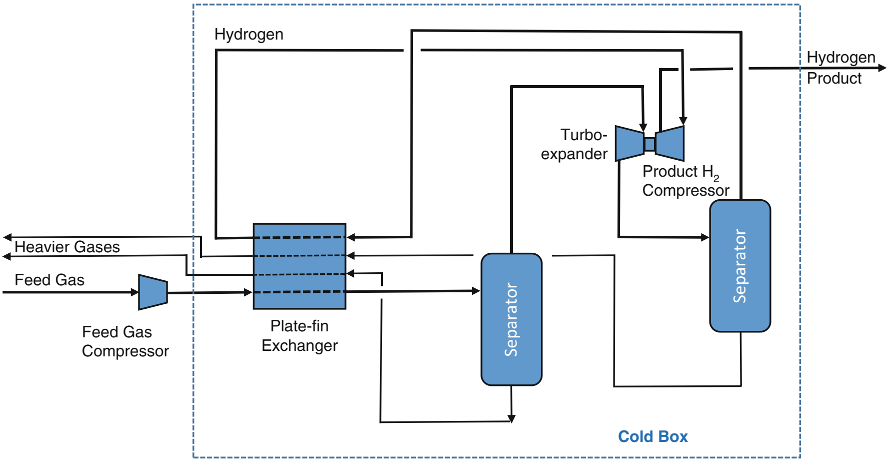


Fig. 23 Simplified flow diagram of one type of cryogenic hydrogen recovery process (Reference: Faraji et al. 2005)

LPG and fuel gas. The product hydrogen can be further upgraded by PSA or membrane. Cryogenic product hydrogen purities of 95–99 % and recoveries of 90–98 % of hydrogen are possible with appropriate process changes.

Cryogenic units are somewhat more difficult to operate and more expensive than the alternative technologies if your primary objective is hydrogen recovery. These units may be justified by the value of the other products recovered in some cases.

Because these are not common in refinery hydrogen systems, they are not discussed further here. Refer to the available references for suppliers of these systems.

Refinery Hydrogen Management

Ideally, all the hydrogen produced in a refinery would be used in upgrading the refined products to more and cleaner fuels. In reality, some of the hydrogen is inevitably lost to fuel or flare.

General Management Concepts

The purpose of hydrogen management is to minimize these losses through design, monitoring, and allocation of hydrogen to the users.

There are a few principles that guide hydrogen management:

- Treat the hydrogen system like any other process system – have a process flow diagram with critical controls shown and a material balance for the system.
- Meter all the hydrogen streams to and from units.
- Know the compositions of the hydrogen streams to and from units.
- Make or buy the lowest amount of “on-purpose” hydrogen possible.
- Preferentially use hydrogen in the highest value units.
- Minimize the need to recompress hydrogen by cascading from high to low pressure where possible.
- Keep hydrogen out of the fuel gas system and flare.
- Recover hydrogen where feasible.
- In refinery planning, the refinery LP should consider hydrogen.
- With good practices, a refinery should be able to use more than 90 % of the hydrogen generated.
- A periodic review by a company experienced in hydrogen system studies is advisable (e.g., Air Liquide, UOP, Air Products, etc.).

An example of a hydrogen system in a full-conversion refinery is illustrated in Fig. 24. There are a series of hydrogen generators (naphtha reformers, SMR plants) connected to hydrogen headers. The headers distribute the hydrogen to the users. There may also be intermediate hydrogen headers at different pressures and purities. Headers may be sweet or sour, depending on the design choices made

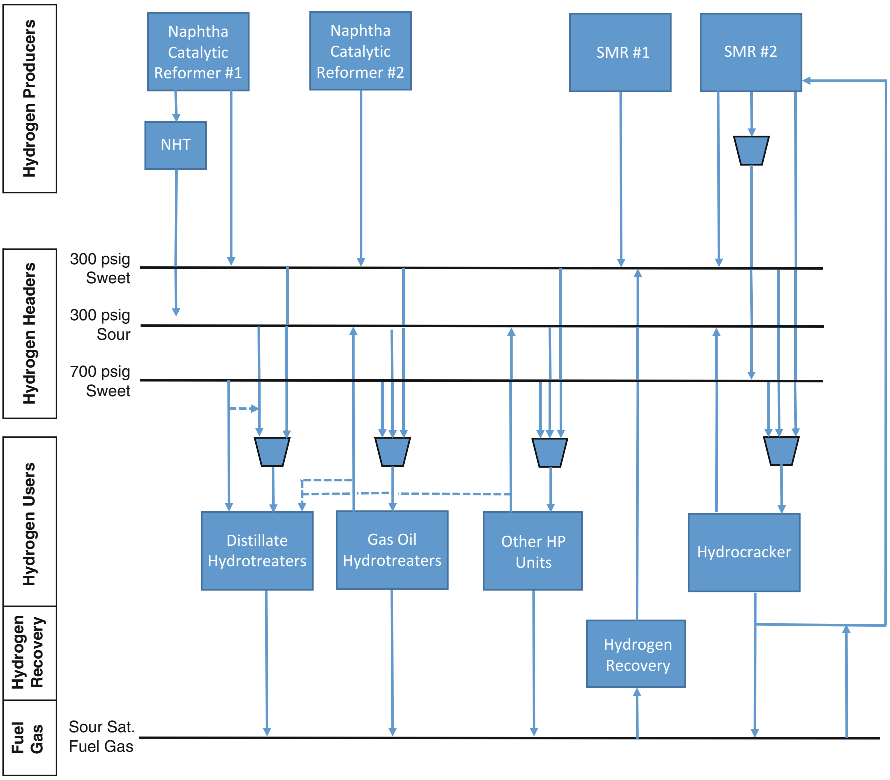


Fig. 24 Typical full-conversion refinery hydrogen management approach

for a facility. There may also be hydrogen recovery systems from fuel gas, refinery or petrochemical gases, and purge gases that make up into the headers.

Along with the process flow diagram, there should be a spreadsheet and/or simulation model that provides material balance calculations for the system. The model can use typical hydrogen consumptions and production for users based on feed rates or can be more sophisticated and account for feed quality as well as rates. Having these tools available will allow more intelligent use of hydrogen in a refinery, especially by operations personnel.

Hydrogen Headers

Fresh Hydrogen

The fresh hydrogen header takes hydrogen from the producers and distributes it to the initial users. Incoming hydrogen may originate from the SMR hydrogen plant (s), over-the-fence supply, or catalytic naphtha reformer(s). Incoming hydrogen may also be supplied by recovery unit(s).

One of the suppliers must be used as the swing unit to control the header pressure. The other suppliers should then be base loaded or may have rates that are set by other factors. For example, a naphtha reformer's hydrogen production will more often be set by the required naphtha octane and the catalyst age. You would not normally set naphtha reformer rate just to supply hydrogen, although that is an option.

The swing unit is usually an SMR unit that is large enough to control the fresh hydrogen header pressure. The SMR is able to react more quickly than many other units. An SMR does not like to be swung around too frequently, however; so, a swing SMR may end up producing a small excess of hydrogen that is lost. One objective is to minimize that loss.

Sour Hydrogen

Often, hydrogen is cascaded from high-pressure to low-pressure units for conservation and reuse. The hydrogen picks up H_2S the first time it is used. Some refineries scrub the H_2S out of purged gases from the higher-pressure units, but others purge sour gases.

The sour hydrogen is normally handled in a separate header. The gas from this header can be used in lower-pressure or less severe units. It can also be used for presulfiding or activation of hydrotreating catalysts.

Surplus hydrogen on the sour header may be cascaded to fuel gas.

Header Pressures

There are a number of strategies used to determine where to set hydrogen header pressures during design. The philosophy described here is one of the more common approaches.

The pressure for the fresh hydrogen header could be set at the maximum makeup pressure required for the highest pressure user (hydrocracker or gas oil hydrotreater), but this would mean compressing all the gas to the highest pressure all the time. That would be wasteful.

It is similarly not optimum to just supply hydrogen at low pressure, like naphtha reformer outlet pressure of 200–300 psig. That would mean installing compressors at many different users or creating another header for higher pressures.

A compromise that works well is to compress and distribute the fresh hydrogen supply at the makeup pressure required by the diesel hydrotreater (DHT). This usually means the fresh header runs 700–1,000 psig. This eliminates the need to compress within the DHT and most other units. It allows the DHT purge to be cascaded to lower-pressure services. If a refinery has a hydrocracker or high-pressure gas oil hydrotreater, the hydrogen for those services still requires additional compression.

In any event, the best practice for a given refinery is to select header pressures that result in the best economics, including the cost of compression.

Managing Hydrogen Users

Allocation of Hydrogen

Someone needs to “own” the hydrogen system in a refinery and that person has to be able to make decisions about the system. Short-term, on-shift decisions are normally made by someone in the shift operations organization. Overall decisions day-to-day are usually a joint effort of the operations and planning staffs. Longer-term planning and improvements are the purview of engineering staff.

Allocation of hydrogen is especially important when a facility is tight or short of hydrogen. To maximize the refinery profitability, hydrogen needs to go to the units that will make the most value per cubic foot (or cubic meter) of hydrogen used. All impacts need to be considered however. For instance, allocation of hydrogen to a high value unit that could force a cut in crude rate to the refinery because another unit was starved for hydrogen would not be wise.

Factors Affecting Usage and Generation

Hydrogen is primarily used to:

- Eliminate sulfur, nitrogen, and other impurities from products or feedstocks.
- Upgrade product values (ULSD, dewaxing, isomerization).
- Crack heavier hydrocarbons (gas oils) to lighter hydrocarbon products (naphtha, distillates).
- Supply reducing gas to sulfur plants (in some cases).

Changes in crude slate and rates impact all these factors. A heavy, sour crude will require more hydrogen to refine than a light, sweet crude. Higher rates in a hydrocracker or gas oil unit (possible due to crude changes) will require more hydrogen. Deeper HDS or increasing conversion will increase consumption.

On the supply side, lower reformer severity, increasing catalyst age, or less naphtha available to reform will all reduce cat reformer hydrogen makes. Changes in SMR hydrogen plant feedstocks, catalyst age, capacity, or firing/recovery limits may reduce the amount of hydrogen an SMR can make.

It is advisable to have a simple model that predicts hydrogen consumption or production for each unit based on feed rate and quality to estimate changes. These models would be incorporated into the material balance model for the system overall.

Overall Planning

Good, active hydrogen management practices will ensure that the least amount of valuable hydrogen is wasted in a refinery. The operations organization can manage the day-to-day hydrogen system, but the planning organization should include the hydrogen system in their process using the refinery LP or another model to avoid arriving at an infeasible plan.

Concluding Remarks

The production and use of hydrogen in a refinery is becoming increasingly important as refined product specifications drive toward zero sulfur, high H/C ratio fuels of all boiling ranges. There are several options for providing hydrogen to a refinery. Many of these have been discussed in this section. This is, by no means, all inclusive, however. Many variations exist among facilities and new options for production or recovery of hydrogen continue to grow.

Appendix Example SMR Hydrogen Plant Material Balance and Monitoring Parameters Development

To calculate the key monitoring parameters for an SMR plant, consider the following example that is typical of the sort of calculations needed. This example is for an SMR feeding natural gas plus refinery saturated off-gas that has been scrubbed free of sulfur (for simplicity). Hydrogen purification is by PSA unit. The plant only has high-temperature shift.

The objectives are to calculate:

- Material balance around the reforming furnace, shift converter, and PSA
- Approach to equilibrium in reformer
- Approach to equilibrium in shift converter
- PSA recovery efficiency
- Shift condensate rate
- Normalized reformer pressure drop
- Actual steam/carbon ratio

The following data are given:

Flow rates
  - Sweet feed gas = 6.87 MMscfd
  - Product hydrogen (99.9999 % H2) = 20.6 MMscfd
  - Raw hydrogen to the PSA = 31.8 MMscfd
  - Process steam rate = 66,500 lbs/h

Temperatures
  - Reformer outlet temperature = 1,500 °F
  - HTSC outlet temperature = 810 °F

Pressures
  - Reformer inlet = 315 psig

- Reformer outlet = 290 psig
- Shift converter outlet = 280 psig
- Product hydrogen from PSA = 260 psig

Dry gas analyses, vol % by GC

Component	Feed gas	PSA inlet
Hydrogen	9.3	69.5
Methane	79.7	2.3
Ethane	3.4	0.0
Propane	1.9	0.0
Mixed butanes	1.6	0.0
Mixed pentanes	1.3	0.0
Hexane and heavier	0.2	0.0
CO	0.3	3.0
CO_2	0.6	15.7
N_2	0.7	7.3
O_2	0.0	1.9

Solution

1. Normalize the dry gas analyses to 100 %. Notice that the analysis of the raw gas to the PSA inlet contains a lot of oxygen and nitrogen. This indicates air contamination and is typical of GC results. The air has to be backed out of the analysis. So remove the 1.9 % oxygen and 7.1 % nitrogen (79/21 × 1.9). This leaves 0.2 % nitrogen in the PSA inlet. Normalize the PSA inlet gas to 100 % without the air. The final normalized PSA Inlet gas is:
   - Hydrogen = 76.7 %
   - Methane = 2.5 %
   - CO = 3.3 %
   - CO_2 = 17.3 %
   - N_2 = 0.2 %
2. Set up a material balance spreadsheet for the composition, molar flow rate, mass flow rate, pressure, and temperature at each key location in the unit:
   - Feed gas
   - Reformer inlet feed gas
   - Process steam
   - Reformer outlet
   - HTSC outlet
   - Process condensate (shift condensate)
   - PSA inlet gas
   - PSA product hydrogen
   - PSA off-gas
3. Assume the feed gas flow rate is correct and use the feed gas analysis to calculate the moles of carbon and hydrogen per hour in the feed. Do not forget to include any CO and CO_2 in the carbon. We are assuming no

moisture in the feed. Use these values to calculate alpha (α) for use in Eq. 20. In this case, we have 816.2 mols of carbon per hour and 3,105.5 mols hydrogen per hour:

$$2\alpha = 3,105.5/816.2 = 3.80$$
$$\alpha = 3.80/2 = 1.90$$

4. Calculate the steam/carbon ratio (X) at the reformer inlet by converting the steam rate to moles per hour and dividing it by the moles per hour of carbon:
   66,500 lb/h steam/18 = 3694.4 mols/h steam
   Steam/Carbon = 3694.4/816.2 = 4.53 S/C Ratio = X
5. Calculate the wet shift converter outlet composition using the following equation and knowing α and X from above. The methane, CO, and CO_2 proportions (1-a-b, a, and b) come from the PSA inlet dry gas. The steam portion is calculated from the equation. Hydrogen falls out in the calculation. Remember that the nitrogen will come through as an inert:

$$\begin{aligned} CH_{2\alpha} + XH_2O \longleftrightarrow\ & aCO + bCO_2 + (1-a-b)CH_4 \\ & + (X-a-2b)H_2O + (3a+4b+\alpha-2)H_2 \end{aligned} \quad (31)$$

   where
   α = factor based on feed C/H molar ratio
   X = steam/carbon molar ratio
   a, b = coefficients for CO and CO_2 concentrations, respectively, at any point in the process
6. The shift or process condensate should be the residual water from the reaction. Use this as the process condensate flow rate. You can include dissolved CO_2, but the amount of dissolved CO_2 is not significant in the overall process.
7. Now check the overall balance in the unit by adding the feeds (feed gas plus steam plus any recycle hydrogen) and comparing to the HTSC outlet (PSA inlet gas plus calculated process condensate). Check the carbon and hydrogen balances also. Make adjustments to flow rates until you closed the balance. This sometimes means compromising on rates or slight adjustments to compositions. There are many sources of possible error in these calculations so flexibility is needed. If the balance can be closed to +/−2 %, that is good enough for the analysis.
8. Now estimate the reformer outlet composition.
   - Assume the HTSC outlet (in moles) is the correct methane slip from the reforming furnace. Here the slip is 2.5 v% of the dry gas or about 87 mols/h.
   - Calculate the CO and CO_2 proportions by assuming the gas is at water-gas shift equilibrium at the reformer outlet. The CO and CO_2 proportions can be derived by iteration until the calculated K_{WGS} at the reformer

outlet matches the K_{WGS} at the reformer outlet temperature of 1,500 °F. Use the definition:

$$K_{WGS} = (P_{H_2} \times \ P_{CO_2})/P_{H_2O} \times P_{CO})$$

where the partial pressures are in atmospheres in the *wet* gas.

Use the equation for K_{WGS} for the SMR process discussion.

An easier approach with sufficient accuracy is to use the equilibrium charts provided in the SMR monitoring discussion for methane to estimate the % CO and CO_2 in the dry gas at the reformer outlet. From the chart, the CO at the reformer outlet should be about 11.5 v% and CO_2 would also be about 11.5 v%. We brought in 816.2 mols/h carbon. 87 mols/h stayed in methane as methane slip. The remaining 729 mols per hour is roughly split evenly between CO and CO_2 at the reformer outlet (about 365 mols/h each). Iterative calculations give values of about 359 mols/h for CO and 370 mols/h for CO_2.

Check to be sure the reformer outlet mass balances, including C and H.

9. Calculate the partial pressures of methane, CO, CO_2, hydrogen, and water in the wet gases at the outlet of the reforming furnace and shift converter. The partial pressures must be in atmospheres absolute.
10. Calculate K_{SMR} at the reformer outlet and K_{WGS} at the shift converter outlet using the definitions in the SMR process discussion.

Reformer outlet actual $K_{SMR} = \sim 298$ (Table is reciprocal of this)

Shift converter outlet actual $K_{WGS} = \sim 6.23$

11. Calculate the equivalent equilibrium temperatures using the equations in the SMR process discussion or use the charts in that section.

Reformer actual equilibrium temperature $= \sim 1,515$ °F

Shift converter actual equilibrium temperature = 878 °F

12. Finish the material balance streams and check the overall, carbon, and hydrogen balances.
13. The key monitoring parameters can now be calculated:
    - *Overall material balance* was derived as part of the calculations. See Table 15 for the basic material balance.
    - *Approach to equilibrium (ATE) in the reformer*

$$\text{Reformer ATE} = \text{actual} - \text{calculated} = 1,500 - 1,515°\text{F} = -15°\text{F}$$

- *Approach to equilibrium (ATE) in the shift converter*

$$\text{Shift ATE} = \text{actual} - \text{calculated} = 878 - 810\ °\text{F} = +68\ °\text{F}$$

- *PSA recovery efficiency*

$$\text{Recovery} = (\text{mols } H_2 \text{in product} * 100\%)/\text{mols } H_2 \text{in feed}$$

$$\text{Product } H_2 = 20.6 \text{ MMscfd} \rightarrow\ 2,262.0 \text{ mols/h}$$

$$\text{PSA inlet } H_2 = 76.8\% \text{ of } 31.8 \text{ MMscfd} \rightarrow 2,721 \text{ mols } H_2/\text{h}$$

$$\text{Recovery} = 100\% * 2,262/2,721 = 83.1\%$$

- *Shift condensate rate*

This falls out of the material balances as 2, 378 mols/h (leftover process steam) = 42.3 Mlb/h or ~85 gpm.

- *Actual steam/carbon ratio*

This also fell out of the calculations as X = 4.53.

- *Normalized pressure drop*

For normalizing the pressure drop, prior history and a normalization basis (reference conditions) are required. Here, from prior development work, the equation for normalization of dP was found to be

$$dP_{norm} = dP_{meas} \times \left[(Q_{feed} + Q_{steam})_{norm}/(Q_{feed} + Q_{steam})_{meas}\right]^{1.6}$$

where:
dP_{norm} = normalized dP at reference conditions
dP_{meas} = measured dP at actual conditions
Q_{feed} = inlet volumetric flow of feed, reference or actual
Q_{steam} = inlet volumetric flow of steam, reference or actual
Here:

$$dP_{meas} = 315 - 290\ \text{psig} = 25\ \text{psig}$$

$$Q_{feed,\,meas} = 6.87\ \text{MMscfd}$$

$$Q_{steam,\,meas} = 66,500\ \text{lb/h} \times 24\ \text{h/day} \times 379.45\ \text{scf/18 lbs} \rightarrow 33.6\ \text{MMscfd}$$

$(Q_{feed} + Q_{steam})_{norm} = 51.9$ MMscfd (for normalization reference case)
So

$$dP_{norm} = 25 \times [51.9/(6.9 + 33.6)]^{1.6} = 37\ \text{psi}$$

14. From the parameters monitored, we can observe that:
    - Depending on how much adjustment was needed to get a good material balance, flow meter, instrument, or analytical issues may be indicated that would bear some evaluation.
    - The reformer approach to equilibrium is fairly good. Trending the calculated value would provide an indication of deactivation rate.
    - The shift converter ATE should also be trended over time for complete analysis. An ATE of 68 °F is a little high and may indicate the shift converter catalyst has deactivated some or the temperature is not optimum. It could also indicate bad data.
    - The PSA recovery efficiency of 83 % is lower than you should expect. Recovery of at least 85 % should be achievable. This would bear further investigation.
    - The shift condensate rate is informational primarily. It may be needed for loading evaluation of the degasifier on occasion.

Table 15 Example SMR hydrogen plant material balance development

		Feed					Steam					
Component			6.87	MMscfd			66.5 Mlb/h		Ref In			
	mw	v%	mols/h	lbs/h	mols \ C/h	mols \ H/h	mols/h	mols \ H /hr	mols/h	lbs/h	C mols/h	H mols/h
H_2	2	9.3	70	140	0	140	0	0	70	140	0	140
C_1	16	80.7	609	9,741	609	2,435	0	0	609	9,741	609	2,435
C_2	30	3.4	26	769	51	154	0	0	26	769	51	154
C_3	44	1.9	14	631	43	115	0	0	14	631	43	115
C_4	58	1.6	12	700	48	121	0	0	12	700	48	121
C_5	72	1.3	10	706	49	118	0	0	10	706	49	118
C_6	86	0.2	2	130	9	21	0	0	2	130	9	21
CO	28	0.3	2	63	2	0	0	0	2	63	2	0
CO_2	44	0.6	5	199	5	0	0	0	5	199	5	0
N_2	28	0.7	5	148	0	0	0	0	5	148	0	0
H_2O	18	0.0	0	0	0	0	3,694	7,389	3,694	66,500	0	7,389
		100.0	754	13,227	816	3,104	3,694	7,389	4,449	79,727	816	10,492
				H/C Rat	3.802		Stm/Carb		4.53			
				Alpha	1.901							
		Reforming		CH_{2a}	+	XH_2O	<=>	a CO	+	b CO_2	+	(1-a-b)CH_4
			mols/h	816.2		3694.4		359.1459		369.8		87.3
			coeff.	1.000		4.526		0.440		0.453		0.107
			atm					1.26		1.30		0.31
			H	3.80		9.05		0.00		0.00		0.43
				Total In: 12.855				Total Out: 12.855				
		HTSC										
			mols/h	816.2		3694.4		114.3		614.7		87.3
			Coeff	1.000		4.526		0.140		0.753		0.107
		20.05 Atm		2.78		12.57		0.39		2.09		0.30

Reformer outlet				HTSC outlet			PSA prod			Shift condensate	
				Dry gas	31.8 MMscfd		20.6 MMscfd	PSA off-gas			
mols/h	C mols/h	H mols/h	PP, atm	v%	mols/h	lbs/h	mols/h	mols/h	v%	mols/h	lb/h
2,476	0	4,952	8.71	76.8	2,721	5,442	2,262	459	35.8	0	0
87	87	349	0.31	2.5	87	1,397	0	87	6.8	0	0
0	0	0	0.00	0.0	0	0	0	0	0.0	0	0
0	0	0	0.00	0.0	0	0	0	0	0.0	0	0
0	0	0	0.00	0.0	0	0	0	0	0.0	0	0
0	0	0	0.00	0.0	0	0	0	0	0.0	0	0
0	0	0	0.00	0.0	0	0	0	0	0.0	0	0
359	359	0	1.26	3.2	114	3,200	0	114	8.9	0	0
370	370	0	1.30	17.4	615	27,045	0	615	48.0	0	0
5	0	0	0.02	0.1	5	148	0	5	0.4	0	0
2,596	0	5,191	9.13		2,351	42,315	0	0	0.0	2,351	42,315
5,893	816	10,492	20.73	100.0	5,893	79,546	2,262	1,280	100.0		
5,893			20.73	Dry gas							
			Dry gas	mols C	816						
				mols H	10,492						
+	(X-a-2b) $H_2$0	+	(3a+4b +α-2)H_2			Actual		@Act	EquivT	ATE	
	2595.7		2475.9		1,500 F	K_{WGS}	0.982	0.98	1,500	0	
	3.180		3.033		1,500 F	K_{SMR}	298.1	239.5	1,515	−15	
	9.13		8.71							Act - Equiv	
	6.36		6.07								
	2350.8		2720.8			Actual		@Act	EquivT	ATE	
	2.880		3.333		810 F	K_{WGS}	6.23	8.61	878	68	
	8.00		9.26							Equiv-Act	

  - The normalized pressure drop of 37 psi is somewhat high for most reformers and may indicate some catalyst crushing or coking from age or an incident. 37 psi is not particularly alarming. This value should be trended over time.
  - The steam carbon ratio at 4.53 is a little high for most PSA-type units, but would be common in older units using solvent CO_2 cleanup. It could probably be lowered.
15. These calculations can be built into a spreadsheet, including the trial-and-error, iterative solution to the reformer outlet composition and material balance closure. This would save a significant amount of time and enable more detailed operations evaluation to be completed more often.

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