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Monitoring Hydrogen Plant Performance

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Process monitoring is an indispensable practice to keep track of key performance indicators of the Hydrogen plant. A good system of process monitoring not only ensures safe and reliable plant operation but also helps in making strategic decisions such as catalyst change out schedules. If the performance is not monitored closely, there can be situations where the expected yields are not achieved, and this would not only affect the economics of Hydrogen plant but also of the entire refinery complex as the downstream hydrotreated/ hydrocracked product yields are also affected. This will have a direct implication on the overall refinery margin.

Knowing the fundamentals of performance indicators is imperative for better monitoring and control. Performance monitoring requires operating data inputs from plant which is normally accessible from the intranet servers or from DCS. It also requires stream analyses from laboratory (or online analyzers) to understand how each reactor is performing with respect to conversion/ yield. The laboratory testing frequency of such streams is normally decided by the Process Engineering department in conjunction with Laboratory Section.

The main objective of this paper is to guide the Hydrogen plant process engineers in the following ways:

- Perform a detailed mass balance across the Hydrogen flowsheet using available information such as dry analysis of outlet streams. Doing such a balance will help identify bottlenecks across each reactor. The focus would be to see how much hydrogen is being made before the final stream enters the Pressure Swing Adsorption (PSA) unit. This mass balance will also help estimate the outlet stream composition on wet basis thereby facilitating estimation of equilibrium constants (Keq values) for Steam Methane Reforming (SMR) and Water Gas Shift (WGS) reactions which in turn will help calculate the Approach to Equilibrium Values. These values, which are important in understanding the catalyst activity, can then be compared with the kinetic model values provided by the catalyst supplier.
- Monitor other critical parameters and key performance indicators across each reactor in Hydrogen flow sheet.

Feed Definition and characterization

Two feed types are considered; Case 1 is a Natural Gas (NG) feed and case 2 is a Naphtha feed. Please note that the flow, composition and operating conditions are purely assumptions based on author's experience and doesn't correspond to any specific plant.

For case 1, A 1000 kmol/h of (NG + recycle H₂) is assumed with the following composition

H₂ = 2%, N₂ = 5.0%, CH₄=90%, C₂H₆ = 2%; C₃H₈ = 1%;

This combined stream of NG and Recycle H₂ contains 10 ppmv H₂S and 5 ppmv each of methyl mercaptan and Di Methyl Di Sulphide (DMDS).

For case 2, 80 Kmol/h of Naphtha with 20 kmol/h of recycle H₂ is assumed. The most common laboratory information we have for naphtha is ASTM D-86 distillation and specific gravity.

ASTM D-86 °F Naphtha

T10%	110 °F
T30%	128 °F
T50%	135 °F
T70%	145 °F
T90%	155 °F

The reported specific gravity is 0.716

Naphtha needs to be characterized further based on the above available information. °F and °K units for temperature will be used only for the below estimations.

Naphtha characterization

- Find Volume Average Boiling Point
- VABP, °F = (T10% + T30% + T50% + T70% + T90%)/5 = 134.6 °F
- Correction factor
 - Slope = (T90% - T10%)/80 = 0.563
 - $\ln \Delta = \{-0.94402 - 0.00865(\text{VABP} - 32)0.6667 + (2.99791 \times \text{Slope}0.333)\}$
 - $\Delta = 3.825 \text{ °F}$
- Mean Average Boiling Point (MeABP) = VABP – $\Delta = 134.6 - 3.825 = 130.8 \text{ °F} = 328.03 \text{ °K}$
- Molecular weight (Riazi and Daubert) (Riazi, M.R., 2005)

$$= 1.6607 \times 10^{-4} \times (\text{MeABP})^{2.1962} \times (\text{Sp. Gr.})^{-1.0164}$$

$$= 1.6607 \times 10^{-4} \times (328.03)^{2.1962} \times (0.716)^{-1.0164} = 78.2 \text{ kg/kmol}$$
- C/H weight ratio =

$$3.4707 \{ \exp^{(0.01485 \text{ Tb} + 16.94 \times (\text{sp. Gr.}) - 0.012492 \text{ Tb} \times (\text{sp. Gr.}))} \times \text{Tb}^{-2.725} \times (\text{sp. Gr.})^{-6.798}$$

Substituting Tb = MeABP
C/H wt = 6.022

There is another simple estimation formula which is not very accurate and hence shall not be considered.

$$C/H \text{ wt} = [74 + 15x(\text{sp.gr.})]/[26-15x(\text{sp.gr.})]$$

- Molar H/C = $12.01/(C/H \text{ wt}) = 1.9944$
- Now, we know the empirical formula of naphtha which is $CH^{1.9944}$
- Empirical molecular weight = $1 \times 12 + 1.9944 \times 1.008 = 14$
- Carbon No °F Naphtha = Actual Molecular wt./ Empirical Molecular wt. = $78.2/14 = 5.586$

Feed Purification Section 1: Hydrogenator

The feed along with recycle H_2 first enters the Hydrogenator reactor.

Primary functions of Hydrogenator:

- Conversion of organic Sulphur compounds such as mercaptan, sulphides, disulphides and thiophenes to H_2S and organic chlorides (if present) to HCl by reaction with H_2 .
- Hydrogenation of olefins present in the feed

Key Parameters to be monitored:

- Recommended hydrogen level for each type of feed or combination of feeds. This is generally suggested by the catalyst supplier and the process engineer should confirm the same from the catalyst supplier in case of any deviation in feed specs. The recommended outlet H_2 level normally is 2% for Natural Gas feeds and about 26% for high aromatic naphtha feeds.
- The optimum operating temperature is in the range of 350 – 400°C. For LPG feed, the maximum temperature limit may be lower due to susceptibility to form carbon. Operating at higher than the recommended maximum temperature may cause carbon deposition on the catalyst and upstream pre-heat coil thereby leading to high pressure drop issues. Operating at lower than the recommended minimum temperature may cause organic Sulphur or chloride to slip through and poison the downstream reforming catalysts.

Key Performance Indicators:

• Pressure Drop

The Hydrogenator being the first reactor in a typical H_2 flow sheet is vulnerable to pressure drop issues. Some general reasons for pressure drop increase across any fixed bed are as follows

Breakage or erosion of catalyst particles – mainly due to poor handling and loading

Disintegration of catalyst pellets, mainly the top layer owing to poor inlet gas distribution and/or due to inadequate hold-down layer on the top. In some cases, the disintegration of poor-quality hold-down layer itself contributes to high pressure drop.

Carryover on catalyst bed – This is one of the most likely reasons for high pressure drop across the hydrogenator. Any debris upstream of the reactor, if not properly removed, can get carried over to the top of the catalyst leading to high pressure drop. There are specialized foulant trapping materials commercially available which can address this issue

Deformation of catalyst pellets due to accidental wetting of the catalyst causing decrease in catalyst strength leading to deformation and in worst case disintegration. This kind of issue can be encountered in High Temperature or Medium Temperature Shift reactors where there is likelihood of upstream boiler water leaks

Collapse of bed support grid or any damage to the outlet collector can also result in high pressure drop

Operating the reactor (hydrogenator and pre-reformer) at higher than recommended temperature can cause thermal cracking of the hydrocarbon feed thereby depositing carbon over the catalyst ultimately leading to high pressure drop. Additionally, for pre-reformers processing naphtha feeds, there is a minimum bed temperature below which there could be issues °F polymeric carbon formation which again ultimately leads to pressure drop increase.

It is important to monitor the pressure drop trend closely right from the time the catalyst has been put in operation. If the pressure drop increases suddenly, then that time period (before and after) should be isolated and investigated in detail. This generally applies to all reactors in the flowsheet.

Feed Purification Section 3: H₂S Absorbers (ZnO)

Primary function:

Absorption of H₂S which is present either in the feed or which is formed across hydrogenator (from organic Sulphur). Mainly seen as two vessels in lead-lag arrangement or a single vessel when the Sulphur levels are very low.

Key Performance Indicators:

- Outlet H₂S (<0.1 ppmv) versus inlet H₂S
- Life – depends on pick up/capacity. The process engineer should have the information of expected pick up from the catalyst supplier
- Pressure drop

A note on pick up/capacity: The process engineer should ask the catalyst supplier for actual pick up and not theoretical pick up. The theoretical pick up might be much higher than actual pick up.

For case 1 example; 1000 kmol/h of (NG + recycle H₂) with 25 ppmv H₂S.

Theoretical pick up = 600 kgS/m³
Actual pick up = 500 kgS/m³

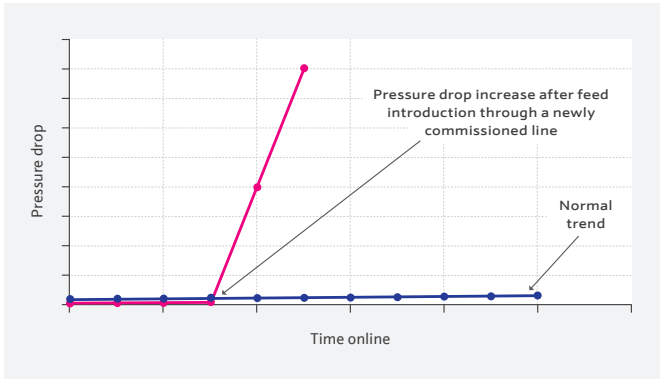
Again, the pick up figures are just an assumption and doesn't correspond to any specific product.

Volume of each bed = 10 m³

S to be removed = $(25/1000000) \times 1000 \text{ kmol/h} \times 24$
= 0.6 kmol H₂S/day = 20.4 kg H₂S/day = 20.4 x 32/34 = 19.2 kgS/day

Therefore, expected life = $500 \text{ kg S/m}^3 \times 10 \text{ m}^3 / 19.2$ = 260 days

The most economical way of operating a lead-lag is to allow the lead bed to operate till near saturation, that is, until the outlet H₂S from lead bed is 90% of the inlet H₂S.



• Inlet and outlet Sulphur and chlorides

It is important to monitor the inlet and outlet levels of Sulphur and chlorides. In most Hydrogen plants, the feed is analyzed on a daily basis and so the inlet Total Sulphur and chlorides are known. The outlet H₂S and HCl can be routinely measured by the process engineers using detector tubes or can be analyzed in the laboratory. The outlet H₂S measurement gives an idea if the hydrogenator is converting all organic S to H₂S

For example, if the feed (NG + recycle H₂) as in case 1 containing 10 ppmv H₂S and 5 ppmv each of methyl mercaptan and Di Methyl Di Sulphide (DMDS) is passing through Hydrogenator, then the outlet should measure the below calculated H₂S value

$10 \text{ ppmv H}_2\text{S} + 5 \text{ ppmv} \times 1 \text{ (methyl mercaptan)} + 5 \text{ ppmv} \times 2 \text{ (DMDS)} = 25 \text{ ppmv of H}_2\text{S}$

Feed Purification Section 2: Chloride Absorber (not common; required only when the feed contains chlorides)

Primary function:

Absorption of HCl either present in the feed or which is formed across Hydrogenator (from organic Chlorides).

In most cases, this catalyst is installed as a small layer below the hydrogenator. In some flowsheets, it is also installed above the H₂S absorber.

Key Performance Indicators:

- Outlet chloride (<0.1 ppmv) versus inlet chloride
- Life – depends on pick up/capacity. The process engineer should have the information of expected pick up from the catalyst supplier.

Feed Purification Section 3: Ultra-purification (Not common in all flowsheets)

Primary function:

- Polishing of H₂S to few ppb levels.
- Usually seen as a small layer beneath the ZnO absorber(s)

Key Performance Indicators:

- It may be difficult to measure very low ppb levels of H₂S using detector tubes or in the laboratory. However, the economic benefit of having this layer can be realized in terms of extended life of the pre-reformer catalyst. Ultra-purification also helps extend the life of primary reformer catalysts in highly stressed reformers.
- H₂S pick up/capacity

Pre-reformer

Pre-reformers are not found in all flowsheets. Of all the merits of having a pre-reformer, the most important one is flexibility to process different feeds.

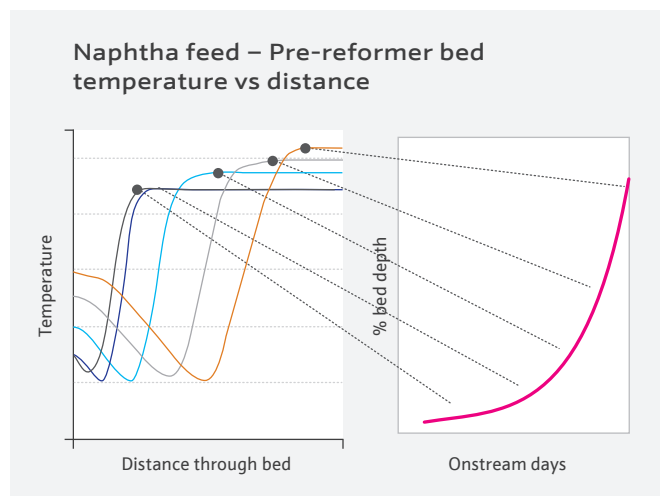
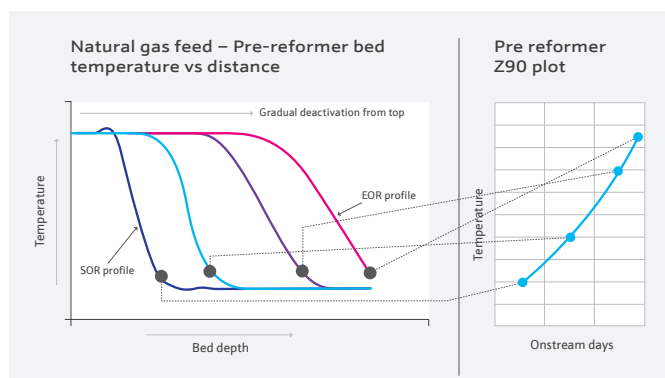
Primary function:

Conversion of C₂₊ present in feed to C₁ and Hydrogen

Key Parameters:

Steam to carbon ratio, Inlet temperature, pressure, Z₉₀ progression, pressure drop

Z₉₀ is an important trend which needs to be monitored closely as this determines the timing of pre-reformer catalyst change out. The typical Z₉₀ plots for natural gas and naphtha feeds are shown below:



Key Performance Indicators:

C₂₊ slip, pressure drop, Z₉₀ progression

Approach to Equilibrium (ATE) is not a key performance indicator for pre-reformer as the Steam Methane Reforming (SMR) ATE would be close to zero throughout the expected life of the catalyst (as long as the C₂₊ is within the guaranteed limit). However, the SMR and WGS equilibrium temperatures can be calculated and compared with the observed temperatures.

Mass balance across Pre-reformer:

Case 1: 1000 Kmol/h of treated (NG + recycle H₂) with composition: H₂ = 2%, N₂ = 5.0%, CH₄=90%, C₂H₆ = 2%; C₃H₈ = 1%; Inlet S/C (mol/mol) = 3.0; outlet pressure = 24.2 bara (23.9 atma), Inlet temperature = 450°C; outlet temperature = 400.2°C

Outlet composition (dry basis) reported by laboratory:

H₂ = 18.00%, N₂ = 4.00%, CH₄=73.00%, CO=0.03%; CO₂=5.00%

Unknowns: Outlet Dry flow rate, outlet steam (as we don't know how much steam has been consumed in the reactions to make products)

Let 'd' be the outlet dry flow rate and 's' be the moles of steam at outlet.

	Inlet moles kmol/h	Outlet moles Kmol/h
H ₂	20.00	0.18d
N ₂	50.00	0.04d
CH ₄	900.00	0.73d
C ₂ H ₆	20.00	0.00
C ₃ H ₈	10.00	0.00
CO ₂	0.00	0.05d
CO	0.00	0.0003d
H ₂ O	3.0 x [900 + 20x2 + 10x3] = 2910.00	s

Doing 'C' balance:

$$900 + 20 \times 2 + 10 \times 3 = 0.73d + 0.05d + 0.0003d$$

d = outlet dry flow rate = 1243.11 kmol/h

Doing 'O' balance:

$$2910 = 2 \times 0.05 \times 1243.11 + 0.0003 \times 1243.11 + s$$

S = outlet steam = 2785.3 kmol/h

$$\text{Total wet outlet flow} = 1243.11 + 2785.3 = 4028.4 \text{ kmol/h}$$

	Inlet kmol/h	Outlet kmol/h	Outlet wet mol fraction
H ₂	20.00	223.76	0.056
N ₂	50.00	49.72	0.012
CH ₄	900.00	907.47	0.225
C ₂ H ₆	20.00	0.00	0.000
C ₃ H ₈	10.00	0.00	0.000
CO ₂	0.00	62.16	0.015
CO	0.00	0.37	0.000093
H ₂ O	2910.00	2785.32	0.691

Now, calculating the SMR equilibrium constant

$$K_p (\text{SMR}) = P^2 \times \frac{[\text{CO}_2][\text{H}_2]^3}{[\text{CH}_4][\text{H}_2\text{O}]} = 23.92 \times$$

$$(0.000093 \times 0.056^3) / (0.225 \times 0.691) = 6 \times 10^{-5}$$

Substitute the above in the equation (Twigg, M.V., Catalyst Handbook second edition, Appendix 6, pg 537) below to get equilibrium temperature in °K

$$\ln(1/K_p) = 0.2513Z^4 - 0.3665Z^3 - 0.58101Z^2 + 27.1337Z - 3.2770$$

Where Z = (1000/T) -1; T is in °K

$$\ln(1/K_p) = \ln(1/6 \times 10^{-5}) = 9.721$$

Solving the above equation using goal seek or solver in excel, Z = 0.485; T_{eq} = 673.4 oK = 400.2°C

Therefore, approach to SMR equilibrium in pre-reformer = T-T_{eq} = 400.2-400.2 = 0°C

Case 2: Doing a similar balance for treated naphtha feed: 80 Kmol/h of naphtha (estimated C No = 5.586); S/C = 3.0 mol/mol; outlet pressure = 24.1 bara = 23.8 atma; inlet T = 450°C; outlet T = 477 °C

Outlet composition (dry basis) reported by laboratory:

$$\text{H}_2 = 21.50\%, \text{CH}_4 = 54.00\%, \text{CO} = 0.50\%; \text{CO}_2 = 24.00\%$$

Unknowns: Outlet Dry flow rate, outlet steam (as we don't know how much steam has been consumed in the reactions to make products)

Let 'd' be the outlet dry flow rate and 's' be the moles of steam at outlet.

	Inlet moles kmol/h	Outlet moles Kmol/h
H ₂	20	0.215d
Nap Carbon	80 x 5.586 = 446.88	0
H ₂ O	3 x 446.88 = 1340.64	s
CO ₂	0	0.24d
CO	0	0.005d
CH ₄	0	0.54d

Doing 'C' balance:

$$446.88 = 0.24d + 0.005d + 0.54d$$

d = dry outlet flow rate = 569.3 kmol/h

Doing 'O' balance:

$$1340.64 = s + 2 \times 0.24 \times 569.3 + 0.005 \times 569.3$$

s = 1064.53 kmol/h

$$\text{Total wet outlet flow} = 569.3 + 1064.53 = 1633.83 \text{ kmol/h}$$

	Inlet kmol/h	Outlet kmol/h	outlet wet mol fraction
H ₂	20	122.39	0.0749
Nap Carbon	446.88	0.00	0.000
H ₂ O	1340.64	1064.53	0.6517
CO ₂	0	136.63	0.0836
CO	0	2.85	0.00174
CH ₄	0	307.41	0.1882

Now, calculating the SMR equilibrium constant

$$K_p (\text{SMR}) = P^2 * \frac{[\text{CO}_2] [\text{H}_2]^3}{[\text{CH}_4] [\text{H}_2\text{O}]} = 23.8^2 \times (0.00174 \times 0.0749^3) / (0.1882 \times 0.6517) = 3.38 \times 10^{-3}$$

Substitute the above in the equation below to get equilibrium temperature in °K

$$\ln (1/K_p) = 0.2513Z^4 - 0.3665Z^3 - 0.58101Z^2 + 27.1337Z - 3.2770$$

Where Z = (1000/T) -1; T is in °K

$$\ln (1/K_p) = \ln (1/3.38 \times 10^{-3}) = 5.691$$

Solving the above equation using goal seek or solver in excel, Z = 0.333; T_{eq} = 750 °K = 476.9 °C

Therefore, approach to SMR equilibrium in pre-reformer = T - T_{eq} = 477 - 476.9 = 0.1 °C

Primary Steam Reformer

Every hydrogen process engineer knows this is the 'heart' of the entire hydrogen flowsheet.

Primary function:

Conversion of methane and higher hydrocarbons (in absence of pre-reformer) in the feed to hydrogen (along with CO and CO₂)

Key Parameters:

Steam to carbon ratio, outlet temperature, pressure, pressure drop, tube wall temperature, reformer firing and flame characteristics, tube appearance

Key performance indicators:

Methane conversion (as indicated by methane slip) and pressure drop are the two major performance indicators.

Approach to equilibrium is a theoretically important parameter in this section as it indicates the performance of catalyst whilst other parameters such as outlet temperature, S/C ratio, pressure are held constant. This value will be useful for the process engineers during the technical evaluation stage of catalyst offers. It is to be understood that the reactions occurring in the reformer are equilibrium limited and therefore the methane slip observed at zero (or close to zero) ATE indicates the minimum thermodynamically possible methane slip at the given conditions. The process engineers should be knowledgeable enough to do a sanity check to see if the methane slip is in line with the equilibrium approach.

Another advantage of calculating the equilibrium temperature is that it gives an indication of the exact outlet process gas temperature. As WGS reaction is quick, it can be assumed to be in equilibrium always at the reformer outlet conditions.

Normally, in most reformers, the reformer outlet temperature indication (TI) is located few meters away from the tube outlet (where the catalyst ends) and there is always some heat loss which needs to be assumed from tube end to TI point.

Mass balance across primary reformer:

The pre-reformer effluent will be the feed to the reformer. Depending on the flowsheet, there could be some additional steam added at the reformer inlet. In reformers in HyCO plants, recycle CO₂ is normally added at reformer inlet with the intention to maximize CO yield. However, for the examples here let us assume no additional steam is added for case 1 and some steam added for case 2. Again, these are purely assumptions and bear no similarity to any existing unit.

Case 1: Total Flow = 4028.4 kmol/h (outlet of pre-reformer, reformer inlet temperature = 500 °C, reformer outlet temperature = 840 °C. Assume 15 °C heat loss from tube end to TI, so tube outlet temperature = 855 °C, outlet pressure = 22 bara (21.7 atma)

Outlet composition (dry basis) reported by laboratory:

H₂ = 72.40%, CH₄=4.57%, CO=13.61%; CO₂=8.10%; N₂ = 1.35%

Let 'd' be the outlet dry flow rate and 's' be the moles of steam at outlet.

	Inlet kmol/h	Outlet kmol/h
H ₂	223.76	0.724d
N ₂	49.72	0.0135d
CH ₄	907.47	0.0457d
CO ₂	62.16	0.081d
CO	0.373	0.1361d
H ₂ O	2785.32	s

Doing 'C' balance; 907.47 + 62.16 + 0.373 = 0.0457d + 0.081d + 0.1361d

d = outlet dry flow rate = 3691 kmol/h

Doing 'O' balance; 2x62.16 + 0.373 + 2785.32 = s + 2x0.081x3691 + 0.1361x3691

s = outlet steam = 1809.73 kmol/h

	Inlet kmol/h	Outlet kmol/h	outlet wet mol fraction
H ₂	223.76	2672.30	0.486
N ₂	49.724	49.83	0.009
CH ₄	907.47	168.68	0.031
CO ₂	62.156	298.97	0.054
CO	0.373	502.35	0.091
H ₂ O	2785.32	1809.71	0.329

Now, calculating the SMR equilibrium constant

$$K_p(\text{SMR}) = P^2 * \frac{[\text{CO}][\text{H}_2]^3}{[\text{CH}_4][\text{H}_2\text{O}]} = 21.72 \times (0.091 \times 0.4863) / (0.031 \times 0.329) = 482.3$$

Substitute the above in the equation below to get equilibrium temperature in °K

$$\ln(1/K_p) = 0.2513Z^4 - 0.3665Z^3 - 0.58101Z^2 + 27.1337Z - 3.2770$$

Where Z = (1000/T) -1; T is in °K

$$\ln(1/K_p) = -6.179$$

Solving the above equation using goal seek or solver in excel, we ultimately get T_{eq} = 846.3 C

Therefore, approach to SMR equilibrium in reformer = T - T_{eq} = 855.0 - 846.3 C = 8.7 C

WGS Approach can be calculated using the below equations:

$$K_p(\text{SMR}) = P^2 * \frac{[\text{H}_2][\text{CO}_2]}{[\text{H}_2\text{O}][\text{CO}]} = (0.486 \times 0.054) / (0.329 \times 0.091) = 0.8766$$

$$\ln(K_p \text{ WGS}) = 0.63508Z^3 - 0.29353Z^2 + 4.1778Z + 0.31688$$

(Twigg, M.V., Catalyst Handbook second edition, Appendix 7, pg 543)

Solving the above equation using Goal seek or solver in excel, we get T_{eq (WGS)} = 845.9°C

Case 2: For naphtha case:

Let us assume an additional steam of 165 kmol/h is added at the inlet of reformer. Reformer inlet temperature = 500°C, reformer outlet temperature = 840 °C. Assume 15C heat loss from tube end to TI, so tube outlet temperature = 855 °C; outlet pressure = 23 bara (22.7 atma)

Outlet composition (dry basis) reported by laboratory:

H₂ = 68.53%, CH₄=2.76%, CO=15.86%; CO₂=12.85%;

Doing C and O balance as explained earlier, we get:

	Inlet kmol/h	Outlet kmol/h	outlet wet mol fraction
H ₂	122.39	973.14	0.417
H ₂ O	1064.53	915.48	0.392
CO ₂	136.63	182.47	0.078
CO	2.85	225.22	0.096
CH ₄	307.41	39.19	0.017
Addl. H ₂ O	165.0		

Solving the equations as before, we get

$$K_p(\text{SMR}) = 538.3; K_p(\text{WGS}) = 0.864$$

$$T_{\text{eq}(\text{SMR})} = 851.4^\circ\text{C}; T_{\text{eq}(\text{WGS})} = 850.1^\circ\text{C}$$

Therefore, approach to SMR equilibrium in reformer = T - T_{eq} = 855.0 - 851.4 C = 3.6 °C

The process engineer should ask the catalyst supplier what the expected Approach is and compare the same with the calculated values.

Tube wall Temperature:

Besides catalyst activity, the approach and the methane slip also depend on how well the reformer is being operated. Improper heat distribution across the tubes will increase the approach and therefore the methane slip would be more than expected, although the catalyst is perfectly normal in terms of its activity.

Tube wall temperatures need to be measured on a regular basis using a simple handheld pyrometer or a more advanced thermal imaging equipment. The tube wall temperatures of all tubes after applying suitable correction for background radiation, shall indicate how balanced the reformer heat distribution is. A spread (Max - Min) of > 70 °C normally indicates there is scope for improving the heat distribution. The measured TWT of tubes can also be compared with the expected TWT profile as per catalyst supplier's kinetic model.

Pressure drop across steam reformer:

This is another critical parameter which needs close monitoring. The rate of pressure drop increase depends on how well the reformer is being operated. Frequent trips or shutdowns can break the catalyst pellets due to expansion and contraction of tubes. The broken pellets can contribute to higher pressure drop. A sudden increase in pressure drop would need the time period to be isolated and any event in that period to be investigated. In most of the plants, the pressure drop is measured between the reformer inlet and waste heat boiler (WHB) or process gas boiler (PGB) outlet. Therefore, any fouling in WHB/PGB can also affect the pressure drop. The process engineer should have a record of number of trips/shutdowns and the reason for such a trip/shutdown. In many instances, a step increase in pressure drop is observed right after starting up post sudden trip.

Shift Reactor

Primary function:

To convert CO formed in the reformer to hydrogen by reacting with steam.

Key parameters:

Inlet temperature, outlet temperature, steam to dry gas ratio, pressure drop, temperature profile

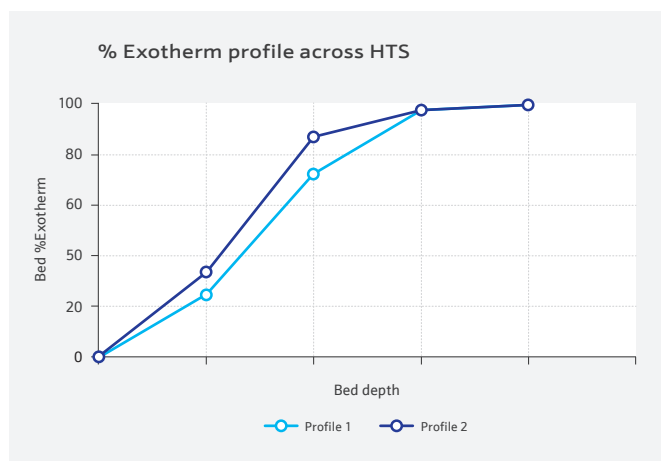
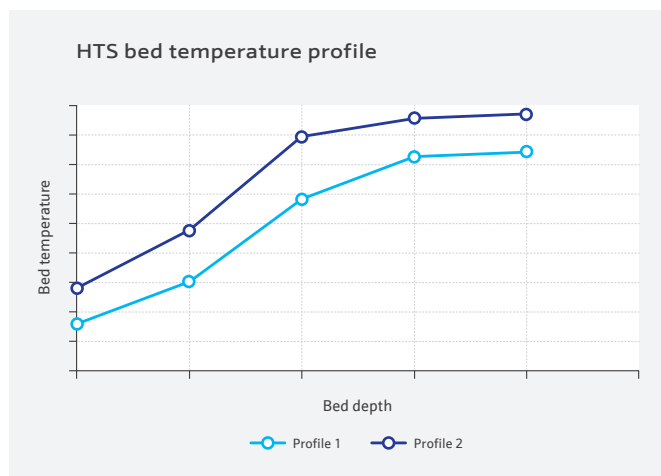
Key Performance Indicators:

CO conversion, pressure drop, WGS approach

Plotting of temperature profile is helpful in understanding how the catalyst activity declines with age. A clear trend can be obtained by plotting the %exotherm profile rather than temperature profile.

%exotherm@ any particular bed temperature
= $\frac{(T-T_{min})}{(T_{max}-T_{min})} \times 100$

A sample illustration of both bed temperature and %exotherm plots across a High Temperature Shift Reactor (HTS) is shown below



Pressure drop:

The shift reactor (HTS or MTS), being just downstream of the WHB/PGB, is vulnerable to fouling issues due to upstream boiler water leaks. This causes pressure drop to increase due to build up of boiler solids. The pressure drop trend is to be carefully monitored especially after a trip incident. Also, any wetting incident can reduce the strength of catalyst pellets thereby crushing it contributing to high pressure drop. Also, inappropriate or inadequate hold down layer on top can cause high pressure drop issues.

Mass balance across Shift reactor:

Let's assume we have a High Temperature Shift reactor in the flowsheet and continue with the mass balance.

Case 1: Inlet temperature = 320°C; outlet temperature = 394 °C;

Outlet composition (dry basis) reported by laboratory:

H₂ = 74.86 %, CH₄=4.16%, CO=3.38%; CO₂=16.36%; N₂=1.23%

Doing 'C' and 'O' balance as explained earlier:

	Inlet kmol/h	Outlet kmol/h	outlet wet mol fraction
H ₂	2672.30	3038.25	0.552
N ₂	49.83	49.92	0.009
CH ₄	168.68	168.84	0.031
CO ₂	298.97	663.98	0.121
CO	502.35	137.18	0.025
H ₂ O	1809.71	1444.85	0.263

So, at the end of the shift reactor, 3038.25 kmol/h of H₂ is produced in case 1.

Using the equations:

$$K_p(\text{WGS}) = \frac{[\text{H}_2][\text{CO}_2]}{[\text{H}_2\text{O}][\text{CO}]}$$

$$\ln(K_p \text{ WGS}) = 0.63508Z^3 - 0.29353Z^2 + 4.1778Z + 0.31688$$

We get,

$$K_p(\text{WGS}) = 10.2; T_{\text{eq}}(\text{WGS}) = 403.2 \text{ }^\circ\text{C}$$

$$\text{WGS Approach} = T_{\text{eq}}(\text{WGS}) - T = 403 - 394 = 9.2 \text{ }^\circ\text{C}$$

Case 2: for naphtha case, inlet temperature = 320 °C, outlet temperature is 396 °C

Outlet composition (dry basis) reported by laboratory:

H₂ = 71.96 %, CH₄=2.46%, CO=3.20%; CO₂=22.37%

Doing C and O balance across shift reactor:

	Inlet kmol/h	Outlet kmol/h	outlet wet mol fraction
H ₂	973.14	1147.25	0.491
H ₂ O	915.48	741.34	0.317
CO ₂	182.47	356.64	0.153
CO	225.24	51.02	0.022
CH ₄	39.19	39.22	0.017

So, at the end of shift reactor 1147.25 kmol/h of hydrogen is produced in case 2

$$K_p(\text{WGS}) = 10.8; T_{\text{eq}}(\text{WGS}) = 397.1 \text{ }^\circ\text{C}$$

$$\text{WGS Approach} = T_{\text{eq}}(\text{WGS}) - T = 397.1 - 396 = 1.1 \text{ }^\circ\text{C}$$

PSA section

Generally, the Hydrogen recovery across PSA is between 85 to 90%. Assuming 87% hydrogen recovery across PSA, the hydrogen production in case 1 would be 3038.25 x 0.87 = 2643.3 kmol/h and in case 2 would be 1147.25 x 0.87 = 998.1 kmol/h. This needs to be cross-checked with the PSA purge gas flow and the hydrogen content in it.

Conclusion

There is no denial to the fact that proper checks and balances in the plant are crucial for ensuring maximum operational efficiency. Mass balance is one of those crucial checks. Also, the primary objective of this 'practice-oriented' paper is that the process engineer understands the significance of key performance indicators across each section of the plant and is confident in doing calculations such as Approaches to Equilibrium using the available plant and lab information. By following the monitoring aspects highlighted in this paper, the process engineer will be in a better position to make sound technical judgements when doing a technical evaluation of bid and also when doing routine plant evaluations.

References:

1. Riazi, M. R., (2005). Characterization and Properties of Petroleum Fractions, ASTM International.
2. Twigg, M.V., Catalyst Handbook, Second Edition
4. Ramakumar, K.R., Detect Boiler leaks upstream of the shift reactor in Hydrogen plants, Hydrocarbon Processing, March 2016
5. Ramakumar, K.R., Sultan Orman, Ismail Bahadir Kara, Pre-reformer catalyst in a Hydrogen Plant, Catalysis (PTQ) 2020, pg. 61-63

Appendix

Using Goal Seek (from 'what if analysis' in excel) to find the solution °F 'Z' equation

The screenshot shows an Excel spreadsheet with the following data:

	G	H	I	J	O	P	Q	R	S	T	U
4											
5											
6											
7											
8											
9											
10											
11											
12											
13											
14											
15											
16											
17											
18											
19											
20											
21											

The Goal Seek dialog box is open, showing the following settings:

- Set cell: I14
- To value of: 6.3036
- By changing cell: I15

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