

OPERATION HYDROGEN

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review the design nuances of a modern hydrogen plant.

Hydrogen is an essential feedstock in today's refining operations. There are two main reasons for this increased importance. The crudes that refineries now use are becoming heavier in nature and also contain additional sulfur and nitrogen species. Environmental regulations also continue to reduce the level of sulfur in both gasoline and diesel products. These trends have led to higher hydrogen requirements for both hydrotreating and hydrocracking operations within the refinery.

Hydrogen can be produced from a variety of feedstocks, which can range from natural gas to coal and include all hydrocarbons in between. The selection of feedstocks can limit the options in choosing a hydrogen generation technology. There are four technologies that are typically employed to produce hydrogen: steam methane reforming (SMR); SMR followed by an oxygen reformer (O_2R); auto thermal reformer (ATR); or partial oxidation (POX). Each of these technologies produces different natural H_2/CO ratios. Therefore, for a hydrogen plant, a technology that produces a high H_2/CO ratio would be preferred. Figure 1 illustrates the natural H_2/CO ratios for the four given technologies based on a natural gas feedstock.

As seen in Figure 1, SMR produces the highest natural H_2/CO ratio. This is a mature technology and is the typical choice for hydrogen generation. In fact, SMRs generate the majority of the world's on purpose hydrogen. Therefore, the rest of this discussion will focus on SMR based hydrogen plants and the design nuances that are now typically part of designing a modern hydrogen plant. There are three areas of focus in designing a modern hydrogen plant:

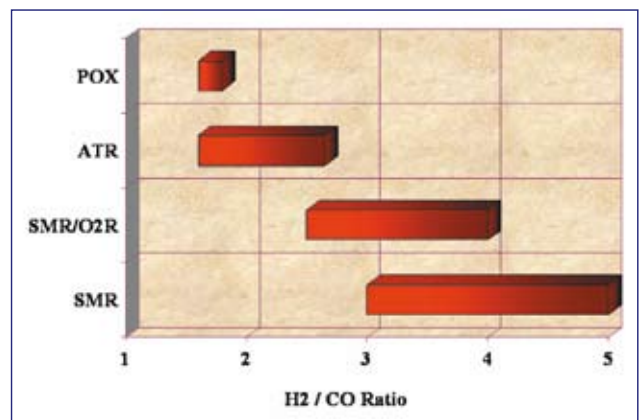


Figure 1. Natural H_2/CO ratios with natural gas feedstock.

- Capability to handle multiple feedstocks.
- Setting an export steam amount that will fit within a refinery's steam balance.
- Controlling the export steam purity.

MULTIPLE FEEDSTOCKS

In the past, natural gas or naphtha were the primary feedstocks used for the hydrogen generation. However, as governmental agencies intensify their focus on emissions, and with the refiner's growing need for additional hydrogen, refiners have begun to look at sending various refinery offgases, in addition to natural gas or naphtha, to the hydrogen unit for use as feedstocks. This can alleviate some of the refiner's emissions concerns since they would not be flaring

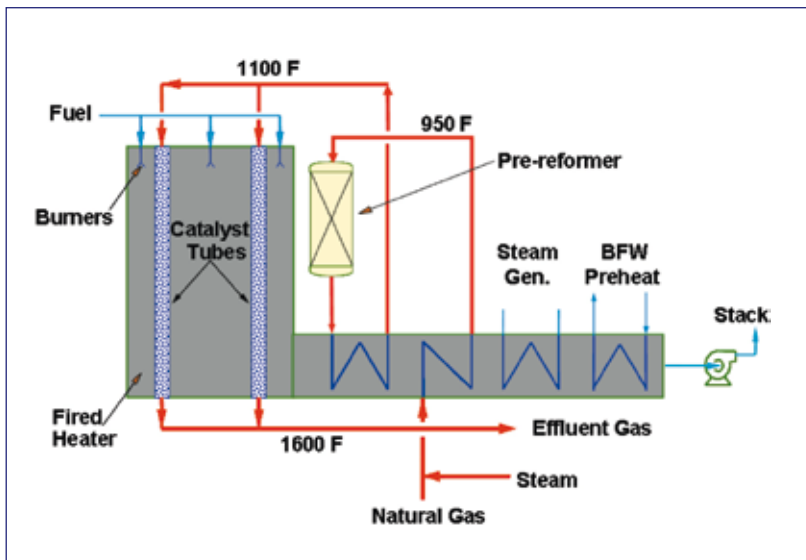


Figure 2. SMR with addition of a prereformer.

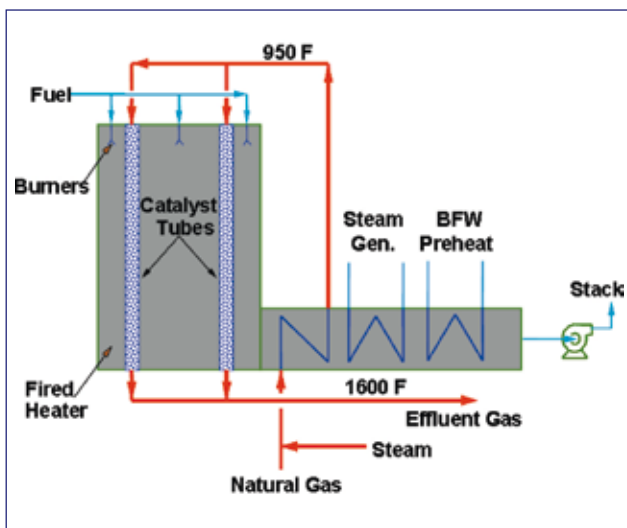


Figure 3. Typical configuration for a maximum steam export SMR hydrogen plant.

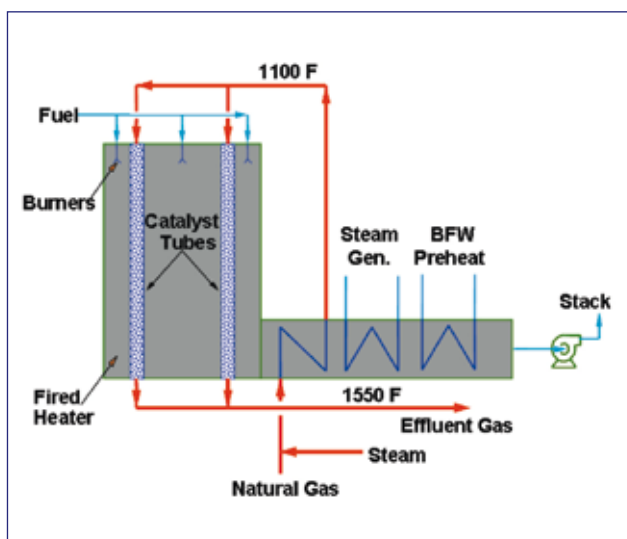


Figure 4. Reduction of export steam production by altering reformer inlet and outlet temperatures.

the offgases. Refinery offgases typically consist of hydrogen, carbon monoxide, carbon dioxide, nitrogen,

hydrocarbons through octane, and sulfur compounds. However, refinery offgases can vary greatly both in composition and flow due to changes in upstream unit operations.

In the past, these fluctuations would be very difficult to handle for a hydrogen plant due to the heavier components that could be found in these offgases. The main concern is centered around the reforming catalyst and its ability to handle the significant swings in feedstock composition. However, today's typical steam methane reforming catalysts can handle natural gas through butane as feedstocks without the need for a catalyst changeout. Accurate flow measurement and compositional measurement are required to ensure proper steam to carbon ratio adjustment. Therefore, as long as adequate instrumentation is in place, the hydrogen plant can be operated successfully, utilizing various refinery offgases as feedstocks.

However, this hydrogen plant design can sometimes be viewed by refiners as an operational concern. This is due to the possibility of having heavier components in the feedstock such as pentane. In addition, higher regularity of instrumentation checks is required to ensure proper operation. One technique that can be employed to lessen an operator's anxiety is to put in an adiabatic prereformer. The prereformer is a vessel filled with high activity reforming catalyst that is placed before the primary reformer (Figure 2). The prereformer partially reforms the hydrocarbon feed to produce a methane/syngas mixture. The prereformer acts as a guard bed for the primary reformer. The prereforming catalyst is easily poisoned by sulfur and would protect the primary reformer tubes from overheating due to catalyst deactivation by sulfur poisoning. Since the prereformer partially reforms the hydrocarbon stream to CH_4 , CO , CO_2 , H_2O and H_2 , then methane is the only hydrocarbon that is sent on to the primary reformer. The primary reformer would not see fluctuations in feedstock composition since the prereformer would convert the heavier hydrocarbons. This also minimizes the possibility of thermally cracking the feedstock prior to entering the primary reformer since methane has a high cracking temperature. Table 1 illustrates the expected utility usage for new plant designs utilizing a prereformer for natural gas feed and naphtha feed respectively.

The addition of a prereformer to an existing hydrogen plant can increase the capacity of the plant. The addition of a prereformer can alleviate a portion of the absorbed duty of the primary reformer since it has partially reformed the feedstock stream. However, the reforming capacity is all in the same heat envelope. Therefore, additional capacity is gained only by reheating the prereformer effluent. This allows the primary reformer additional capacity for firing. In Figure 2, a prereformer effluent convective coil has been inserted into the waste heat recovery unit to allow greater plant capacity. This addition has a twofold effect:

- Reduces the heat load on the primary reformer.
- Reduces the steam make of the plant.

The duty required for reheating of the prereformer effluent is taken from the steam generation of the

waste heat recovery unit. Therefore, the steam make of the plant will decrease. The amount of reduction is dependent on the feedstocks that are used to the plant. For a natural gas fed plant, the prereformer is endothermic in nature. For a heavy hydrocarbon feed such as naphtha, the prereformer is exothermic in nature. Obviously, the heat load on the primary reformer is also tied to the type of feedstocks that are used. For a plant with natural gas feedstock, the use of a prereformer could reduce the absorbed duty of the primary reformer by approximately 6%, whereas for a naphtha fed plant, the absorbed duty could be reduced by approximately

11%. This reduction of absorbed duty then allows for increased capacity of the plant. Table 2 illustrates the expected plant capacity increase and the utility usage for an existing plant design revamped by the addition of a prereformer for natural gas feed and naphtha feed respectively.

The decision to include a prereformer in the original design of a hydrogen plant should be made both on technical and economic considerations. The prereforming catalyst can be two to three times the cost of traditional reforming catalyst. The expected catalyst life for prereforming catalyst is approximately three years. This is two years less than what is expected for traditional reforming catalysts. The cost of the additional convective coil and its impact on the design of the induced draft fan must also be factored in to the decision making process. The addition of a prereformer with effluent reheating will decrease the steam production of the plant. A prereformer can aid the operation of a new hydrogen plant utilising multiple feedstocks. However, the practical benefit of adding a prereformer appears to be most advantageous for capacity expansion options in an existing hydrogen plant.

New plant configuration	Prereformer natural gas	Prereformer naphtha
Utilities, units/M ft ³ H ₂		
Feed, million btu LHV	0.346	0.356
Fuel, million btu LHV	0.092	0.123
Feed and fuel, million btu LHV	0.438	0.479
Export steam, lb	75	84
BFW, lb	106	127

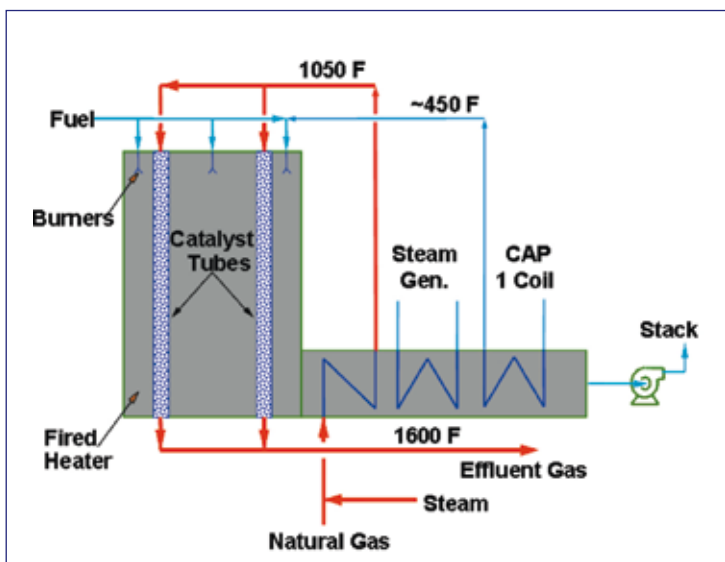


Figure 5. Reduced steam configuration utilising one coil of combustion air preheat.

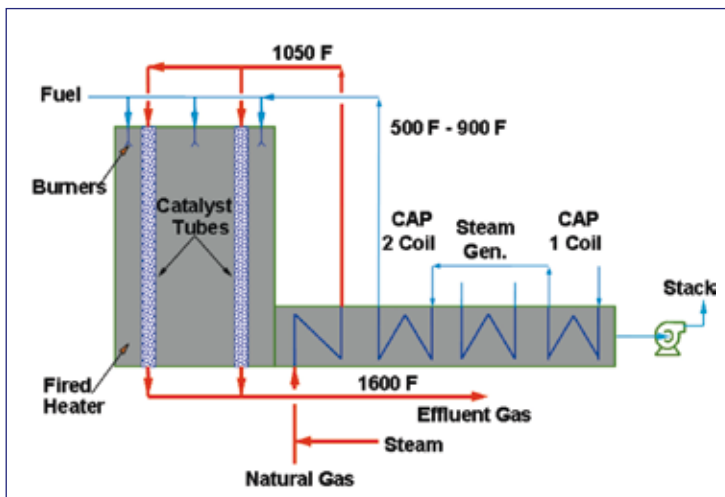


Figure 6. Reduced steam configuration utilising two coils of combustion air preheat.

STEAM PRODUCTION

The second area of focus in designing a modern hydrogen plant is the steam system. A hydrogen plant produces steam as a byproduct. The process requires a portion of the steam, but a significant quantity is available for export. Most refiners today have optimised their steam systems. Therefore, refineries may not be able to accept the maximum amount of export steam from a new hydrogen plant. The hydrogen plant design must incorporate the customer's export steam requirements. There are typically three options to reduce the export steam from a hydrogen plant:

- Minimise steam without combustion air preheat (CAP).
- Maximise steam production with CAP.
- Minimise steam production with CAP.

The first method to reduce steam production is to alter the temperatures entering and exiting the reformer. Figure 3 illustrates the typical temperatures entering and exiting the reformer for a maximum steam export plant. To reduce the steam production, the inlet temperature to the reformer can be raised to approximately 1100 °F. This change decreases the required firing in the reformer as well as reduces the duty in the convection section for steam production. The exit temperature of the reformer can be lowered to approximately 1550 °F. This change also reduces the absorbed duty of the reformer which reduces the required firing. However, lowering the outlet temperature of the reformer also reduces the hydrogen production. Additional throughput is required to maintain hydrogen production. Figure 4 illustrates the temperature options for this method.

The second method to reduce steam production is to add one coil of CAP. In this scenario, the boiler feedwater preheat coil is replaced with a plate type recuperative convective coil for the preheating of combustion air. Preheating of the combustion air lowers the required firing in the reformer and also replaces duty that was used

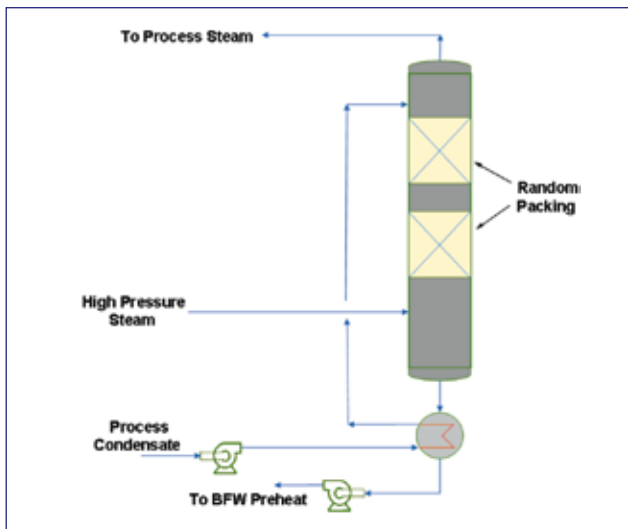


Figure 7. High pressure stripper.

Existing plant configuration case	Prereformer natural gas	Prereformer naptha
Capacity increase, %	5	10
Utilities, units/M ft ³ H ₂		
Feed, million btu LHV	0.346	0.356
Fuel, million btu LHV	0.091	0.130
Feed and fuel, million btu LHV	0.437	0.485
Export steam, lb	74	90
BFW, lb	105	133

Plant configuration case	Max steam	Reduced steam	CAP-1 coil	CAP-2 coils
Utilities, units/M ft ³ H ₂				
Feed, million btu LHV	0.346	0.373	0.346	0.346
Fuel, million btu LHV	0.119	0.064	0.070	0.050
Feed and fuel, million btu LHV	0.465	0.438	0.416	0.393
Export steam, lb	97	71	62	42
BFW, lb	128	103	92	72

previously for boiler feedwater preheating. This method is usually combined with an increase in the process inlet temperature to the reformer. Figure 5 illustrates this method. One coil of CAP would typically produce a combustion air temperature of approximately 450 °F. This temperature is dependent on the steam production pressure and the desired stack outlet temperature.

The third method to reduce steam production is to add two coils of CAP. The second coil is typically placed before the steam generation coil in the convection section. Since the flue gas temperature in this zone is higher, it allows higher preheat temperatures for the combustion air. Typically, this method is combined with an increase in the process inlet temperature to the reformer. Figure 6 illustrates this method. Two coils of CAP could typically produce a combustion air temperature in the range of 500 - 900 °F.

The expected plant utilities for these three methods are compared to a maximum steam plant's utilities in

Table 3. As can be seen, the export steam quantity can be customised for a given situation.

EXPORT STEAM PURITY

In the majority of hydrogen plants today, the process condensate is used as makeup water to the steam generation system of the plant. The process condensate from a typical hydrogen plant contains impurities such as dissolved gases, ammonia and methanol. The dissolved gases consist of the components found in the syngas downstream of the reformer (CO, CO₂, H₂, N₂, CH₄). Ammonia is formed in the reformer of a hydrogen plant. The amount of ammonia production is dependent on the amount of nitrogen in the feedstock. Methanol is produced as a byproduct in the shift converters. The formation of methanol is equilibrium based for a high temperature shift converter but is also related to the catalyst characteristics and kinetics of the low temperature shift converter.

The dissolved gases have historically been stripped from the condensate via a deaerator, which would also strip a portion of the ammonia and methanol. Therefore, the deaerator vent would contain methanol and ammonia as emissions. However, some quantity of the methanol and ammonia may not be stripped from the condensate and may end up in the export steam of the plant. These components could be detrimental to downstream processes that utilise the steam and could affect additional downstream emission points.

One solution that can be used to produce an export steam with low ppm levels of ammonia and methanol is the use of a high pressure stripper. In this scenario, the process condensate is stripped in a high pressure column that utilises packed beds for additional contact.

Figure 7 illustrates this design scheme. The majority of the ammonia and methanol are stripped from the condensate. The contaminants are recycled back to the reformer in the form of process steam. The ammonia/methanol system reaches a state of equilibrium. The ammonia and methanol are partially destroyed due to the high temperatures of the reformer and their production is limited due to the equilibrium nature of the reactions that form them. This solution is advantageous to refiners as it also eliminates the methanol emission from the deaerator vent.

CONCLUSION

Hydrogen continues to be an essential component in refinery operations due to the use of heavier crudes and lower sulfur specifications for transportation fuels. Therefore, it is important to provide the refiner with a hydrogen plant that not only meets their hydrogen demand but also their steam and emission demands. The proper process design of a hydrogen plant must incorporate these issues in addition to the economic considerations associated with each refinery.

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