

PROCESS OPTIMIZATION

Optimize your hydrogen plant operations

Proper unit monitoring is necessary to achieve this goal

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Global demand for hydrogen (H_2) continues to grow due to heavy crude processing and stricter governmental mandates to reduce sulfur content in transportation fuels. This has led to increased H_2 requirements for both hydrotreating and hydrocracking operations within a refinery (Fig. 1). Thus, it is important for refiners to maintain or, in some cases, increase H_2 production from existing units. Proper plant monitoring is essential to achieving this objective. There are several areas to focus on when monitoring H_2 plant performance, including feedstock, catalyst, reformer and the steam system.

FEEDSTOCK

Analyses should be regularly conducted, as it is important to know stream content being fed to the H_2 plant. The feed's olefin and impurity content will indicate pretreatment requirements and can be used to calculate catalyst bed life.

Overall feed composition may also be used to adjust the downstream steam-to-carbon ratio. Unexpected heavy hydrocarbon liquids in a feed gas may lead to compressor damage or fouling of the feed preheat exchanger, while the amount of sulfur in the fuel will predict possible sulfur dew point corrosion in the waste heat recovery unit.

CATALYST MONITORING

Proper catalyst performance is an important aspect in any H_2 plant, and catalyst activity should be monitored in various operations within the H_2 unit.

Hydrotreater and desulfurizers. Sulfur compounds are a poison to the downstream reforming and shift conversion catalysts, and unsaturated hydrocarbons can cause carbon deposition on the downstream reforming catalyst. Thus, a hydrotreater is used to convert sulfur compounds to hydrogen sulfide (H_2S) and to saturate any olefins.

Since H_2 is required for this process, it is recommended to have excess H_2 in the hydrotreater effluent to ensure there is adequate hydrotreating. If there is no H_2 in the feed, a slip



FIG. 1 Typical 50 million standard cubic ft/day H_2 plant.

stream of H_2 product can be recycled for this purpose. Once the sulfur compounds have been converted to H_2S , the zinc oxide (ZnO) catalyst in the desulfurizers reacts with the H_2S to form zinc sulfide (ZnS), which is retained by the catalyst. This reaction goes to completion under ideal operating conditions and reduces the sulfur content down to a level of less than 0.1 parts per million volume (ppmv).

For a two-bed lead/lag desulfurization system, the lead bed should be allowed to operate until approximately 90% of the incoming sulfur is found in its effluent. This optimizes bed usage by allowing it to become saturated with sulfur. At this point, the lead bed should be taken out of service to have its catalyst replaced with a fresh charge. If the effluent of the lag bed shows higher levels of H_2S , which is anything greater than 0.1 ppmv, the bed may be saturated with H_2S and needs to be changed, or it could be releasing its H_2S .

If the feedstock has relatively high concentrations of H_2 and carbon dioxide (CO_2) with relatively low moisture, water (H_2O) can be generated by the reverse shift reaction:

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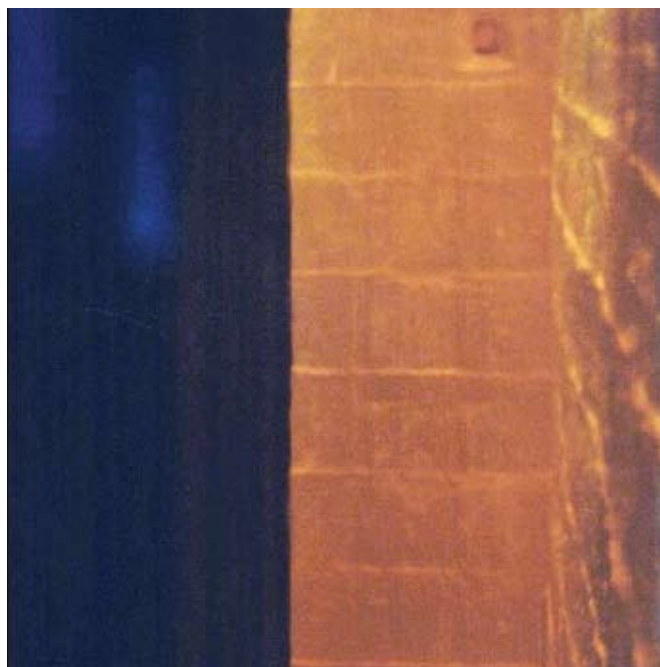
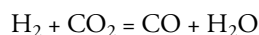


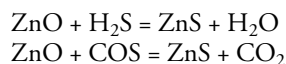
FIG. 2 Reformer tubes in normal operation (note uniform dark color).



FIG. 3 Reformer tubes exhibiting the possible effects of carbon formation, sulfur poisoning, catalyst deactivation and/or catalyst attrition.



At the same time, the desulfurization catalyst removes sulfur by the following reactions:



Thus, the presence of CO_2 or H_2O in the feedstock or the formation of H_2O in the reverse shift reaction could strip off sulfur from the desulfurization catalyst.

If sulfur compounds other than H_2S are found in the effluent, the hydrotreating catalyst may not be performing adequately. The first thing to verify would be bed operating conditions. Hydrotreating catalysts are active in the temperature range of 450°F – 800°F . In addition, pressure drop readings across the bed should be tracked over time to watch for possible catalyst attrition. If the bed pressure drop is exceeding design limits, it may be time to change the catalyst due to degradation and activity loss.

Reformer. Pressure drop measurements should be monitored across the catalyst-filled tubes in the reformer. If the pressure drop increases with time, it could be an indication that catalyst attrition or possibly carbon formation on the catalyst is taking place. The catalyst activity can be checked by utilizing a methane analyzer in the reformer effluent process gas.

The design methane slip should be maintained by slowly increasing the reformer outlet temperature as the catalyst ages. If the pressure drop increases or the activity has decreased to end-of-run catalyst conditions, it is probably time to change the reforming catalyst.

Shift converter. H_2 plants typically use a shift converter (high-temperature, medium-temperature and/or low-temperature) to increase the plant's H_2 yield by the H_2O -gas shift reaction:



The high-temperature shift catalyst is relatively durable and insensitive to poisons and chlorides. However, periodic pressure drop readings should be taken across the bed. If H_2O comes into contact with the catalyst, it can agglomerate the catalyst and form a crust on the bed, resulting in a higher pressure drop across the bed. If the activity decreases, the bed may have experienced a temperature set phenomenon. If the bed temperature is increased, maintained for more than 30 days and then decreased to the former temperature, catalyst activity will not return to previous levels.

Medium- and low-temperature shift catalysts are susceptible to poisoning by chlorides and sulfur. Upstream feed pretreatment should be monitored to ensure that only clean gas is sent to the shift converter. Another possible source of chlorides would be leaking boiler H_2O from upstream exchangers. H_2O from these sources would also damage the catalyst bed.

Periodic readings of the carbon monoxide (CO) conversion across the shift converter catalyst bed should be taken. In addition, temperature profiles across the bed should be taken. This data can be used to forecast the need for a fresh catalyst charge.

Pressure swing adsorption (PSA). This unit is used to purify H_2 . The adsorbent in the PSA is expected to last the unit's lifetime, but the product purity should be tracked to check for possible adsorbent poisoning. There are several possible scenarios for a reduction in product purity, including additional nitrogen (N_2) in the feedstock, H_2O , improper cycle time, high syngas temperature and improper valve operation:

- N_2 is one of the more difficult components to remove from syngas. If the feedstock's N_2 content increases, product purity may decrease as N_2 or additional components such as CO slip through the bed.

- Monitoring the incoming syngas composition on a regular basis is also important. Changes to the reformer or shift con-

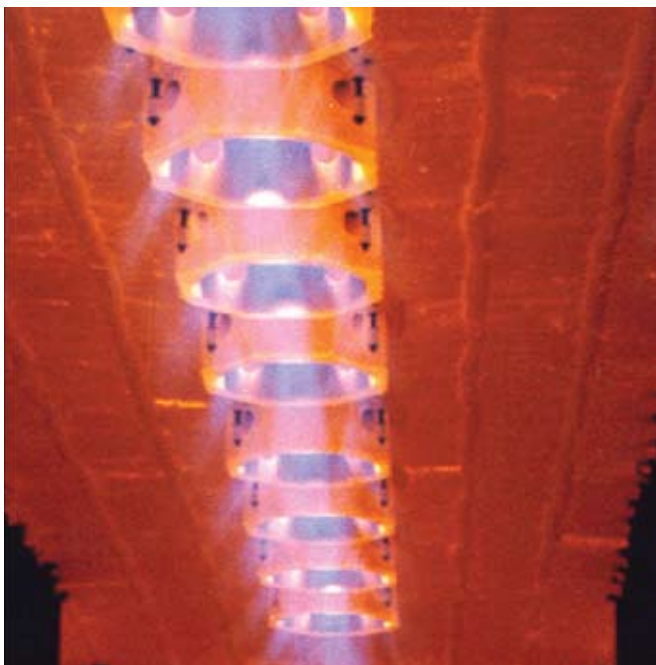


FIG. 4 Properly adjusted reformer burners in operation.



FIG. 5 Erratic flame pattern due to lack of oxygen.

verter operation can change the syngas composition and, in some instances, reduce the amount of H₂ sent to the PSA unit.

- H₂O is considered a poison to the mol sieve adsorbent in the PSA unit. If H₂O comes into contact with the mol sieve, it will likely never regain its adsorbing capacity.

- The cycle time may be too long for a given set of operating conditions. Keeping a bed online longer than design could induce component breakthrough, thus reducing product purity.

- The optimum adsorbing temperature range for the PSA is approximately 90°F–120°F. If the temperature approaches 140°F, the PSA adsorption capacity can decrease significantly. Therefore, it is crucial for the final process gas cooling to be monitored. The cooling capability of the syngas coolers can be exceeded by running a higher than design steam-to-carbon ratio, by elevated cooling H₂O and ambient air temperatures, or by surpassing the syngas design flow through the system.

Leaking or improperly operating valves on a PSA unit can prevent a bed from properly desorbing the impurities during its depressurization and repressurization steps. Since the valves on the PSA are in a highly cyclic service, the valves should be inspected annually and rebuilt every two years.

REFORMER MONITORING

Not only is this the most important piece of equipment in a H₂ plant, but it also operates in the most severe environment. It is recommended that tube wall temperature surveys of the reformer be conducted regularly. There are many devices available that can read tube wall temperatures. The industry standard, however, is an optical pyrometer.

When measuring tube wall temperatures in a furnace, the optical pyrometer should have its emissivity set to 1.0. Then for each tube wall temperature taken, a background temperature should also be recorded. To correct tube wall readings due to the effects of background radiation, the following equation can be used:

$$T_a = \left[\frac{(T_m + 460)^4 - (1 - e)(T_b + 460)^4}{e} \right]^{1/4} - 460 \quad (1)$$

where: T_a = actual tube temperature, °F
 T_m = measured tube temperature, °F
 T_b = background temperature, °F
 e = tube emissivity (0.85 is a typical value for reformer furnaces)

These temperatures should be recorded to illustrate historical trends in unit operation, and they can show possible momentary changes in unit operating conditions (Fig. 2). For instance, an increase in tube wall temperature could be the result of many different variables, including, but not limited to:

- Excessive firing
- Compositional swings in the feed or fuel
- Burner issues
- Improper flow distribution through the reformer
- Catalyst deactivation
- Catalyst attrition.

If tube discoloration or hot spots are observed, it could represent sulfur poisoning of the catalyst, carbon formation on the catalyst, catalyst attrition or possible flame impingement on the tubes (Fig. 3). Brighter areas of the tube should be watched closely to ensure they do not exceed the tube's design temperature.

All reformers are designed for specific amounts of excess oxygen to ensure complete combustion. The radiant section pressure is maintained by the fan damper setting, while the excess air is regulated by the burner air register settings for any given pressure. Most designs utilize a 10% or possibly 15% excess air requirement, depending on the composition of the makeup fuel.

However, an increase in air flow will require additional firing to keep the reformer process outlet temperature at its desired setpoint. The additional firing could increase the reformer tube wall temperatures, as well as impact the coils in the plant's waste

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heat recovery section as the flue gas flow increases. The excess air can be monitored by the oxygen analyzer in the flue section of the reformer. For most designs, the excess oxygen should be approximately 1.5% (wet basis) for a 10% excess air case and 2.2% (wet basis) for a 15% excess air case.

Conversely, a deficit of combustion air can damage the reformer. Uncombusted fuel at the burner will burn once it combines with the required amount of oxygen. This “afterburning” condition can be harmful to the reformer tubes and the downstream convection section equipment. Properly monitoring the excess oxygen can reduce over-firing in the reformer, which will decrease makeup fuel usage and, in some cases, lower elevated reformer tube wall temperatures (Fig. 4).

Regular visual inspection of the reformer radiant section should also be performed to ensure that stable flame patterns are maintained. Irregular air register settings, improper radiant section pressure and plugged burner tips may all lead to an erratic flame pattern (Fig. 5). If left unchecked, these problems could lead to flame impingement on the tubes and/or insulation—ultimately causing equipment failure.

The waste heat recovery should also be monitored. Flue gas temperature and pressure drop readings across the coils have to be checked. These data can be used to identify possible problems such as reformer tube failure, coil tube failure and coil tube fin pluggage.

The reformer and other plant equipment should be monitored during a regular plant walk-through. Hot spots or discoloration observed on the outside of the reformer may indicate a ruptured tube and/or insulation damage. Heat-sensitive paint applied to refractory-lined equipment and piping will indicate if operating conditions have exceeded design or indicate possible internal refractory damage. Visual inspection may also reveal possible maintenance and safety issues, such as flange leaks.

STEAM SYSTEM

Monitoring the steam system of an H₂ plant ensures continued stable operation. If the steam quality decreases or the steam

drum is overflowed, it can lead to solids carryover from the steam drum. These solids will plate out in the feed preheat coil and/or the steam superheat coil of the convection section and can subsequently lead to equipment failure and plant shutdown. To reduce the probability of an upset, the steam drum should be manually blown down on a regular basis. This reduces the dissolved solids and other impurities. Proper instrumentation should also be in place to alert operations of a high level in the steam drum.

Some plants use condensate from the process as boiler feed H₂O. This stream is usually degasified to remove CO₂ and other dissolved gases. The process condensate is typically acidic after being degasified. Therefore, it is important to have pH control of the boiler feed H₂O as part of the overall boiler treatment program. Additionally, the incoming boiler feed H₂O makeup should be regularly analyzed to ensure that the treatment it is receiving is adequate for the desired steam generation conditions. Inadequate treatment can lead to equipment damage. **HP**

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