Question 32: A) What are the variations of target efficiency that can be achieved in hydrogen plant operation? B) What are the operational factors that impact efficiency?

LONG (HollyFrontier Corp - Navajo)

Hydrogen plants have several areas to target, when it comes to efficiency. There are several factors that contribute to energy efficiency, and all process variables vary greatly from plant to plant.

I am going to start with the pressure swing absorber. The main target production efficiency of a hydrogen plant is the PSA (pressure swing adsorber) efficiency. This is calculated as a ratio of PSA product hydrogen to inlet PSA hydrogen. A PSA efficiency greater than 85% is considered to be adequate. Another ratio to consider is efficiency of conversion, which is the unit feedstock- to-hydrogen production ratio. This efficiency of conversion has an impact on total plant operations. Typical efficiency of conversion is 2.1 to 2.4, and variations in the plant average value can indicate operational upset. Operational impacts on PSA efficiency consist of valve switching failures and PSA feed gas. As carbon monoxide concentrations increase in feed gas, the efficiency of the PSA is reduced. Another way to measure energy efficiency is by evaluating the energy conserved per unit of hydrogen produced.

Now we move on to the reformer. The factors that can impact energy efficiency in a steam methane reformer (SMR) indicate catalyst activity, burner operations, heat lost to atmosphere, furnace operation, heating values in BTU (British thermal unit), tube life, shift equilibrium or steam-to-carbon ratio S/C, and potentially ambient temperature. A direct-monitored target for SMR consists of methane slip and outlet target temperature, which varies from plant to plant. Methane slip consists of 1.5 to 5 dry mol% and impacts heating values, in terms of BTU. Methane slip is controlled in the reformer by shifting the equilibrium or manipulating the steam-to-carbon ratio and SMR outlet temperature. Typical steam-to-carbon ratio is 2 to 3.5, but this ratio can greatly vary; again, from plant to plant.

If the reformer reaction equilibrium was shifted to increase hydrogen make, steam, or temperature, this modification will reduce methane content in the PSA off-gas in the reformer heater. As BTU values of the off-gas decrease, the secondary burners may have to be fired harder, which will require an increased amount of purchased natural gas. Increasing methane slip correlates to an increase of heating efficiency and – potentially – an increase of reformer tube life. Increasing methane slip is achieved by decreasing the steam-to-carbon ratio or decreasing reformer outlet temperature. To increase hydrogen, make, the steam-to-carbon ratio can be increased; however, impacts, heating value, and tube life should be considered. It should also be noted that operating at higher reformer temperatures will directly decrease tube life and catalyst life.

In the high-temperature shift converter, the factors that impact energy efficiency in the shift converter are the inlet temperature and catalyst activity. The shift converter should target constant inlet temperatures as temperature swings impact catalyst activity.

The exotherm across the shift converter should be monitored, as well as CO slip. Inlet temperature can be increased to maintain constant exotherm as catalyst deactivates. The local startup temperature differential is 100ºF, and a target startup run temperature is below normal. It is common to have temperature step changes that occur every six months. If a plant is short on hydrogen, the inlet temperature can be increased to promote CO conversion. The target shift converter CO slip consists of 1.5 to 3 dry mol% and indicates catalyst deactivation. This percentage depends on each facility, as well as start-of-run conditions. The operational factors that impact efficiency of carbon monoxide slip are inlet temperature and the steam-to-carbon ratio. CO slip can be decreased by increasing inlet temperature or increasing the steam-to-carbon ratio. The temperature differentials will be indicated by catalyst activity. Inlet temperature can also be increased to achieve the target temperature differential, which changes from plant to plant.

Lastly, the sulfur guard: Frontend sulfur removal has an impact on catalyst efficiency in the hydrogen plant. The sulfur component being removed is H_2S (hydrogen sulfide) and variations of mercaptans. The desulfurization previously consisted of activated carbon at ambient temperatures. Desulfurizers have used several types of media, from zinc oxide to carbon beds. The media type can impact efficiency, depending on the plant design and temperature parameters.

AGGUS (Becht Engineering Co., Inc.)

All I will add about efficiency is that a lot of the people who designed the plant – CB&I, in particular – use a plant efficiency term. It is not just the amount of natural gas you convert to hydrogen; you have to throw the steam in there as well. I do not know how many hydrogen plant unit engineers we have here. But to those who are in the audience, I want to say that it is a good exercise to add this efficiency calculation to your daily monitoring. You want to take the amount of feed on a heating value basis, the fuel that is going into the furnace, and then the difference between your energy and boiler feed water to steam, and then divide that by the hydrogen product. If you monitor those values every day, you will be doing a good job of taking care of your SMR. If only it was that simple, right?

The heavy hitter, as far as energy usage and efficiency in your SMR, is the furnace. It is just like any furnace: You want to be able to monitor your excess oxygen and excess air. So, try to maintain 2.5 to 3% excess O_2 in the furnace. What also really affects the efficiency of hydrogen recovery, as Sarah said, is the PSA. The unit temperature is easy to monitor. Make sure you are staying below 110ºF. It is your PSA. You will have best absorption efficiency if you do that. Then if you are really nice to your process control engineers, you can also play with the cycle time on the PSA. So, longer absorption times will give you less hydrogen loss and blowdown repressurization and should increase your recovery.

LEWIS LUDWIG (UNICAT Catalyst Technologies, Inc.)

I will just say that the typical minimum for steam-to-carbon ratio is 2.8. I think the panelist said 2. We think you would run into real problems running at 2. The other important point is pressure: the lower the pressure you can run on the outlet of the SMR, the better the equilibrium. However, that is usually a design consideration and not something that the operator can do with an existing SMR.

KEN CHLAPIK (Johnson Matthey)

I have a few comments. One, in tomorrow's P&P session, we will have Air Products talk to us about some of their experiences in dealing with efficiency through the decades that they have been producing hydrogen. It will be an operator's view, so you are welcome to experience that at 8:00 tomorrow morning.

We put a lengthy answer in the Answer Book, and I want to add two comments about efficiency now. We are hearing that a lot more hydrogen plant operators want to address and improve on efficiency. As you start to change some of these variables, monitoring your unit will become even more important. The steam methane reformer, as has been said by the panelists, is a critical part of that hydrogen production unit. We have been working with Daily Thermetrics over the last decade and have developed and established the application of their CatTracker® thermometry for in-tube reformer thermometry. CatTracker® for reformers gives you a "sight glass" in that reformer, with respect to the reactions that are going on in the tube. When running the reformer at these more efficient conditions, the operator can see the quick response of operating changes as they are made. This enables the operator to maintain reliability at these new conditions, which is so important in hydrogen production.

My other comment is that there are operators who are trying to look at low capital ways to address efficiency and production. Usually when you start looking at improving efficiency at low capital, this limits the number of options. Johnson Matthey has a step out reforming technology in our CATACELJMSSR, a stackable structure reactor that replaces the catalyst pellets in the reformer tube. SSR enables an operator to make a step change in efficiency through improved heat transfer, activity, and pressure drop in the reformer tube allowing the same production with 5 to 10% less firing or 5 to 10% more production prior to plant modifications.

ROBERTSON (AFPM)

Since there are no other questions, we will now conclude this Question & Answer session. Thank you, again, to all of the panelists for their informative presentations and responses today. We appreciate all of their efforts and contributions. And, thanks to all of you here today for your participation, as well.

BRANT AGGUS (Becht Engineering)

When discussing efficiencies, it is important to define the plant efficiency term. In most cases, hydrogen plant efficiency is measured by calculating the energy [BTU/scf (British thermal unit/standard cubic foot)] required to generate product hydrogen. This calculation involves adding input streams on an energy basis (feed and fuel), subtracting the output streams (export steam, other export streams, etc.), and then dividing the result by the product hydrogen flow (see equation below).

<u>Efficiency (BTU/scf) LHV:</u> (Feed + Fuel – Steam)/Hydrogen Product

The export steam term is based on the energy difference between the export steam conditions and the incoming boiler feedwater conditions. This simple formula is used by technology licensors, like CB&I, to benchmark unit performance. It is a good idea to include it in daily unit monitoring and long-term trending.

Plant configuration, particularly the addition of combustion air preheat, will affect efficiency; so, it is important to compare like-to-like.

In addition to the items Sarah covered about operational factors that impact efficiency, I will add that furnace-side operation has a large impact on overall plant efficiency. Excess air should be minimized (typically to 10%, or 3% excess O_2).

For the PSA unit, the cycle time can be maximized to decrease the hydrogen loss associated with the blowdown and repressurization steps. In addition, the inlet temperature should be maintained below 110°F for optimal performance of the unit.

SARAH LONG (HollyFrontier Corp - Navajo)

Hydrogen plants have several areas to target when it comes to efficiency. There are several factors that contribute to energy efficiency, and all process variables vary greatly from plant to plant.

Pressure Swing Adsorber (PSA)

The main target production efficiency of a hydrogen plant is the PSA efficiency. PSA efficiency is calculated as a ratio of PSA product hydrogen to inlet PSA hydrogen. A PSA efficiency greater than 85% is considered to be adequate. Another ratio to consider is efficiency of conversion, which is the unit feedstock-to-hydrogen production ratio. The efficiency of conversion has an impact on total plant operations. Typical efficiency of conversion is from 2.1 to 2.4, and variations in the plant average value can indicate operational upset. Operational impacts on PSA efficiency consists of valve switching failures and PSA feed gas. As carbon monoxide (CO) concentrations increase in the feed gas, the PSA efficiency reduces.

Another way to measure energy efficiency is by evaluating the energy consumed per unit of hydrogen produced.

Reformer

The factors that impact energy efficiency in the steam methane reformer (SMR) include catalyst activity, burner operation, heat loss to atmosphere, furnace operation, heating values (BTU), tube life, shift equilibrium or steam-to-carbon ratio (S-C), and potentially ambient temperatures. A direct monitoring target for the SMR consists of methane slip and outlet temperature, which vary from plant to plant. Methane slip consists of 1.5 to 5 mol% dry and impacts heating values, in terms of BTU. Methane slip is controlled in the reformer by shifting the equilibrium or by manipulating S-C and SMR outlet temperature.

Typical S-C is 2 to 3.5, but it can greatly vary from plant to plant.

If reformer reaction equilibrium was shifted to increase hydrogen make, the result will also be in a reduction in methane content in the reformer heater PSA off gas. As BTU value of off gas decreases, the secondary burners may have to be fired harder. This shift to increase hydrogen make requires an increased amount of purchased natural gas. Increasing methane slip correlates to an increase of heating efficiency and potentially an increase of reformer tube life. Increasing methane slip is achieved by decreasing S-C ratio or decreasing reformer outlet temperature (temperature is in range). To increase hydrogen, make, S-C can be increased, but increasing hydrogen can have an impact on heating values and tube life should be considered. It should be noted that operating at higher reformer temperatures directionally decreases tube life and catalyst life.

High-Temperature Shift Converter (HTSC)

The factors that impact energy efficiency in the shift converter are the inlet temperature and catalyst activity. Shift converters should target constant inlet temperatures as temperature swings impact catalyst activity. The exotherm across the shift converter should be monitored, as well as the CO slip. Inlet temperature can be increased to maintain a constant exotherm as catalyst deactivates. The local startup dT (delta T; temperature differential) is 100°F, and a target SOR (start-of-run) temperature is below normal. It is common to have temperature step changes occur every six months. If the plant is short on H2, the inlet temperature can be increased to promote CO conversion. The target shift converter CO slip consists of 1.5 to 3 dry mol% and indicates catalyst deactivation. These process conditions depend on each facility and on SOR conditions. The operational factors that impact this efficiency or CO slip are inlet temperature and S-C ratio. CO slip can be decreased by increasing inlet temperature or increasing S-C ratio. The temperature differentials will indicate catalyst activity. Inlet temperature can also be increased to achieve the target temperature differential, which changes from plant to plant.

Sulfur Guard

Front-end sulfur removal has an impact on catalyst efficiency in the hydrogen plants. The sulfur component being removed is H2S and variations of mercaptans. The desulfurizers previously consisted of activated carbon beds at ambient temperatures. Desulfurizers have used several types of media from zinc oxide to carbon beds. The media type can impact efficiency depending on plant design and temperature parameters. Desulfurizers have gone into the direction of a variation of zinc oxide catalyst. Zinc oxide catalyst can increase carbonyl sulfide removal, along with increase efficiency by decreasing heat requirements, with regard to CSO. To increase sulfur removal efficiency, a layer of HDS catalyst can provide increased removal of organic sulfur compounds.

ABIGAIL SUP (Johnson Matthey Inc.)

Part A: Modern hydrogen plants are around 5 to10% more efficient than those built in the 1990s. These improvements have been achieved through flowsheet modifications such as pre- and post-reforming [for example, a GHR (gas-heated reformer), MTS (medium-temperature shift), pressure swing absorption (PSA), and the use of combustion air preheat, as well as advancements in catalyst technology (e.g., Johnson Matthey’s CATACEL SSR). Modern flowsheets can be very efficient with estimates approaching the theoretical minimum amount of energy required to produce a unit of hydrogen with values of just over 300 BTU/scf of hydrogen (taking credit for steam export) being quoted for some plants. Though for typical hydrogen plants in operation today, energy efficiency values generally are in the range of 350 to 425 BTU/scf of hydrogen.

The thermal efficiency of a hydrogen plant will depend on the:

- Quantity of heat recovered from the process gas.
- Amount of heat recovered from the flue gas.
- Total heat loss to the environment (function of size, design, condition of reformer).
- CH4 (methane) slip from the reforming section (impacted by steam-to-carbon (S-C) ratio, catalyst selection and age, reformer balancing, reformer design, material limitations, etc.).

- CO slip from the WGS (wet gas scrubber section) (catalyst selection and age, configuration: HTS, MTS, HTS+LTS, WHB size); and/or,
- Downstream purification design (PSA versus CO2 removal/methanation, PSA efficiency).

For new plant designs, improvements in energy efficiency are generally evaluated against any increases in capex (capital expense) and/or opex (operating expense) required. For example, an MTS flowsheet may achieve a lower CO slip compared to an HTS, but the value of the additional hydrogen may not be able to off-set the additional capex required, such as the cost of a larger waste heat boiler (WHB), a more expensive catalyst, larger catalyst volumes, greater susceptibility to poisoning, and a reduction system.

The optimal plant efficiency for any plant will vary due to factors such as the:

- Cost of feed,

- Cost of fuel,
- Cost of power, and
- Value of steam.

There are also numerous other factors that impact plant design, which then affect the efficiency of the plant. Some of these factors include plant scale, feedstock flexibility, turnaround schedule, payback targets, compression requirements, pressure drop versus vessel cost.

Part B: A hydrogen plant is designed with a specified arrangement for heat integration which sets the theoretical limit for the plant's efficiency. The operational factors that provide the largest impact in moving a plant towards this limit include the following:

- Plant rate: Generally, the plant is less efficient at lower rates due to the relatively higher heat losses and difficulty in maintaining good distribution, which can result in a higher CH4 slip or require a higher S-C.

- Reformer balance: maintenance of burners, adjustment of air dampers and fuel pressure, condition of tunnels, etc.

- Ability to properly identify and measure plant bottlenecks; e.g., accuracy of tubewall temperatures (TWTs), sampling analysis, instrumentation, etc.

- Determining the optimum steam-to-carbon ratio: reducing steam requirement without compromising catalyst life/performance.

- Minimizing excess oxygen: decreasing fuel usage while still maintaining reliable operation.

- Optimization of inlet temperatures to the HTS/MTS/LTS bed for minimum CO slip.

- Monitoring of purification section to prevent poisoning of downstream units, which can significantly impair the ability to run at optimal operating conditions.

- Startup and shutdown procedures, which can affect catalyst life and performance.

- Heat loss: refractory condition, insulation, wind shield, etc.

- Catalyst selection, which affects CH4 slip over life of charge, heat transfer, pressure drop, carbon formation, etc.

- Routine cleaning and maintenance of heat exchangers.

When pursuing improvements in energy efficiency, it is important to consider the impact of any proposed changes to ensure continued safe and reliable operation. For example, reducing the steam-to-carbon ratio too far could result in carbon formation on the reforming catalyst or over-reduction of the HTS catalyst. This change to the process could adversely impact the plant's long-term efficiency or its ability to achieve maximum rates prior to the next scheduled changeout.

For this reason, daily plant monitoring becomes more critical when pushing a plant towards optimal efficiency because the plant is most efficient when it is running closer to its limits. To safely and reliably maintain operation at optimal conditions, operators need to be able to respond to any changes or deviations that could move the plant outside of designated limits (e.g., TWTs, carbon forming conditions, minimum excess oxygen, etc.)

One monitoring tool that can help in this area is Daily Thermetric’s CatTracker® technology, which can be placed directly inside a reformer tube with catalyst loaded around it is using Johnson Matthey’s proprietary loading method. CatTrackers® can measure the process gas down the length of the tube, giving operators continuous feedback on the reformer’s condition. This information can enable operators to detect poisoning, carbon formation, or other issues before they significantly affect performance.

As noted in the list above, catalyst selection also provides an opportunity to relieve operational constraints and improve a plant’s efficiency with minimal capital investment. For example, Johnson Matthey’s promoted reforming catalyst, KATALCO 25-4Q, allows operators to run at lower steam-to-carbon ratios – compared to traditional catalysts – without the risk of carbon formation at more severe conditions. Also, Johnson Matthey’s CATACELSSR can provide a step change in performance by lowering fuel usage for the same capacity, decreasing TWTs allowing the plant to run more aggressively, reducing pressure drop across the reformer, and even allowing an increase in capacity, if needed.

When searching for efficiency improvement opportunities, it is recommended to seek input from a catalyst vendor, such as Johnson Matthey. Johnson Matthey has the tools, modelling capabilities, and knowhow to help operators identify improvement opportunities, evaluate their relative impact/benefit, and provide recommendations that enable customers to improve their overall efficiency. This expertise includes onsite reformer surveys and data analysis, as well as kinetic modelling of the unit operations to predict the impact of operational changes. For more capital-intensive improvements, such as looking for step changes in capacity and efficiency, Johnson Matthey conducts revamp studies.

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