Worldwide hydrogen demand continues to grow in today’s refineries as a result of two main drivers. One, governmental regulations continue to reduce the accepted sulfur levels in gasoline and diesel transportation fuels. Two, many refiners are moving to heavier crude slates that typically contain higher levels of sulfur and nitrogen species. Because these two drivers place additional requirements on refiners’ hydrotreating and hydrocracking capabilities, more hydrogen is needed to feed these essential processes.

While hydrogen is generated in certain refinery processes, refiners are increasingly finding it necessary to generate hydrogen in greater quantities. Steam methane reforming has been the typical technology of choice for the production of on-purpose hydrogen in a refinery, with natural gas or...
naphtha serving as the traditional feedstocks to the steam
methane reformer (SMR). However, with the increasing
demand for hydrogen, refiners have begun to evaluate the
use of various refinery offgases as additional feedstocks
to the hydrogen plant.

Refinery offgases present an economic substitute for
the primary feedstock to the hydrogen plant. These
offgases are typically high in hydrogen content and thus
allow the refiner to reduce the amount of primary feed-
stock and fuel to the SMR. The refinery can also benefit
from an emissions standpoint since the firing in the SMR
has been decreased, and the refinery may be able to
reduce the flare load.

However, the use of refinery offgases as additional feed-
stocks to a hydrogen plant must be evaluated carefully due
to their flowrate and compositional variations. The primary
concern with these fluctuations in composition and flow
is the ability of the plant to handle these changes without
jeopardising the operation of the SMR. Various solutions are
available for handling these changes, including feed pretreat-
ment, monitoring of the feedstocks, and the use of a prere-
former.

**Feed pretreatment**

Refinery offgas feeds often contain components that can be
detrimental to the operation of the SMR. These offgases typi-
cally consist of hydrogen, carbon monoxide, carbon dioxide,
nitrogen, hydrocarbons through octane, various sulfur com-
pounds, chlorides and olefins. The components that could
be harmful to downstream plant operations, if not dealt with
properly, are the sulfur compounds, the chlorides and the
olefins.

**Sulfur**

Sulfur is a poison to the reforming catalyst and will result in
a reduction of catalyst activity. If this situation is not rectified,
the end result can be excessive reformer tube wall tempera-
tures, which reduce tube life and can cause potential tube
ruptures. Pretreatment, in the form of hydrotreating and des
sulfurisation, can prolong catalyst activity and tube life.

Hydrotreating is required for the feedstock when it con-
tains sulfur compounds that are heavier than propyl mercap-
тан. Hydrotreating converts the sulfur compounds to
hydrogen sulfide. Hydrogen sulfide is then easily removed
in the downstream desulphurisers, where the zinc oxide cat-
alyst reacts with the sulfur to form zinc sulfide. The reac-
tion goes to completion and removes all sulfur down to
less than 0.1 ppmv. The desulphurisation system typically
consists of two vessels piped in a lead/lag configuration.
This configuration allows the operator to replace the des-
sulfurisation catalyst while the plant is online (Figure 1).
Depending on the amount of sulfur in the feed stream, an
economic evaluation may be required to decide if addi-
tional pretreatment is necessary.

**Chlorides**

Chlorides are a mild poison to the SMR catalyst and a
major poison to low temperature shift catalyst. Therefore,
a guard bed should be used to remove chlorides ahead of
the reformer. For effective removal, the chlorides should be
in the hydrochloride form. For that reason, the guard bed
is typically placed downstream of the hydrotreater. How-
ever, the guard bed must also be placed before the desul-
furisers. The zinc oxide adsorbent in the desulphurisers will
pick up chlorides in the form of zinc chloride. Since oper-
ating temperatures are in excess of 500 °F, the zinc chlo-
ride would be volatile and would desorb from the bed and
to the plant. Therefore, proper placement of the chloride
guard bed is imperative. The guard bed can be placed at
the bottom of the hydrotreater or at the top of the desul-
furisers (Figure 2).

**Olefins**

Refinery offgas streams often contain olefins that must be
hydrogenated to prevent carbon deposition on the reforming
reactor. Hydrogenation of olefins can result in a sig-
nificant temperature rise across the hydrotreater. This
temperature rise is dependent on the type and quantity
of olefins, as well as the heat capacity of the feed stream.
In addition, if oxygen is present in the offgas, the tem-
perature rise will be significantly greater. The maximum
temperature rise that can be tolerated is approximately
250 °F. This would correspond to a 500 °F inlet tempera-
ture to the hydrotreater and a 750 °F outlet temperature.
The inlet temperature of 500 °F is a preferred minimum

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**Figure 2. Chloride guard beds added to the pretreatment section of the hydrogen plant.**

**Figure 3. Hydrotreater recycle loop for reduction of temperature rise due to olefins.**

**Figure 4. Addition of a hydrocarbon analyser for steam/carbon ratio control.**
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temperature to ensure good hydrotreating catalyst activity. If the temperature rise is greater than 250 °F, a heat sink must be provided to lower the temperature rise.

One solution to decrease the temperature rise is to recycle a cooled portion of the hydrotreater effluent back to the inlet of the hydrotreater. Figure 3 illustrates this approach. A compressor or blower must be employed to bring the effluent pressure back to that of the inlet gas stream entering the hydrotreater. Another option is to recycle the hydrotreater effluent to the inlet of the feed preheater. By using a bypass with the feed preheater, the hydrotreater inlet temperature can be controlled.

**Monitoring the feedstocks**

Controlling the steam to hydrocarbon-carbon ratio (Stm/HC-C) is crucial in the operation of a hydrogen plant. One, it helps in the prevention of carbon formation in the reformer tubes, and two, it controls the efficiency of the plant. With natural gas feed only, the Stm/HC-C ratio is relatively easy to control. However, when multiple feeds are present, it becomes more difficult due to the compositional and flow swings from multiple sources.

The typical hydrogen plant utilizes flow control valves on the natural gas feed and process steam. Since natural gas normally has a minimal compositional swing, the natural gas flow control valve can be programmed on a flow basis to adjust the process steam control valve. This assumes there is no compositional change in the natural gas. For a plant with a refinery gas feed or multiple feeds, the typical flow control setup will not be as effective.

One method of improving the accuracy of the flow control setup is to use a gas chromatography (GC) analyser, which can be installed on the gas line directly. The GC analyser provides a composition of the gas by separating it into its individual components. While the GC analyser is accurate, the lag time associated with the analysis may be a problem where the feedstock composition changes rapidly.

Another way to increase accuracy is to install a hydrocarbon analyser on either the combined feeds or on each of the individual feeds. The hydrocarbon analyser uses a flame ionisation detector (FID) to determine the methane equivalent percentage of hydrocarbons. While the hydrocarbon analyser will provide a faster response, it is not recommended for direct input to the Stm/HC-C control. By not using direct input, steady feed flow control can be achieved without the influence of small compositional changes or analyser malfunction. It is recommended that an alarm be used to alert operations when a large discrepancy exists between the analyser reading and the fixed carbon number for the feedstock. Then adjustments can be made as needed, resulting in a more stable operation of the plant (Figure 4).

**Prereforming**

At present, typical steam methane reforming catalysts can operate with feedstocks, such as natural gas and butane, without the necessity of a catalyst change out. Heavier components that can be found in refinery offgas streams, such as pentane, are a concern to the typical reforming catalyst. Heavier components can crack and lay down carbon on the reformer catalyst, which will result in catalyst deactivation and shorter tube life. One method that can be employed to cope with this possibility, as well as the compositional swings in the offgas streams, is the addition of an adiabatic prereformer.

The prereformer functions as a guard bed for the primary SMR. A prereformer partially reforms the feedstock to produce a methane/syngas mixture. Since methane is the only hydrocarbon that is sent on to the primary reformer, the primary reformer can operate with the more active reforming catalyst. In addition, the primary reformer would not see the fluctuations in hydrocarbon content of the feedstocks. This would ensure a more stable operation of the primary reformer.

The prereformer is a vessel loaded with a highly active reforming catalyst that is placed before the primary reformer (Figure 5). The prereforming catalyst is easily poisoned by sulfur and thus acts as a guard bed for the primary reformer.

The decision to include a prereformer in the design of a hydrogen plant should be made using both technical and economic considerations. The cost of the prereformer and the additional convective coil for reheating the prereformer effluent must be factored into the decision making process. In addition, the prereforming catalyst, which can cost three times as much as a traditional reforming catalyst and has an expected catalyst life of approximately three years, two years less than the expected life for traditional reforming catalysts, should also be considered.

Likewise, the plant’s utilities should be factored into the economic considerations. Steam production of the plant will decrease, as well as fuel usage due to the addition of a prereformer. One other consideration is the effect of the prereformer on the capacity of an existing plant. With the reheating of the prereformer effluent, the reformer will be able to handle an increase in the feed rate; thereby, increasing the reforming capacity of the hydrogen plant. The plant capacity increase will vary depending on various factors that exceed the scope of this discussion.

**Conclusion**

Hydrogen will continue to be a vital component in the operation of refineries due to the use of heavier crudes, increasingly strict sulfur regulations for fuels, and more stringent emission limits for flares. These reasons have compelled refiners to investigate the use of refinery offgases as feedstocks to the hydrogen plant. Although there are challenges with these refinery offgases, there are solutions that can be implemented to aid refiners in utilising offgases as feedstocks to the hydrogen plant, thereby allowing them to generate hydrogen in greater quantities.

**References**