Features in Ammonia Plant Design for Maximising Heavy Water Production

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1.0 Introduction

Presently Heavy Water Plants in India are built either on Mono Thermal NH_3-H_2 exchange or Bi-thermal H_2S-H_2O exchange technology.

Several plants on NH_3-H_2 exchange are now successfully operating in India. Some more plants are planned. Large capacity & high stream efficiency of Ammonia plant favours economics of Heavy Water Plant operation.

2.0 Performance of Heavy Water Plants

Earlier Heavy Water plants suffered much from non-availability of gas at rated capacity. Thanks now to the improved and established technology of large single stream ammonia plants and availability of uninterrupted power supply from the captive power plants, very high stream efficiency is assured. Experience of the recently gas based built plants is that they operate consistently at near or above rated capacity. Purity of the syn. gas is also assured by use of ultra methanation Catalyst. It is however the D_2-concentration and pressure of the syn. gas which have now emerged as major constraints on HWP performance.

The O_2 concentration in the gas is far below the O_2-content in the feed gas/raw-water and the pressure of the gas as well is generally below the specified normal operating pressure. Before further discussing these variables, it is necessary to briefly describe the Ammonia Plant Process & its linkage with HWP.

3.0 Ammonia Process Integration with HWP

The modern Ammonia Plants are based on high temperature catalytic steam - hydrocarbon reformation route. The feedstock hydrocarbon is natural gas or associated gas containing mainly methane with a deuterium content of 120-130 ppm. The reaction steam is generated from naturally occuring water containing about 140-150 ppm of deuterium.

The reformed gas, containing mainly hydrogen; carbon dioxide and carbon monoxide, is passed through CO-shift converters wherein carbon monoxide reacts with steam to yield hydrogen and carbon dioxide. The shift conversion reaction takes place in two or three stages operating at varying temperatures. The converted gas is cooled and the process condensate is separated out prior to CO_2-removal. The decarbonated gas is finally passed through a methanation reactor to convert the residual CO and CO_2 to methane and obtain make-up synthesis gas mixture containing about 75% H_2 and 25% N_2 which is compressed in a make-up gas compressor to suit the requirements of ammonia synthesis loop. The compressed make-up synthesis gas is utilized as process feed in

Heavy Water Plant for isotopic exchange between H_2 and liquid NH_3 lean in deuterium. This results in enrichment of ammonia and depletion of hydrogen with respect to their deuterium concentration. The deuterium content of synthesis gas mainly depends on the content of the same in the feed hydrocarbon and process steam used for its generation. A booster compressor is provided in Heavy Water Plant to take care of the pressure drop of the gas in the isotopic exchange column and associated equipment and piping loop. The return make-up synthesis gas, depleted in deuterium, joins the recycle gas stream to recycle gas compressor in Ammonia plant.

The process condensate, separated from the converted gas as mentioned earlier, is stripped off the impurities like CO_2, methanol, ammonia etc. with steam before it goes to D.M. Water plant and mixed with turbine condensate, steam condensate and make-up raw water.

4.0 Sources of D_2 loss in Ammonia Plants

It is established that transfer of D_2 to steam from the process gas takes place in the shift conversion section resulting in short-fall of D_2 content in synthesis gas compared to the stoichiometric value. As can be seen from the following equilibrium equation, this isotopic transfer is more favourable at lower temperatures.

$$k = e^{464/T - 0.27}$$

where

k = co-efficient of distribution of D_2 between water and hydrogen.
T = Temperature, °K

At the low shift converter exit at 197°C, the k-value is 2.04. Bulk of the process condensate is separated after shift conversion and from the overhead CO_2 condenser. Some D_2 rich water vapour is carried by the synthesis gas as well as CO_2 gas and is collected after methanated gas water cooler and CO_2 compressor water cooler respectively. The loss of D_2 or depletion of D_2 in synthesis gas can be to the extent of 30% depending upon the extent of utilisation of the D_2 rich process condensate in the process stream.

Any loss or dilution of D_2-rich process condensate, therefore, is the principal factor accountable for the lower D_2 content in the synthesis gas. The loss/dilution of the D_2-rich process condensate can be attributed to the following reasons:

i) Mixing of process condensate with turbine condensate, steam condensate and make-up raw water;
ii) Back-washing & rinsing in D.M. Water Plant;
iii) Steam export from Ammonia plant;
iv) Occasional draining of condensate and venting of steam;
v) Mal-functioning of steam traps;
vi) Steam leakage from joints and valve glands;
vii) Boiler blow-down;
viii) Deaerator vent;
ix) Loss of compressor (syn.gas and CO_2) interstage cooler condensate.
etc.,etc.

5.0 D_2 Conservation Schemes

Two schemes are available for total D_2 conservation, namely Process Condensate stripping and dedicated boiler. In both the schemes entire D_2 rich process condensate is recycled within the front end of the plant thus enabling conservation of entire D_2 content of Hydrocarbon feed gas and raw water.

1. Process Condensate Stripping :

The scheme envisages the installation of a steam - process condensate stripper at a pressure suitable to match the requirement of primary reformer instead of the low pressure one as in the existing Ammonia plants. The entire D_2-rich process condensate is fed to this stripper and stripped with superheated steam from the extraction of syn. gas compressor steam turbine. The D_2-enriched steam exit the stripper is utilized as the process steam in the primary reformer. The depleted process condensate after polishing in a mixed bed ion exchanger is used as Boiler Feed Water.

2. Dedicated Boiler :

The entire D_2 rich process condensate is fed to boiler to generate the MP steam which in turn shall be utilised in the primary reformer. The balance quantity of steam for primary reformer is drawn from the existing MP Grid to meet the total.

Since the entire process condensate is recycled back into the process system, there is no dilution with respect to D_2 and D_2 concentration in Syn. gas to Heavy Water Plant is achieved to maximum possible level.

In both the schemes the investment is recovered in about 3 to 4 months time considering the present level of D_2 content.

Both the schemes are suitable for retrofit in existing Ammonia Plants coupled to Heavy Water Plants. For new plants, Process Condensate Stripping is recommended.

6.0 Other Design Features

In addition to what has been discussed above, there are certain other features also which should be reviewed and finalized at the stage of basic design of Ammonia Plant so that the interests of Heavy Water Plant are safe-guarded. These are mainly:

i) Operating pressure of Ammonia synthesis loop;
ii) Introduction of purge gas recovery unit;
iii) Selection of CO_2 - removal process;
iv) Selection of Make-up gas/Recycle gas compressor;
v) Provision of ultra-methanator.

Presently the trend is towards operation of ammonia synthesis loop at a lower pressure. There is also a move towards introducing the Purge gas recovery unit. Both of these are, no doubt, helpful in reducing the specific energy consumption for ammonia production. But they act against the basic process needs of the Heavy Water Plant.

It is, therefore, necessary to optimize the NH_3 syn. loop design for higher pressure commensurate with the needs of HWP without sacrificing NH_3 plant economics. H_2 recovered from PGR shall be introduced into the loop through a separate booster compressor. CO_2-removal process design should aim at avoiding the dilution of D_2 in the process condensate by minimizing the use of any import steam. Similarly, proper selection of Make-up gas/Recycle gas compression system can prevent the mixing of recycle gas with the make-up synthesis gas (which is the feed for heavy water production) and thus check any dilution of D_2-content in the same.

7.0 Conclusion

Whenever an ammonia plant is linked with heavy water production, it is suggested that at the design stage itself, a system should be foreseen for total conservation of D_2 in synthesis gas and zero D_2 loss. The process should ensure recycle of D_2 rich condensate within the front end. This alone would be the single most important factor for improving heavy water production. Similarly synthesis loop pressure should be chosen keeping in view the interests of HWP. PDIL has a package for total D_2 conservation. With vast experience of engineering of NH_3 & HWP plants, it is favourably placed for integrating HWP requirements at the design stage itself.