Optimised hydrogen production by steam reforming: part I

Modelling optimisation of process and design parameters for minimising natural gas consumption in hydrogen production by steam reforming

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Hydrogen is a particularly important feedstock in refineries because of stringent environmental legislation for producing low-sulphur gasoline and diesel fuels. The refinery hydrogen requirement is fulfilled through the route of steam methane reforming (SMR) of natural gas. SMR is a highly energy-intensive technology and this energy requirement can be minimised by combining various reforming techniques. In this article, process optimisation of the hydrogen plant is carried out to minimise natural gas consumption by considering operating parameters such as the steam-to-carbon ratio, various reactor configurations, methane slip, choice of product purification step, and natural gas composition in a conventional SMR process.

In a second article to follow, new process schemes incorporating an autothermal reformer (ATR) and a heat exchange reformer (in series and parallel combination with the ATR) offered by licensors are evaluated and compared with the conventional process. It has

been observed that the new schemes, from the point of view of natural gas consumption, are more beneficial compared with the conventional process but at a cost of lower steam production from the hydrogen plant. Hence, where the natural gas price is substantial and dominates the plant operating cost, the new process scheme should be utilised.

Along with increased hydrogen consumption for deeper hydrotreating, additional hydrogen is needed for processing heavier and higher sulphur crude slates. In many refineries, hydroprocessing capacity and the associated hydrogen network limits refinery throughput and operating margins. Furthermore, higher hydrogen purities within the refinery network are becoming more important to boost hydrotreater capacity, achieve product value improvements and lengthen catalyst life cycles. Improved hydrogen utilisation and expanded or new sources for refinery hydrogen and hydrogen purity optimisation are now required to meet the needs of the future

market for transportation fuels and the drive towards higher refinery profitability.

A variety of process technologies can be used for hydrogen production, including steam reforming, cracking, gasification and electrolysis. The choice depends on the scale of production required and the cost of available feedstocks.

For large-scale production, the steam reforming of natural gas has become the preferred solution. In some cases, partial oxidation has also been used, particularly where heavy oil is available at low cost. However, oxygen is then required and the capital cost of producing oxygen plant makes partial oxidation expensive. On the other hand, the steam reforming of natural gas offers an efficient, economical and widely used process for hydrogen production, and provides near- and mid-term energy security and environmental benefits. The efficiency of the steam reforming process is about 65% to 75%, among the highest of current commercially available production methods.
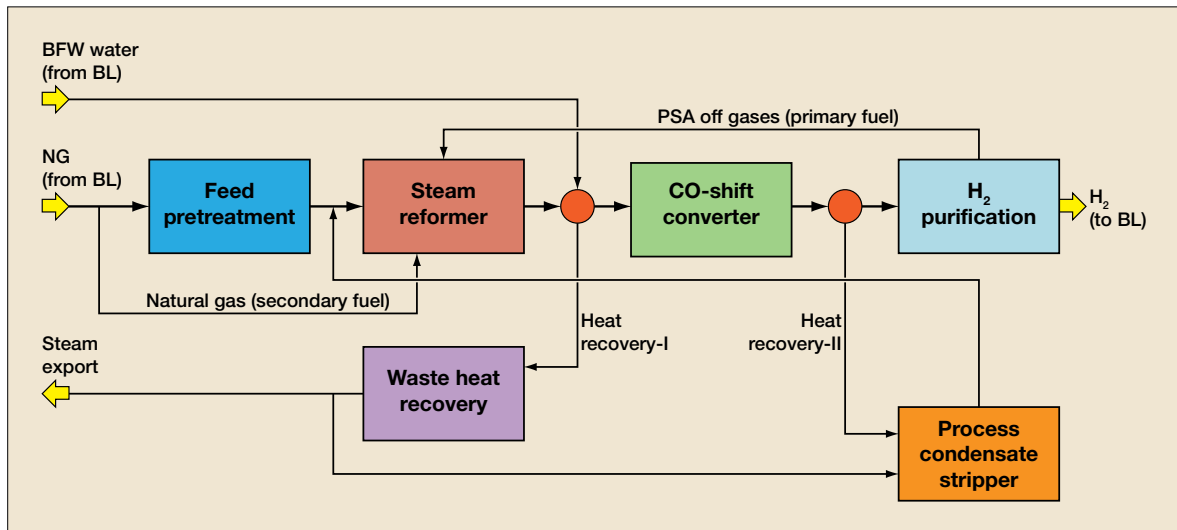
Figure 1 Typical steam methane reformed hydrogen plant block diagram

The SMR process is divided into sections: feedstock purification for the removal of sulphur and other impurities; steam reforming for synthesis gas generation; shift conversion/carbon monoxide removal; and hydrogen purification. A general block diagram with natural gas as the feedstock is shown in Figure 1.

Natural gas feed is preheated in coils in the waste heat section of the reformer, and sulphur is removed over a zinc oxide catalyst. Process steam is added, and the mixture of natural gas and steam is further preheated before entering the tubular reformer. Here, conversion to equilibrium of hydrocarbons to hydrogen, carbon monoxide and carbon dioxide takes place over a nickel-based reforming catalyst. The gas exits the reformer and is cooled by steam production before entering the shift converter. Over the shift catalyst more hydrogen is produced by converting carbon monoxide and steam to carbon dioxide and hydrogen. The shifted gas

is cooled further to an ambient temperature before entering the pressure swing adsorption (PSA) unit. High-purity hydrogen product is obtained, and the off-gas from the PSA unit is used in the reformer as fuel supplemented with natural gas fuel. Combustion air for the tubular reformer burners can be preheated in coils in the reformer waste heat section. Part of the steam produced in the hydrogen plant is used as process steam; the excess steam is exported.

The objective of this study is to analyse the process parameters of the present configuration and to identify optimum conditions to enhance the process performance. Different process layouts with high, medium- and low-temperature shift reactors and also with different purification processes (PSA and methanator) are studied and compared.

Identification and optimisation of process parameters
The study focuses on the optimisation of process/design

parameters for the minimisation of natural gas consumption. The study is particularly useful in countries such as India, where natural gas prices dominate operating cost. The most important parameters to influence natural gas consumption are:
- Methane slip
- Steam-to-carbon ratio
- Natural gas composition
- Shift converter configuration
- Choice of hydrogen purification step.

The following assumptions were made while carrying out the analysis:
- Impurities in feed are efficiently removed in the feed purification stage. The total volume of reactors in the purification stage does not change within the variation of operating parameters under study
- Hydrogen production is fixed at 90 000 Nm^3/h for any variation in the operating parameter
- PSA efficiency is 89%
- The kinetics of the reaction are taken from the open literature and are not specifically applicable to any particular catalyst.

Methane slip

The steam methane reforming reaction is strongly endothermic and is therefore favoured by a higher temperature. Typical reformer outlet temperatures fall in the range 810–900°C. As the temperature is increased, the hydrogen yield increases, which is observed as a reduction in the methane concentration in the reformer effluent, known as methane slip. The higher the yield, the less the amount of feedstock that will be consumed.

Due to the lower methane slip, the calorific value of the PSA off-gas is reduced and, since this stream is the base load fuel for the reformer, the supplementary fuel (natural gas) imported to the hydrogen unit increases (see Figure 2). This effect is enhanced because the higher reformer outlet temperature increases its radiant duty. The supplementary fuel has a relatively small flow and is strongly influenced by small changes to the reformer heat balance so that, in this case, there is a small increase in the total feed/fuel consumption. This effect is due to the increase in radiant duty and reduction in the steam requirement for the process feed, giving the net increase in the steam available for export. The higher reformer outlet temperature shifts the heat balance to produce more steam from more feed/fuel.

Steam-to-carbon ratio

The feed gas to the reformer is a mixture of steam and hydrocarbon gas. The mixture is characterised by the steam-to-carbon ratio, wh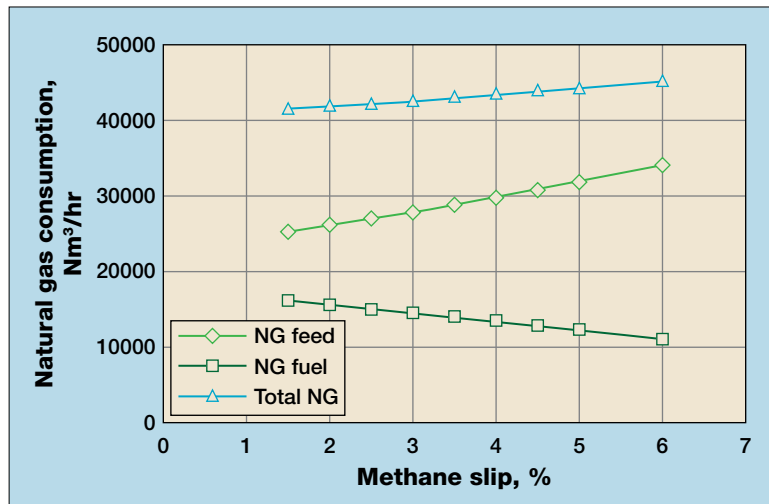ich is the molar ratio of steam to the reactive carbon contained in the hydrocarbon gas. A higher steam-to-carbon ratio drives the reaction closer to the equilibrium and increases the hydrogen yield.

Reforming catalysts require steam to be present in excess, increasing the volumetric throughput and cost of the plant, so there is always interest in reducing the steam-to-carbon ratio. In doing so, there is an increase in feedstock consumption, which is almost balanced by a decrease in demand for supplementary fuel (see Figure 3). The mechanism of these effects is opposite to that for a higher reformer outlet temperature, in that the methane slip increases and the PSA off-gas contains more calorific value. The decrease in steam-to-carbon ratio gives rise to an increase in the reformer radiant duty,
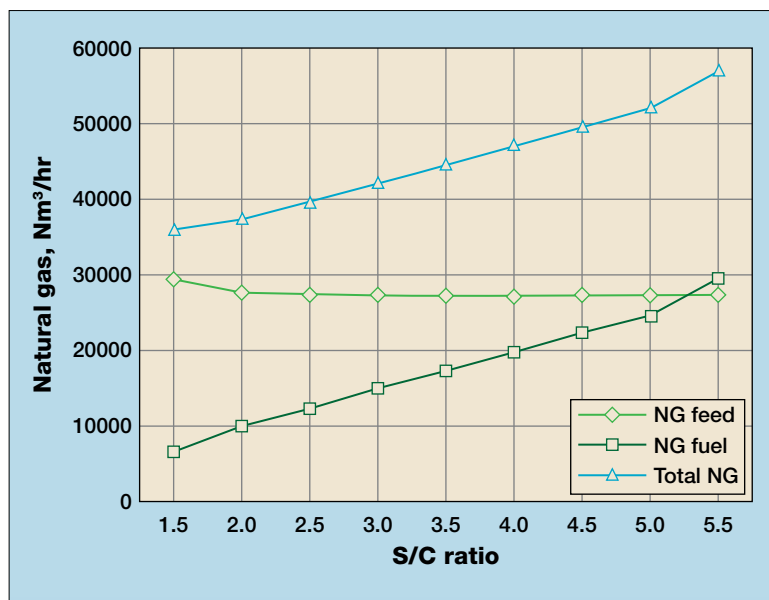

Figure 2 Effect of methane slip on natural gas consumption

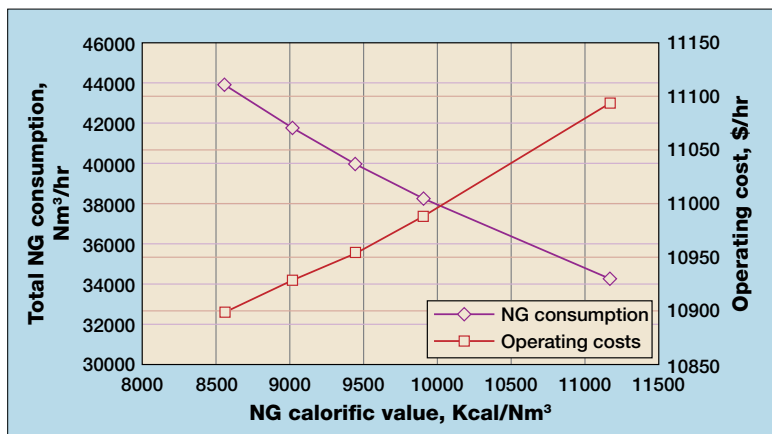**Figure 3** A wide range of ADZs for all applications

Figure 4 Effect of methane content in natural gas on specific energy

which increases the steam generated in the convection section. Less steam is used in the process and the steam exported from the plant is further increased. In this case, the significant benefit of a lower steam-to-carbon ratio is clearly shown. A lower steam-to-carbon ratio is limited by the catalyst performance and tendency of the feedstock to form carbon at the reformer inlet.

Natural gas composition

Natural gas mainly contains methane in the range (75–98% by volume) along with higher hydrocarbons (C_2+ components) and inert gases. The higher hydrocarbons contribute to the calorific value of the natural gas as well the hydrogen production. The inerts in natural gas add only to the natural gas volumetric flow rate and thus contribute only to capital cost (due to an increase in the piping and equipment sizes) and operating cost (higher power consumption in compressor). The cost of the natural gas is calculated on the basis of the calorific value. Here it should be noticed that higher HC content in the natural gas contributes to higher hydrogen production for the same quantity of feed gas. Hence, the natural gas consumption as feed decreases with the calorific value. Higher HC in the feed also contributes to more CO_2, resulting in higher off-gases from the PSA. Thus, for the same methane slip, the contribution from the off-gas is more in the case of higher HC natural gas, resulting in a reduction in the supplementary NG fuel requirement. The following graph is plotted as calorific value against the total NG consumption for the given hydrogen production. The graph also provides the operating cost for the natural gas for the hydrogen plant within the range of calorific values considered. The operating cost is calculated by multiplying x-axis and y-axis value by the NG unit cost, which is considered as 29$/Gcal with reference to the Indian scenario. Hence, for case 1, the operating cost due to NG works out to be:

=8565(X-axis value, Kcal/Nm³)*43878(Y-axis value, Nm³/hr) *29($/Gcal)
= 10899$/hr.

From Figure 4, it can be seen that even though NG consumption reduces with the increase in calorific value, the operating cost increases.

Shift reactor configuration

A typical steam-to-carbon ratio in a configuration containing an HTS reactor is 2.8. The steam-to-carbon ratio will depend not only on the pre-reformer/reformer catalyst but also on the type of shift converter catalyst. All HTS catalysts are based on Fe-Cr oxides that over-reduce when the steam-to-hydrogen ratio drops below certain limits. The consequence of this over-reduction is the formation of higher hydrocarbons and oxygenates by the Fischer-Tropsch reaction.

The steam-to-dry gas ratio will be 0.46–0.52 for HTS catalysts and 0.39 for MTS catalyst at the converter inlet. Different shift converter configurations were studied by fixing the natural gas feed flow rate and the steam-to-carbon ratio. The reformer outlet temperature is maintained at 860°C. A prereformer/reformer/HTS/LTS scheme is optimum and provides ~3.5% savings in natural gas consumption over a reformer/HTS combination (see Figure 5a).

The prereformer helps in the reduction of natural gas consumption as feed as well as fuel. Above that, the prereformer offers other advantages such as flexibility in handling natural gas feed composition, a reduction in reformer heat duty, and reformer catalyst protection. Hence, it has become an essential part of hydrogen plants. Even though MTS saves on natural gas

consumption, the catalyst volume requirement is very high compared to other shift configurations (see Figure 5a). As a result, MTS is only used for smaller capacity hydrogen plants, while for larger plants it is used in combination with LTS.

Hydrogen purification

In modern plants, PSA is used for the final hydrogen purification instead of CO_2 absorption followed by a methanator. PSA gives a high-purity hydrogen product of 98–99%, while an absorption/methanator combination provides purities in the range 90–94% (see Figure 5b). Natural gas consumption will be 12% less than with a PSA purification step. Hence, in refinery operations where hydrogen purity is not essential, a hydrogen plant with the later combination may be preferred.

Generation of base case with optimised parameters and comparison with operating data

Overall hydrogen production depends upon the consumption of utilities, which typically include feed, fuel, boiler feed water, electrical power, cooling water and steam production/import. Of these utilities, feed and fuel contribute more than 90% of the total utilities cost. The major utility besides natural gas is steam, as it is produced as by-product in the plant. The credit given for export steam can have a significant impact on utility costs, especially when refinery utility costs are favourable for steam production.

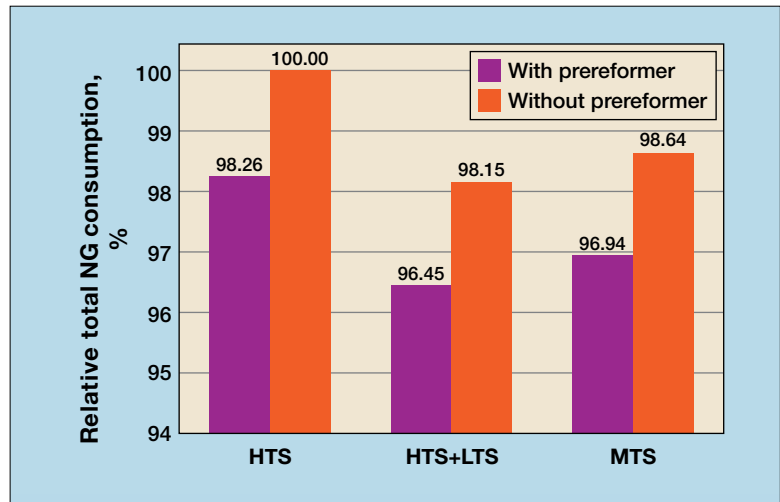The steam produced in the plant has internal consumers

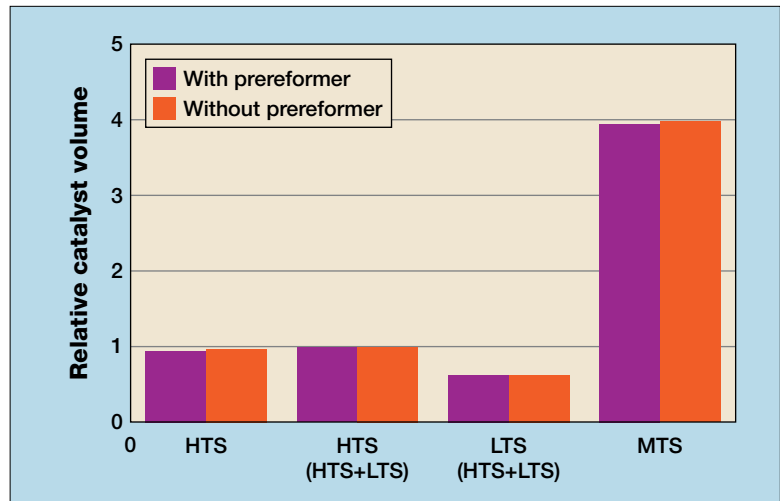**Figure 5a** Effect of shift reactor configuration on natural gas consumption

Figure 5b Catalyst requirement for shift reactor configuration

within boundary limits. Most important among them are steam-driven turbines for BFW pumps, ID and FD fans, process steam for reforming, process condensate stripper, while other consumers include steam tracing, lube oil heating, losses and so on. Steam production within the plant should be adequate for these contributors, and surplus steam is exported. A simulation carried out for the entire hydrogen plant is shown in Table 1, along with the set of optimised parameters studied.

Conclusion

Natural gas offers greater advantages over other feedstocks for hydrogen production in terms of simplicity of use, operating cost and capital cost. For economic production of hydrogen utilities such as natural gas as feed, fuel and steam are the important parameters. However, steam export is important only when there is a need from other parts of the refinery. Hence, the overall objective should be to minimise natural gas consumption for the hydrogen plant.

Utilities consumption in a hydrogen plant				
Operating parameters	Calculated	Reference I	Reference II	Reference III
Approx. capacity, Nm³/hr		50 000	100 000	40 000
Methane slip	3.92	6.74	2.69	6.74
Steam-to-carbon ratio	2.6	2	2.59	2.0
NCV, Kcal/Nm³	11 211	9393	9765	9393
Shift reactor configuration	MTS+LTS	MTS	MTS+LTS	MTS
Purification step	PSA	PSA	PSA	PSA
Utilities, per Nm³ of hydrogen	Calculated	Reference I	Reference II	Reference III
Natural gas feed, Nm³/Nm³	0.257	0.352	0.278	0.352
Natural gas fuel, Nm³/Nm³	0.064	0.025	0.086	0.023
Total feed + fuel, Nm³/Nm³	0.321	0.377	0.363	0.375
HP export steam, kg/Nm³	0.424	0.695	0.620	0.674
Electric power, kWH/Nm³	0.0012	0.017	0.038	0.017
BFW requirement, kg/Nm³	1.222	1.166	1.142	1.145
CW req., kg/Nm³	2.34	1.9	11.3	1.9

Table 1

Hydrogen plant capacity, end use and export steam requirement usually govern the selection of an optimum set of operating parameters for a new hydrogen plant.

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