

Optimised hydrogen production by steam reforming: part 2

Emerging technologies for hydrogen production from steam reforming are modelled

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Stringent emission control legislations and a well-informed market have compelled refiners to build highly complex refineries for producing cleaner and more efficient fuels. With crude slates getting heavier and sour, the demand for hydrogen is rapidly increasing and refiners are looking into new reforming technologies and schemes for optimum hydrogen production. In a previous article (PTQ, Q1 2012), we identified and

optimised process parameters that affect the energy performance in hydrogen plants with conventional steam methane reforming (SMR) technology. Autothermal reforming (ATR) and gas heating reforming (GHR) are among the new technologies available at present, and future developments are focused on economical and environmentally friendly plant operations in a sustainable manner. Process schemes such as GHR in series or parallel

combination with SMR and ATR are gaining prominence, as these are expected to have lower capital and operating costs and plot space requirements, as well as a reduction in flue gas emissions.

In the present study, a mathematical model is developed for a greater understanding of the functioning of GHR. A simulation model is then developed to optimise the performance of a SMR/ATR + GHR combination and the

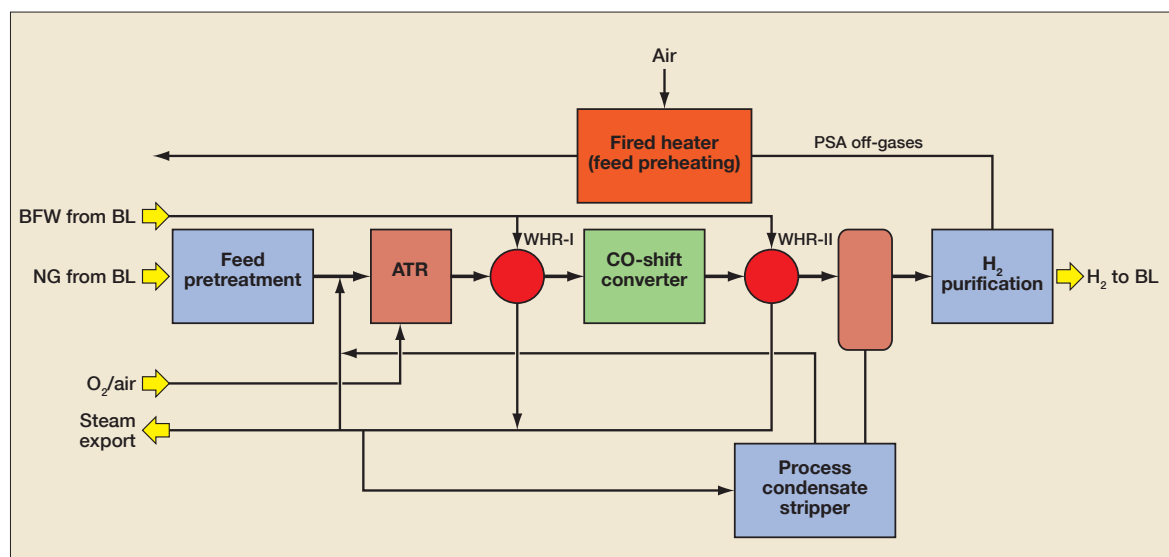


Figure 1 Schematic of hydrogen production by autothermal reforming

results are validated with reference data. The model is used to study the effect of operating parameters such as S/C and O₂/C ratios, the extent of feed preheating and the natural gas feed split on specific energy consumption and export steam production. Performance comparisons indicate that a saving in natural gas consumption and a reduction in flue gas emissions of 6-7% is possible with new reforming technologies and process schemes when compared to a conventional SMR configuration for refinery hydrogen generation.

Increased hydrogen demand

In the last decade, the worldwide refining industry has been impacted by several trends that have increased hydrogen demand significantly. First, in aggregate, crude oil has been getting heavier and contains more sulphur and nitrogen; second, a decreasing heavy fuel oil demand requires more bottoms upgrading; and, third, increasingly stringent environmental regulations require cleaner transportation fuels production. These factors have led to a substantial increase in hydrogen consumption in a refinery complex. Generally, complex refineries source 30-60% of their total hydrogen requirements from on-purpose hydrogen capacity. Overall, approximately 95% of the on-purpose hydrogen is supplied by steam reforming of light hydrocarbons.

The hydrocarbons such as natural gas (mainly methane) up to naphtha and refinery off-gas can be converted into hydrogen by either steam

reforming technology or through partial oxidation and a combination thereof. The future advances in reforming technology are focused primarily on reducing energy consumption and stack flue gas emissions. This article evaluates various reforming technology options available on an industrial scale, compares the performance parameters based on a simulation model and suggests an optimal configuration.

Autothermal reforming

The ATR unit is a refractory-lined pressure vessel containing a burner, a combustion chamber and a catalyst bed. The hydrocarbon feedstock is mixed with steam and pure oxygen, enriched air and air at the top of the reactor. In the combustion chamber, partial oxidation reactions take place and the generated heat is utilised within for endothermic steam reforming reactions. In the lower section of the reactor (loaded with reforming catalyst), the steam reforming and shift conversion reactions occur as the gas passes through the fixed bed, generating a gas mixture of H₂ and CO. A general schematic of ATR is shown in Figure 1.

Gas-heated reformer

GHR uses the heat available in the process gas at the reformer exit for steam reforming in a heat exchanger type of reactor. This scheme is available in series or parallel combination with SMR or ATR. In a parallel combination with the available heat, up to 20% of the feed can be split and taken to GHR. Normally, export steam produc-

tion is minimum in these configurations.

Process scheme: GHR with SMR

Since the outlet temperature of GHR is less than the SMR outlet temperature, the methane slip is higher in GHR. The higher methane slip can be counteracted by adjusting the steam-to-carbon (S/C) ratio and the inlet temperature to GHR. This option is available in the case of a parallel arrangement only, as it allows for adjustment of the operating parameters to obtain the perfect balance between the size of GHR and combined outlet composition.

Process scheme: GHR with ATR

The purpose is to increase the ratio between steam reforming and partial oxidation so that the synthesis gas will have a higher hydrogen-to-carbon monoxide (H₂/CO) ratio than ATR alone. This will also result in a reduced high-cost oxygen consumption and load on the shift section. In a series arrangement, all gas passes through the steam reforming unit and then through ATR. This will mean that the reforming catalyst may set a lower limit for the S/C ratio. In a parallel arrangement, the two reformers are fed independently, giving the freedom to optimise the S/C ratio individually. However, the gas heated reformer must operate at a higher temperature than in a series arrangement in order to obtain a low methane concentration in the synthesis gas. The GHR arrangement in parallel with SMR/ATR is shown in Figure 2.

A comparison between various reforming schemes is shown in Table 1.

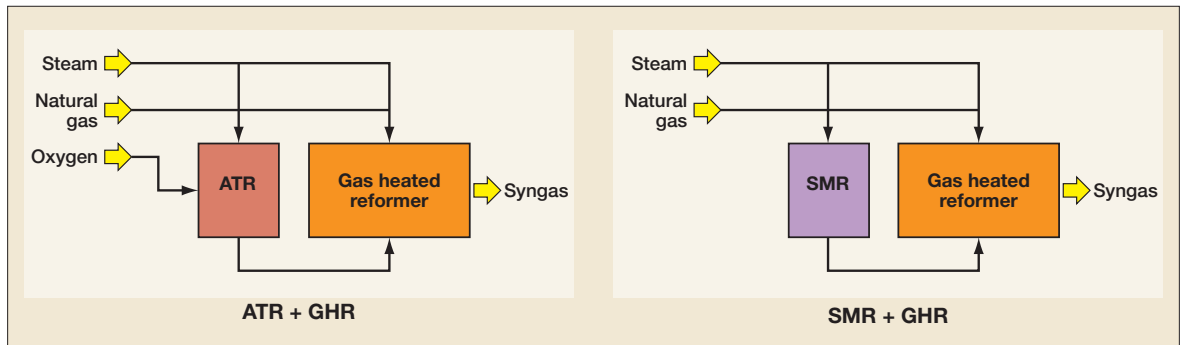


Figure 2 GHR arrangement in parallel with ATR/SMR

Basis of simulation

Model development and process simulation are carried out on the following basis:

- Impurities in the feed are efficiently removed in the feed treatment stage and hence do not influence reforming reactions

- The calorific value of natural gas available at the battery limit is

11211 kcal/Nm³ with a methane content of 72% and a pressure of 37.5 bar

- The hydrogen product flow rate requirement is 100 kNm³/hr with a purity of >99.5%

- The kinetics of the reforming and shift reactions is taken from the open literature and is not specifically applicable to any particular catalyst

- The final purification is achieved by pressure swing adsorption operating with a working efficiency of 89%

- A HT shift and LT shift reactor configuration is considered for the water gas shift reaction.

For the SMR scheme:

- Ten per cent excess air is considered in the reformer burner

- The reformer outlet temperature is fixed at 920°C

- S/C ratio is considered as 2.5

- PSA off-gas is recycled back

as supplementary fuel for the reforming section.

For the ATR scheme:

- Oxygen purity is considered as >99%

- The reformer outlet temperature is fixed at 1050°C

- S/C and O₂/C ratio is kept minimum and adjusted to match the required reformer outlet temperature

- PSA off-gas is fired in a heater for the feed preheating requirement.

For the GHR scheme:

- The natural gas feed is split (based on the heat content of the reformer exit gas)

- The GHR outlet temperature for the combined gas is fixed at 820°C

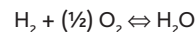
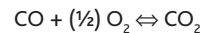
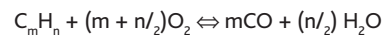
- The S/C ratio is maintained at 3.0.

A simulation model is developed for the hydrogen plant flow sheet for four process schemes (SMR, ATR, GHR in parallel combination with ATR and SMR) using commercial

steady-state simulation software Aspen Hysys 7.3. Model development of ATR and validation with reference data is described below.

Simulation model for ATR

ATR is modelled as two reactors in series. In the first reactor, the mixture of hydrocarbons is partially burned as per the following chemical reaction. In addition to that, complete oxidation of CO and H₂ will compete:



In the second reactor, leftover hydrocarbon after partial oxidation is reformed and a shift reaction takes place over the catalyst, as per the following chemical reaction:



Comparison of various reforming schemes

Parameters	SMR	ATR	SMR + GHR	ATR + GHR
Steam export	High	High	Some or none	Some or none
Oxygen/enriched air	No	Yes	No	Yes
Natural gas consumption	High	High	Low	Medium
Relative stack emission	High	High	Medium	Medium
Plot space required	High	Low	High	Medium

Table 1

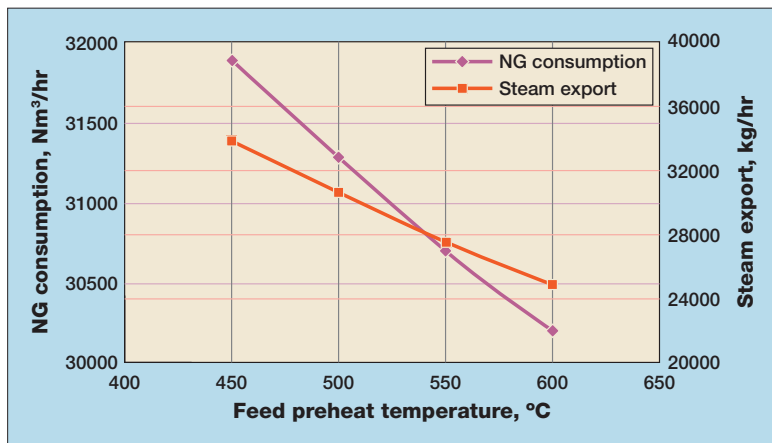
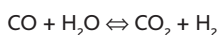


Figure 3 Effect of feed preheat on natural gas consumption in ATR



The exit temperature of the ATR reactor is maintained at a constant value, thereby fixing methane slip by adjusting the inputs of steam and oxygen. Using the simulation model, the reactor exit conditions in terms of composition and temperature are predicted and compared, with reference data available in the literature. The comparison details are given in Table 2. The marginal deviation in the simulated results may be due to the kinetic data considered for partial oxidation

and catalytic reforming reactions.

Parametric analysis for ATR Preheat temperature

High preheat temperatures reduce oxygen consumption, thereby lowering the content of CO₂ in the product gas and increasing the H₂/CO ratio. This will reduce natural gas consumption and steam export. The effect of feed split to GHR on natural gas consumption and steam export is also analysed.

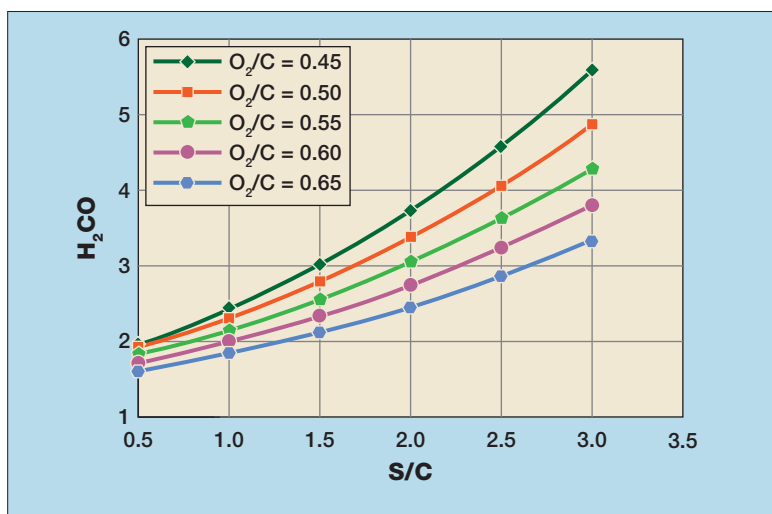


Figure 4 Optimum O₂/C ratio for a given S/C ratio

Comparison between reference and simulation

Reference	Simulation	
Input		
Natural gas feed, Nm ³ /h	20 000	
P _{exit} , bar	23.8	
T _{exit} , °C	1050	
Results		
H ₂ /C	0.60	0.64
O ₂ /C	0.64	0.54
H ₂ /CO	2.4	2.1
H ₂ + CO, dry mol%	89.6	93.5
CO ₂ + CH ₄ , dry mol%	6.6	6.0

Table 2

S/C and O₂/C ratios

The higher the O₂/C ratio, the more energy will be produced in the ATR unit, which in turn increases the extent of steam reforming in the catalyst zone. Thus, a higher outlet temperature and lower methane slip is obtained at the outlet of the ATR unit. Higher O₂/C ratio operation consumes more natural gas for the same quantity of hydrogen production. Also, more combustion increases the proportion of CO₂, which, in turn, increases the load on the purification stage. From an operational point of view, in order to reduce the possibilities of soot formation, the S/C ratio is kept high for a higher O₂/C ratio.

Parametric analysis for a GHR + SMR combination

Feed split ratio

The higher feed split means that more natural gas will bypass the SMR unit. This has two impacts: the bypassed gas does not require fuel to be fired, so there is a saving in terms of natural gas as fuel, but, at the same time, energy in the effluent of the reformer is not available for heat recovery and for steam production. Hence, with an increase in the

GHR feed ratio, natural gas consumption as fuel goes down along with steam production from the plant.

Results and discussion

Reforming is a highly endothermic process and needs natural gas as feed as well as fuel for the production of hydrogen. An approximately 90% contribution to total specific energy consumption is by natural gas alone. Credit is given for export from the hydrogen plant to the high-pressure steam generated within the plant and off-gases if these are not utilised within the plant. The simulation results for the various reformer configurations are analysed in terms of product composition, total natural gas consumption and steam production, and the details are given in Table 3.

Natural gas consumption

The hydrocarbon feed requirement will be identical for the same production of hydrogen, while the amount of hydrocarbon required as fuel will vary, depending upon the choice of reforming technology. In schemes with GHR, the fuel saved is directly proportional to the amount of feed that has bypassed SMR/ATR. Hence, a considerable amount of natural gas can be saved. The maximum amount of feed that can be taken to GHR depends upon the heat content in the reformer exit gas, and it is possible to take natural gas feed up to 20% for both ATR + GHR and SMR + GHR schemes, restricting the combined methane slip at the exit to 3%.

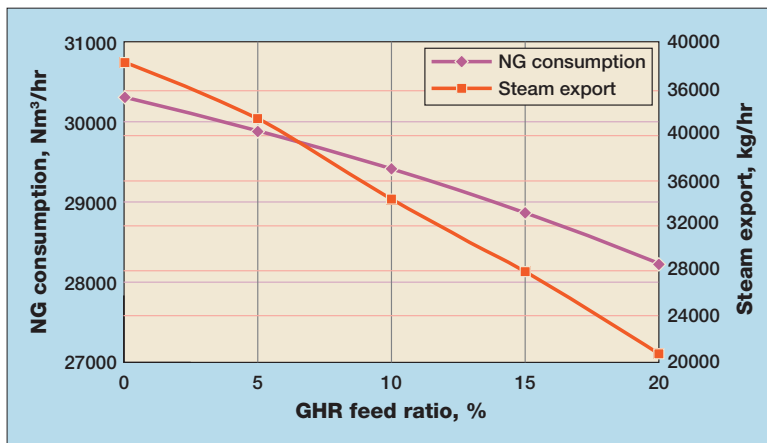


Figure 5 Effect of GHR/SMR feed ratio on natural gas consumption and steam production

Synthesis gas composition

In the ATR unit, the amount of CO produced due to the partial oxidation of hydrocarbons is higher than that formed due to reforming reactions. Hence, the H₂/CO ratio achieved in ATR is 2.3-2.6 compared to a H₂/CO ratio of ~4 in SMR. This results in an additional load on shift reactors for hydrogen generation. The composition of CO₂ is less in the ATR outlet stream as compared to SMR. This is

because a higher operating temperature in ATR restricts the exothermic water shift reaction. In ATR, the amount of oxygen fed stoichiometrically consumes the hydrogen part of the feed hydrocarbon not contributing to hydrogen production. Even though the process steam required for reforming at the inlet of the ATR unit is less when compared to SMR, additional steam is needed at the inlet of

Process parameters comparison				
Process parameters	SMR	ATR	SMR + GHR	ATR + GHR
Hydrogen production, KNm ³ /h	100			
Oxygen requirement, TPD	-	722	-	549
Natural gas feed split to GHR, %	-	-	20	20
Natural gas consumption, Nm ³ /h				
Natural gas feed	25 200	30 000	24 000	28 500
Natural gas fuel	5100	-	4150	-
Total natural gas	30 300	30 000	28 150	28 500
Relative total natural gas consumption, %	100	99	93	94
Synthesis gas composition at reformer exit, dry mole basis				
H ₂ /CO ratio	4.0	2.3	3.9	2.6
H ₂ + CO, %	88.8	92.1	89.9	91.4
CO ₂ + CH ₄ , %	10.8	7.4	9.8	8.2
Steam balance mass flow, kg/h				
Steam flow at reformer inlet	70 985	34 101	70 868	45 315
Steam added at shift reactor inlet	0	28 131	0	16 879
HP steam export	33 221	33 000	0	3000
Steam consumption - turbines	15 438	25 730	12 141	19 285
Total steam production	119 644	120 962	83 009	84 479
Relative flue gas emission, CO ₂ %	100	100	93.7	95.3

Table 3

Relative natural gas consumption: PSA off-gas export

Process parameters	SMR	ATR	SMR + GHR	ATR + GHR
Relative total natural gas consumption,%	100	88	91	84
Relative CO ₂ emissions (feed preheating only), %	100	62	81	58

Table 4

the shift section for a similar CO slip.

Steam production

Ideally, the supply of energy should be just sufficient for fulfilment of the energy requirement of the reforming reaction. Due to system limitation, higher energy must be supplied and this is recovered through steam generation in the plant. Steam is generated in the heat recovery sections between reforming and shift and in between shift reactors. This steam is internally consumed in stripping dissolved gases from generated process condensate, steam turbine drives and process steam.

Distinctively, the choice of reforming technology depends upon the steam requirement of the entire refinery complex. Even under highly optimised conditions, it is difficult to reduce the steam production below a certain amount for SMR/ATR schemes. The excess steam produced within the hydrogen plant battery limit is at the expense of natural gas as fuel. Steam production can be reduced by adding GHR, where a larger portion of energy in the reformer product stream is utilised for reforming. This reforming is achieved without firing natural gas as fuel.

PSA off-gas export

PSA off-gas is used as a fuel for feed preheating in a

reformer or in a separate fired heater in ATR. If PSA off-gas is not utilised in the plant, total natural gas consumption will increase to account for the feed preheating requirement. The details of relative total natural gas consumption and CO₂ emissions for feed preheating only are shown in Table 4.

Conclusion

SMR is a well-proven technology conventionally used in refineries for hydrogen generation. With rapidly increasing hydrogen demand and volatile natural gas prices, refineries are looking into alternative technologies for optimum hydrogen production. New process schemes such as the autothermal reformer and the gas-heated reformer in series or parallel combination with SMR or ATR are gaining prominence, as they offer potential in reducing energy consumption and flue gas emissions.

ATR is simpler and more compact than steam reforming. However, the cost of oxygen supply makes it less attractive than SMR even for large-scale plants. The H₂/CO ratio achieved is ideally suited for methanol and Fischer-Tropsch synthesis.

GHR utilises the energy in reformer effluent for hydrogen production, thus saving on natural gas as fuel at the expense of steam production. It is ideally suited to projects

where no steam export is required.

A simulation model is developed for the hydrogen plant flow sheet with various reformer process schemes, and it is observed that savings in total natural gas consumption in the range of 6-7% are possible with GHR schemes at the expense of export steam production.

The scheme with a gas-heated reformer in parallel combination with SMR is a good option for new refinery hydrogen plants. The scheme of GHR with ATR may be considered in future when a low-cost oxygen source is available and sufficient operational experience is gained in ATR technology.

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