

Converting CO₂ to valuable synthesis gas

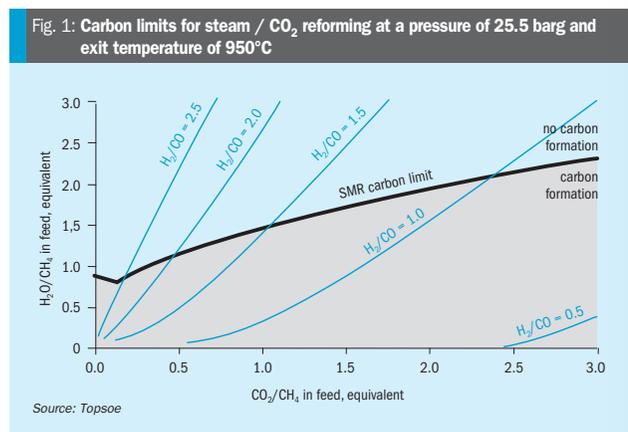
M. Østberg and **M. Rautenbach** of Haldor Topsoe describe ReShift™ technology, a new high temperature CO₂ reforming process, where preheated CO₂ is added directly downstream of a main reformer and then equilibrated in an adiabatic reactor. This new technology makes use of the high temperature of the reformer effluent to circumvent carbon formation, while at the same time maintaining an overall minimum steam to hydrocarbon carbon ratio, depending on process specific conditions. An increase in the amount of CO₂ added to the process will result in an increased fraction of CO in the produced synthesis gas. Synthesis gas with H₂/CO ratios in the range 0.5-3 can be produced. These CO-rich gases are typically utilised in the production of functional chemicals and synthetic fuels.

Important bulk chemicals such as hydrogen, ammonia and methanol are produced in a multiple step process. The first step is typically conversion of natural gas, or a similar feedstock, to produce hydrogen or synthesis gas (a mixture consisting of mainly hydrogen and carbon monoxide). This is followed by the actual synthesis and purification. The synthesis gas production step is often carried out by reforming of the feedstock with mixtures of steam and carbon dioxide (henceforth referred to as CO₂ reforming).

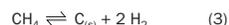
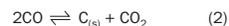
CO₂ reforming is an environmentally interesting process as it offers a way of utilising CO₂, which is a polluting greenhouse gas, and in many industries often considered as a waste product. CO₂ reforming is a process which can be designed with overall negative CO₂ emissions, or in other words can be designed to utilise more CO₂ than what is emitted. It is therefore expected to play an important role in combination with CO₂ capture technologies.

The technology presented in this article is a promising solution within the area of CO₂ utilisation, converting CO₂ to valuable synthesis gas with a high content of CO, but without the traditional limitations requiring large amounts of steam addition. It can be used to retrofit an existing unit for more CO production or included in new projects and is an excellent match in cases where excess CO₂ is available.

The CO₂ reforming reaction (1), also



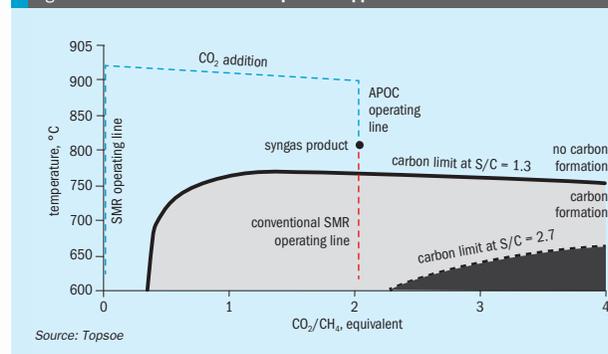
referred to as dry reforming, is an ideal way to obtain a 1:1 ratio of hydrogen and carbon monoxide in the product synthesis gas. Obtaining a catalyst that would enable dry reforming has therefore always been pursued by the scientific community. However, formation of carbon by any of the given reactions (2)–(4) remains a challenge.



Some catalyst systems have allowed for operation inside the traditional carbon forming area using, for example, noble metal catalyst or sulphur passivation (the SPARG™ process), but carbon formation has remained an issue and addition of steam a necessity. Therefore, CO₂ reforming will always occur together with steam reforming (5) and water gas shift, or in the case with addition of large amounts of CO₂, reverse water gas shift (6).



Fig. 2: Illustration of the ReShift™ process approach



Looking at a traditional reforming process with CO₂ addition, the operation window as limited by carbon formation is shown in Fig. 1. Here it is indicated that the lowest allowable H₂O addition is around 0.8 (illustrated as H₂O to C ratio, with all hydrocarbons as CH₄, i.e. S/C). As more CO₂ is added, more steam is required. So, if the desired product is a syngas with H₂:CO ratio of 1, it is necessary to operate with a S/C ratio of at least 2 and an addition of CO₂ corresponding to a CO₂:CH₄ ratio of about 2.4. Usually, some safety margin is added for process fluctuations, feed variations etc. and therefore the industry applied steam and CO₂ additions will be higher.

The ReShift™ technology introduced by Haldor Topsoe is a new process approach to achieve a CO-rich synthesis gas, while operating at lower S/C and with less CO₂ addition without getting into the carbon formation area dictated by thermodynamic affinity as graphite, meaning that it is a process wise very safe approach.

Introducing the ReShift™ process approach

In this new process approach being introduced to the market, it is made possible to keep a low S/C ratio by introducing the CO₂ to the process after the main

part of the steam reforming has occurred and a high temperature syngas has been obtained (at this point still with a high H₂:CO ratio). This is illustrated in Fig. 2, which shows the operation line of a steam reformer (SMR) operating at S/C 1.3 with an exit temperature of 920°C. At this point, preheated CO₂ is mixed with the product gas from the SMR and the mixed process gas is equilibrated in an adiabatic reactor, named an adiabatic post converter (APOC), producing the final syngas with a low H₂:CO ratio (CO-rich).

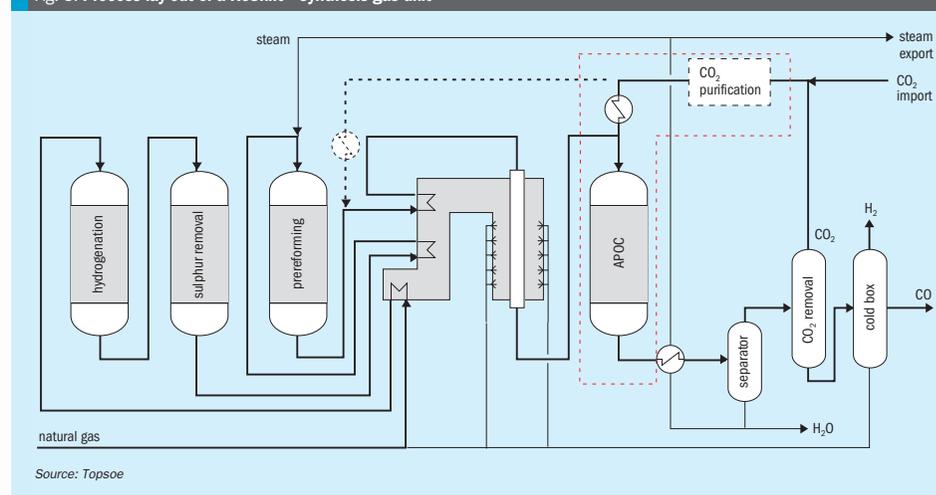
To produce the same synthesis gas in the traditional way by mixing the CO₂ upstream of the SMR, it would require a S/C ratio of 2.7 to avoid carbon formation.

The layout shown in Fig. 3 indicates by means of the dashed line, the changes required compared to a traditional synthesis gas unit based on tubular reforming. All it requires to introduce the ReShift™ process is the APOC reactor, with the addition of high purity, preheated CO₂. This enables introduction of the ReShift™ for revamps of existing plants with a possibility to expand the capacity with increased CO production.

Features of the APOC

A core element in the ReShift™ technology is the APOC (Fig. 4). This has been designed based on industrially proven technology. The catalyst used is a nickel-based catalyst, working as a hybrid between

Fig. 3: Process lay-out of a ReShift™ synthesis gas unit



a traditional tubular steam reforming catalyst and a secondary / autothermal reforming catalyst, with more activity than the high temperature catalyst, but keeping the thermal robustness of these catalysts. The high temperatures require a refractory-lined reactor similar to the well-known secondary reformers.

The last important feature is the outlet flow distributor, not trivial to the design of a fixed bed reactor operating at these high temperatures. Also here features of the industrially proven Topsøe SynCOR™ technology are used. As for secondary reformers, the footprint of the APOC is limited compared to the associated tubular reformers.

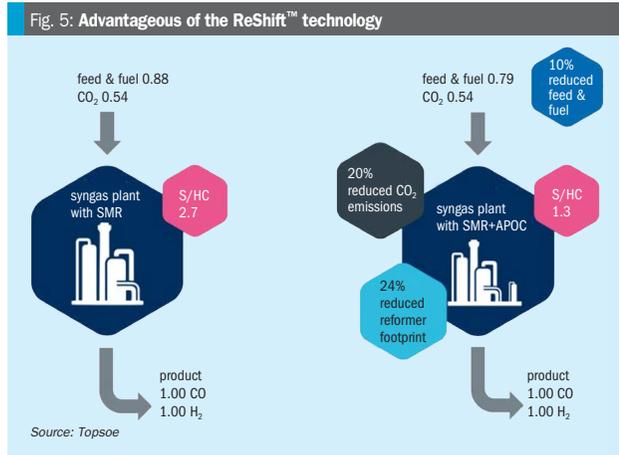
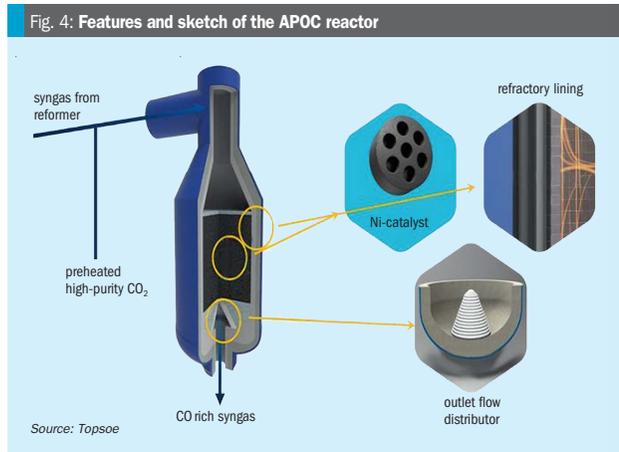
The conversion in the reactor will be a combination of methanation (reverse steam reforming) and reverse water gas shift reaction (rWGS), having the methanation dominating the upper part giving a slight temperature increase because of the highly exothermicity of this reaction. Subsequently, the rWGS will take over leading to an overall temperature decrease in the reactor. Besides the production of CO from CO₂ and H₂, a slight increase of CH₄ also takes place.

Advantages of the ReShift™ technology

The ReShift™ technology introduces the possibility to make a CO-rich synthesis gas based on a tubular reforming step operating with an absolute minimum steam to carbon ratio, while at the same time having no affinity for forming carbon according to any of the given reactions (2)-(4). The process uses traditional nickel based catalyst and all features of the additional reactor are industrially proven in secondary or autothermal reactors.

The steam addition to the tubular reformer can be significantly reduced, either resulting in a smaller tubular reformer or a possibility to increase capacity. CO₂ import is needed and as the energy needed for the tubular reforming in terms of fuel requirements are reduced at the same time, this also gives lower overall CO₂ emissions from the plant, as emitted through the flue gas.

To make a 1:1 H₂:CO ratio syngas, the amount of feed + fuel can be reduced by 10%, producing the same amount of syngas. The reformer footprint can be reduced by 24% or a similar capacity expansion can be achieved (Fig. 5).



Conclusions

It has been the objective of this article to present the advantages of the new ReShift™ technology offered by Haldor Topsøe if a CO-rich synthesis gas is desired. The technology is based on introducing an adiabatic post converter (APOC), equilibrating a low CO containing syngas, after mixing with preheated CO₂, to produce a CO-rich product. All elements of the APOC stem from industrially proven technology.

The technology is available for both new

Significant savings on feed + fuel are possible, reducing the CO₂ emissions from the plant.

builds and revamps of existing plants, for now mainly focusing on tubular reformers. It enables significant reduction of the steam to carbon ratio of the main reformer and is a great fit where import CO₂ is available. Significant savings on feed + fuel is possible, thereby reducing the overall CO₂ emissions from the plant.

As the APOC reactor is compact compared to a tubular reformer, the overall footprint of the reforming section itself is also significantly reduced which is an advantage especially in revamp cases. ■

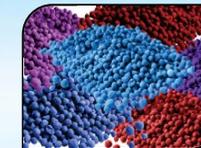
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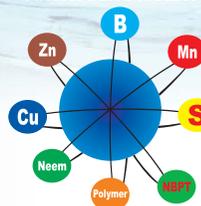
DUST SUPPRESSOR



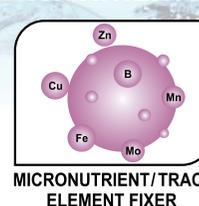
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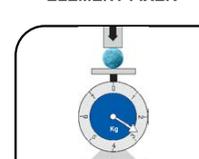
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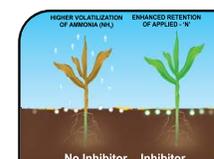
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