



Steam Reforming Catalysts





Steam Reforming Catalysts

The steam reformer is a vital part of hydrogen plants and of the gas preparation section in plants producing ammonia, methanol, and other types of syngas.

Developments in metallurgy have allowed steam reformers to operate at increasingly higher levels of temperature, pressure and heat flux. Use of a variety of feedstocks as alternative to natural gas has made selection of proper catalyst more important than in the past. New process technology in other parts of the plants has in many instances made the steam reformer the bottleneck for further capacity increase.

Topsøe's steam reforming catalysts combining high activity with favourable heat transfer and pressure drop characteristics have made it possible to significantly increase the throughput at unchanged pressure drop and tube wall temperatures.

Haldor Topsøe has for more than 35 years delivered catalysts and technology for the steam reforming process. Topsøe's catalysts are used in all types of reforming furnaces and have reached lifetimes unsurpassed by any competitive catalyst used in the same service.

The Reforming Process

Steam reforming can be described by the irreversible reaction(s)



combined with the reversible reactions

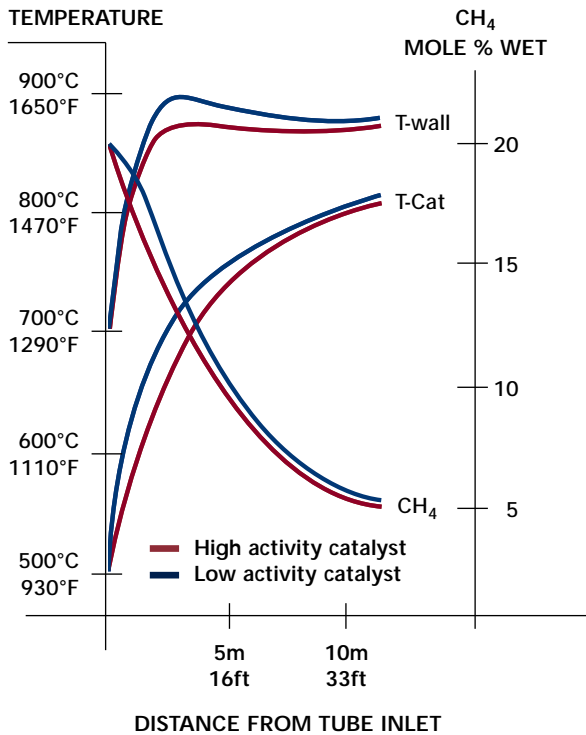


The total of these reactions is strongly endothermic and in the presence of a nickel catalyst, the gas mixture will be close to equilibrium at the exit of the furnace. The molar steam to carbon ratio, temperature and the pressure largely determine the final composition of the gas leaving the reformer. It is evident that higher temperatures result in less methane and more carbon monoxide in the equilibrated gas. A large surplus of steam favours both low methane and low carbon monoxide, whereas high pressure increases the methane content.

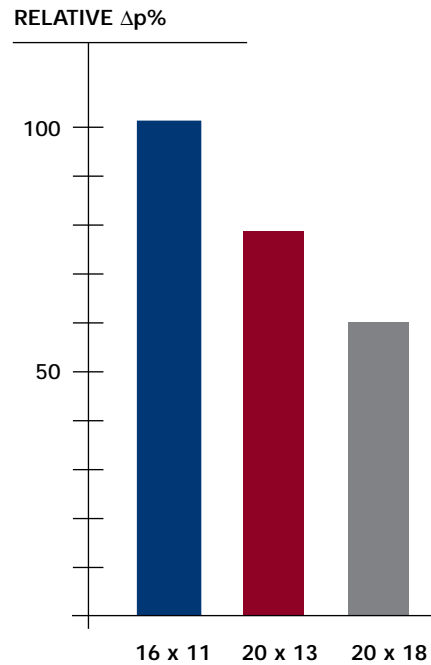
Benefits obtained by High Activity Catalyst

For a given reformer and process conditions the approach to equilibrium at the exit of the tubes is a function of catalyst activity. For typical ammonia plant conditions an approach to equilibrium below 10°C (18°F) is achievable for many years.

Tube wall, catalyst temperatures and methane conversion profile in top-fired furnace.



Pressure drop characteristics of different catalyst sizes (mm).

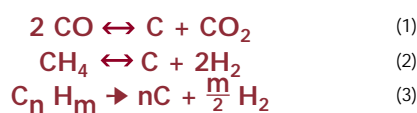


Generally, the difference between performance of a high and low activity catalyst is much more pronounced in the upper part of the tubes than in the lower part. As exemplified in the above figure at a given point in the tube, the more active catalyst will operate at a lower temperature as the higher reaction rate will make the endothermic reforming reaction proceed closer to equilibrium.

High activity is particularly desirable in top of the tubes and as a larger part of the pressure drop is generated in the bottom half, an optimal catalyst charge will often be a combination of a relatively small catalyst size in the top and a larger size in the lower part of the tubes. The above graphic illustrates pressure drop characteristics of different sizes of Topsøe's main steam reforming catalysts.

Carbon Free Operation and Protection against Carbon Formation

Carbon may be formed on the catalyst or on the tube wall according to following reactions:



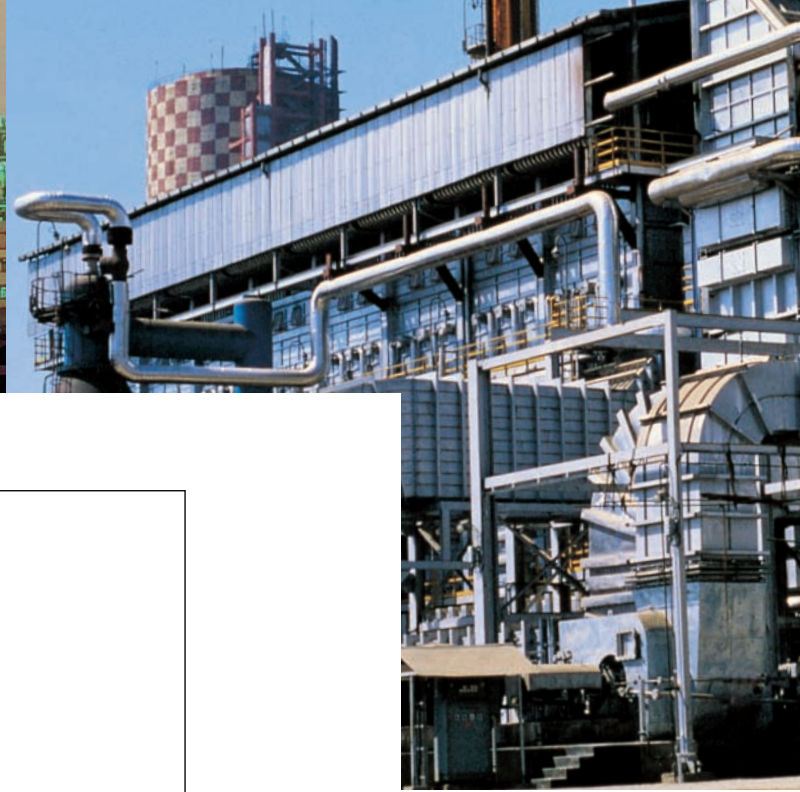
The Boudouard (1) and methane cracking (2) reactions will not take place in reformers operating at process conditions of conventional ammonia,

methanol and hydrogen plants. These reactions could be responsible for carbon formation only in cases of maloperation or in plants operating at extremely low steam to carbon ratio.

However, thermal cracking of higher hydrocarbons (3), which results in carbon lay-down, is possible even at conditions where there is no affinity for carbon formation according to Boudouard and methane cracking reactions. This problem may occur if steam reforming of higher hydrocarbons is not completed at the relatively low temperature prevailing in the upper part of the tubes. In such cases, thermal cracking is initiated at a threshold temperature typically reached 1-4 meters (3-12 feet) from the inlet and observed as hot spots (hot bands) on the tubes due to carbon lay-down.

A prerequisite for carbon-free operation is a catalyst with high activity at low temperatures near the inlet of the tubes, and a catalyst with few acidic sites known to be initiators of cracking reactions. Magnesium aluminate chosen as carrier for Topsøe's main steam reforming catalyst is a less acidic oxide than pure alumina which is a major constituent of other commercially available steam reforming catalysts.

The high reforming activity of the catalyst and the non-acidic nature of its carrier are sufficient to ensure carbon free operation. However, in some top-fired



furnaces, where the critical temperature for thermal cracking is reached close to the inlet and for hydrocarbon feeds containing higher hydrocarbons we recommend using our low alkali-promoted catalysts. The low alkali catalysts are installed in the critical upper part of the tubes.

For reforming of naphtha feeds, Topsøe provides high alkali-promoted catalysts as the required extra protection against carbon formation. Depending on characteristics of naphtha and operating conditions, the high alkali catalysts are used in combination with a bottom layer of a low alkali catalyst or Topsøe's normal steam reforming catalyst.

Catalyst Poisoning

Whereas performance of steam reforming catalyst could be impaired by carry-over of any compound, which may deposit as a solid on the catalyst, sulphur is clearly the most severe poison to consider. Although the high nickel surface area offered by Topsøe's reforming catalysts can accommodate a relatively large quantity of sulphur, the sulphur levels should be minimised to ensure benefits of high activity throughout the catalyst lifetime.

Catalyst Reduction

The catalyst is activated by reduction of nickel oxide to metallic nickel. Traditionally, steam reforming catalyst is reduced by the steam/feed gas mixture at a relatively high steam to carbon ratio.

Reduction is initiated by hydrogen formed by thermal cracking of hydrocarbons. Since elementary nickel becomes available, the steam reforming process is triggered and the additional hydrogen formed accelerates catalyst reduction.

Catalyst reduction above the ignition zone will proceed by back diffusion of hydrogen at a gradually decreasing rate towards the cool top of the tubes.

To speed up the reduction process, a portion of the catalyst is provided in a prereduced form, which is charged in the top 10-15% of the tubes. This ensures that steam reforming and production of hydrogen take place as soon as hydrocarbon is introduced and the reduction of catalyst loaded below the pre-reduced inlet layer is completed in minimum time.

The prereduced catalyst has been reduced in our manufacturing facilities in dry hydrogen at optimal conditions, which results in higher activity than what is obtained by in-situ reduction.

Oxidation of the top catalyst by steaming during shutdowns is slow due to the prevailing modest temperatures. Therefore restart of a catalyst after a shutdown takes place almost like the initial start-up with prereduced catalyst in top of the tube.

Technical Service

Besides preparing tailor made catalyst and technology solutions, Topsøe provides on-site assistance and follow-up service according to the needs of the producer.

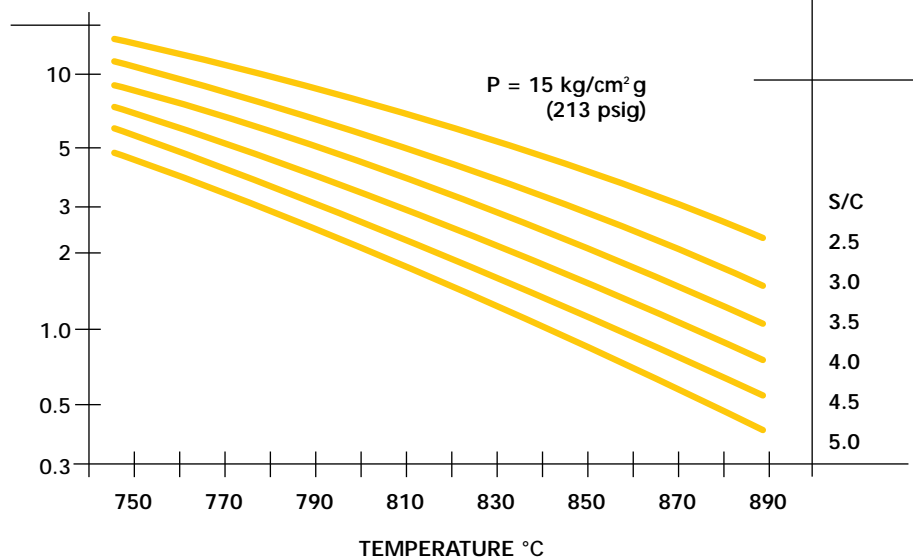
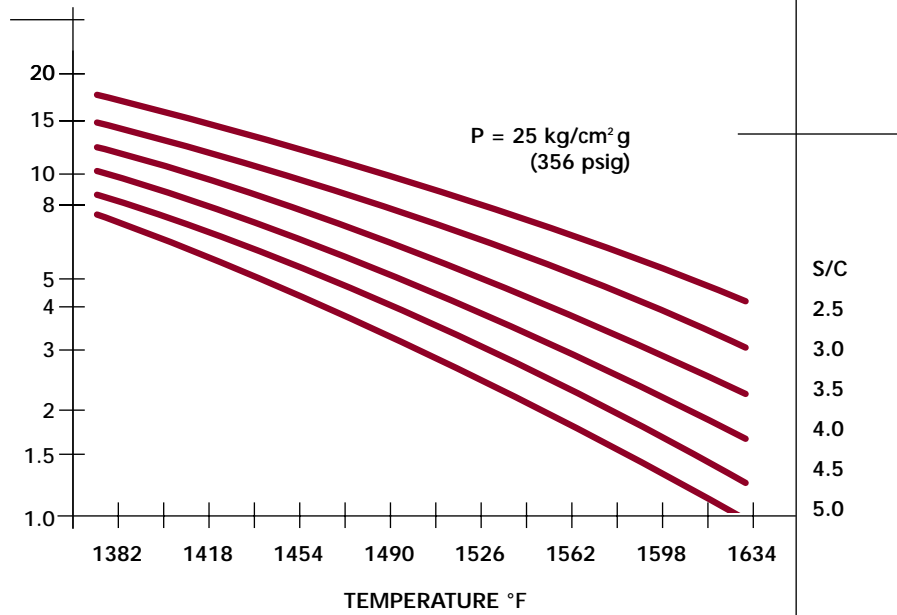
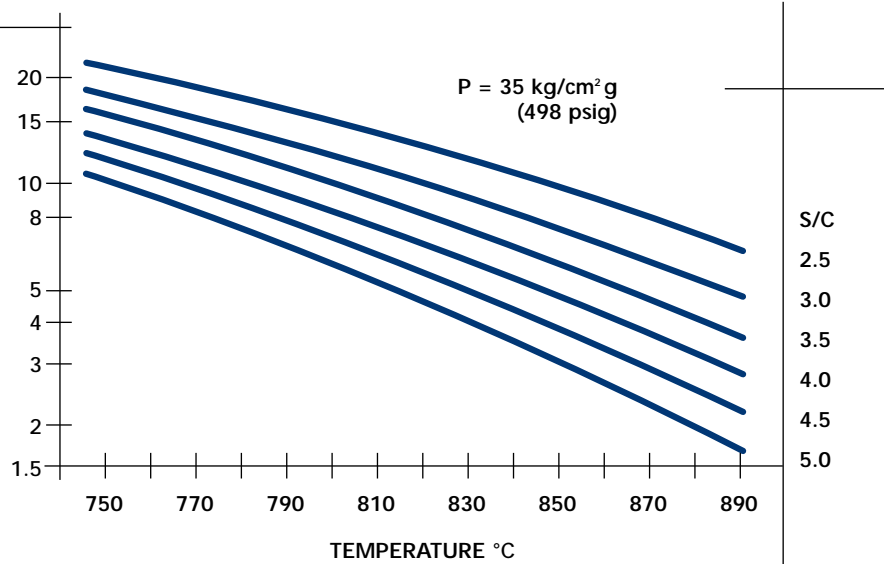
This service includes:

- Supply of manuals for loading and operation of the catalyst.
- Supervision during loading and initial start-up as required.
- Analysis of operating data, evaluation of catalyst performance and of remaining life.
- Advice on measures to improve performance.
- Troubleshooting.
- Analysis of samples of used catalyst.
- Assistance in disposal of spent catalyst through arrangements with catalyst reclaimers.

Proven by Performance

Equilibrium content of CH₄ in dry reformer effluent versus temperature for various steam to carbon ratios and at three different pressures, 35 kg/cm²g, 25 kg/cm²g, and 15 kg/cm²g. Feed gas assumed to be 100% CH₄. The three pressure levels are typical exit pressures from the steam reformers in ammonia, hydrogen and methanol plants.

CH₄ % (dry)



Topsøe R & D

Topsøe's worldwide services to the chemical, petrochemical and refining industries are based on a fundamental understanding of heterogeneous catalysis, including development and production of catalysts, process technologies and engineering services.

Quality catalysts – proven by performance

Topsøe's unique integrated approach has resulted in profitable solutions providing catalysts in the areas of:

- Feed Purification
- Adiabatic Steam Reforming
- ▶ **Steam Reforming**
- CO Shift Conversion
- Methanation
- Ammonia Synthesis
- Methanol Synthesis
- Formaldehyde
- Sulphuric Acid
- Refinery Hydroprocessing
- DeNOx and DeSOx
- Combustion of VOC

Based on many years of experience, the development of Topsøe catalysts is dedicated to provide a second-to-none performance. This means that focus always is on key factors such as enhancement of high and stable activity, long operating life, high resistance to poisoning, low pressure drop, energy savings and reduced emissions.

Customised after sales service

Topsøe's after sales service relies upon an on-going exchange of information between the client and us, to provide clients with relevant and most up-to-date information. The four pillars in Topsøe's service programme are:
Frequent Contact and Discussions,
On-site Supervision, Evaluation of Plant Performance and Troubleshooting.

Visit www.haldortopsoe.com for more information.

The information and recommendations have been prepared by Topsøe specialists having a thorough knowledge of catalysts. However, any operation instructions should be considered to be of a general nature and we cannot assume any liability for upsets or damage of the customers' plants or personnel. Nothing herein is to be construed as recommending any practice or any product in violation of any patent, law or regulation.

Denmark

HALDOR TOPSØE A/S
P.O. Box 213
Nymøllevej 55
DK-2800 Lyngby
Denmark
Phone: + 45-45 27 20 00
Telefax: + 45-45 27 29 99

India

**HALDOR TOPSØE
INTERNATIONAL A/S**
India Liaison Office
Apt. A-5, Qutab Hotel
Off Sri Aurobindo Marg,
New Delhi 110016
Phone: + 91-11-686 4735
Telefax: + 91-11-686 2252

Japan

**HALDOR TOPSØE
INTERNATIONAL A/S**
Tokyo Branch Office
Kioicho Building, 14th Floor
3-12, Kioi-cho
Chiyoda-Ku
Tokyo 102-0094
Phone: + 81-3-5210 2751
Telefax: + 81-3-5210 2754

People's Republic of China

**HALDOR TOPSØE
INTERNATIONAL A/S**
Beijing Representative Office
Room 1008, Scitech Tower
22 Jianguomenwai Dajie
100 004 Beijing
Phone: + 86-10-6512 3620
Telefax: + 86-10-6512 7381

Russia

HALDOR TOPSØE A/S
Moscow Representative Office
Bryusov Street 11, 4th Floor
103009 Moscow
Phone: +7-095-229 6350
+7-503-956 3274
Telefax: +7-503-956 3275

ZAO HALDOR TOPSØE

42 Respublikanskaya St.
150040 Yaroslavl
Phone: +7-0852-730173
Telefax: +7-0852-252558

USA

HALDOR TOPSOE, INC.
17629 El Camino Real
Houston, Texas 77058
Phone: + 1-281-228-5000
Telefax: + 1-281-228-5109

HALDOR TOPSOE, INC.
Refining Technology Division
770 The City Drive
Orange, CA 92868
Phone: + 1-714-621-3800
Telefax: + 1-714-748-4188