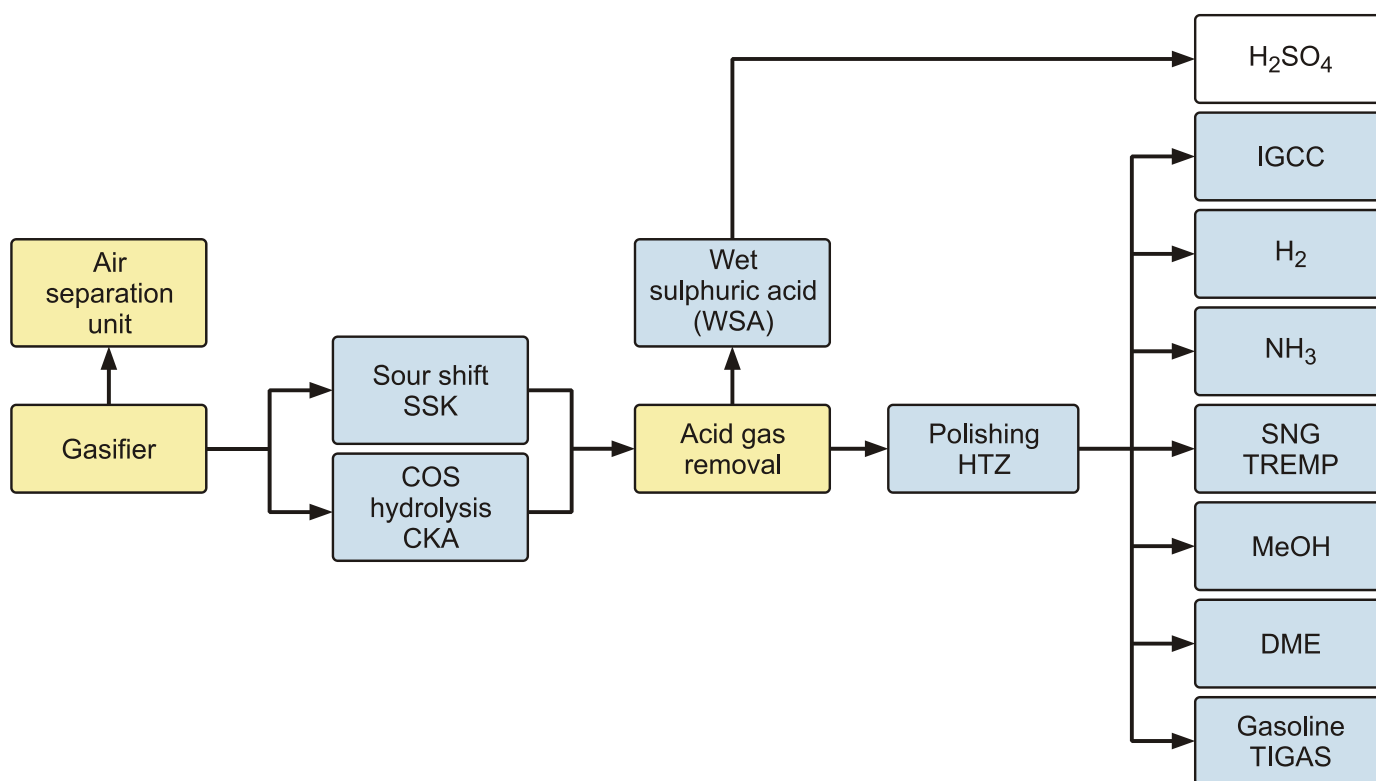


# Optimising the synthesis of your desired energy-carrying product

Topsøe downstream gasification technologies

RESEARCH | TECHNOLOGY | CATALYSTS

WWW.TOPSOE.COM



## Introduction

The improvement of living standards coupled with demographic expansion increases national energy consumption. At the same time, existing or developing infrastructure and technology constrain the form in which energy carriers may be used. Availability of resources, security of supply and the environment all influence the choice of the energy source.

Haldor Topsøe licenses a number of technologies for the production of energy carriers, ranging from basic chemicals to transportation fuels. As a key player in the business of energy conversion, we have further developed our well-established

processes based on natural gas and naphtha-derived synthesis gas to include also gasification-based synthesis gas.

Understanding that your choice of energy resource and energy products is specific for your application, we are dedicated to optimising our proprietary processes to your particular demand.

Read more about Topsøe's technology portfolio and how Topsøe's experience can make a difference for your project.

## Downstream gasification technologies

The diagramme on the cover shows the technologies in Topsøe's downstream gasification technology portfolio. Gasification, air separation, and acid gas removal are not catalytic processes and are not licensed by Topsøe. However, Topsøe cooperates with the most prominent licensors of these technologies and we are accustomed to establishing collaboration that allows you, as our client, to obtain the highest benefits from the integration of the packages.

Topsøe downstream gasification technologies belong to the areas of:

- module adjustment: correction of the ratio between CO, H<sub>2</sub> and CO<sub>2</sub> to the value required by the synthesis – the technologies are sour shift (SSK) and hydrolysis of COS (CKA)
- sulphur treatment: polishing of sulphur from the process stream by means of the HTZ sorbent and recovery of sulphur in the form of sulphuric acid by means of the WSA technology
- synthesis including pure hydrogen (for hydrogen or ammonia), synthesis gas adjusted to the requirements of carbon capture and storage (CCS) for the power industries (in integrated gasification combined cycle units – IGCC), methanol, dimethyl ether, substitute natural gas (SNG) and gasoline for use as chemicals or fuels

## Water-gas shift catalysis (sour shift)

The synthesis gas leaving the gasifier has a variable composition given by the gasification process and the fuel. As each synthesis process operates optimally at a specific ratio of H<sub>2</sub>, CO and CO<sub>2</sub>, the concentration of these three components has to be adjusted to your specific application. This operation is carried out using the water-gas shift reaction:



The reaction can be carried out fully, if your application requires no CO but only hydrogen, or only on a fraction of the gas, if CO is required in the feed to the synthesis gas (module adjustment).

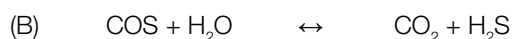
For downstream gasification, the water-gas shift technology of choice is typically "sour shift", SSK. SSK can simultaneously perform the hydrolysis of carbonyl sulphide - COS (see next paragraph). The SSK technology is also called "sulphur resistant water-gas shift" as it is placed before the acid gas removal, where the gas still contains sulphur.

Carrying out the shift reaction at sour conditions is highly desirable, as it improves the plant energy efficiency: SSK allows saving one cooling and heating cycle across the dew-point compared to a conventional sweet shift. The large operative flexibility of the Topsøe SSK catalyst permits operation with very little steam in the gas and a large span in temperature. SSK acts both as a high-temperature shift and a low-temperature shift catalyst. The heat generated by the reaction may be recuperated as high pressure steam.

In some specific cases, a sweet shift process, i.e. positioned after the acid gas removal, may be more appropriate. Topsøe also supplies suitable catalysts for this process. The choice is mostly dictated by the sulphur concentration in your gas. We are pleased to tailor your plant design to maximise the benefits you are searching for.

## COS hydrolysis

If the acid gas removal technology of choice is unable to absorb COS (carbonyl sulphide), typically present in the raw gas, Topsøe can provide you with a unit (CKA) carrying out the hydrolysis of COS to H<sub>2</sub>S (hydrogen sulphide). This is the sulphur species that acid gas removal technologies are normally designed to remove. The chemical reaction is as follows:



This reaction also occurs spontaneously across an SSK catalyst type. If your application requires only an adjustment of the ratio between CO to H<sub>2</sub> via the water-gas shift, the CKA reactor is typically positioned in parallel with the SSK technology.

## Sulphur guard

Topsøe has supplied desulphurisation absorbents to more than 250 industrial plants and various applications worldwide. Final desulphurisation of synthesis gas (polishing) is typically positioned after the acid gas removal. Final desulphurisation is needed to decrease the concentration of H<sub>2</sub>S to more or less "zero" (a few ppb), thereby optimising the lifetime of the downstream catalysts.

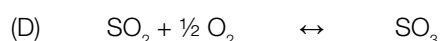
Topsøe's polishing technology (HTZ) is based on a series of solid sorbents, the choice of which depends on the characteristics of the gas at the inlet. As some of the most effective metals for adsorbing sulphur also have catalytic activity towards other reactions, any design for desulphurisation of synthesis gas by adsorption should specifically suppress side reactions. The design of such a unit is therefore highly critical and requires specific knowledge.

## Wet sulphuric acid (WSA)

Topsøe's proprietary technology for the recovery of sulphur from acid gas removal is Wet sulphuric acid (WSA), the product of which is highly concentrated sulphuric acid (>98%). The main unit operations in the process are the combustion of H<sub>2</sub>S to SO<sub>2</sub> (mostly non-catalytic and self-sustained):



the catalytic oxidation of SO<sub>2</sub> to SO<sub>3</sub>:



and the reaction of SO<sub>3</sub> with water, with subsequent condensation of H<sub>2</sub>SO<sub>4</sub>:



Contrary to alternative technologies for the recovery of sulphur, WSA does not need additional fuel. The technology also produces a significantly larger amount of high pressure steam, and it has a lower investment. As the chemical in largest demand worldwide, sulphuric acid is a highly marketable and valuable product. Sulphuric acid is the only chemical product of this technology meaning that you will avoid the inconvenience of dealing with the disposal of by-products. Today, Topsøe has more than 80 references for WSA plants worldwide.

## IGCC and hydrogen

If the product of your interest is hydrogen or CO<sub>2</sub>-free power (integrated gasification combined cycle with carbon capture and storage – IGCC-CSS), there is no additional synthesis operation to carry out. The water-gas shift process is optimised to achieve the required conversion of carbon monoxide into hydrogen. Depending on the application, additional unit operations specific to the purification of hydrogen might be needed. This is typically obtained either via a catalytic process (for example methanation) or by absorption (pressure swing absorption).

Topsøe has 60 years of experience and 30% of the world market of hydrogen plants. We have optimised our solutions to the needs of a vast number of clients and are always available to envisage new solutions if the existing ones do not represent the best for your application.

## Ammonia

As the largest ammonia technology licensor worldwide, Topsøe can make use of all the experience in this technology acquired through decades of activity. Topsøe has gained and maintained its leading position in the world market by continually improving the process efficiency. Part of this development aims at the refinement of the reactor technology. Topsøe is world-renowned for the invention and development of the radial flow ammonia converter, allowing significantly lower pressure difference and higher activity per volume than traditional axial-flow fixed beds. There are more than 130 Topsøe radial flow converters in operation worldwide. Particularly, the latest development, the S-300, is a huge commercial success, with more than 30 references since 1999.

For coal-based ammonia synthesis, the purification of the gas-stream after the acid gas removal is performed by means of a cryogenic wash with liquid nitrogen (already available from the air separation unit). This allows an inert-free process gas that eliminates the need of a purge and has a significantly higher activity than inert-containing gas from natural gas-based processes.



WWW.TOPSOE.COM

## Substitute natural gas – TREMP™

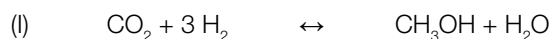
TREMP™ (Topsøe recycle methanation process) is Topsøe's proprietary process for manufacture of substitute natural gas, a gas blend mostly constituted by methane. Given the nature of methane as a clean combustion fuel, which is easy and cheap to transport, there is currently a huge commercial interest in SNG. The methanation reaction occurs according to the following stoichiometry:



Thanks to the high activity and ruggedness of the methanation catalyst MCR and to the optimum integration and reliability of the equipment in the steam superheating section, TREMP™ is able to recover roughly 80% of the energy in the syngas as methane. Roughly 85% of the remaining energy may be recovered as super-heated high pressure steam for your utilities integration processes. These exceptional performances provide you, as our client, with maximum profit from your syngas and are only possible thanks to the perfect integration of catalysis and technology mastered at Topsøe.

## Methanol

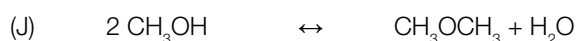
Methanol is a versatile molecule, used widely as a chemical in itself, as a feedstock for chemical synthesis and as a fuel (Otto engines). The methanol synthesis takes place according to the reactions:



Methanol production consists of synthesis and distillation from water and by-products. Topsøe offers the full manufacturing process. Whereas the distillation process depends on the required purity of methanol, the characteristics of the synthesis section are linked to the size of the plant. For the synthesis, Topsøe offers technologies based on cooled as well as adiabatic reactors. All technologies feature the proprietary Topsøe methanol catalyst. Topsøe methanol technology is a commercial success, demonstrated by the 14 references accumulated just in the last 3 years.

## Dimethyl ether (DME)

Similar to methanol, DME may be applied as an individual chemical, as a feedstock to further synthesis and as a fuel (LPG substitute, diesel engines or gas turbines). DME is formed by dehydration of methanol according to the reaction:



Topsøe's DME process is a compact unit, which can either be built as an add-on unit to an existing methanol plant or as a stand-alone unit that imports methanol. The unit is highly heat integrated and comprises essentially two distillation columns, an adiabatic reactor and a purge gas scrubber. This layout is very cost efficient and guarantees propellant-grade DME if the methanol purity is high. However, DME fuel grade can be produced with Topsøe's DME technology also from fuel grade methanol, giving to the process a significant Opex and Capex advantage.

## Topsøe Integrated Gasoline Synthesis (TIGAS)

In addition to our technology portfolio, TIGAS is our proprietary process for the production of gasoline. TIGAS is based on the conversion of synthesis gas to methanol and DME first. The TIGAS technology achieves the integration of gasoline, methanol and DME conversion. This permits to adjust the gas composition at the inlet of the methanol reactor for maximum efficiency of gasoline conversion, allowing energy efficiency benefits. The TIGAS technology is demonstrated at a pilot scale and is well under way to commercialisation.

## Combined synthesis: ammonia + methanol + DME ....

The economy of scale, particularly for the air separation unit, and the price fluctuation in the petrochemical market favour plants combining multiple syntheses. Studies show that co-production of methanol and ammonia can lead to 10-15% lower Capex with respect to stand-alone plants. Topsøe has two references for this process concept in China and is always available to support you in your decision about how to combine multiple productions.