Sulphur resistant/ sour water-gas shift catalyst

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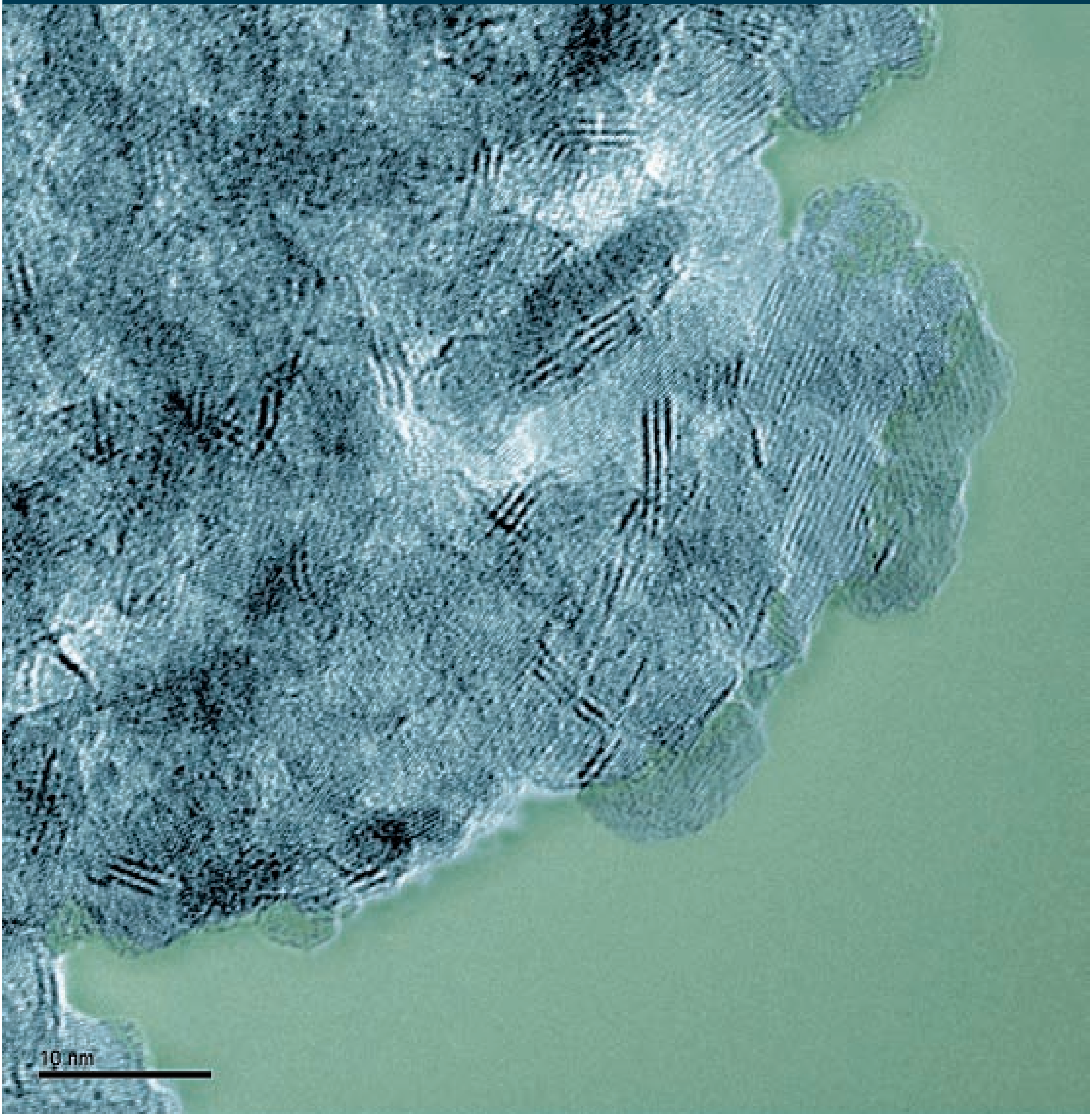
HALDOR TOPSØE
CATALYSING YOUR BUSINESS



Haldor Topsøe's SSK catalyst – sulphide particles and slabs photographed by transmission electron microscope

Superior catalyst performance for sour syngas conversion

Maximising efficiency

The world's decreasing reserves of oil and natural gas call for the use of unconventional carbon sources such as coal, biomass, waste and petcoke for the production of synthesis gas. Today's energy conversion technologies allow efficient use of these solid fuels with practically zero emission.

Sulphur resistant water-gas shift – or sour shift – is an important process step in the efficient conversion of solid fuels to syngas which is then converted into liquid fuels and chemicals. The sour shift catalyst uses sulphur – which is a poison for a traditional sweet shift catalyst – to assist in the catalysis of the water-gas shift reaction.

Client benefits

Topsøe's sour shift technology including the proprietary SSK catalyst offers a number of client benefits:

- superior shift activity in a sulphur-containing syngas, resulting in significant process simplification and reduced energy consumption compared to the traditional sweet shift catalyst
- the catalyst can operate in a broad temperature range and a wide range of steam to carbon monoxide ratios, resulting in increased flexibility in the operation of the water-gas shift section
- flexible shift trains consisting of one or multiple reactors with inter-cooling either for maximum carbon monoxide (CO) conversion or for production of syngas with a wide range of hydrogen to CO ratios
- conversion of carbonyl sulphide to hydrogen sulphide by hydrolysis
- the use of simple adiabatic shift reactors reduces capital cost and ensures simple operation

Topsøe's process designs are tailor-made to meet clients' requirements, and our engineers will design the best solution according to site specific conditions while obtaining maximum heat recovery.

The water-gas shift reaction

The sour shift catalyst requires sulphur in the syngas to stay in its active phase.

The well known stoichiometry of the water-gas shift reaction is:

$$CO + H_2O \leftrightarrow H_2 + CO_2 + \text{Heat}$$

Furthermore, COS is converted into hydrogen sulphide:

$$COS + H_2O \leftrightarrow H_2S + CO_2$$

The metal oxide in the sour shift catalyst reacts with the sulphur and forms metal sulphides. This sulphided state is the active state of the catalyst.

In an efficient heat integration scheme, the heat of reaction can be recovered as superheated high pressure steam.

Sour versus sweet water-gas shift

Sweet shift

The classic sweet water-gas shift process requires relatively high steam to dry gas ratio to prevent iron carbide formation on the iron-based high temperature shift catalyst. Furthermore, if a copper-based low temperature shift step is required the gas must be completely free of sulphur (figure 1).

Sour shift

The Topsøe sour shift technology greatly simplifies the process layout, as removal of hydrogen sulphide before the water-gas shift step is not required (see figure 2).

This layout ensures significant energy reduction.

The sour shift catalyst also allows operation at a lower steam to carbon monoxide ratio than sweet shift. This reduces the mass flow through the plant resulting in smaller-sized pipes and vessels.

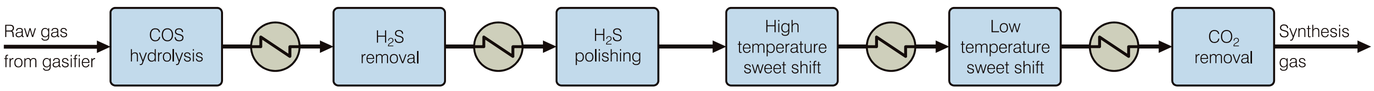


Figure 1: The sweet shift process

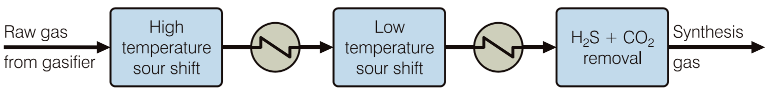


Figure 2: The sour shift process

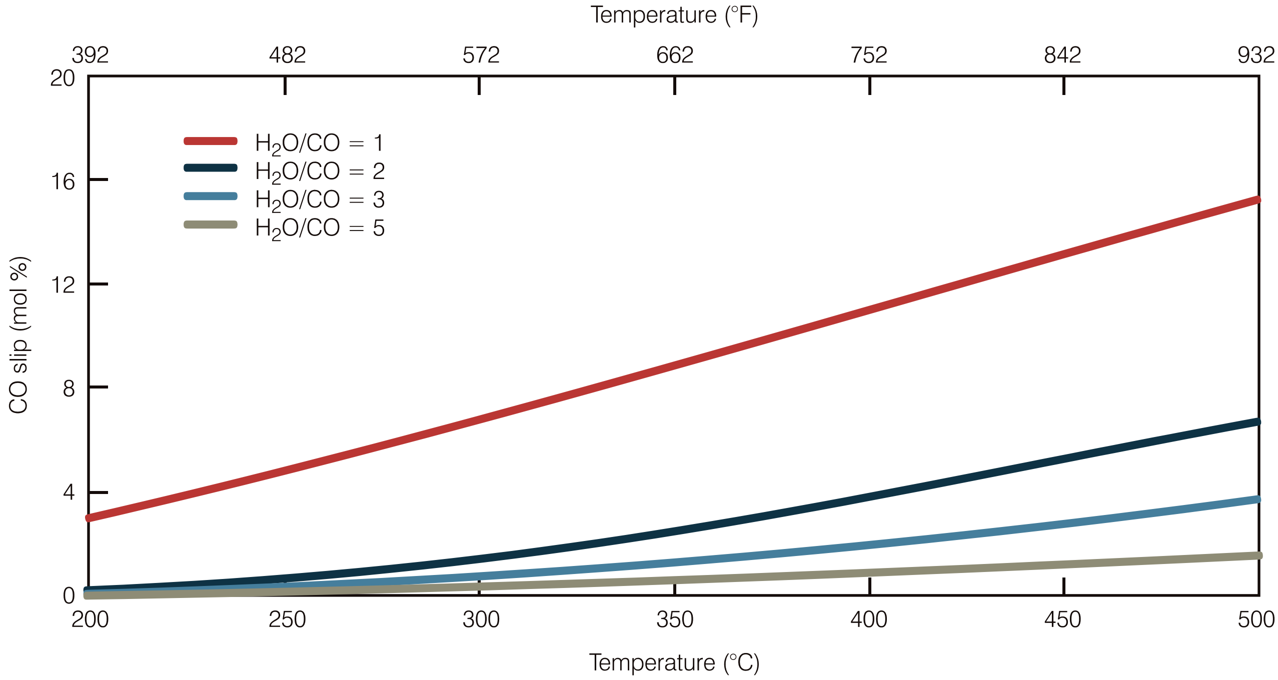


Figure 3: The effect of steam/CO and temperature on the CO slip for a typical gasifier-syngas composition

Process

Topsøe's sour shift technology can be tailored to clients' needs for instance by adjusting the steam to CO ratio in the gas. We can also design for the flexibility of co-production of power, substitute natural gas, hydrogen, ammonia, methanol and other chemicals.

As the water-gas shift is an equilibrium-limited reaction, the CO slip – CO concentration in the exit gas – depends on the reaction temperature and the syngas composition. The composition of the syngas is given by the gasifier. The steam concentration before shift can be adjusted.

A low CO slip can be achieved by increasing the steam to CO ratio or by decreasing the exit equilibrium temperature by cooling between two or more sour shift reactors.

If low CO slip is not a requirement, the Topsøe sour shift process and catalyst can operate at very low steam to CO ratio. The large flexibility in the choice of the operating conditions makes it possible to optimise the technology to maximise heat recovery by the production of high pressure steam.

Depending on process requirements, the configuration of a sour shift train may require one or two to three reactors in series.

Moisturisation of the raw syngas

The different gasification technologies produce a syngas with a different content of steam. Gasification technologies which are not utilising full quench will often require steam addition to obtain proper process conditions for the shift reactor.

Topsøe offers several methods to adjust the amount of steam in the raw syngas, so the optimal steam content can be obtained at lowest cost. An energy efficient moisturising process will lead to savings in the steam and energy consumption and reduce the amount of process condensate minimising the size and cost of a water treatment unit.

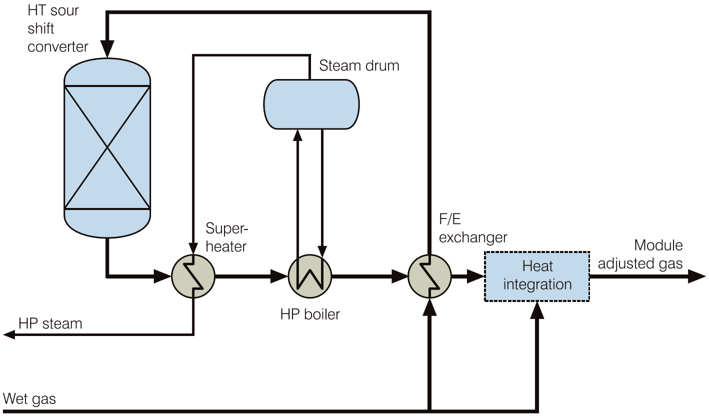


Figure 4: Partial conversion process layout

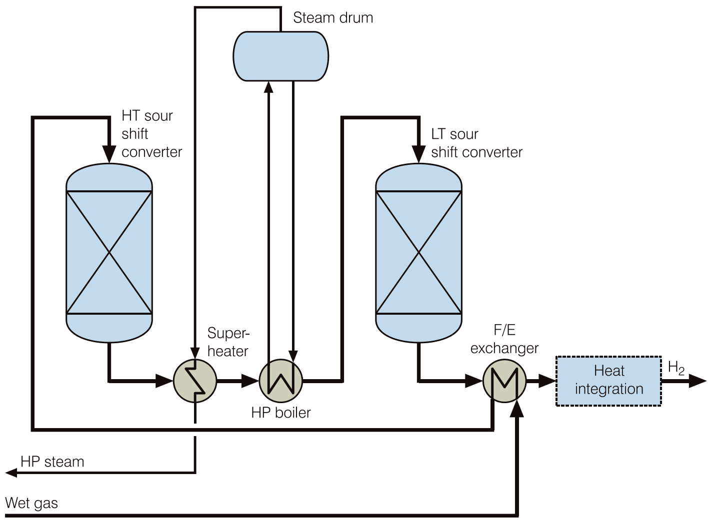


Figure 5: Full conversion process layout

Partial conversion

For methanol, substitute natural gas and liquid fuels syntheses, only a partial conversion of carbon monoxide is required. The typical configuration of a shift section consists of only one high temperature reactor with heat recovery in feed/effluent exchangers producing high pressure superheated steam.

COS hydrolysis

In this case, only part of the feed is passed to the sour shift reactor. The remaining fraction simply by-passes the shift reactor. The by-pass stream may be treated with Topsøe CKA catalyst to convert the carbonylsulphide (COS), as required by the downstream process units.

Full conversion

For hydrogen, ammonia as well as integrated gasification combined cycle and carbon capture and storage, high conversion of carbon monoxide is necessary.

The water-gas shift reaction is carried out in two reactors in series with intercooling. The heat of the exit gas from the first reactor (high temperature shift) is recovered as high-pressure superheated steam. The heat of the exit gas of the second reactor (low temperature shift) is recovered in the feed/effluent heat exchanger and other heat integration steps, such as boiler feed water preheating.

For processes requiring minimal CO slip, a layout including three reactors is available. In this case, the final hydrogen clean up is achieved through a methanation step rather than a Pressure Swing Adsorption (PSA).

Partnerships turning knowledge into business

The optimal solution

The optimum process configuration depends on the final product, the required purity of the product and the available options for heat integration. Additional integration of feed purification units, such as carbonyl hydrolysis, may be necessary, particularly in cases with a by-pass around the sour shift section. In each case, the optimal layout is achieved through a close cooperation between the client and the Topsøe design team.

The Topsøe proprietary catalyst for sour shift, SSK, provides our clients with an unmatched operating flexibility. For example, the high activity at low temperatures ensures very low CO slippage in applications targeting high conversion, and the stable performance at high temperature allows for the production of superheated high-pressure steam.

Your technology partner

Since 1940, Topsøe has specialised in heterogeneous catalysis, process development and engineering. A continuous focus on research and development has ensured that Topsøe's technologies and catalysts remain second to none. The many different types of process plants designed by Topsøe promote synergy and give our clients the benefit from the experience gained from these plants.

Topsøe's product portfolio ranges from catalyst production, licensing and engineering of proprietary catalytic processing units to in-house process development, project management and technical service. Proprietary know-how of all these fields ensures clients a competent business partner.

The Topsøe business portfolio

The firm commitment to catalysis and process technology has strengthened Topsøe's position in a wide range of additional business areas: Development and supply of catalysts and technologies for the production of ammonia, methanol and other petrochemicals, for gas conversion, oil refining and for emission control for the power and automotive industry.

Working with Topsøe, clients will benefit not only from our long-term knowledge of syngas related processes, but also from a broad portfolio of other technologies and catalysts:

- hydroprocessing and hydrogen production in the refining and petrochemical industry
- ammonia, methanol, DME, substitute natural gas (SNG) and coal to liquid (CTL) in coal based industries
- eliminating sulphur and other contaminants from off-gases – the WSA process

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