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The Claus process: teaching an old dog new tricks

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Abstract

The potential of integrating reaction with adsorption in a single piece of equipment to favourably displace chemical equilibria has attracted considerable attention in recent years. In contrast to the most such multifunctional reactor concepts investigated so far, the aim of our work is to study an industrially relevant chemical system with all its peculiarities.

The feasibility of enhancing conversion in fixed-bed adsorptive reactors has been evaluated for the Claus reaction used in sulphur recovery, which is usually carried out in a multistage process, to counteract the severe equilibrium limitations at high conversions. Both experimental and simulation results indicate that the adsorption/reaction kinetics and the adsorbent capacity have to exhibit appropriate and compatible values in order to overcome the equilibrium limitation and attain high conversions in a single-step process.

A crucial point is the selection of suitable reaction conditions, since the occurrence of undesirable side-reactions (e.g. suppression of COS elimination in the case of the Claus process) may be amplified by the distorted concentration profiles in adsorptive reactor operation. In industrial applications such by-products may be of particular importance and thus exert a decisive influence on the concentration profile modifications possible.

Keywords: Multifunctional reactor; Adsorptive reactor; Claus process; Sulphur recovery; Adsorption; Zeolites

1. Introduction

1.1. Claus reaction

Many of the catalysts used for the treatment of hydrocarbons in the petrochemical industry are highly susceptible to poisoning by sulphur compounds. It is thus essential to separate hydrogen sulphide from feedstocks such as sour natural gases or crude oil. Sulphur recovery typically involves application of the Claus process using the synproportionation reaction between hydrogen sulphide and sulphur dioxide yielding elemental sulphur and water vapour:

$$2H_2S\,(g) + SO_2\,(g) = \frac{3}{n}S_n\,(g) + 2H_2O\,(g),$$

$$\Delta_r H_m^\circ = -108\,\text{kJ/mol} \qquad (1)$$

High conversions for this exothermic, equilibrium-limited reaction call for low temperatures, the use of which, however, leads to low reaction rates, so that a catalyst must be employed. Even so, high sulphur yields still necessitate a multistage process with inter-stage cooling and sulphur condensation [5,8]. Increasingly restrictive environmental regulations mean that existing processes must be improved or new concepts developed to maximise hydrogen sulphide conversion [1,9]. The technological challenge is aggravated by the increasing need to exploit feedstocks having higher sulphur contents, due to the depletion of high quality resources (Fig. 1).

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Nomenclature

a	parameter of the Freundlich isotherm $(\mathrm{mol/m^3})^{0.25}$
c_i	concentration of component i (mol/m^3)
c_p	heat capacity (J/(K kg))
D_{ax}	axial dispersion coefficient (m^2/s)
ΔH_{m}	molar enthalpy (kJ/mol)
k_1	rate constant of the forward reaction (mmol/(kg s mbar$^{1.25}$))
k_2	rate constant of the reverse reaction (mmol/(kg s mbar))
K_p	equilibrium constant
p_i	partial pressure of component i (mbar)
p^0	standard pressure (mbar)
q_i	moles of adsorbate per volume adsorbent (mol/m^3)
r_{m}	catalyst mass based reaction rate (mmol/(kg s))
t	time (s)
T	temperature (K)
u	interstitial fluid velocity (m/s)
z	reactor length (m)

Greek symbols

α_1	coefficient in the mass balance (kg/m^3)
α_2	coefficient in the mass balance (–)
β_1	coefficient in the energy balance (kg/m^3)
β_2	coefficient in the energy balance (–)
λ_{eff}	effective thermal conductivity coefficient (W/(K m))
ν_i	stoichiometric coefficient for component i (–)
ρ	density (kg/m^3)

Subscripts and superscripts

ads	adsorption
eq	equilibrium
F	fluid phase
r	reaction
S	solid phase

1.2. Adsorptive Claus reaction

According to Le Chatelier's principle, the removal of a reaction product results in an equilibrium displacement to higher conversion. The conventional Sulfreen process is based upon the withdrawal of sulphur by in situ condensation within the reactor [10]. The selective removal of water should, however, be a far more effective technique, as its effect on the equilibrium composition in the mass action equation is much greater:

$$K_p(T) = \frac{p^2(\mathrm{H_2O})\,p^{3/8}(S_8)}{p^2(\mathrm{H_2S})\,p(\mathrm{SO_2})}(p^0)^{5/8} \tag{2}$$

The in situ combination of the heterogeneously catalysed Claus reaction and an adsorptive water separation seems especially promising, as both reaction and adsorption exhibit similar kinetics and pressure can be adapted to the needs of the adsorptive separation. Such an adsorptive reactor will lead to almost complete conversion as long as the adsorption capacity is not exhausted. There are numerous possibilities for implementing these two functionalities, ranging from fixed-beds with homogeneous catalyst/adsorbent mixtures to spatially structured distributions or even fluidised beds.

The operation of adsorptive fixed-bed reactors is inherently periodic due to the need for adsorbent regeneration once its adsorption capacity has been exhausted. The zeolite adsorbent used can be regenerated effectively using an inert sweep gas. Fig. 2 shows a flowsheet for the cyclic operation of such a process with at least two adsorptive reactors, operated alternately in the adsorption or regeneration mode. The sulphur is condensed and removed between the reactors. The virtually water- and sulphur-free gas emerging from the condenser can be heated and used as the inert sweep gas for the regeneration of the second reactor. Once the adsorbent in the adsorptive reactor is fully loaded, the direction of flow is reversed, so that the regenerated reactor now serves as the adsorptive stage while the adsorptive reactor from the previous half cycle is regenerated. Alternatively, continuous operation is possible using rotating, moving or fluidised bed systems [2,6].

In the case of the Claus reaction zeolite-3A seems to be the most promising adsorbent for in situ physisorption of water, due to its high adsorptive capacity, its excellent selectivity and rapid adsorption kinetics. Furthermore, facile regeneration by pressure swing operation or with inert sweep gas and/or temperature modulation is feasible. Compared to pressure swing operation, which is fast and can be used to enhance

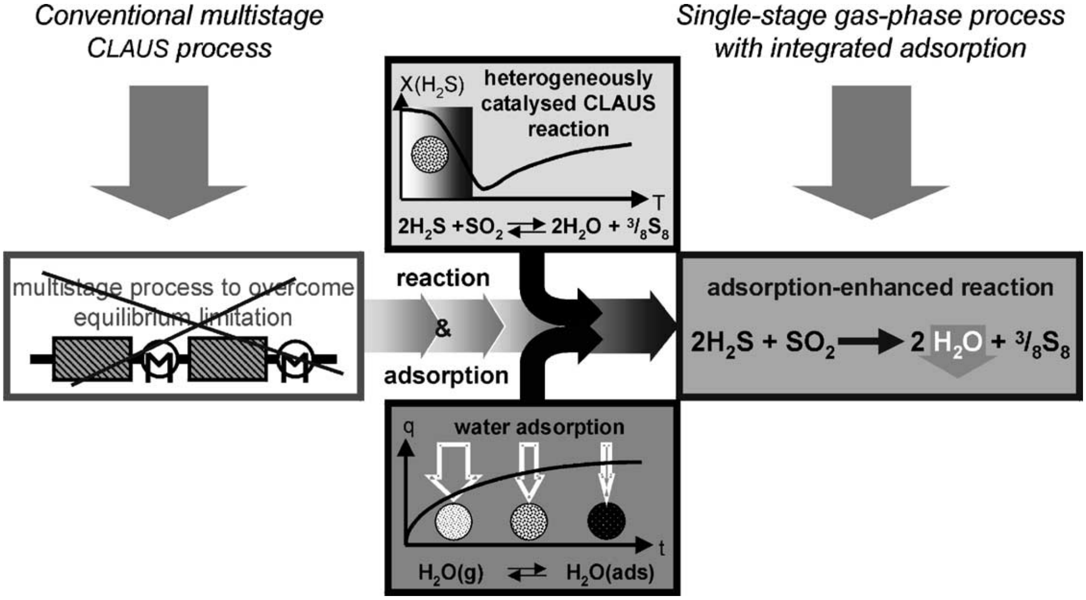

Fig. 1. Single-stage adsorptively enhanced Claus process as alternative to conventional multistage processes.

adsorption, temperature changes are rather slow, due to the thermal inertia of the system. This leads to extended regeneration periods and, consequently, the need for additional reactors in quasi-continuous operation.

A commercial Na_2O-promoted Al_2O_3 catalyst (CR 4/8, Procatalyse) was used to catalyse the reaction.

The conceptual design of an adsorptive Claus reactor requires preliminary kinetic studies of both the adsorption and the reaction process. The adsorptive capacity must also be determined. High adsorptive capacity under reaction conditions and an appropriate catalyst to adsorbent ratio are prerequisites for lengthy adsorption periods. Nevertheless, not just the adsorption period and high conversion must be considered, the regeneration is also an important aspect in designing and evaluating adsorptive reactors.

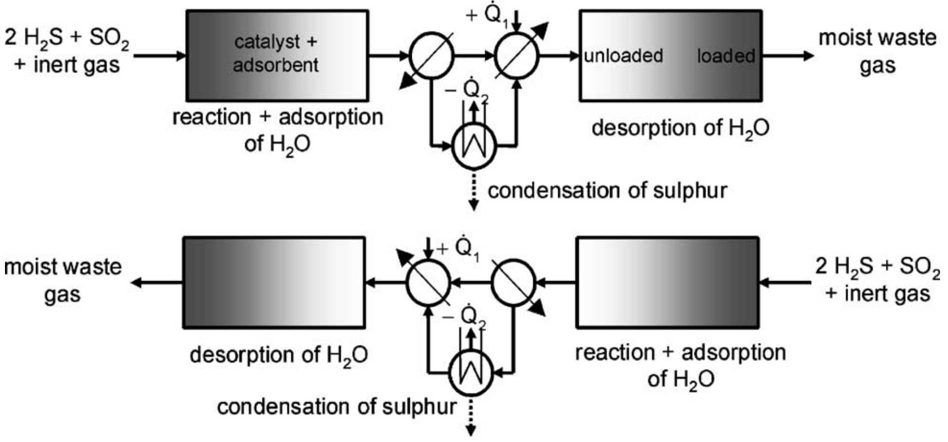

Fig. 2. Reverse flow adsorptive reactor concept for single-stage high conversion Claus process.

2. Investigation of individual process functions

2.1. Reaction kinetics

The kinetics of the Claus reaction were studied in the temperature range of 200–300 °C and at H_2S concentrations between 0 and 15 vol.% in a Berty-type reactor. The experimentally observed results can be described well by the following empirical equation:[1]

$$r_m = k_1(T)p(H_2S)p^{0.25}(SO_2) - k_2(T)p(H_2O) \quad (3)$$

From the temperature coefficients of the rate constants, the activation energies were found to be 49.4 kJ/mol for the forward and 89.3 kJ/mol for the reverse reaction. It is stressed once more that the kinetics are described by a simple statistical equation which may include mass transport phenomena. This might be also the reason why the difference of the determined activation energies do not fit to the reaction enthalpy. A comparison between experimental and calculated values for the reaction rate indicates an agreement entirely adequate for the purposes of a basic reactor design.

2.2. Adsorption kinetics and capacity

Due to comparatively mild temperatures of around 250 °C, commercially available zeolitic adsorbents are eminently suitable for the adsorptive Claus reaction. For selective water adsorption, a zeolite-3A (SYLOBEAD™ MS 562 C, Grace Davison GmbH) was chosen which, owing to its pore diameter, adsorbs neither SO_2 nor H_2S.

The determination of the adsorption kinetics was carried out by chromatographic techniques and with direct TEOM measurements (Tapered Element Oscillating Microbalance). In the temperature and concentration range relevant for Claus reaction, the adsorption isotherms could be fitted well using the Freundlich equation (see footnote 1):

$$q_{eq}(H_2O) = a(T)c_{eq}^{0.75}(H_2O),\quad \Delta_{ads}H_m^{\circ} = -30.5\,\text{kJ/mol} \quad (4)$$

Moreover, for modelling the adsorption kinetics a simple LDF model (Linear Driving Force) was chosen, which also describes the experimental values very satisfactorily. The adsorptive capacity of the zeolite was also found to be sufficiently large. No reactant adsorption on the zeolite could be detected, in accordance with the high selectivity for water vapour expected.

2.3. Modelling

The fixed-bed reactor was simulated using a one-dimensional, dynamic dispersion model under both isothermal and adiabatic conditions, assuming that the fixed-bed comprises a homogeneous mixture of catalyst and adsorbent (Fig. 3):

$$\frac{\partial c_i}{\partial t} - D_{ax}\frac{\partial^2 c_i}{\partial z^2} + \frac{\partial(uc_i)}{\partial z} = \alpha_1 \nu_i^{\text{reaction}} r + \alpha_2 \nu_i^{\text{adsorption}}\frac{\partial q_i}{\partial t} \quad (5)$$

For adiabatic operation, the energy balance must also be solved:

$$\bar{\rho}_S\bar{c}_{p,S}\frac{\partial T}{\partial t} - \lambda_{eff}\frac{\partial^2 T}{\partial z^2} + \bar{\rho}_F\bar{c}_{p,F}\frac{\partial(uT)}{\partial z} = \beta_1 r(-\Delta_r H_m) + \beta_2\sum_{(i)}\frac{\partial q_i}{\partial t}(-\Delta_{ads}H_{m,i}) \quad (6)$$

This one-dimensional parabolic system of differential equations was discretised using finite QUICK differences (quadratic interpolation between each two discrete elements) according to the Leonard scheme [7] and solved numerically with gPROMS® [4].

2.4. Comparison of reaction and adsorption

A comparison of reaction and adsorption kinetics indicates that they are of the same order of magnitude and thus meets an important criterion for adsorptive reactors. This result can be illustrated by comparing the lengths of reaction and adsorption zones that are necessary to adsorb the entire amount of water produced at a given temperature [2]. A further matter to be clarified is the optimal catalyst to zeolite ratio in a homogeneous fixed-bed. By ascertaining the breakthrough time for various values of this ratio, an adsorbent fraction of 43 vol.% was found to be optimal under the prevailing operating conditions. The conversion

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[1] Both equations, reaction and adsorption, are only valid under the mentioned conditions for Claus process.

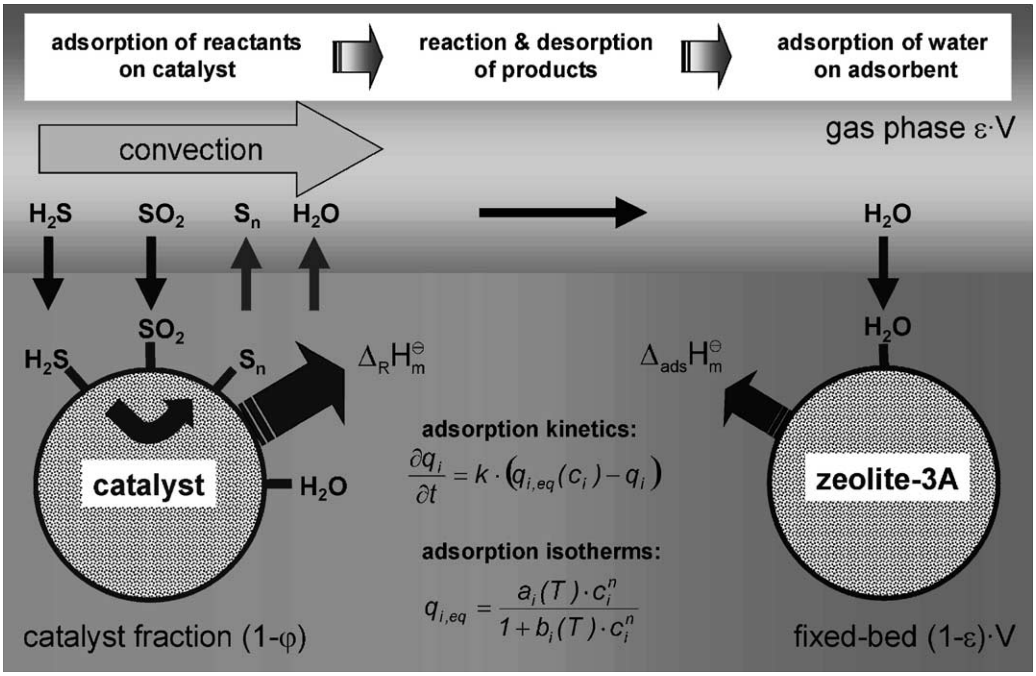

Fig. 3. Individual steps consisting of adsorption of the reactants on the catalyst, reaction, desorption of the products together with the adsorption of water vapour on the adsorbent are the basis for the model describing the phenomena within the adsorptively enhanced Claus reactor.

enhancement in an adsorptive reactor was evaluated under isothermal conditions at a series of temperatures. Above a temperature of 210 °C the adsorptive reactor was predicted to yield noticeably higher conversion values than at equilibrium and the maximum value of more than 99.5 % was attained at about 250 °C.

3. Experiments on the adsorptive Claus reaction

3.1. Experimental equipment

A pilot-scale test facility was constructed to validate the conversion enhancement predicted based on the positive simulation results. This Claus pilot-plant was designed for the temperature range of 250–350 °C and a total feed of 2.5 Nm^3/h containing up to 15 vol.% H_2S. The reactor is equipped with a vacuum jacket and an additional insulation to minimise heat loss and permit investigation of the reaction under virtually adiabatic conditions.

The problems associated with sulphur condensation were be overcome by extensive electric line heating and precise temperature control. Failure to avoid local sulphur desublimation leads to pressure build-up due to plugged lines. The sulphur formed is condensed at the reactor outlet in a sequence of two water-cooled sulphur condensers at different temperature levels. Inside these condensers a rotating scraper blade removes the sulphur and guarantees a minimal thickness of the sulphur film for reasonable rates of heat transfer. Most of the sulphur is separated in the first condenser and the gas leaving the second condenser is nearly sulphur-free.

Both feed composition and reactor outlet were analysed for H_2S, SO_2 and N_2 (inert) using gas chromatography.

3.2. Experimental results

Several experiments were carried out with a stoichiometric H_2S:SO_2 ratio and H_2S contents between 5 and 10 vol.% in the temperature range of

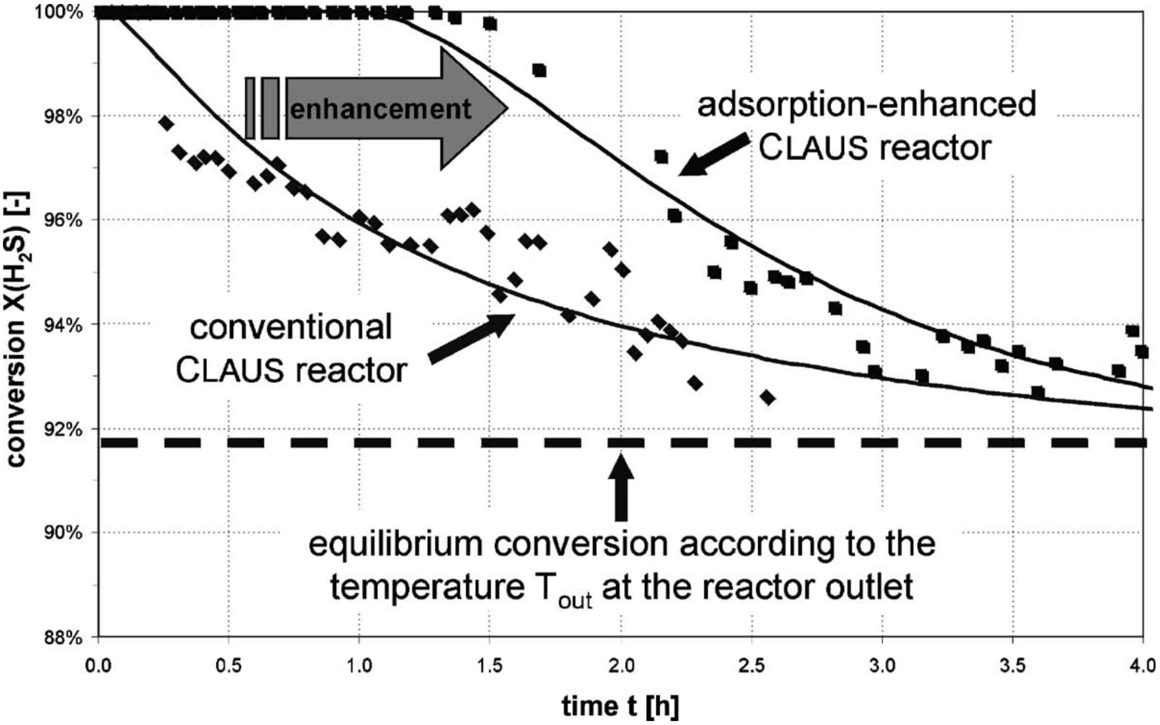

Fig. 4. Comparison between the experimental data obtained under conventional and adsorptively enhanced Claus reactor operation and under adiabatic conditions (H_2S-content: 10 mol%, H_2S:SO_2 ratio = 2:1, reactor inlet temperature: $T_{in} = 250\,^{\circ}C$).

250–350 °C. The reactor was filled with a homogeneous mixture of catalyst/adsorbent or catalyst/inert containing 43 vol.% of adsorbent/inert, respectively. The experimental results thus allow a direct comparison between the conventional and the adsorptively enhanced reactor operation.

Fig. 4 depicts this comparison for an experiment with a reactor inlet temperature of 250 °C and a H_2S content of 10 vol.%. The experimental results clearly demonstrate that the in situ adsorption of the water formed in the reaction increases the sulphur yield for a period of more than 60 min prior to H_2S breakthrough. As a consequence of the zeolite becoming saturated with water vapour and the increased temperature of the fixed-bed (adiabatic operation) the H_2S conversion subsequently approaches the equilibrium value representing the upper limit of conventional operation.

These initial experimental results show that the principle of an adsorptive-enhanced reactor is sound and promise illuminating insights and interesting further developments for the Claus reaction and similar systems.

In addition, the experiments in the adsorptively enhanced Claus reactor revealed further phenomena not anticipated in the original analysis. The catalyst, for example, exhibited a certain amount of reactant sorption, probably consisting of a combination of rapid H_2S adsorption and slow SO_2 chemisorption. The latter effect is consistent with the somewhat sparse information provided in the literature dealing with this topic [3]. The irreversible chemisorption of the SO_2 on the alkaline γ-Al_2O_3 has been modelled approximately with a "shrinking core model" for particles of unchanging size. It was found that the chemisorption proceeds under diffusion control with an effective diffusion coefficient of about $4.7 \times 10^{-9}\ m^2/s$ at 250 °C. For the gas–solid reaction itself first order kinetics with respect to the gas phase reactant were assumed. From the Arrhenius plot the activation energy was determined to be 61.7 kJ/mol. Additional reactant adsorption experiments on this catalyst were used to extend the existing mathematical models to incorporate reactant adsorption. This refinement yielded even better agreement between calculated and experimental values.

Another effect of interest results from the thermal inertia of the reactor system. In the adiabatic reactor, periods of 10–15 h are necessary for reactor to achieve thermal equilibrium. A regeneration of the adsorbent by temperature swing desorption is thus not feasible, since the time off-line becomes excessive. As a consequence only pressure change or sweep gas desorption with more favourable dynamics and suitability for reverse flow operation are realistic options. The thermal inertia of the fixed-bed does, however, avoid the heat liberated by the reaction interfering with the adsorption process in adiabatic operation.

4. Conclusion and future work

The potential and pitfalls of an adsorptively enhanced Claus reactor concept were analysed in detail. The kinetics of the Claus reaction and for the adsorption of water on zeolite-3A, together with the adsorption isotherms, were established from experimental data. A simple empirical relationship was used for the description of the reaction kinetics on a commercial Al_2O_3 supported catalyst. Furthermore, a suitable adsorbent was identified and characterised with respect to its adsorption kinetics and capacity. The results indicate that under the operating conditions chosen the capacity of the zeolite-3A for water vapour is adequate. An LDF model was found to give a good fit to the adsorption data. The mathematical models developed were validated in a pilot-plant and subsequently refined. The superior performance of in the adsorptively enhanced reactor in comparison to the conventional operation could be verified. The adsorptive Claus reactor would thus seem to be a promising subject for future research. Such work should address features such as adsorbent regeneration and the influence of side-reactions, which have been largely neglected so far.

Even though the adsorption of water on zeolite has been investigated thoroughly, a large amount of modelling and experimental work remains in order to develop a suitable regeneration strategy for the adsorbent chosen. At this point, the potential available in structuring the catalyst and adsorbent composition of the fixed-bed and in an intelligent temperature control concept will become important.

Another key issue is the undesirable side-reactions occurring in the Claus reaction, which are well known from the conventional process. In particular, the formation of carbonyl sulphide COS from the H_2S and CO_2 usually present in the Claus gas is especially problematical, and has already been qualitatively observed to take place to a small extent. In contrast to the conventional process, where COS is hydrolysed by the excess water vapour present, such a fortuitous decomposition reaction is precluded in the adsorptive reactor. What is more, the adsorptive Claus reactor would actually be expected to increase COS formation due to the high degree of water removal.

A matter of particular interest is the chemical resistance of the catalyst and, even more so, of the zeolite to the aggressive gas system. The key factor would seem to concern the possible effect of SO_2 on the loaded zeolite. Microscopic and chemical analyses of the zeolite and catalyst surfaces could help clarify this issue.

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