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IN-SITU STRIPPING OF H_2S IN GASOIL HYDRODESULPHURIZATION
Reactor Design Considerations

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In order to meet future diesel specifications the sulphur content of diesel would need to be reduced to below 50 ppm. This requirement would require improved reactor configurations. In this study we examine the benefits of counter-current contacting of gas oil with H_2, over conventional co-current contacting in a trickle bed hydrodesulphurization (HDS) reactor. In counter-current contacting, we achieve *in-situ* stripping of H_2S from the liquid phase; this is beneficial to the HDS kinetics. A comparison simulation study shows that counter-current contacting would require about 20% lower catalyst load than co-current contacting. However, counter-current contacting of gas and liquid phases in conventionally used HDS catalysts, of 1.5 mm sizes, is not possible due to flooding limitations. The catalysts need to be housed in special wire gauze envelopes as in the catalytic bales or KATAPAK-S configurations. A preliminary hardware design of a counter-current HDS reactor using catalytic bales was carried out in order to determine the technical feasibility. Using a realistic sulphur-containing feedstock, the target of 50 ppm S content of desulphurized oil could be met in a reactor of reasonable dimensions. The study also underlines the need for accurate modelling of thermal effects during desulphurization. Our study also shows that interphase mass transfer is unlikely to be a limiting factor and there is a need to develop improved reactor configurations allowing for increased catalyst loading, at the expense of gas–liquid interfacial area.

Keywords: hydrodesulphurization; reactor design; catalytic bales; counter-current flow; NEQ-model

INTRODUCTION

Present regulation in the European Union (EU) and USA on the maximum levels of undesirable compounds in transport fuels has triggered an intensive search for new catalytic systems and reactor technologies (Babich and Moulijn, 2003; Ma *et al.*, 1994; Song and Ma, 2003). For diesel, the EU has a commitment to reduce the sulphur content to below 50 ppm and aromatics to 0.0 vol%, as well as to improve the cetane number to a minimum of 51. The fulfilment of this legislation presents a serious challenge for the refining industry. With the use of conventional catalytic systems and one-stage trickle bed reactor (TBR) technology, typical HDS plants are able to reduce the S content in their diesel feedstock to levels of around 700–500 ppm. Deeper conversion levels are only possible with the use of two-stage technology and catalyst profiling, as practiced by the SynSat and Arosat processes (Song and Ma, 2003; Trambouze, 1990). The key strategy used in these processes, i.e. the removal of H_2S after the first stage, has proved to be beneficial in the context of reaching ultra-low levels of both S and aromatics in a second stage. It is well recognized that HDS reactions are adversely affected by the presence of H_2S. An alternative strategy is to use counter-current contacting of gas and liquid phases (Krishna, 2002; Mochida *et al.*, 1996; Sie, 1999; Trambouze, 1990). In counter-current contacting of oil and H_2 we achieve *in-situ* stripping of H_2S (see Figure 1) and refractory S compounds at the bottom of the catalyst bed are brought into contact with fresh H_2. Counter-current operation of gas and liquid phases using present day catalyst, with sizes of the order of 1.5 mm, is not feasible because of severe pressure drop and flooding constraints. New generation hardware configurations such as the catalyst bales of CDTech (Subawalla *et al.* 1997; Xu *et al.*, 1997) and KATAPAK-S structure of Sulzer (Ellenberger and Krishna, 1999; Moritz and Hasse, 1999) need to be used, wherein the conventional catalysts are housed in wire gauze envelopes (see Figure 2).

The major objective of our work is to carry out a comparison of counter-current vs. co-current for the hydrodesulphurization (HDS) of diesel in order to underline the advantages of counter-current contacting. Furthermore, a detailed hardware design is carried out for the counter-current reactor concept using Catalyst Bales as catalyst-

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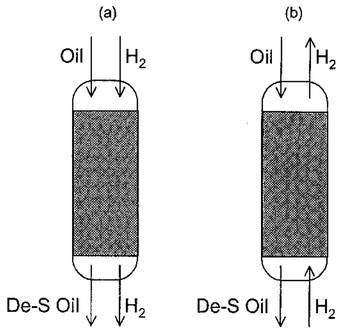

Figure 1. Hydrodesulphurization of gas oil carried out in (a) co-current trickle bed reactor and (b) counter-current reactor with *in-situ* stripping of H_2S.

bearing packing elements in order to show the practical feasibility of this hardware configuration.

SULPHUR COMPOUNDS IN GAS OIL AND THEIR REACTIVITY

Sulphur compounds in petroleum fractions span a wide range of molecular structures with remarkable differences in reactivity (Froment *et al.*, 1994; Gates and Topsoe, 1997; Schulz *et al.*, 1999a, b). From a structural viewpoint, we can distinguish between non-aromatic S components—mercaptans R-SH, sulphides *R-S-R′*, disulphides *R-S-S-R′* and polysulphides $R\text{-}S_n\text{-}R'$—and aromatic S components—thiophene (T), benzothiophene (BT), dibenzothiophene (DBT), multi-ring molecules and all their alkyl derivatives. The relative and absolute contribution of these families to the total S content plays an important role in the operation conditions inside the reactor and in the catalyst selection. Experimental data (Ma *et al.*, 1994; Mochida *et al.*, 1996; Schulz, *et al.*, 1999a, b) have shown that there are mainly three reactive behaviors of S species.

Components that Rapidly React at Reactor Inlet Conditions

Here we include BT, T and lighter S components. Approximately 50–70% of the total S content in straight rung gas oil comes from these families. The amounts of these sulphur compounds have a significant influence on reactor design because of the large heat of reaction and the amount of H_2S released. Usually the co-current trickle bed reactor (see Figure 1a) needs a quenching section with fresh H_2 in order to reduce the liquid temperature and to increase the H_2 partial pressure. At common HDS conditions, a major portion of these components is converted. Conventional $CoMo/Al_2O_3$ catalysts are suitable for this reaction duty.

Components with a Mild Reactivity and Presence through Most Part of the Reactor Length

All the alkyl-dibenzothiophenes, excluding 4-MeDBT and 4,6-DiMeDBT, are included here. The impact of these compounds on reactor design is related to the catalyst demand, and their total content determines the severity of

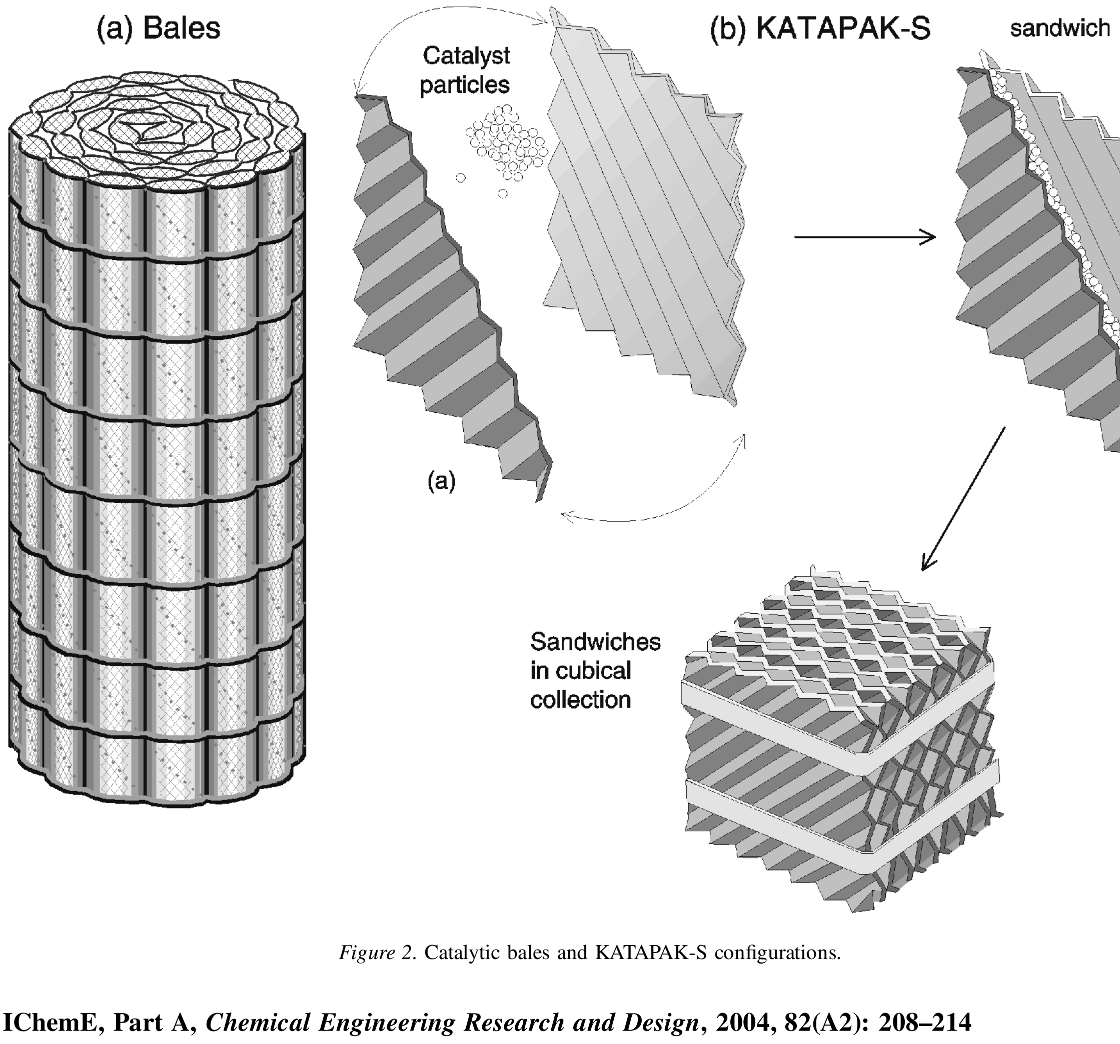

Figure 2. Catalytic bales and KATAPAK-S configurations.

the process. Again, CoMo/Al_2O_3 and also NiMo/Al_2O_3 are suitable catalysts.

Highly Refractive Components

Here we include sulphur species with an intrinsic hindrance of the S atom by a hydrocarbon group like 4-MeDBT, 4,6-DiMeDBT and higher boiling point components with similar hindrance pattern with two or three aromatic rings. With the present catalysts and reactor volumes it is still very difficult to convert them to levels higher than 50%, and an important portion of their initial content remains almost intact when undergoing HDS. Catalysts with an improved acid function and higher hydrogenation capabilities perform better for these molecules.

COMPARISON OF CO- AND COUNTER-CURRENT CONTACTING

In order to demonstrate the advantages of counter-current contacting we consider the desulphurization of a liquid feed of *n*-hexadecane, nC_{16}, (model compound representing the diesel fraction), containing 1.82 wt% (18,200 ppm) DBT, representing the most refractory S species. The molar flows of C_{16} and DBT are 85.6 and 12.2 mol s^{-1}, respectively. The entering gas phase consists of 91.8 mol s^{-1} H_2 and 56.8 mol s^{-1} CH_4. Inlet temperature and pressure are kept constant during the simulations. The inlet temperatures of gas and liquid phases are set at 590K and the reactor is maintained at a pressure of 50 bar. The reaction rate for DBT is of the Langmuir–Hinshelwood type and is taken from the literature (Vanrysselberghe *et al.*, 1998). Both gas and liquid phases as assumed to flow through the reactor in plug flow. The equilibrium stage (EQ) model (Taylor and Krishna, 1993) was adopted for reactor design, while allowing for finite reaction HDS reactions in the liquid phase. Reaction in gas phase is not considered. Neither mass nor energy transport limitations within the catalyst particle are taken into account (effectiveness factor of unity). For co-current simulations we used one additional equilibrium stage without catalyst (stage 0), so that entering liquid and gas at the top of the reactor (stage 1) are indeed an L/V mixture in equilibrium at the given temperature and pressure. This configuration resembles industrial conditions with a trickle-bed reactor. For counter-current, liquid and gas are fed at the top (stage 1) and bottom (stage N) of the reactor without any additional preparation. The Peng–Robinson equation of state is used to describe the gas phase. The number of equilibrium stages was taken to be 30 ($N = 30$); a higher number of stages did not produce significant improvement in the conversions.

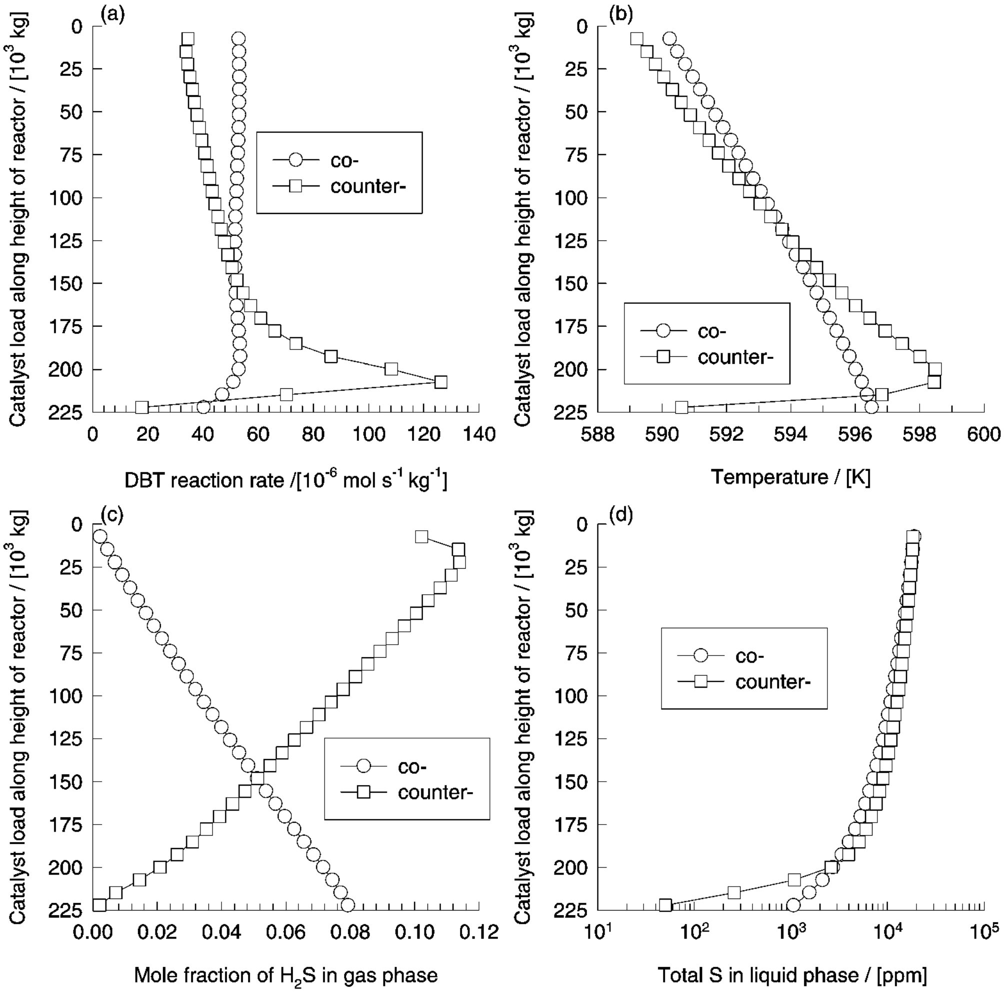

Figure 3. EQ stage model simulations for (a) co-current and (b) counter-current contacting. The total catalyst inventory is 222 tonnes for both cases.

In the first set of simulations we consider a reactor with a catalyst inventory of 222 tonnes, distributed uniformly over the 30 equilibrium stages. The simulation results using the EQ model for co- and counter-current operation are shown in Figure 3. The reaction rate of DBT (see Figure 3a) for counter-current operation is significantly higher at the bottom of the bed, where the fresh H_2 is brought into contact with the liquid leaving the reactor. This underlines the main advantage of counter-current operation. Another way of looking at the counter-current configuration is to consider this as a reactor wherein the dissolved H_2S in the liquid phase is *stripped* into the gas phase; this is evident when we observe the gas phase compositions in Figure 3(b); the H_2S mole fraction increases from zero at the bottom to its maximum value at the top of the reactor. Since the presence of dissolved H_2S is detrimental to desulphurization, *in-situ* stripping is beneficial. In the conventional co-current operation, the H_2S concentration is the highest at the bottom, where the residual refractory compounds are to be found; clearly this situation is not ideal.

The S content of the liquid phase, expressed in ppm, is plotted in Figure 3(d). We note that for counter-current operation the S content of the exiting liquid is 50 ppm, whereas for co-current operation it is 1070 ppm. Clearly for the chosen catalyst load (222 tonnes), co-current operation is unable to meet the desired 50 ppm specifications.

Another way to compare co- and counter-current operation is to consider designs in which the 50 ppm specification on the S content of the desulphurized oil is met in *both* cases. From simulations of various configurations we established that, for the co-current case, a total catalyst load of 267 tonnes will be required, i.e. about 20% more than for the counter-current case. The simulation results are illustrated in Figure 4. From Figure 4(a) we note that the reaction rate for DBT for the co-current case progressively reduces to zero as we proceed down the column as the 50 ppm specifications are approached, underlining the difficulty of obtaining deep hydrodesulphurization in this case.

Another important point to note is the sharp reduction in the S content for the counter-current case, as we move down the bottom of the reactor; see Figure 4(d). For the co-current case the reduction in S content is much more gradual, in view of the progressive reduction in the DBT reaction rate (see Figure 4a) to near-zero values.

HARDWARE DESIGN FOR COUNTER-CURRENT REACTION

Having established the advantages of counter-current contacting, we now proceed with the hardware design aspects of this configuration by performing a detailed

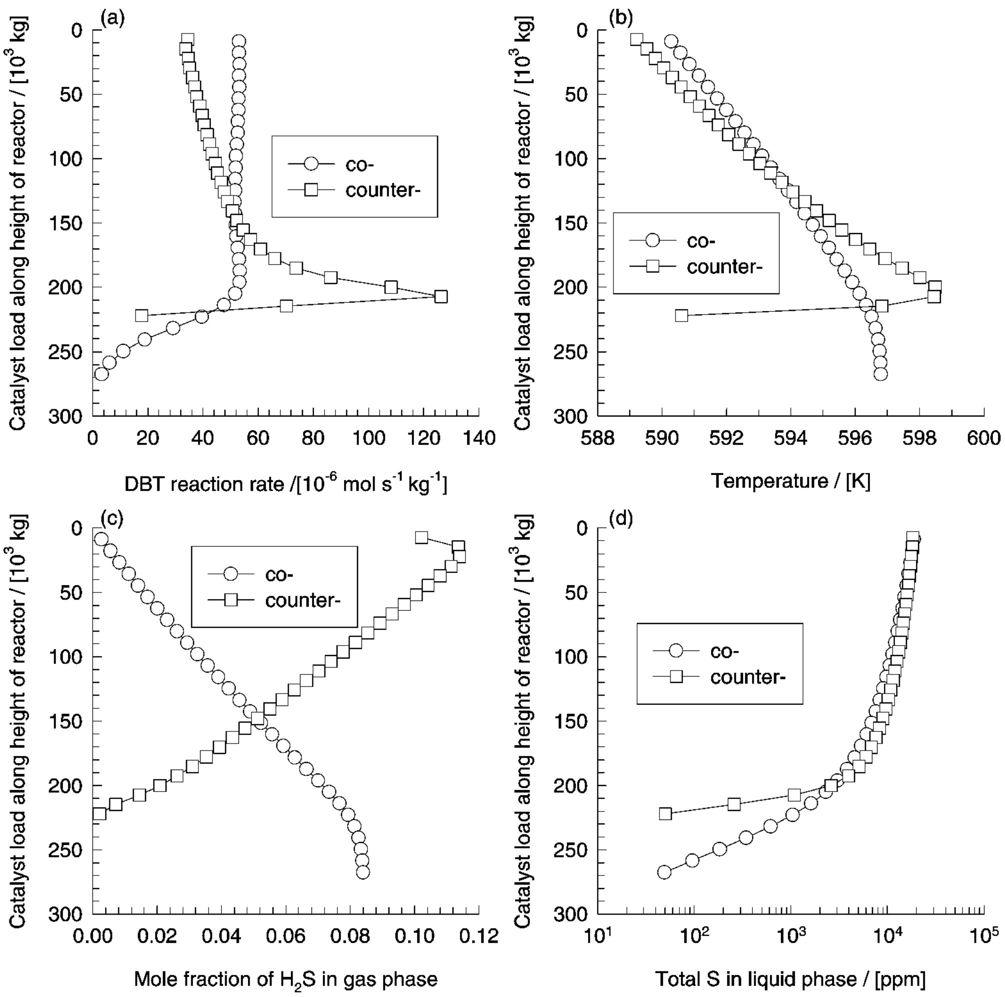

Figure 4. EQ stage model simulations for (a) co-current (catalyst load = 267 tonnes) and (b) counter-current (catalyst load = 222 tonnes) contacting.

Table 1. Hardware details for counter-current reactor with catalytic bales.

Height, m	30
Diameter, m	2.75
Catalyst load, tonnes	30
Liquid flow at top of reactor, mol s^{-1}	nC_{16}: 85.6; BT: 8, DBT, 4 (in Figures 5 and 7) In Figure 6, BT = 5, 6, 7, 8 and 9; DBT = 4
Gas flow at bottom of reactor, mol s^{-1}	H_2, 91.8; CH_4, 56.8
Pressure in reactor, bar	50
Temperature of entering gas, K	590
Temperature of entering liquid, K	590
Specific area of Catalyst Bale packing, m^{-1}; this represents the surface area of the cloth containing the catalyst	169
Void fraction of catalyst bales	0.76
Catalyst inside bales	Co/Mo catalyst
Catalyst bed density expressed per m^3 of total column volume, kg m^{-3}	170

design of the reactor employing catalytic bales, pictured in Figure 2(a). In catalytic bale packing (Subawalla *et al.*, 1997), the catalyst is enclosed within several pockets in a cloth belt, with cloth dimension varying according to the size of the bale. The open ends of the pockets are sewn closed, and the belts are then rolled up with alternating layers of an open stainless steel knitted mesh, to form a cylindrical bale of desired dimensions. The stainless steel mesh provides both structural strength and the open configuration required for counter-current vapour and liquid flow. Several of these bales are then packed tightly into a column such that the pockets are vertical in a spiral arrangement. The catalytic bed density expressed as kg of catalyst per cubic meter of column is 170 kg m^{-3}, which is approximately four times lower than that of a trickle bed reactor. The hardware details are summarized in Table 1.

For the S compound in the feed we consider a more realistic feed containing 8 mol s^{-1} of BT and 4 mol s^{-1} of DBT. We shall also consider the influences of varying BT/DBT ratios in the feed of 5/4, 6/4, 7/4 and 9/4. The other flows are the same as in the study considered above.

Preliminary calculations indicated that the constraint of 50 ppm total S in the desulphurized oil can be met with a catalyst load of 30 tonnes and that 20 theoretical stages will be required for separation (*in-situ* stripping purposes). Using the hydrodynamics and mass transfer parameters for catalytic bales (Bornhutter and Mersmann, 1993; Subawalla *et al.*, 1997) we choose a column diameter of 2.75 m and a total packed height (catalytic bales) of 30 m. The choice of the column diameter ensures that the expected vapour and liquid loads are well below the flooding limits.

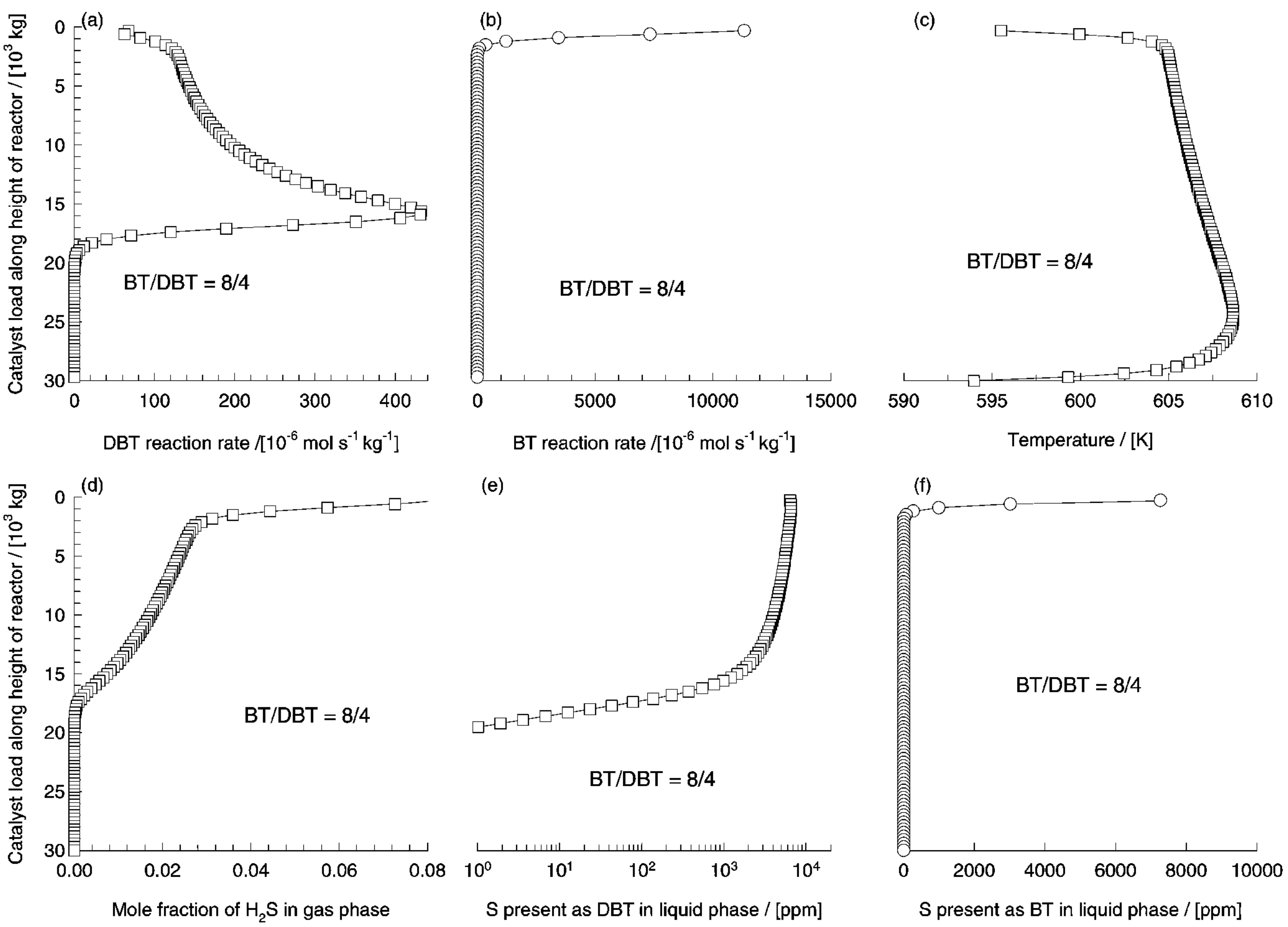

Figure 5. NEQ simulation results for counter-current HDS reactor with 20 tonnes of catalyst inventory. The column diameter = 2.75 and the total packed height (catalyst bales) is 30 m. The BT/DBT ratio in the liquid feed to the reactor is 8/4.

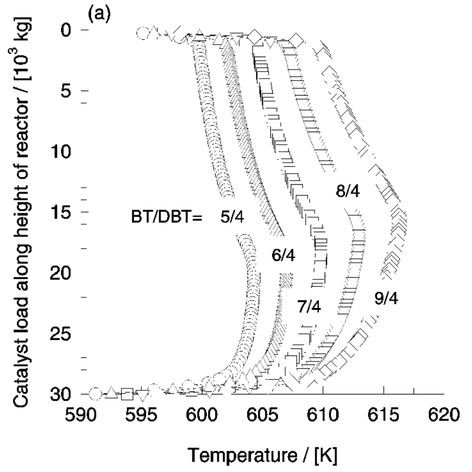

Figure 6. Influence of BT/DBT ratio on (a) temperature and (b) total S content in the liquid phase. NEQ simulation results for counter-current HDS reactor with 30 tonnes of catalyst inventory. The column diameter = 2.75 and the total packed height (catalyst bales) is 30 m.

In order to check the feasibility of the proposed hardware configuration, we carried out a rigorous non-equilibrium (NEQ) simulation of the counter-current HDS reactor using the methods described in earlier publications (Baur and Krishna, 2002; Taylor and Krishna, 2000).

The NEQ simulation results for BT/DBT = 8/4 are shown in Figure 5. The BT reaction rate is highest at the top of the reactor near the liquid inlet. All the BT is converted within the first few metres of packing; see Figure 5(f). The DBT reactivity is highest near the bottom of the reactor where the fresh H_2 enters the reactor. The maximum DBT reaction rate corresponds to the maximum in the temperature in the reactor; compare Figure 5(a) and (f). Total S content in the liquid leaving the bottom is 0.25 ppm (DBT = 0.15, BT = 0.1 ppm), well below the 50 ppm target level. The catalyst inventory of 30 tonnes allows for the presence of even more refractory S compounds than allowed in the kinetics used for DBT in this study.

The sensitivity of the results to varying BT/DBT ratios in the feed are studied in the simulations presented in Figure 6. Figure 6(b) shows a paradoxical result that *increasing* the total BT in the liquid feed leads to a *lower* total S content in the liquid effluent from the reactor. The reason for this is to be found in the temperature profile; Figure 6(a). With increasing BT content of the feed the heat liberated by the exothermic desulphurization of BT is higher, leading to a higher temperature and a higher reaction rate. Note the sharp increase in the temperature at the top of the reactor. At the bottom of the reactor, the situation is different. Here the entering gas (at 590 K) cools the liquid. The temperature profiles for varying BT/DBT ratios, all show a maximum about 7 m above the bottom of the reactor. This temperature maximum corresponds with the maximum in the DBT reaction rate. These results underline the need to model the heat transfer process accurately in the reactor.

In the foregoing simulations the interfacial area between the gas and liquid phases is calculated to be 169 $m^2 m^{-3}$, for the bale packing. For the base case, detailed in Table 1, we also carried out a set of simulations with varying interfacial areas of 100, 50, 25 and 10 and the results are shown in Figure 7. As regards the S content of the effluent liquid, it is

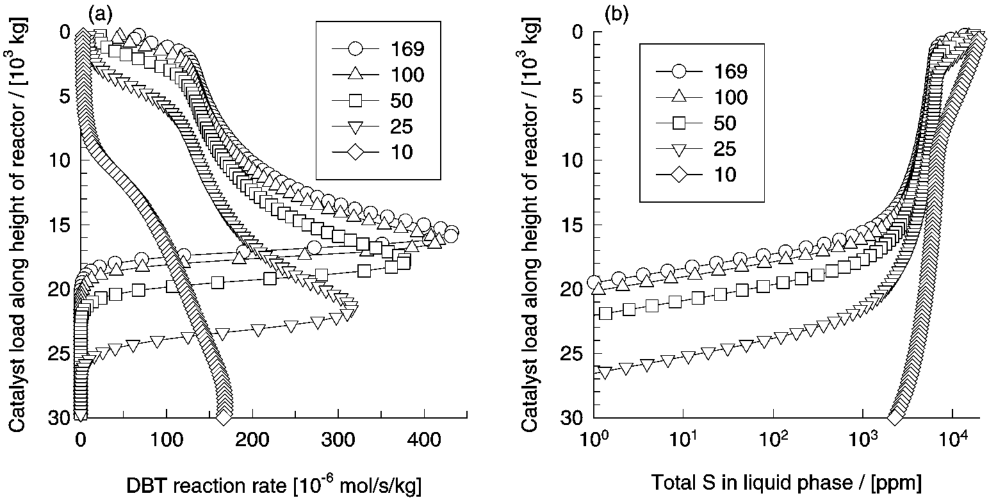

Figure 7. Sensitivity of design to specific interfacial area of packing. Values of specific interfacial areas in the simulations are 169, 100, 50, 25 and 10 $m^2 m^{-3}$.

seen that only when the interfacial area is reduced to below $25\,m^2 m^{-3}$ is there a danger that the 50 ppm specification is not met. In other words, mass transfer limitations is not a major issue in counter-current HDS reactor design. There is therefore a scope of improving the hardware configurations by allowing for more catalyst inventory, while reducing the open area between the catalyst containing envelopes.

CONCLUSIONS

In this study we examine the benefits of counter-current contacting of gas oil with H_2, over conventional co-current contacting in a trickle bed HDS reactor. In counter-current contacting, we achieve *in-situ* stripping of H_2S from the liquid phase; this is beneficial to the HDS kinetics. A comparison simulation study shows that counter- current contacting would require about 20% lower catalyst load than co-current contacting. For counter-current contacting, the DBT reaction rates are particularly high near the bottom of the bed and this portion is very effective in reducing the S content to below 50 ppm. In co-current contacting it is very difficult to reduce the S levels to below about 1000 ppm, because the DBT reaction rate progressively reduces as we proceed down the bed; see Figure 4(a).

A preliminary hardware design of a counter-current HDS reactor using catalytic bales was carried out in order to determine the technical feasibility. Using a realistic sulphur containing feedstock, the target of 50 ppm S content of desulphurized oil could be met in a reactor of reasonable dimensions (2.75 m diameter, 30 m height, packed with 30 tonnes of CoMo catalyst). Simulations with varying amounts of BT in the liquid feed led to the paradoxical conclusion that increasing BT in the feed leads to a lower S content in the liquid effluent. This finding can be rationalized by the fact that the high exothermicity of the BT reaction; a higher temperature leading to a higher DBT reaction rate.

Interfacial mass transfer is not likely to be a limiting factor in counter-current HDS reactors and there is a need for improved catalyst envelop design giving more catalyst inventory at the expense of smaller open area, and concomitant higher pressure drop.

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