

Advantages of Counter-current Operation for Hydrodesulfurization in Trickle Bed Reactors

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Abstract—The deep desulfurization of oil fraction is a central matter of concern to every refinery. Hydrogen sulfide is the product of hydrodesulfurization reaction and it is the inhibitor of the reaction. When products inhibit the reaction, the counter-current operation is expected to have an advantage over the co-current operation. Hydrodesulfurization of vacuum gas oil in a trickle bed reactor was simulated for both models of co-current operation and counter-current operation. The models were simulated on high and low gas and liquid velocities. Hydrogen sulfide was affected by mass transfer resistance in both gas-liquid and liquid-catalyst interface. The other component mass transfer resistances were negligible. When the deep desulfurization was required, simulation results showed that the counter-current operation was superior to the co-current operation in organic sulfur conversion.

Key words: Hydrodesulfurization, Trickle Bed Reactor, Counter-current Operation, Co-current Operation, Simulation

INTRODUCTION

The deep desulfurization of oil fraction is a central matter of concern to every refinery. To maximize the yield of high quality products containing low sulfur content, we must know how the process operations affect desulfurization. There are many papers on desulfurization. Song [2003] reviewed both catalyst and process of desulfurization of fuels.

Hydrodesulfurization is one of the desulfurization methods. Korsten and Hoffman [1996] made a model for hydrodesulfurization of the vacuum gas oil in a trickle bed reactor. The simulation results showed good agreement with experimental data over a wide range of temperature, pressure, space velocity and gas/oil ratio.

Chowdhury et al. [2002] expanded Korsten's model and applied it to desulfurization and dearomatization of the diesel oil. Inert particles were put on the catalyst to transfer hydrogen from gas to liquid. Dearomatization reaction and gas-liquid mass transfer in non-active zone were added to Korsten's model. Simulation results of desulfurization and dearomatization agreed with the experimental data.

Hydrogen sulfide inhibited desulfurization of oil [Papayannakos and Marangozis, 1984]. When products inhibit the reaction rate, the counter-current operation is expected to have advantages over the co-current operation. van Hasselt et al. [1999] compared the co-current trickle bed reactor with the three-levels-of-porosity reactor and the internally finned monolith reactor on hydrodesulfurization of the vacuum gas oil. It was found that the results of counter-current flow in the novel reactors had significant increase of conversion.

Goto and Smith [1978] compared the co-current operation and counter-current operation in the trickle bed reactor. The catalytic oxidation of sulfur dioxide on activated carbon in the presence of liquid water was selected as a model reaction. The counter-current operation had higher conversion than the co-current operation.

In this work, the co-current operation and the counter-current

operation in the trickle bed reactor were simulated and compared. Desulfurization of vacuum gas oil was selected for the reaction.

SIMULATION CONDITION

Hydrodesulfurization of the vacuum gas oil in a trickle bed reactor is simulated. We cite the co-current flow model and parameters, such as mass transfer coefficient and reaction rate constant, from Korsten and Hoffmann [1996]. Their simulation model is as follows. Fig. 1 shows the mass transfer model.

The general reaction equation is as follows.

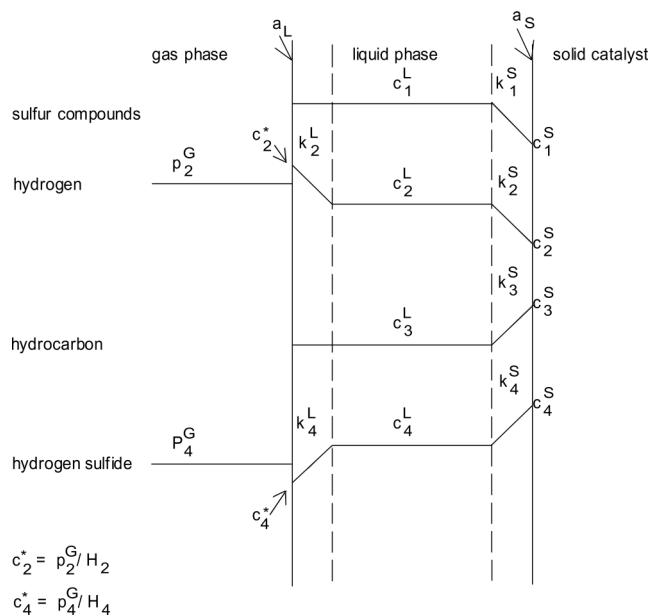
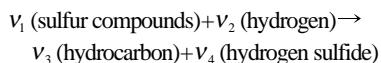


Fig. 1. Mass transfer model.

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Sulfur compounds are hydrocarbon sulfide. Stoichiometric coefficients of the overall reaction are estimated experimentally; they are $v_1=1$, $v_2=15$ and $v_4=9$. Since Hydrocarbon is the main component of vacuum gas oil, the concentration of hydrocarbon does not change significantly by hydrodesulfurization. Hydrocarbon is not taken into further consideration.

By formulating the mass transfer equations, the following assumptions are made.

- (1) Gas and liquid velocities do not change through the reactor.
- (2) There are no radical concentration gradients.
- (3) The catalyst activity does not change with time.
- (4) Vaporization and condensation of oil do not take place.
- (5) The temperature is isothermal and the pressure is constant.
- (6) Chemical reactions only take place at the solid catalyst.

Mass-balance equations for co-current operation are as follows.

Gas phase:

$$\text{Hydrogen: } (u_G/(R T)) (dp_2^G/dz) + k_2^L a_L (p_2^G/H_2 - c_2^L) = 0 \quad (1)$$

$$\text{Hydrogen sulfide: } (u_G/(R T)) (dp_4^G/dz) + k_4^L a_L (p_4^G/H_4 - c_4^L) = 0 \quad (2)$$

Liquid phase:

$$\text{Sulfur compounds: } u_L (dc_1^L/dz) + k_1^S a_S (c_1^L - c_1^S) = 0 \quad (3)$$

$$\text{Hydrogen: } u_L (dc_2^L/dz) - k_2^L a_L (p_2^G/H_2 - c_2^L) + k_2^S a_S (c_2^L - c_2^S) = 0 \quad (4)$$

$$\text{Hydrogen sulfide: } u_L (dc_4^L/dz) - k_4^L a_L (p_4^G/H_4 - c_4^L) + k_4^S a_S (c_4^L - c_4^S) = 0 \quad (5)$$

Solid catalyst:

$$\text{Sulfur compounds: } k_1^S a_S (c_1^L - c_1^S) = v_1 (\rho \zeta \eta r_c) \quad (6)$$

$$\text{Hydrogen: } k_2^S a_S (c_2^L - c_2^S) = v_2 (\rho \zeta \eta r_c) \quad (7)$$

$$\text{Hydrogen sulfide: } k_4^S a_S (c_4^L - c_4^S) = -v_4 (\rho \zeta \eta r_c) \quad (8)$$

ρ , ζ and η are bulk density of catalyst pellets, ratio of the catalyst bed diluted by inert particles and catalyst effective factor, respectively.

Reaction rate, r_c , is as follows.

$$r_c = k_{app} (c_1^S) (c_2^S)^{0.45} / (1 + 0.7 c_4^S) \quad (9)$$

We expand Korsten's model to the counter-current operation. Eqs. (1) and (2) are changed as follows for the counter-current operation.

$$\text{Hydrogen: } -(u_G/(R T)) (dp_2^G/dz) + k_2^L a_L (p_2^G/H_2 - c_2^L) = 0 \quad (1')$$

$$\text{Hydrogen sulfide: } -(u_G/(R T)) (dp_4^G/dz) + k_4^L a_L (p_4^G/H_4 - c_4^L) = 0 \quad (2')$$

The same mass transfer coefficient values are used for the co-current and the counter-current operation to clarify the kinetic effects. Reactions on a laboratory scale that has low liquid velocity and industrial scale that has the high liquid velocity are simulated. Table 1 shows reaction conditions for both cases.

Korsten and Hoffmann [1996] used hydrogen-saturated oil. On the other hand, our initial hydrogen concentration in oil is zero to simulate the co-current and the counter-current operation under equal initial conditions. Our simulation model has good agreement with Korsten's results when saturated oil is used in the co-current trickle

Table 1. Reaction conditions

	Laboratory	Industry
Hydrogen velocity [m/s]	1.61×10^{-3}	0.112
Oil velocity [m/s]	7.52×10^{-5}	5.27×10^{-3}
Reactor length [m]	0.7	4
Internal diameter [m]	0.03	0.03
Temperature [K]	543	543
Pressure [MPa]	4	4

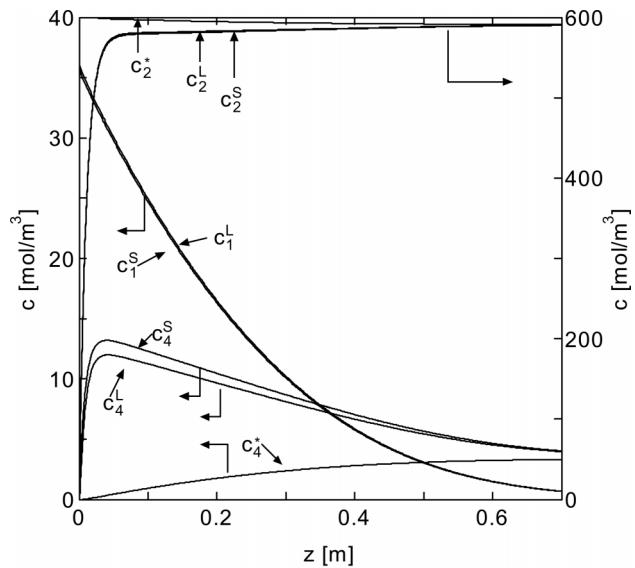


Fig. 2. Concentration profiles of co-current flow in laboratory scale.

bed reactor.

RESULTS AND DISCUSSION

1. Laboratory Scale Simulation

Fig. 2 shows the liquid concentration profiles through the reactor with the co-current operation. The reactant, sulfur compound, concentration in the liquid phase (c_1^L) decreases through the reactor. The reactant concentration at the outlet is 0.68 mol/m^3 . The conversion is 98%. The reactant concentration at the catalyst surface (c_1^S) is very close to the reactant concentration in the liquid phase. Mass transfer resistance between catalyst and liquid is negligible. Hydrogen concentrations in the liquid phase (c_2^L) and at the catalyst surface (c_2^S) are very close. Mass transfer resistance between catalyst and liquid is negligible. Hydrogen concentration in the liquid phase increases rapidly and approaches to the concentration at gas-liquid interface (c_2^*). Hydrogen dissolving rate is very high. Hydrogen sulfide concentration in the liquid phase (c_4^L) and at the catalyst surface (c_4^S) increases and then decreases. The value of c_4^S is a little larger than that of c_4^L . The mass transfer resistance from catalyst to liquid causes this difference. Hydrogen sulfide concentration at the gas-liquid interface (c_4^*) increases through the reactor. There are large differences between c_4^* and c_4^L . Gas-liquid mass transfer resistance is large.

To compare the counter-current operation with the co-current operation, hydrodesulfurization with the counter-current operation

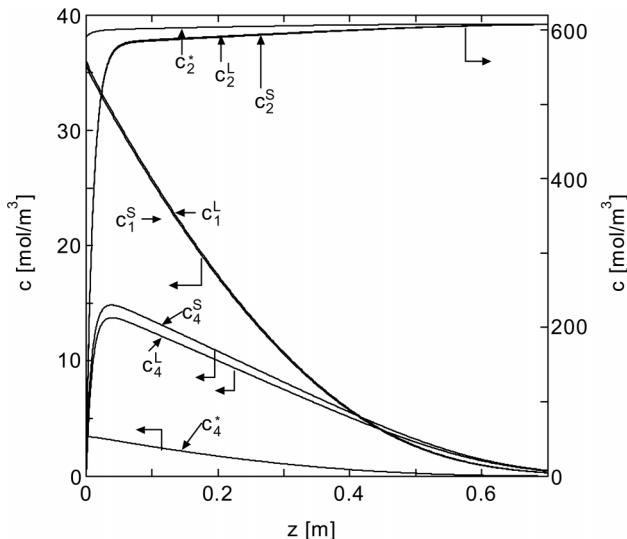


Fig. 3. Concentration profiles of counter-current flow in laboratory scale.

is simulated.

Fig. 3 shows the concentration profiles through the reactor. Tendencies for concentration profiles in the liquid phase and at the catalyst surface are similar to those of the co-current operation. Tendencies for concentration profiles of hydrogen and hydrogen sulfide at the gas-liquid interface are opposite for the co-current operation. Sulfur compounds concentration of the outlet is 0.30 mol/m^3 which is about half of the co-current operation. However, sulfur compounds concentration of the co-current operation is lower than that of the counter-current operation until $z=0.39 \text{ m}$. The concentration profile of hydrogen sulfide at the catalyst surface is the reason for this result. Hydrogen sulfide is the inhibitor of hydrodesulfurization reaction as shown in Eq. (9). The counter-current oper-

ation has high hydrogen sulfide concentration around the inlet, which makes the reaction rate lower than that of the co-current operation. On the other hand, the counter-current operation has low hydrogen sulfide concentration at high conversion. This low concentration makes the reaction rate higher than that of the co-current operation. The counter-current operation is superior to the co-current operation for deep desulfurization.

The hydrogen velocity (u_g) is varied. Fig. 4 shows the simulation results. $u_g=1.61 \times 10^{-3} \text{ m/s}$ is the standard condition used in Fig. 2 and 3. The sulfur compounds concentration of outlet ($c_{1,out}^L$) increases with decrease of the hydrogen velocity. The concentration of counter-current operation is lower than that of co-current operation and the difference increases with decrease of the hydrogen velocity. The counter-current operation needs 36% hydrogen flow rate of the co-current operation for $c_{1,out}^L=0.68 \text{ mol/m}^3$.

2. Industrial Scale Simulation

The gas and liquid velocities in the industrial scale trickle bed reactors are usually one or two orders of magnitude higher than those in laboratory scale reactors. Increasing of gas and liquid flow rates decreased external effects of catalyst. The reaction rate was increased with increase of liquid flow rate [Yamada et al., 1999]. Reaction profiles at industrial scale are simulated. Fig. 5 shows the concentration profiles through the reactor. The gas and liquid velocities are increased 70 times. The reaction rate constant on industrial scale is 22 times as great as that of laboratory scale operation. Since wet efficiency of catalyst is increased. The increase of reaction rate increases hydrogen sulfide concentration in the liquid phase. The effect of hydrogen sulfide in industrial scale is greater than that in laboratory scale. Sulfur compounds concentration of outlet is 0.45 mol/m^3 .

The counter-current operation is also simulated. Fig. 6 shows the simulation results. Sulfur compounds concentration of outlet was 0.22 mol/m^3 . The counter-current operation was superior to the co-current operation even with high gas and liquid velocities.

The hydrogen velocity is varied. Fig. 7 shows the simulation results. $u_g=0.112 \text{ m/s}$ is the standard condition used in Fig. 5 and 6. The sulfur compounds concentration of outlet increases with decrease

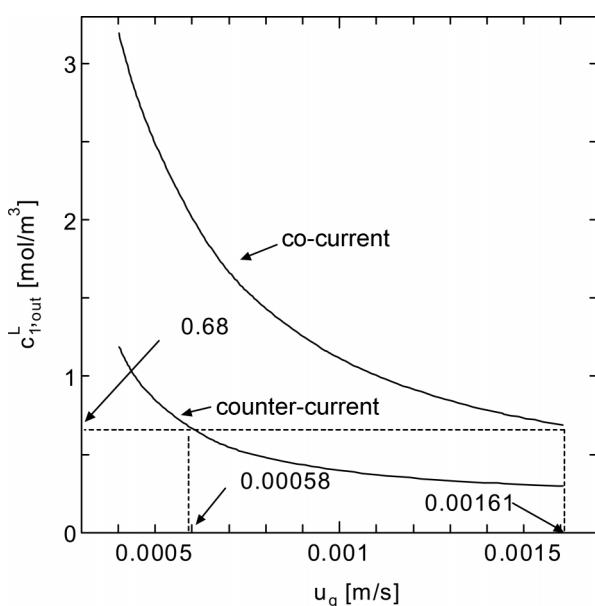


Fig. 4. Effect of hydrogen velocity on outlet concentration in laboratory scale.

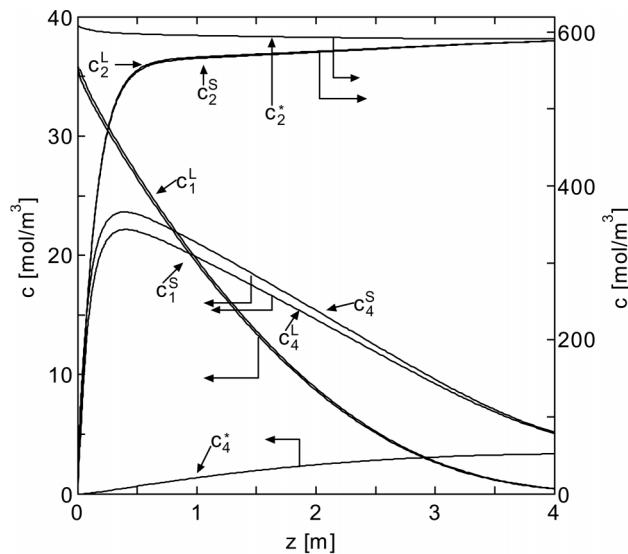


Fig. 5. Concentration profiles of co-current flow in industrial scale.

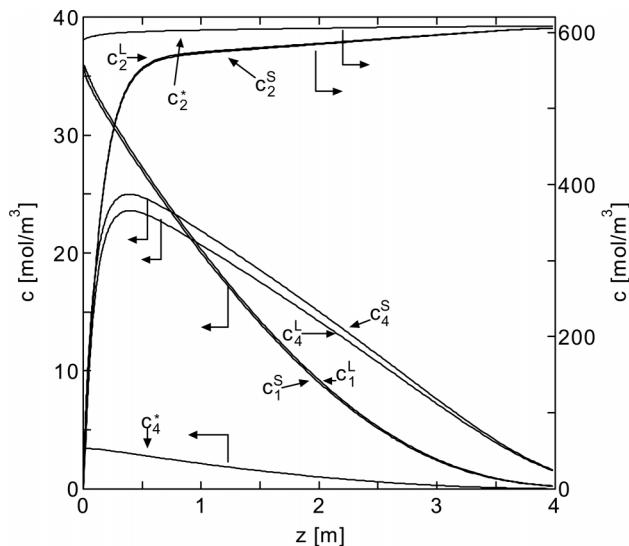


Fig. 6. Concentration profiles of counter-current flow in industrial scale.

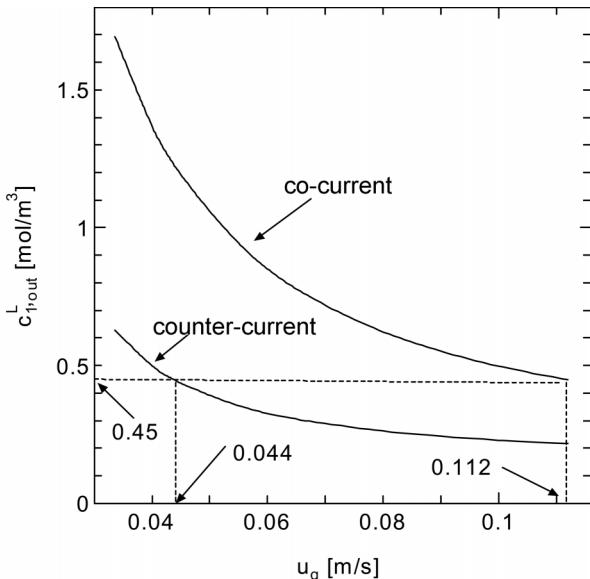


Fig. 7. Effect of hydrogen velocity on outlet concentration in industrial scale.

of the hydrogen velocity. The counter-current operation needs 39% hydrogen flow rate of the co-current operation for $c_{1,out}^L = 0.68 \text{ mol/m}^3$.

CONCLUSION

Hydrodesulfurization of the vacuum gas oil in the trickle bed reactor was simulated. When deep desulfurization was required, the product of the counter-current operation had lower sulfur compounds concentration than that of the co-current operation in the wide range of gas and liquid velocities. The hydrogen velocity in the counter-current operation is much lower than that in the co-current operation.

NOMENCLATURE

a	: specific surface area [1/m]
c	: concentration [mol/m ³]
H	: Henry's law constant [Pa m ³ /mol]
k	: mass transfer coefficient [m/s]
k_{app}	: apparent rate constant [(m ³ /(kg-cat s))(mol/m ³) ^{1.55}]
p	: partial pressure [Pa]
r_c	: reaction rate [mol/(kg-cat s)]
R	: gas-law constant [J/(mol K)]
T	: reaction temperature [K]
u_g	: hydrogen velocity [m/s]
z	: reactor length [m]
ρ	: bulk density of catalyst pellets [kg-cat/m ³]
ζ	: ratio of the catalyst bed diluted by inert particles [-]
η	: catalyst effective factor [-]

Subscripts

1	: organic sulfur compound
2	: hydrogen
3	: hydrocarbon
4	: hydrogen sulfide
,out	: of outlet

Superscripts

L	: liquid phase
S	: catalyst surface
*	: gas-liquid interface

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