

HYDRODESULFURIZATION OF A VACUUM GAS OIL IN A SLURRY BED AND IN A TRICKLE-BED REACTOR: A COMPARATIVE STUDY

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INTRODUCTION

Partial wetting of catalyst pellets is an important characteristic of trickle-bed reactors (Satterfield, 1975; Herskowitz and Smith, 1983; Gianetto and Specchia, 1992). Two kinds of wetting must be considered for porous catalysts, internal wetting, defined as the ratio between the wetted pellet volume and the total pellet volume and external effective wetting that is the fraction of the external area of the pellet effectively wetted. Many investigations have dealt mostly with external wetting efficiency by tracer (Mills and Dudukovic, 1981) and reaction (Herskowitz et al., 1979; Ring and Missen, 1989; Morita and Smith, 1978) methods and by computational simulations (Ring and Missen, 1986; Yentekakis and Vayenas, 1987). Total internal wetting of the catalyst pellets is normally assumed due to capillary effects.

With the exception of few studies aiming at the determination of catalyst wetting under industrial reaction conditions (Ruecker and Akgerman, 1987; Ring and Missen, 1989; Al-Dahhan and Dudukovic, 1995), reaction methods used have determined wetting efficiencies at low pressures and temperatures (Herskowitz et al., 1979; Morita and Smith, 1978).

In this investigation effective catalyst wetting was estimated for a trickle-bed reactor for the HDS of a vacuum gas oil at high pressure (60atm) and temperatures (280-330°C). The wetting efficiencies were accounted for by expressing the global rate in terms of an overall effectiveness factor, which is a function of internal and external wetting efficiencies, internal diffusion and intrinsic kinetics. External mass and heat transfer limitations were negligible. The modified Thiele modulus proposed by Dudukovic was used and intrinsic kinetics were determined by batch experiments.

EXPERIMENTAL

The 15%MoO₃-4.5%NiO/ γ -Al₂O₃ catalyst was prepared by incipient wetness co-impregnation of 1/16" γ -Al₂O₃ extrudates with the appropriate solutions. The catalyst was calcined at 110°C overnight and at 500°C for 5h. The presulfidation of the catalyst was accomplished by exposure to a H₂S/H₂ mixture at 360°C, preceded and followed by a 1h He purge. The presulfation time was adjusted accordingly so that the total amount of H₂S passed over the catalyst contained approximately 6 times more sulfur than the stoichiometric amount needed for the sulfidation of the Mo, Ni oxides. The feedstock used was a vacuum distillate obtained from the refinery of LPC Hellas with a total sulfur content of 0.45% wt. The density of the lube oil was 0.86 g/ml at 20°C, the kinematic viscosity at 40 and 100°C was 39 and 6.14cSt respectively giving a viscosity index of 103. The sulfur content of the feed and product oils were determined by an ASOMA sulfur analyzer (200T-series) based on X-ray fluorescence analysis.

The HDS of the vacuum gas oil was carried out in both a stirred batch autoclave and a concurrent downflow trickle-bed reactor. The batch autoclave had a volume of 300ml and the catalyst to oil mass ratio was equal to 1/10. The reactor operating time was counted from the moment the temperature of the reactor reached the desired value and the pressure was fixed at 880psi (\approx 60atm). A more detailed description of the setup and performance of the batch reactor is given elsewhere (Yiokari et al., 1997). The trickle-bed reactor was a stainless steel tube of 15mm i.d. and 300mm length arranged inside a heater. The 15ml catalyst bed was placed at the bottom of the reactor while the rest of the tube was filled with γ -Al₂O₃ extrudates. The flow rates of the gases were controlled by mass flowmeters and controllers. The viscous liquid feed, which was placed in a piston, was driven into the reactor by pumping distilled water into the other side of the piston with the help of a common HPLC pump. The reactants, both liquid and gas, were mixed and heated before entering the reactor at 150°C. The reactor effluent flowed into a stainless steel cylinder acting as a gas-liquid separator. The liquid product flowed continuously into a sample tank with the help of a solenoid valve whereas the scrubbed gas product flowed into the vent. Control for the pressure and temperature of the catalyst bed were provided. All results were obtained under steady state conditions which were reached approximately 4h after the reaction conditions were applied. According to the work of Fukushima and Kusaka (1977a,b) regarding the boundaries of hydrodynamic flow regions, the range of Reynolds numbers experimentally covered in this work belonged to the trickle flow region ($1 \times 10^4 < Re_L < 1.5 \times 10^5$).

RESULTS

Hydrodesulfurization Kinetics: One of the most important set of reactions that take place during the hydrotreatment of residual oils is the hydrodesulfurization (HDS) of its various sulfur compounds. Since there is a great number of different sulfur compounds in industrial feedstocks, the actual mechanism of the HDS reaction is quite complex. Kinetic studies have shown that the HDS of an industrial feedstock could be described satisfactorily if it is considered as a mixture of two sulfur containing pseudocompounds, which differ considerably in HDS reactivity (Schuit and Gates, 1973). The first pseudocompound represents a reactive group that consists of thionaphthenes, mercaptans and sulfides (S_1), while the second hypothetical compound consist of the less reactive thiophenoaromatics (S_2). Each pseudocompound is assumed to react at a rate proportional to its sulfur concentration. Therefore the HDS reactions can be written simply,



Gel permeation chromatography of the gas oil (Varotsis and Pasadakis, 1997) used in this investigation determined 40% of sulfur pertaining to the less reactive thiophenoaromatics (S_2). Hence the remaining 60% of the gas oil total sulfur content was assumed to be the more reactive pseudocomponent S_1 . The two straight lines illustrated in Figure 1 indicate first order reaction of each sulfur containing pseudocomponent adding up to the curve fitting the data. This type of kinetic behavior can be mistaken for second order reaction kinetics. The distinction between the two parallel first order reactions and one second order reaction was made according to the procedure proposed by Wei and Hung (1974) for sulfur conversions above 97%.

Schuit and Gates (1973) reported that the kinetics regarding hydrogen are dependent on catalyst composition and on the nature of the feedstock. Hence the effect of hydrogen partial pressure on the HDS reaction was investigated. Figure 2 shows that sulfur conversion practically remains constant for hydrogen partial pressures over 20atm, independent of total gas flow rate. Thus the experiments performed in this study were in the region of zero-order kinetics regarding hydrogen.

Assumptions: The absence of external mass and heat transfer limitations was verified in the batch autoclave by choosing the appropriate stirring speed and in the trickle-bed reactor by confirming that the sulfur conversion remained constant when the volume of the catalyst bed and liquid flow rate where both doubled (constant LHSV). The 1/16" diameter pellets assured no internal mass and heat transfer by performing batch experiments with pellets of different sizes. First-order isothermal, irreversible reactions with respect to the reactants in the liquid are considered and the gaseous H_2 is present in great excess so the liquid is always saturated with gas. The catalyst pellets are completely wetted in the batch autoclave. Under these conditions the rate constants derived from the batch autoclave are assumed to be intrinsic rate constants.

Batch Reactor Performance: In the case of the batch reactor, one has:

$$\frac{dC_{S,i}}{dt} = \left(\frac{v_{cat}}{v_{liq} + v_{cat}} \right) \cdot r_i \quad (2)$$

where r_i is the reaction rate and $C_{S,i}$ the concentration of the sulfur-containing pseudocomponent i and v_{cat} and v_{liq} are the volume of the catalyst bed and the extra liquid in the batch autoclave respectively. For first order reaction regarding the sulfur component and zero order reaction regarding H_2 , one has:

$$r_i = k_{B,i} \cdot C_{S,i} \quad (3)$$

where $k_{B,i}$ is the rate constant of the sulfur containing pseudocomponent i . Substituting equation (3) in equation (2) and integrating, one obtains:

$$C_{S,i} = C_{S0,i} \cdot \exp\left(-\frac{k_{B,i}}{ELHSV}\right) \quad (4)$$

where ELHSV is an equivalent liquid hourly space velocity and can be defined for the batch autoclave as:

$$ELHSV^{-1} = \left(\frac{v_{cat}}{v_{liq} + v_{cat}} \right) \cdot t \quad (5)$$

Therefore the total sulfur concentration is:

$$C_S = C_{S1} + C_{S2} = \frac{C_S}{C_{S0}} = \alpha_1 \cdot \exp\left(-\frac{k_{B,1}}{ELHSV}\right) + \alpha_2 \cdot \exp\left(-\frac{k_{B,2}}{ELHSV}\right) \quad (6)$$

where α_1 and α_2 express the percentage of the pseudocompounds S_1 and S_2 and depend on the feedstock used. In this study α_1 and α_2 are 0.6 and 0.4 respectively as discussed above.

Trickle-bed Reactor Performance: Considering a differential volume element across the reactor, one has:

$$F \cdot C_{S0,i} \cdot dx_S = r_i \cdot dV \quad (7)$$

where F is the liquid flow rate, x_S is the sulfur conversion and V is the volume of the catalyst bed. Considering first order reaction regarding the sulfur component and zero order reaction regarding H_2 we substitute equation (3) in equation (7) to obtain:

$$C_{s,i} = C_{s0,i} \cdot \exp\left(-\frac{k_{T,i}}{\text{LHSV}}\right) \quad (8)$$

where LHSV is the liquid hourly space velocity and is defined for the trickle-bed reactor as:

$$\text{LHSV}^{-1} = \frac{V}{F} \quad (9)$$

and $k_{T,i}$, $i=1,2$, are the apparent first order kinetic constants for trickle-bed operation. Therefore the total sulfur concentration for the trickle-bed reactor is:

$$C_s = C_{s,1} + C_{s,2} \Leftrightarrow \frac{C_s}{C_{s0}} = \alpha_1 \cdot \exp\left(-\frac{k_{T,1}}{\text{LHSV}}\right) + \alpha_2 \cdot \exp\left(-\frac{k_{T,2}}{\text{LHSV}}\right) \quad (10)$$

Figures 3 and 4 illustrate the kinetic behavior of the batch and trickle-bed reactors, for the four temperatures studied, respectively. As expected sulfur concentration decreases with increasing LHSV⁻¹ and temperature. The total gas flow rate for the trickle-bed reactor is equal to 200ml/min. The removal of sulfur from the vacuum gas oil is greater in the batch reactor for given reaction conditions. The values of the rate constants derived for both the batch autoclave and the trickle-bed reactor are summarized in Table 1. The rate constants of group S₁ are 5-35 times greater than those of group S₂ depending on the reaction temperature. It is important to note that the ratios $k_{T,1}/k_{B,1}$ and $k_{T,2}/k_{B,2}$ remain practically constant with temperature and that the latter is larger since it corresponds to the slower reaction.

DISCUSSION

In the absence of mass transfer effects one would expect that the rate constants derived from equation (10), $k_{B,i}$, would be equal to the ones derived from equation (6), $k_{T,i}$, but this is not the case (Table 1). The essential difference of the two reactors is illustrated in Figure 5, where one can see that the rate of the HDS reactions is affected only by the partial wetting of the catalyst in the case of the trickle-bed reactor since other factors which affect it are the same (hydrogen excess, feed, etc.) and internal and external mass and heat transport limitations are negligible.

For a non ideal trickle-bed reactor, equation (10) can be written again by substituting $k_{T,i}$ with $(k_{B,i} \cdot \eta_{T,i})$, as:

$$\frac{C_s}{C_{s0}} = \alpha_1 \cdot \exp\left(-\frac{k_{B,1} \cdot \eta_{T,1}}{\text{LHSV}}\right) + \alpha_2 \cdot \exp\left(-\frac{k_{B,2} \cdot \eta_{T,2}}{\text{LHSV}}\right) \quad (11)$$

where $\eta_{T,i}$, $i=1,2$ are overall catalyst effectiveness factors for trickle-bed reactor for reactions (1). Therefore $k_{T,i}/k_{B,i}$ is equal to $\eta_{T,i}$ ($i = 1,2$).

For particles of irregular shape and in two-phase systems, it has been established by Aris (1957) that the effectiveness factor can be approximated by:

$$\eta_i = \frac{\tanh \Phi_i}{\Phi_i} \quad (12)$$

$$\text{where } \Phi_i = \frac{V_p}{S} \sqrt{\frac{k_{B,i}}{D_{\text{eff},i}}} \quad (13)$$

V_p is the catalyst volume, S is the catalyst external surface and $D_{\text{eff},i}$ is the diffusivity of pseudocomponent i . Diffusivities of the sulfur-containing pseudocompounds were calculated using the Wilke-Chang correlation with $V_{S_1}=80.8$ cm³/mole and $V_{S_2}=190$ cm³/mole (Reid et al., 1977). Effective diffusivities were computed assuming a porosity/tortuosity factor of 0.1 (Yitzhaki and Aharoni, 1977). The dynamic viscosity of the lube oil at a given temperature was calculated by multiplying the kinematic viscosity with the density of the lube oil at that temperature. The variances of density and dynamic viscosity with temperature were calculated with the Watson-Gamson and Guzman-Andrade equations respectively.

To account for the partial external wetting of the catalyst particles one can use the modified Thiele modulus for trickle-bed reactors proposed by Dudukovic (1977). This modulus is based on the effective wetted external area, S_{eff} and wetted internal volume of the pellet, $V_{p,\text{eff}}$ and can be written as:

$$\Phi_{T,i} = \frac{V_{p,\text{eff}}}{S_{\text{eff}}} \sqrt{\frac{k_{B,i}}{D_{\text{eff},i}}} \Rightarrow \Phi_{T,i} = \frac{f_{\text{int}}}{f_{\text{ext}}} \cdot \Phi_i \quad (14)$$

where f_{int} and f_{ext} are the internal and external wetting efficiencies respectively, defined as:

$$f_{\text{int}} = \frac{V_{p,\text{eff}}}{V_p} \quad \text{and} \quad f_{\text{ext}} = \frac{S_{\text{eff}}}{S_p} \quad (15)$$

From the values of the overall catalyst effectiveness factors $\eta_{T,i}$ (Table 1) and equation (12) the Thiele modulus of the trickle-bed reactor, $\Phi_{T,i}$ (Table 2) is calculated. Using equation (13) we compute Φ_i (Table 2). Therefore from equation (14) the ratio $f_{\text{int}}/f_{\text{ext}}$ is calculated and is summarized for the four temperatures studied and for the two sulfur pseudocomponents in Table 2. Total internal wetting of the catalysts pellets is normally assumed due to capillary effects, hence f_{int} could be considered unity and the external wetting efficiencies are estimated and presented in

Table 2. The computed values of the external wetting efficiencies slightly decrease with decreasing temperature. It is reassuring that similar values are extracted from both pseudocompounds for the preceding analysis. The mean values are 0.45 and 0.39 for pseudocomponents S_1 and S_2 respectively. These values of wetting efficiency are somehow smaller than the ones usually reported in the past (Satterfield, 1975; Gianetto and Specchia, 1992). This could be related to the low liquid flow rates used in the present investigation.

CONCLUSIONS

The HDS kinetics of an industrial feedstock were studied in the temperature range of 280-330°C in both a stirred batch autoclave and a trickle-bed reactor. The feed was considered as a mixture of two sulfur containing groups each reacting according to first order kinetics regarding their sulfur content. Reaction kinetics for hydrogen were zero order in the region of the present investigation.

The rate constants derived from the trickle-bed reactor are smaller than the ones obtained from the batch autoclave. The latter must correspond to intrinsic kinetic constants since internal and external mass and heat limitations were absent and total catalyst wetting was attained. The ratio of the rate constants extracted from the batch autoclave and trickle-bed experiments can be used to estimate the effectiveness factors during trickle-bed operation and thus also estimate the wetting efficiency under reaction conditions.

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TABLE 1- Kinetic rate constants for batch autoclave and trickle-bed reactor.

Temperature, °C	Batch Reactor		Trickle-bed Reactor		$\eta_1 = k_{T,1} / k_{B,1}$	$\eta_2 = k_{T,2} / k_{B,2}$
	$k_{B,1}$, h ⁻¹	$k_{B,2}$, h ⁻¹	$k_{T,1}$, h ⁻¹	$k_{T,2}$, h ⁻¹		
330	23.50	1.43	3.52	0.74	0.150	0.517
315	12.50	0.59	1.88	0.33	0.150	0.559
300	9.00	0.25	1.50	0.15	0.167	0.600
280	1.93	0.21	0.52	0.12	0.269	0.571

TABLE 2- Thiele moduli calculated from equations (12) and (13).

Temperature, °C	Φ_1 (eq. 13)	Φ_2 (eq. 13)	$\Phi_{T,1}$ (eq. 12)	$\Phi_{T,2}$ (eq. 12)	$f_{int,1}/f_{ext,1} = \Phi_{T,1}/\Phi_1$	$f_{int,2}/f_{ext,2} = \Phi_{T,2}/\Phi_2$	$f_{ext,1}$	$f_{ext,2}$
330	3.79	0.94	6.67	1.84	1.76	1.87	0.57	0.54
315	2.84	0.66	6.67	1.67	2.35	2.53	0.43	0.40
300	2.66	0.47	5.99	1.51	2.25	3.21	0.44	0.31
280	1.41	0.50	3.71	1.62	2.63	3.24	0.38	0.31

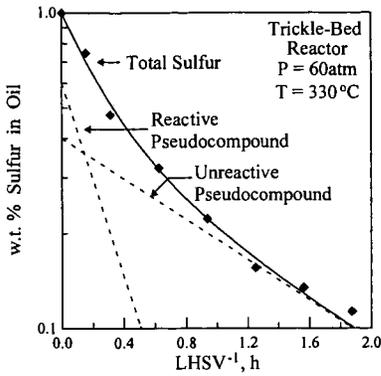


FIGURE 1 - Effect of inverse LHSV on sulfur content of vacuum gas oil and kinetic analysis.

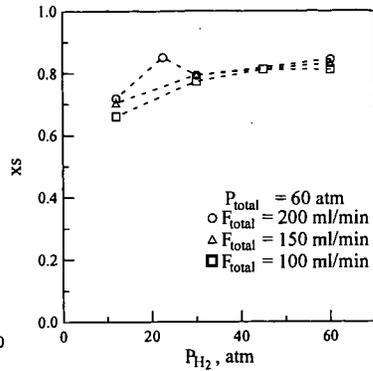


FIGURE 2 - Dependence of sulfur conversion on hydrogen partial pressure. Trickle bed reactor.

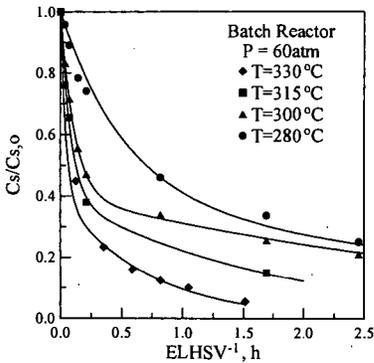


FIGURE 3 - Dependence of sulfur content on the inverse equivalent liquid hourly space velocity and temperature (Batch Reactor).

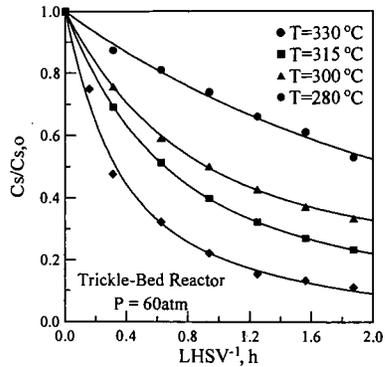
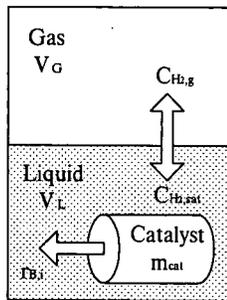
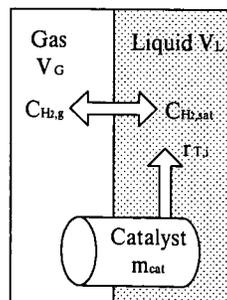


FIGURE 4 - Dependence of sulfur content on the inverse liquid hourly space velocity and temperature (Trickle-Bed Reactor).



Batch Reactor



Trickle-Bed Reactor

FIGURE 5 - Schematic representation of the particle environment in the batch autoclave and the trickle-bed reactors.