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The use of a three phase microreactor to investigate HDS kinetics

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Abstract

Hydrodesulphurization (HDS) kinetics of a straight run heavy gas oil has been studied using data collected from a trickle bed microreactor loaded with a diluted bed of a commercial catalyst. The reactor performance is simulated by a model taking into account the gas–liquid phase equilibrium. The gas oil compounds as well as the sulphur bearing compounds are represented by five pseudo-components. The sulphur removal and the hydrogen consumption are described by a set of parallel reactions of first order with respect to each pseudo-compound concentration. The reactants present in the liquid phase are considered to participate in catalytic reactions.

Keywords: Kinetics; Hydrodesulphurization; Microreactors

1. Introduction

HDS and hydrogen consumption kinetics are important parameters in scaling up, in predicting the performance of industrial reactors and in estimating the efficiency of new catalysts. The vast majority of the data existing in literature to study HDS kinetics with real feeds of petroleum fractions from naphtha to heavy vacuum gas oil, has been collected from bench or pilot scale hydrotreaters. The volume of the catalyst bed in these reactors range from 50 to 200 cm^3 and they operate in a gas–liquid cocurrent upflow or downflow mode. The tests are performed at the same conditions (temperature, pressure, WHSV, gas/liquid ratio) as in industrial hydrotreaters with only one exception. The gas and liquid superficial velocity, which, being proportional to bed length for constant space velocity, is about two orders of magnitude smaller than the corresponding industrial ones. The interest for using even smaller reactors with a bed volume of 5–10 cm^3 is presently increasing although literature references are restricted [1,5,10]. With downscaling, safer, easier and more economic operation can be achieved and these advantages are considered important to support investigations on the use of microreactors for hydrotreatment applications. The most important drawbacks concern reactor hydrodynamics as catalyst incomplete wetting, gas and/or liquid wall flow and axial dispersion effects could be more intense with the decrease of the reactor scale. However, the appropriate bed dilution with small inert particles appears very effective [11] and such small beds can be used to collect reliable data.

In a well wetted catalyst bed, only the compounds present in the liquid phase can come in contact with and react on the catalyst active sites. However, kinetics of reactions occurring during hydrotreatment is usually studied taking into account the concentration of the relevant compounds (S, N, H_2, etc.) in the liquid phase assuming that the liquid feed does not evaporate. The fitting of the data to the power law kinetic equation proposed is good but the kinetics obtained can be used only for the experimental conditions studied and

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Nomenclature

CH	hydrogen consumption (Nl_{H_2}/g_L)
CHT	maximum hydrogen consumption (Nl_{H_2}/g_L)
C_{L,H_2}	hydrogen concentration in the liquid phase (mol_{H_2}/l_L)
C_{L,H_2S}	hydrogen sulphide concentration in the liquid phase (mol_{H_2S}/l_L)
$C_{L,i}$	concentration of the *i*th compound in the liquid phase (mol_i/l_L)
C_S	sulphur concentration (ppm wt.%)
$C_{S,in}$	sulphur content in the liquid feed (ppm wt.%)
$C_{S,out}$	sulphur content in the liquid product (ppm wt.%)
E_H	activation energy for hydrogen consumption reactions (J/mol)
E_S	activation energy for HDS reactions (J/mol)
K_H	constant of hydrogen consumption, $g_L^2/(g_C\,h\,Nl_{H_2}\,bar_{H_2})$ in Eq. (2), $l_L^2/(g_C\,h\,mol_i)$ in Eqs. (8)–(10) and (13)
K_I	inhibition factor, $1/bar_{H_2S}$ in Eqs. (1) and (2), l_L/mol_{H_2S} in Eqs. (7)–(14)
K_S	HDS reaction constant, $g_L\,ppm_S^{1-n}/(g_C\,h\,bar_{H_2})$ in Eq. (1), $l_L^2/(g_C\,h\,mol_{H_2})$ in Eqs. (7), (11)–(14)
L	bed length (dm)
M_C	mass of catalyst (g)
M_L	mass flow rate of gas oil (g/h)
MW_i	molecular weight of the *i*th pseudo-compound
n	reaction order
N_{H_2}	molar rate of H_2 (mol/h)
N_{H_2S}	molar rate of H_2S (mol/h)
N_i	molar rate of *i*th component (mol/h)
Nl	normal litre
P_{H_2}	partial pressure of H_2 (bar)
P_{H_2S}	partial pressure of H_2S (bar)
R_{HDS}	rate of HDS, $g_L\,ppm_S/(g_C\,h)$ in Eqs. (1), (3) and (4), $mol_i/(g_C\,h)$ in Eq. (7)
R_{HDT}	rate of hydrogen consumption, $Nl_{H_2}/(g_C\,h)$ in Eqs. (2), (5) and (6), $mol_{H_2}/(g_C\,h)$ in Eq. (8)
T	temperature (K)
WHSV	weight hourly space velocity ($g_L/g_C/h$)

in many cases only for the equipment used as these equations include the effect of evaporation of the liquid feed. The effect of feed evaporation on the reactor performance has begun to be studied [2,3,8]. When the feed is partially evaporated a part of the reactant is present in the gas phase and cannot directly react on the catalyst. Reaction by-products like H_2S appear first in the liquid phase and then they transfer in the gas phase.

In this paper, a model for the study of sulphur removal and hydrogen consumption kinetics during hydrotreatment of a gas oil taking into account the feed evaporation and the gas–liquid equilibrium along the reactor axis is presented. The experimental data used for the fitting and the estimation of the kinetic parameters has been obtained from an experimental unit equipped with a microreactor.

2. Experimental

A schematic diagram of the unit used to perform the experiments is given in Fig. 1. Commercial $NiMo/Al_2O_3$ catalyst of 5.5 g was diluted with 7 g

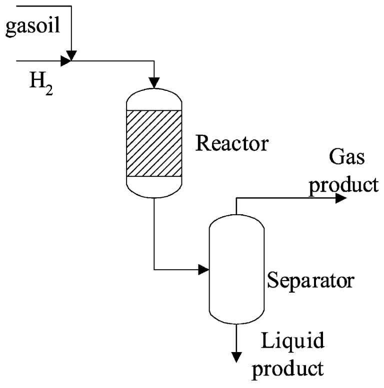

Fig. 1. Schematic diagram of the unit.

of inert SiC particles of mean diameter 0.25 mm in a stainless steel reactor of 8 mm internal diameter. The catalyst was in extrudate form with a diameter of 1.2 mm. Above and below the catalyst bed, glass extrudates were put to support the bed and fill the reactor void volume. The liquid feed, which was a typical heavy gas oil with 1.4% sulphur content, is mixed with H_2 prior to the reactor inlet and the gas–liquid mixture is heated at the reaction temperature before entering the catalyst bed. For the kinetic experiments, the reaction temperature ranged from 320 to 350 °C and the WHSV values were between 1.0 and 4.5 g_L/g_C/h.

3. Mathematical model

Firstly, a simplified mathematical model was used for a first estimation of the kinetic parameters. The fitting was obtained by means of the Simplex optimisation algorithm for non-linear problems [13]. This model is a pseudohomogeneous one assuming no liquid evaporation and taking into account two typical power law kinetic equations with inhibition terms to simulate the sulphur removal and hydrogen consumption. The kinetic equation of sulphur removal (Eq. (1)) depends on H_2 and H_2S partial pressure in the gas phase and is of nth-order with respect to the sulphur concentration. In order to describe the hydrogen consumption, CHT is considered as the maximum possible specific hydrogen consumption, and HC is the real specific hydrogen consumption after some time of hydrotreatment. The hydrogen consumption rate equation (Eq. (2)) is proportional to the square of the difference (CHT−HC).

$$R_{\mathrm{HDS}} = K_{\mathrm{S}}\,\mathrm{e}^{-E_{\mathrm{S}}/RT}\frac{P_{\mathrm{H_2}}C_{\mathrm{S}}^{n}}{1+K_{\mathrm{I}}P_{\mathrm{H_2S}}} \quad (1)$$

$$R_{\mathrm{HDT}} = K_{\mathrm{H}}\,\mathrm{e}^{-E_{\mathrm{H}}/RT}\frac{P_{\mathrm{H_2}}(\mathrm{CHT}-\mathrm{CH})^{2}}{1+K_{\mathrm{I}}P_{\mathrm{H_2S}}} \quad (2)$$

Eq. (3) describes the mass balance based on plug flow for the sulphur removal and Eq. (4) is the mass balance for the H_2S production.

$$M_{\mathrm{L}}\frac{\mathrm{d}C_{\mathrm{S}}}{\mathrm{d}M_{\mathrm{C}}} = -R_{\mathrm{HDS}} \quad (3)$$

$$\frac{\mathrm{d}N_{\mathrm{H_2S}}}{\mathrm{d}M_{\mathrm{C}}} = R_{\mathrm{HDS}}\frac{10^{-6}}{32} \quad (4)$$

For the specific hydrogen consumption the mass balance is given by Eq. (5) and the H_2 molar rate is calculated by Eq. (6).

$$M_{\mathrm{L}}\frac{\mathrm{dHC}}{\mathrm{d}M_{\mathrm{C}}} = R_{\mathrm{HDT}} \quad (5)$$

$$\frac{\mathrm{d}N_{\mathrm{H_2}}}{\mathrm{d}M_{\mathrm{C}}} = -R_{\mathrm{HDT}}\frac{1}{22.4} \quad (6)$$

An improved model has been developed and is presented in this study to simulate the reactor performance. It takes into account the gas–liquid phase equilibrium at reaction conditions in an attempt to estimate the liquid and gas phase concentration of each compound and to propose kinetic models based on the real liquid concentration of reactants and products. For the calculation of the vapour–liquid equilibrium, the liquid feed gas oil was simulated by five pseudocomponents on the basis of its distillation curve. First, the ASTM-D86 curve was converted into the true boiling point (TBP) curve, by Riazi's method [9]. The next step was to break down the gas oil into five pseudocomponents within its boiling temperature range. The boiling point of each pseudocomponent was calculated with the Miquel and Castells' method [7]. The molecular weights were calculated by the Riazi's method [14] and the critical properties by the Lee–Kesler's method [4]. The two phase thermodynamic equilibrium and the Henry coefficient of the hydrogen solubility were estimated by the t-vdW [6] equation of state. In this way, the gas oil was simulated by five pseudocomponents and five sulphur pseudocomponents. The first five pseudocomponents react with H_2 and give five hydrogenated components. These reactions simulate the H_2 consumption. The concentration of sulphur pseudo-components in each fraction was calculated from the sulphur concentration curve. Each sulphur compound reacts with H_2 and gives a sulphur-free compound and H_2S. In this case, the kinetic rates depend on the concentration of the reactants in the liquid phase. Eq. (7) gives the kinetic equation of the HDS and Eq. (8) gives the kinetic equation of the H_2 consumption.

$$R_{\mathrm{HDS}} = K_{\mathrm{S}}\,\mathrm{e}^{-E_{\mathrm{S}}/RT}\frac{C_{\mathrm{L,H_2}}C_{\mathrm{L},i}}{1+K_{\mathrm{I}}C_{\mathrm{L,H_2S}}} \quad (7)$$

$$R_{\mathrm{HDT}} = K_{\mathrm{H}}\,\mathrm{e}^{-E_{\mathrm{H}}/RT}\frac{C_{\mathrm{L,H_2}}C_{\mathrm{L},i}}{1+K_{\mathrm{I}}C_{\mathrm{L,H_2S}}} \qquad (8)$$

Eq. (9) is the mass balance, based on plug flow, of the first five compounds ($1 \leq i \leq 5$), which react with H_2 in order to simulate the H_2 consumption and Eq. (10) concerns the products of this reaction ($6 \leq i \leq 10$). Eq. (11) is the mass balance of the five sulphur compounds ($11 \leq i \leq 15$) that react with H_2 and give five sulphur-free compounds ($16 \leq i \leq 20$) and Eq. (12) gives their mass balance. Eq. (13) describes the mass balance of H_2 ($i = 21$) consumption and Eq. (14) describes the H_2S ($i = 22$) production.

The reactivity of each compound is not the same. The lighter compounds are more reactive than the heavier components. Trytten and Murray [12] found that the HDS and HDN rate constants depend on the molecular weight of the oil fraction. By treating the results of Trytten and Murray, we concluded that the rate constants of HDS and of hydrogen consumption should be proportional to $\mathrm{MW}^{-4.9}$. Each reaction was considered to be of first-order, as the reactions concern compounds in a narrow boiling range.

$$\frac{\mathrm{d}N_i}{\mathrm{d}z} = -\frac{M_{\mathrm{C}}}{L}\frac{K_{\mathrm{H}}}{\mathrm{MW}_i^{4.9}}\mathrm{e}^{-E_{\mathrm{H}}/RT}\frac{C_{\mathrm{L,H_2}}C_{\mathrm{L},i}}{1+K_{\mathrm{I}}C_{\mathrm{L,H_2S}}}, \quad 1 \leq i \leq 5 \qquad (9)$$

$$\frac{\mathrm{d}N_i}{\mathrm{d}z} = \frac{M_{\mathrm{C}}}{L}\frac{K_{\mathrm{H}}}{\mathrm{MW}_{i-5}^{4.9}}\mathrm{e}^{-E_{\mathrm{H}}/RT}\frac{C_{\mathrm{L,H_2}}C_{\mathrm{L},i-5}}{1+K_{\mathrm{I}}C_{\mathrm{L,H_2S}}}, \quad 6 \leq i \leq 10 \qquad (10)$$

$$\frac{\mathrm{d}N_i}{\mathrm{d}z} = -\frac{M_{\mathrm{C}}}{L}\frac{K_{\mathrm{S}}}{MW_i^{4.9}}\mathrm{e}^{-E_{\mathrm{S}}/RT}\frac{C_{\mathrm{L,H_2}}C_{\mathrm{L},i}}{1+K_{\mathrm{I}}C_{\mathrm{L,H_2S}}}, \quad 11 \leq i \leq 15 \qquad (11)$$

$$\frac{\mathrm{d}N_i}{\mathrm{d}z} = \frac{M_{\mathrm{C}}}{L}\frac{K_{\mathrm{S}}}{\mathrm{MW}_{i-5}^{4.9}}\mathrm{e}^{-E_{\mathrm{S}}/RT}\frac{C_{\mathrm{L,H_2}}C_{\mathrm{L},i-5}}{1+K_{\mathrm{I}}C_{\mathrm{L,H_2S}}}, \quad 16 \leq i \leq 20 \qquad (12)$$

$$\frac{\mathrm{d}N_{\mathrm{H_2}}}{\mathrm{d}z} = -3\frac{M_{\mathrm{C}}}{L}K_{\mathrm{H}}\,\mathrm{e}^{-E_{\mathrm{H}}/RT}\frac{C_{\mathrm{L,H_2}}\sum_{i=1}^{5}C_{\mathrm{L},i}/\mathrm{MW}_i^{4.9}}{1+K_{\mathrm{I}}C_{\mathrm{L,H_2S}}} - \frac{M_{\mathrm{C}}}{L}K_{\mathrm{S}}\,\mathrm{e}^{-E_{\mathrm{S}}/RT}\frac{C_{\mathrm{L,H_2}}\sum_{i=11}^{15}C_{\mathrm{L},i}/\mathrm{MW}_i^{4.9}}{1+K_{\mathrm{I}}C_{\mathrm{L,H_2S}}}, \quad i = 21 \qquad (13)$$

$$\frac{\mathrm{d}N_{\mathrm{H_2S}}}{\mathrm{d}z} = \frac{M_{\mathrm{C}}}{L}K_{\mathrm{S}}\,\mathrm{e}^{-E_{\mathrm{S}}/RT}\frac{C_{\mathrm{L,H_2}}\sum_{i=11}^{15}C_{\mathrm{L},i}/\mathrm{MW}_i^{4.9}}{1+K_{\mathrm{I}}C_{\mathrm{L,H_2S}}}, \quad i = 22 \qquad (14)$$

This system of differential equations was solved numerically using the fourth-order Runge–Kutta algorithm. At each differential part of catalyst bed dz, a flash calculation was performed.

4. Results

The use of microreactors allows an economic and safer operation with less energy consumption, less waste oil production and lower investment cost. For the catalyst bed used in this study (5.5 g) and for WHSV = 1 g_L/g_C/h the spent gas oil is 5.5 g/h and the spent H_2 is 3.0 Nl/h. The dead volumes of a microreactor unit are smaller than the respective volumes of a pilot or bench scale unit, resulting in faster response of the unit and faster attainment of steady-state operation. Thus, a typical experimental point can be carried out within 10–12 h. During the steady-state operation, the relative standard deviation of the sulphur concentration of the liquid product is ±1%. As the accumulated volume of the reactants in a microreactor unit is small, the possible leakages or explosion of the reactants in case of an accident are restricted allowing safer operation of the unit.

The simplified model was used only to derive the initial values for the kinetic parameters of the improved model. The activation energy of HDS is estimated as 104 kJ/mol with the simple model and 105 kJ/mol with the improved model. These results are in good agreement with values given in [1]. The activation energy of hydrogen consumption is estimated as 18 kJ/mol with the simple model and 25 kJ/mol with the improved model. The difference in the estimation of the activation energy of the hydrogen consumption is due to the different way of simulation of this group of reactions by the two models. With the simplified model there is a free parameter, the maximum possible hydrogen consumption (CHT), which is optimised, in contrast to the improved model for which the initial concentration of the unsaturated pseudocompounds is predefined.

In Fig. 2, the results of the HDS simulation and reactor performance are shown at several WHSVs and at

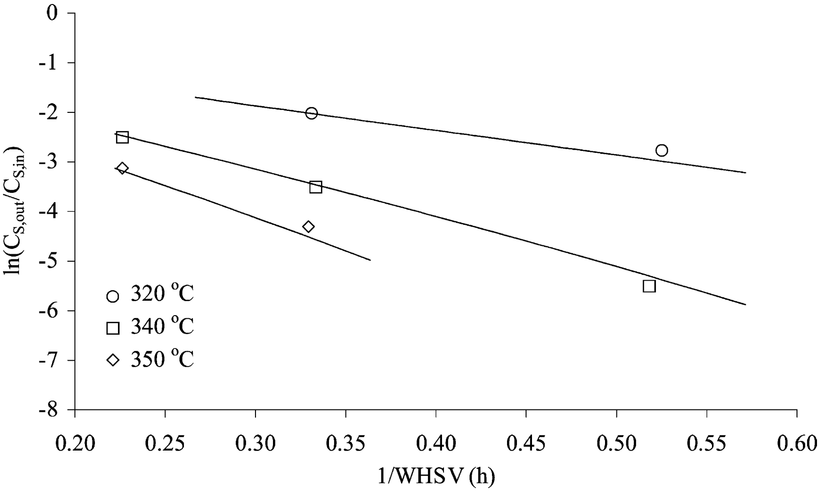

Fig. 2. Reactor performance versus space time. Hydrogen flow rate = 5.7 Nl/h, total pressure = 54 bar.

several temperatures. The pressure was kept constant at 54 bar for all the points and the hydrogen flow rate was 5.7 Nl/h. The experimental results are compared with the predicted results of the improved model. It is obvious that as the space velocity increases the reactor performance becomes worse. This is due to the shorter contact time of the liquid with the catalyst particles. Also, as the WHSV increases and the hydrogen flow rate is kept constant, the gas to oil ratio is reduced, the partial pressure of hydrogen sulphide is increased and the conversion is lower. The reactor performance depends strongly on the reaction temperature. As the temperature increases the evaporation of gas oil increases, there are more organic compounds in the vapour phase and consequently the hydrogen and hydrogen sulphide partial pressure decrease but the concentration of these gases in the liquid phase rises.

In Fig. 3, the sulphur removal versus the hydrogen to oil ratio is shown. The three experimental points presented were performed at total pressure 54 bar, temperature 340 °C and at WHSV = 4.4 g_L/g_C/h. As the gas

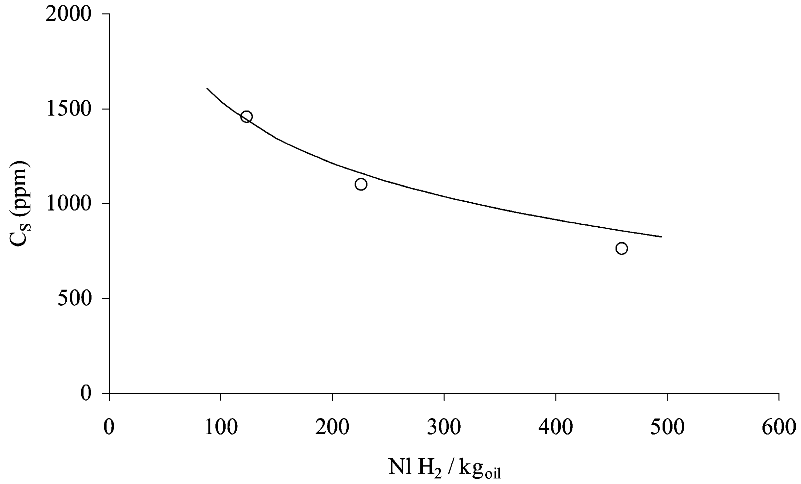

Fig. 3. Reactor performance versus gas to oil ratio. Reaction temperature = 340 °C, total pressure = 54 bar.

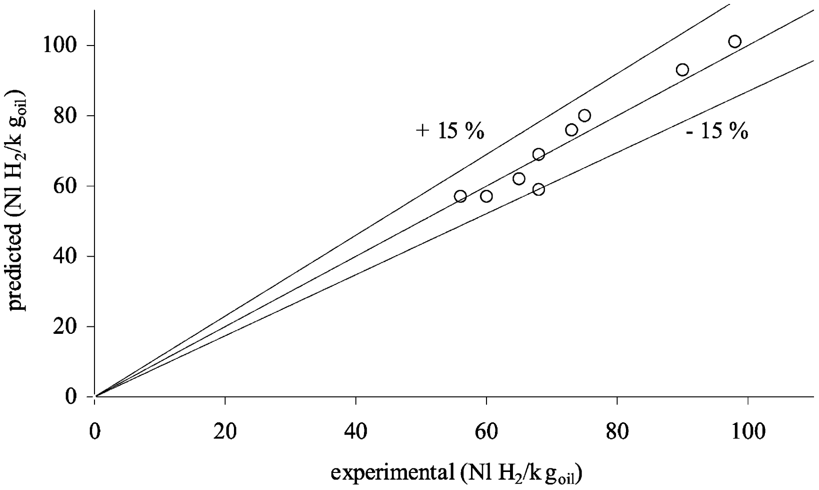

Fig. 4. Parity plot for the specific hydrogen consumption.

to oil ratio increases, the partial pressure of hydrogen sulphide and its liquid concentration diminish (from 2.8 to 0.3 bar and 0.055–0.018 mol/l) and the evaporation of gas oil increases from 12 to 31 wt.%. The hydrogen partial pressure rises from 50.2 to 50.8 bar with the gas to oil ratio, but its liquid concentration keeps practically constant at 0.325 mol/l.

A parity plot is presented in Fig. 4 for the specific hydrogen consumption. For all the points but one, the relative error is less than 6% and only for one point the deviation was 15%. The experimental value of specific hydrogen consumption varied from 56 to 98 Nl H_2/kg_{oil}. As the temperature and the gas to oil ratio increases, the consumption increases. The hydrogen consumption decreases as the WHSV increases.

In Fig. 5, the percentage of each sulphur compound in the ensemble of the sulphur pseudo-compounds in the gas–liquid mixture at each point of the catalytic

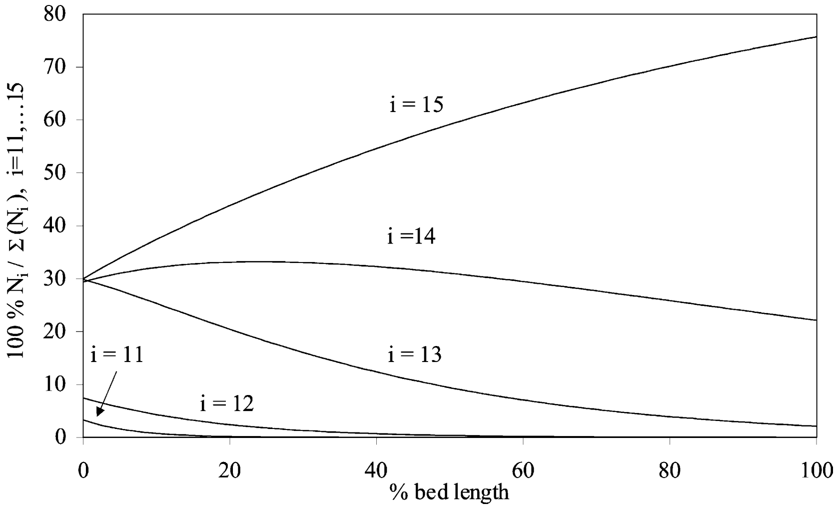

Fig. 5. Percentage of each sulphur pseudo-compound in the ensemble of the sulphur pseudo-compounds along the catalyst bed.

bed is presented. The curves correspond to an experimental test which was carried out at 320 °C at WHSV $= 3.0\,g_L/g_C$/h with a gas to oil ratio $411\,Nl\,H_2/kg_{oil}$. The sulphur concentration in the liquid product was 1790 ppm. At the reactor inlet the lighter fraction ($i = 11$) has the lower concentration and the three heavier compounds ($i = 13, 14, 15$) have approximately the same concentration. The two lighter compounds ($i = 11,12$) react very rapidly and the first one disappears in the first part (20%) of the bed length and the second one in the middle of the bed. At the reactor exit, the product contains practically only the sulphur compounds of the three heavier pseudo-compounds. The percentage of the most refractory sulphur pseudo-compound ($i = 15$) increases as it reacts much slower than the other ones and it prevails in the product.

5. Conclusions

The use of microreactors and the down scaling of experimental units lead to improved process safety, operability and control as well as to minimisation of waste generation, investment and energy consumption. HDS of a real feed has been studied by using a microreactor with a diluted bed of commercial catalyst. The level of the HDS conversion reached 99.6% at WHSV $= 2\,g_L/g_C$/h at 340 °C. The kinetic model, consisting of first-order parallel reactions of five pseudo-components, fits well the experimental points at several conditions. The estimated activation energy for HDS is in good agreement with the values given in literature. The reactor simulation code developed predicts the gaseous and the liquid composition along the reactor length taking into account the liquid evaporation.

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