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# An improved weighted average reactor temperature estimation for simulation of adiabatic industrial hydrotreaters

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## Abstract

A study on the improvement of the representative operating temperature from the temperature profile of an industrial adiabatic reactor is presented. This temperature is used to simulate the reactor performance by small scale laboratory isothermal reactors. An improved methodology for the estimation of a Weighted Average Bed Temperature (WABT) was elaborated to simulate an industrial multi-bed HDS reactor. The improved WABT, so called Weighted Average Reactor Temperature (WART), was compared with the most usually used WABT in a wide range of operational conditions as well as of kinetic parameters. In case of a multi-bed industrial hydrotreater, where quench zones are located between the beds and the  $H_2$  flow rate, which enters each bed, is different, the optimal gas to oil ratio was estimated for the laboratory-scale reactor.

Keywords: WABT; HDS reactor; HDS kinetics; Reactor simulation

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#### 1. Introduction

The reliable simulation of the industrial hydrotreaters has become necessary as the specifications on fuels quality will become stricter in the near future. After 2005, the limitation of sulfur content in diesel will be approximately 50 ppm wt. [1] and the accurate prediction of catalyst and reactor performance will be very crucial for the product quality. A common way to simulate the performance of a commercial HDS reactor is the conduction of kinetic experiments in a laboratory scale reactor using the same catalyst, same operating conditions and a representative feed. To obtain meaningful and ready to use data, it is necessary for the laboratory scale reactors to fulfil some design criteria such as complete catalyst wetting, minimal backmixing effects [2–7] and sufficient gas–liquid mass transfer. Experiments are performed in a wide range of the most critical parameters like reaction temperature and pressure, WHSV and gas to oil ratio. The experimental data are treated with an appropriate model so as to evaluate reaction kinetics, which is necessary for the simulation code of the industrial reactors.

An unavoidable difference in operation between the industrial reactors and the laboratory-scale ones is the catalyst bed temperature profile. In industrial reactors, the adiabatic operation results in an increasing with length temperature profile while small scale reactors operate isothermally. Consequently, it is practically difficult for the pilot reactor to operate maintaining the same temperature profile with the industrial one. Therefore, the kinetic experiments and the modelling of both reactors become indispensable.

Another way to predict the performance of an industrial HDS reactor for a certain set of operating conditions is the use of a Weighted Average Bed Temperature (WABT). All the operational parameters of the laboratory-scale reactor like pressure and WHSV may be the same as those of the industrial reactor while the isothermal temperature of the laboratoryscale reactor corresponds to the WABT of the industrial reactor. This method provides a direct comparison of the performance of both reactors requiring only one experimental point and bypassing the modelling codes. To the best of our knowledge, the literature that concerns the estimation and use of the WABT is still limited [8], although this parameter is an important and practical tool for a refinery engineer. It is not clear whether WABT is applicable in a wide range of operational conditions as well as of kinetic parameters. It is also unknown how the form of the temperature profile works on the WABT performance. Moreover, in case of an industrial reactor which consists of two or even three catalytic beds with intermediate quench zones, a key-parameter is the correct use of the feed gas to liquid ratio in the laboratory-scale reactor. In addition, in multi-bed reactors the temperature profile is not uniform as the gas-liquid stream is cooled in quench zones (Fig. 1).

The aim of this work is to investigate an improved model to predict a representative Weighted Average Reactor Temperature (WART) applied in any single and multi-bed hydrotreater. A theoretical comparison of the performance of adiabatic industrial HDS reactors with isothermal laboratory-scale reactors is presented using as representative temperature the widely used WABT and the proposed one (WART) with the improved methodology.



Fig. 1. The configuration of a laboratory-scale and an industrial-scale reactor.

For the development of the WART equation it was considered that both reactors can be characterised as ideal ones (plug flow, infinite solid–liquid–gas mass/heat transfer, complete catalyst irrigation). First, because the high gas and liquid velocities of the industrial reactor ensures total catalyst wetting and minimization of fluid flow dispersion and second because the laboratory-scale reactor designed for scale up experiments should be operated with bed dilution (in ascending or descending flow) to ensure plug flow for the gas and liquid phases and total catalyst wetting. For the conditions examined in both industrial and laboratory reactors, the gas–liquid flow regime corresponds to trickle flow.

# 2. Mathematical model of an adiabatic reactor

#### 2.1. Simulation of the catalytic beds

The model used in this work for the simulation of an industrial adiabatic reactor, is grounded on a pseudo-homogeneous plug flow pattern with no resistance in mass and heat transfer and complete catalyst wetting. Two typical power law kinetic equations are used to describe the performance of the reactor system. A technical kinetic equation is used to simulate the HDS reaction rate and another one to simulate the hydrogen consumption. It is assumed that the amount of heat produced is due to the reactions of hydrogen consumption, like saturation of olefins and aromatics. The H<sub>2</sub>S is the critical inhibitor of both reactions, so it was taken into account in the kinetic equations. The total HDS reaction rate (Eq. (1)) is assumed to be of *n*th order as for the sulfur which is considered to be concentrated in the liquid phase. The total hydrogen consumption rate (Eq. (2)) is of second order as for the remaining specific H<sub>2</sub> consumption that is observed [9].

$$r_{\rm HDS} = \frac{k_{\rm HDS} \cdot e^{-\frac{E_{\rm HDS}}{R} \cdot T} \cdot C_{\rm S}^n \cdot P_{\rm H_2}}{1 + k_{\rm H_2S} \cdot P_{\rm H_2S}} \tag{1}$$

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$$r_{\rm HC} = \frac{k_{\rm HC} \cdot e^{-\frac{k_{\rm HC}}{R \cdot T}} \cdot (CHT - CH)^2 \cdot P_{\rm H_2}}{1 + k_{\rm H_2S} \cdot P_{\rm H_2S}}$$
(2)

The model described below consists of the differential equations describing the mass balances of sulfur, hydrogen sulphide, hydrogen consumption and hydrogen (Eqs. (3)–(6)) as well as of the differential equation describing the heat balance in the adiabatic reactor (Eq. (7)).

$$\frac{\mathrm{d}C_{\mathrm{S}}}{\mathrm{d}m_{\mathrm{cat}}} = -r_{\mathrm{HDS}} \cdot \frac{1}{M_{\mathrm{oil}}} \tag{3}$$

$$\frac{\mathrm{d}N_{\mathrm{H}_2S}}{\mathrm{d}m_{\mathrm{cat}}} = r_{\mathrm{HDS}} \cdot \frac{10^{-6}}{MB_{\mathrm{H}_2\mathrm{S}}} \tag{4}$$

$$\frac{\mathrm{d}HC}{\mathrm{d}m_{\mathrm{cat}}} = r_{\mathrm{HC}} \cdot \frac{1}{M_{\mathrm{oil}}} \tag{5}$$

$$\frac{\mathrm{d}N_{\mathrm{H}_2}}{\mathrm{d}m_{\mathrm{cat}}} = -r_{\mathrm{HC}} \cdot \frac{1}{22.4} \tag{6}$$

$$\frac{\mathrm{d}T}{\mathrm{d}m_{\mathrm{cat}}} = \frac{N_{\mathrm{H}_{2}} \cdot Cp_{\mathrm{H}_{2}} + N_{\mathrm{H}_{2}\mathrm{S}} \cdot Cp_{\mathrm{H}_{2}\mathrm{S}} + M_{\mathrm{oil}} \cdot Cp_{\mathrm{oil}}}{r_{\mathrm{HC}} \cdot \Delta H}.$$
(7)

## 2.2. Simulation of the quench zones

In case that the reactor employs two or three beds in series with intermediate quench zones, the two-phase mixture, after its exit from the first or second bed, is mixed with a cool gas stream to reduce temperature. Consequently, both the gas flow rate and the mixture temperature will change before the gas–liquid mixture enters the next bed. The hydrogen flow rate after a quench zone  $(N_{\rm H,|after})$  is:

$$N_{\rm H_2}|_{\rm after} = N_{\rm H_2}|_{\rm before} + N_{\rm H_2}^{\rm Q} \tag{8}$$

The temperature at the beginning of the bed after a quench point  $(T_{after})$  is estimated from the solution of the heat balance at the quench, which is:

$$\int_{T_{\text{before}}}^{T_{\text{after}}} M_{\text{oil}} \cdot Cp_{\text{oil}} dT + \int_{T_{\text{before}}}^{T_{\text{after}}} \left( N_{\text{H}_2} \cdot Cp_{\text{H}_2} + N_{\text{H}_2} \text{S} \cdot Cp_{\text{H}_2} \text{S} \right) dT + \int_{T_{\text{before}}}^{T_{\text{after}}} N_{\text{H}_2}^{\text{Q}} \cdot Cp_{\text{H}_2} dT = 0$$
(9)

The above equations are written considering that the gas at the inlet of a reactor as well as the quench gas is pure hydrogen. For the specific heat capacity of the oil mixture appearing in Eqs. (7) and (9), the following correlation is used [10].

$$Cp_{\rm oil} = 4.1868 \cdot \left(\frac{0.415}{\sqrt{d_{15}}} + 0.0009 \cdot (T - 288.15)\right)$$
(10)

In this work, the heat balance equation in a quench zone was solved for  $N_{H_2}^Q$  choosing such a temperature decrease in each quench zone so that the bed outlet temperature to be within the practically acceptable limits.

## 3. Mathematical model of an isothermal reactor

The simulation of an industrial adiabatic reactor, either with or without quench zones, using an isothermal laboratory reactor, requires the solution of the mass balance equations as they were described in Section 2.1.

The solution of the four-equation system prerequisites the estimation of the WABT as well as the estimation of an inlet hydrogen flow rate in occasions of reactors consisting of more than one beds with intermediate quenching zones.

## 3.1. The existing WABT model

The most common WABT equation proposed in literature for the simulation of adiabatic, fixed bed hydroprocessing reactors as well as for the estimation of the deactivation rate of the catalyst used is [8]:

$$WABT = \frac{T_{\rm in} + 2 \cdot T_{\rm out}}{3} \tag{11}$$

where  $T_{in}$  is the temperature at the reactor entrance and  $T_{out}$  is the outlet temperature. The above equation takes the gradient of the temperature increase into account and is applied to single bed reactors. In cases of reactors with more than one bed in series, the WABT put into practice is estimated by the following weighted up expression:

$$WABT = \frac{\sum_{i=1}^{n} WABT_i \cdot m_{\text{cat},i}}{\sum_{i=1}^{n} m_{\text{cat},i}}$$
(12)

where the WABT is calculated by Eq. (9) for each bed and  $m_{\text{cat},i}$  is the catalytic mass of the *i*th bed.

#### 3.2. The improved WART model

In the event of an industrial reactor with more than one bed and intermediate quench zones, one additional weighted up expression is needed, as the gas to oil ratio is different at the entrance of each bed. In case that the industrial reactor consists of three beds, the required flow rate of H<sub>2</sub> in the laboratory-scale reactor entrance  $(N_{H_2}^{IR})$  will be:

$$\frac{N_{\rm H_2}^{\rm IR}}{M_{\rm oil}^{\rm IR}} = \frac{N_{\rm H_2}^{\rm B_1} \cdot m_{\rm cat,1} + \left(N_{\rm H_2}^{\rm B_1} + N_{\rm H_2}^{\mathcal{Q}_1}\right) \cdot m_{\rm cat,2} + \left(N_{\rm H_2}^{\rm B_1} + N_{\rm H_2}^{\mathcal{Q}_1} + N_{\rm H_1}^{\mathcal{Q}_2}\right) \cdot m_{\rm cat,3}}{\left(m_{\rm cat,1} + m_{\rm cat,2} + m_{\rm cat,3}\right) M_{\rm oil}^{\rm AR}}$$
(13)

where  $N_{\text{H}_2}^{\text{B}_1}$  is the molar flow rate of hydrogen at the inlet of the adiabatic reactor and  $N_{\text{H}_2}^{\text{Q}_1}$ ,  $N_{\text{H}_2}^{\text{Q}_2}$  are the molar flow rates of hydrogen in the quench zones before the second and the third bed, respectively.

Replace of the reaction rate for hydrodesulfurization (Eq. (1)) into the differential mass balance equation for the sulfur (Eq. (3)) and integration of the latter over the catalyst mass for both an adiabatic, single bed reactor (Eq. (14)) and its equivalent, isothermal one (Eq. (15)), yields correspondingly:

$$M_{\rm oil} \cdot \int_{C_{\rm S}^{\rm n}}^{C_{\rm S}^{\rm out}} \frac{\mathrm{d}C_{\rm S}}{C_{\rm S}^{n}} = \int_{0}^{m_{\rm cat}} \frac{k_{\rm HDS} \cdot e^{\frac{-k_{\rm HDS}}{R \cdot T}} \cdot P_{\rm H_{2}}}{1 + k_{\rm H_{2}S} \cdot P_{\rm H_{2}S}} \,\mathrm{d}m_{\rm cat}$$
(14)

$$M_{\rm oil} \cdot \int_{C_{\rm S}^{\rm in}}^{C_{\rm S}^{\rm out}} \frac{{\rm d}C_{\rm S}}{C_{\rm S}^{n}} = k_{\rm HDS} \cdot e^{\frac{-E_{\rm HDS}}{R \cdot T}} \cdot \int_{0}^{m_{\rm cat}} \frac{P_{\rm H_2}}{1 + k_{\rm H_2S} \cdot P_{\rm H_2S}} {\rm d}m_{\rm cat}$$
(15)

If Eq. (15) is applied to the isothermal reactor and Eq. (14) is applied to the adiabatic one for the same conversion, the right-hand part of Eq. (14) can replace the left-hand part of Eq. (15) to give:

$$e^{\frac{-E_{\rm HDS}}{R \cdot T_{\rm eq}}} \cdot \int_{0}^{m_{\rm cat}} \frac{P_{\rm H_2}^{\rm IR}}{1 + k_{\rm H_2S} \cdot P_{\rm H_2S}^{\rm IR}} dm_{\rm cat} = \int_{0}^{m_{\rm cat}} \frac{e^{\frac{-E_{\rm HDS}}{R \cdot T}} \cdot P_{\rm H_2}^{\rm AR}}{1 + K_{\rm H_2S} \cdot P_{\rm H_2S}^{\rm AR}} dm_{\rm cat}$$
(16)

where the WART is defined as that temperature at which the operation of the isothermal reactor would give the same sulfur conversion as the actual industrial reactor. Then, Eq. (17) can be derived.

WART 
$$\cdot R \cdot \left\{ \ln \left( \int_{0}^{m_{\text{cat}}} \frac{e^{-\frac{E_{\text{HDS}}}{R \cdot T}} P_{\text{H}_{2}}^{\text{AR}}}{1 + k_{\text{H}_{2}\text{S}} \cdot P_{\text{H}_{2}\text{S}}^{\text{AR}}} dm_{\text{cat}} \right) - \ln \left( \int_{0}^{m_{\text{cat}}} \frac{P_{\text{H}_{2}}^{\text{IR}}}{1 + k_{\text{H}_{2}\text{S}} \cdot P_{\text{H}_{2}\text{S}}^{\text{IR}}} dm_{\text{cat}} \right) \right\}$$
  
=  $-E_{\text{HDS}}$  (17)

Due to the fact that the terms including the hydrogen and hydrogen sulphide partial pressure in Eq. (17) are not sensitive to small variations of  $P_{\rm H_2}$  and  $P_{\rm H_2S}$ , the above equation can be recast into:

WART 
$$\cdot R \cdot \left\{ \ln \left( \frac{\overline{P}_{H_2}^{AR}}{1 + k_{H_2S} \cdot \overline{P}_{H_2S}^{AR}} \cdot \int_0^{m_{cat}} e^{\frac{-E_{HDS}}{R \cdot T}} dm_{cat} \right) - \ln \left( \frac{\overline{P}_{H_2}^{IR}}{1 + k_{H_2S} \cdot \overline{P}_{H_2S}^{IR}} \cdot \int_0^{m_{cat}} dm_{cat} \right) \right\} = -E_{HDS}$$

$$(18)$$

where  $\bar{P}_{H_2}^{AR}$ ,  $\bar{P}_{H_2S}^{AR}$ ,  $\bar{P}_{H_2S}^{IR}$ ,  $\bar{P}_{H_2S}^{IR}$  are the average pressures of hydrogen and hydrogen sulphide in the adiabatic and the isothermal reactor respectively.

Considering that  $\bar{P}_{H_2}^{AR} \approx \bar{P}_{H_2}^{IR}$  and  $\bar{P}_{H_2S}^{AR} \approx \bar{P}_{H_2S}^{IR}$  the above equation can be simplified into:

WART 
$$\cdot R \cdot \left\{ \ln \left( \int_{0}^{m_{\text{cat}}} e^{\frac{-E_{\text{HDS}}}{R \cdot T}} \mathrm{d}m_{\text{cat}} \right) - \ln m_{\text{cat}} \right\} = -E_{\text{HDS}}$$
(19)

Eq. (19) can be applied in cases of one but also of two or more beds in sequence separated by one or more quench zones respectively. Consequently, the proposed equation for the evaluation of the WART is:

WART 
$$\cdot R \cdot \left\{ \ln \left( \sum_{i=1}^{m_{\text{cat},i}} \int_{0}^{m_{\text{cat},i}} e^{\frac{-E_{\text{HDS}}}{R \cdot T(m_{\text{cat}})}} \mathrm{d}m_{\text{cat}} \right) - \ln \left( \sum_{i=1}^{n_{\text{BED}}} m_{\text{cat},i} \right) \right\} = -E_{\text{HDS}}, \quad n_{\text{BED}} \ge 2$$

$$(20)$$

Eq. (20) can be written in terms of bed length:

WART 
$$\cdot R \cdot \left\{ \ln \left( \sum_{i=1}^{n_{\text{BED}}} \rho_{\text{B},i} S_{\text{R},i} \int_{0}^{L_{i}} e^{\frac{-E_{\text{HDS}}}{R \cdot T(x)}} dx \right) - \ln \left( \sum_{i=1}^{n_{\text{BED}}} m_{\text{cat},i} \right) \right\} = -E_{\text{HDS}}$$
(21)

As there is a limited number of thermocouples along industrial beds, it is impossible to acquire the temperature profile for the integration of Eqs. (20) or (21). In this case, an approximation of the temperature profile with a polynomial of second order is attempted  $(T(x)=ax^2+bx+c)$ , using only the temperatures at the inlet, the outlet and at a point near the middle, preferably, of the bed. These values are very likely available for any hydrotreater.

Eq. (21) involves the activation energy of HDS, but the WART is practically very weakly dependent on this kinetic parameter. In Fig. 2, the axial temperature profile of an industrial hydrotreater is presented and for this case the WART is evaluated for several



Fig. 2. The real axial temperature profile and the interpolation polynomials in an industrial reactor with three beds.



Fig. 3. The equivalent temperature of isothermal reactor vs. the activation energy of HDS reactions (three bed reactor).

values of  $E_{\rm HDS}$  and given in Fig. 3. It is obvious that there is a very slight influence of the activation energy ( $E_{\rm HDS}$ ) on the WART. Four times higher activation energy (from 50 to 200 kJ/mol) gives 0.4 K difference on the WART. Therefore, if a typical value of  $E_{\rm HDS}$  is used (100 kJ/mol), Eq. (21) can be simplified in the following form:

WART = 
$$\frac{-12000}{\ln\left(\sum_{i=1}^{n_{\text{BED}}} \rho_{\text{B},i} S_{\text{R},i} \int_{0}^{L_{i}} e^{\frac{-12000}{T(x)}} dx\right) - \ln M_{\text{tot}}}$$
(22)

The inlet hydrogen flow rate in an isothermal reactor for the simulation of a multi-bed adiabatic reactor is estimated by Eq. (13), given before. A similar approach has been used in a recent work [11] mainly concerning single bed reactors, neglecting the correction of the gas/oil ratio from the quench streams and recommending more than five thermocouples for reliable results even for one bed reactor. Experimental evidence of the superiority of this approach is given for cases with one-bed reactor.

## 4. Discussion of results

In this section, the set of the four mass balances describing the isothermal reactor model is solved using both the existing WABT and the improved WART and the results are compared with those calculated from the solution of the equations of the non-isothermal



Fig. 4. Variation of the WABT error with WHSV and  $T_{\rm in}$  for  $E_{\rm HC}$ =13 kJ/mol.

model (Eqs. (3)–(7)) in case of a three bed reactor, as it is considered the most complicated reactor configuration. The procedure was the following. For a given set of kinetic equations the temperature profile of the adiabatic reactor was calculated. Then, the WABT and WART were obtained. These temperature values were used to solve the isothermal reactor model and finally calculate the exit sulfur concentration in each case. A wide range of kinetic and operating parameters have been tested considering the hydrotreatment of a feed ranging from heavy gas oil to diesel oil with a typical 1.4 wt.% sulfur content and total reactor pressure 5.4 MPa. The choice of the range of the kinetic parameters was based on the variation of the sulfur conversion which was in the range from 20% to 99.99%.



Fig. 5. Variation of the WABT error with WHSV and  $T_{\rm in}$  for  $E_{\rm HC}$ =5 kJ/mol.

The values of the kinetic parameters in the case of a three beds reactor	
Kinetic parameters	Three bed
$k_{\rm HDS}  ({\rm kg_{oil} \cdot ppm_{\rm S}^{1-n}/s \cdot kg_{cat} \cdot MPa_{\rm H,})}$	$2.4 \cdot 10^6$
$E_{\rm HDS}$ (kJ/mol)	127
$k_{\rm HC} ({\rm kg}_{\rm oil}^2/{\rm s} \cdot {\rm kg}_{\rm cat} \cdot {\rm MPa}_{\rm H_2} \cdot {\rm Nm}_{\rm H_2}^3)$	$2.8 \cdot 10^{-3}$
$k_{\rm H_2} S (MPa^{-1})$	2.5
$CHT (Nm_{H_2}^3/kg_{oil})$	0.12
n	1.1
$\Delta H (kJ/Nm^{3}H_{2})$	1500

For the comparison of the results, the following error is defined:

$$\operatorname{error} = \left| 1 - \frac{C_{\mathrm{S}}^{est}}{C_{\mathrm{S}}^{\operatorname{pred}}} \right| \tag{23}$$

where:  $C_{\rm S}^{\rm est}$  is the remaining sulfur concentration at the outlet of the adiabatic reactor, as it is calculated from the solution of the non-isothermal model and  $C_{\rm S}^{\rm pred}$  is the remaining sulfur concentration at the outlet of the reactor, as it is calculated from the solution of the isothermal model, using either the WABT or the improved WART.

## 4.1. Three bed reactor

The assessment of the already existing WABT starts by comparing its performance at two different  $E_{\rm HC}$ . In Fig. 4, the WABT error is presented versus WHSV and  $T_{\rm in}$  in case that  $E_{\rm HC}$ =13 kJ/mol. In Fig. 5, the same procedure is followed for  $E_{\rm HC}$ =5 kJ/mol. For both runs, the gas to oil ratio (Q/L) was 290 Nm<sup>3</sup>/m<sup>3</sup> and the values of the other kinetic parameters are presented in Table 1. When higher hydrogen consumption rate occurs and a steeper temperature profile is developed (Fig. 6), the error from the use of the existing WABT becomes quite high (up to 62% for  $E_{\rm HC}$ =5 kJ/mol, against 18% when  $E_{\rm HC}$ =13 kJ/



Fig. 6. Temperature profile in the three-bed adiabatic reactor for two  $E_{\rm HC}$  values.

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Table 1



Fig. 7. Variation of the WABT error with  $E_{\rm HC}$ .

mol). In Fig. 7, the descending line of the WABT error with increasing  $E_{\rm HC}$  is presented. The results of Fig. 7 are given for WHSV=1 h<sup>-1</sup>, Q/L=290 Nm<sup>3</sup>/m<sup>3</sup> and  $T_{\rm in}$ =623 K. The values of the other kinetic parameters are given in Table 1.

Fig. 8 is the respective figure to Fig. 5, where the improved WART is tested for the same values of the operating conditions as well as of the kinetic parameters. The results show that the error values from the use of the improved WART are lower than 11% whereas the respective ones using the existing WABT mode are up to 62%.

In Fig. 9, the error variation versus  $E_{\rm HC}$  is presented using the same parametric and operating values as in Fig. 7. The comparison of the two plots indicates that for the same range of  $E_{\rm HC}$  (5–13 kJ/mol), the error in case of the WABT varies from 4.8% to 28.9% whereas the errors resulting from the use of WART are between 4.8% and 6.6%. It should be mentioned that the values for the operating parameters have been chosen so that the two WABT alternatives are assessed in occasion of deep hydrodesulfurization. The 28.9% error



Fig. 8. Variation of the WART error with WHSV and  $T_{\rm in}$  for  $E_{\rm HC}$ =5 kJ/mol.



Fig. 9. Variation of the WART error with  $E_{\rm HC}$ .

corresponds to 65 ppm outlet sulfur concentration and the 4.8% error corresponds to 235 ppm outlet sulfur concentration.

In Fig. 10, the performance of the proposed WART is evaluated in relation with WHSV (0.5–2.5 h<sup>-1</sup>) and Q/L (200–800 Nm<sup>3</sup>/m<sup>3</sup>) variation. It is observed that all the errors are lower than 8%. The error values are presented for  $T_{\rm in}$ =603 K and for the kinetic parameters given in Table 1.

Finally, in Figs. 11 and 12 the assessment of the WART is realised with respect to the kinetic parameters. More specifically, in Fig. 11, the WART error variation with  $E_{\text{HDS}}$  (84–146 kJ/mol) is presented when  $k_{\text{HDS}}$  varies from  $2.8 \cdot 10^3$  to  $8.3 \cdot 10^6$  kg<sub>oil</sub> ppm<sup>1–n</sup>/s kg<sub>cat</sub> MPa<sub>H2</sub>. In Fig. 12 the WART performance is assessed in relation with  $E_{\text{HDS}}$  (84–146 kJ/mol) for three different reaction orders (n=1, 1.5, 2) with  $k_{\text{HDS}}=2.8 \cdot 10^3$  kg<sub>oil</sub> ppm<sup>1–n</sup>/s kg<sub>cat</sub> MPa<sub>H2</sub>.



Fig. 10. Variation of the WART error with WHSV and Q/L.



Fig. 11. Variation of the WART error with  $E_{\text{HDS}}$  and  $k_{\text{HDS}}$ .

In both cases the values of the operating parameters were considered to be  $T_{\rm in}=603$  K, WHSV=1 h<sup>-1</sup>, Q/L=290 Nm<sup>3</sup>/m<sup>3</sup> and the values of the other kinetic parameters were those of Table 1. It is remarked that the error values are always lower than 8.5%.

## 5. Conclusions

In this work, a comparison between the most commonly used WABT and an improved WABT, so called WART is performed. It should be pointed out that the use of WART needs three known temperature points in an industrial bed (inlet, middle and outlet),



Fig. 12. Variation of the WART error with  $E_{\text{HDS}}$  and n.

whereas the existing WABT needs two temperature points (inlet and outlet). The analysis of the results that was set forth for one-, two- and three-bed reactors showed that the use of the WABT is not authoritative. It may lead either to good or very bad results especially in cases of deep desulfurization. On the contrary, the employment of the improved WART always leads to good predictions. Remark that only results for the three-bed case are presented in this paper since similar trends were obtained when the analysis was applied to the one-or two-bed cases. The appreciation of the WART was realised in a wide range of operating and kinetic parameters and the calculated error in exit sulfur concentration was always lower than 12%.

## Symbols

С	concentration (ppm wt.)
CH	specific hydrogen consumption (Nm <sup>3</sup> H <sub>2</sub> /kg <sub>oil</sub> )
CHT	maximum specific hydrogen consumption (Nm <sup>3</sup> H <sub>2</sub> /kg <sub>oil</sub> )
Ср	specific heat capacity (kJ/kg/K for oil, kJ/kmol/K for H <sub>2</sub> and H <sub>2</sub> S)
$d_{15}$	oil density at 288 K (g/ml)
E	activation energy (kJ/mol)
k <sub>H S</sub>	inhibiting factor $(MPa^{-1})$
$k_{\rm HC}$	frequency factor of HC reaction constant $(kg_{oil}^2/s \cdot kg_{cat} \cdot MPa_{H_1} \cdot Nm_{H_2}^3)$
$k_{\rm HDS}$	frequency factor of HDS reaction constant $(kg_{oil} \cdot ppm_s^{1-n}/s \cdot kg_{cat} \cdot MPa_{H_s})$
$L_i$	length of <i>i</i> th catalytic bed (m)
MВ	molecular weight (g/mol)
m <sub>cat</sub>	mass of catalyst (kg)
$M_{\rm oil}$	mass flowrate of oil (kg/s)
$M_{\rm tot}$	total mass of catalyst for all beds (kg)
N	molar rate (mol/s)
п	reaction order
$n_{\rm BED}$	number of beds
Р	partial pressure (MPa)
Q/L	gas to oil ratio $(Nm^3/m^3)$
r	apparent reaction rate
R	ideal gas constant (8.314 J/mol/K)
$S_{\rm R}$	cross section area of catalytic bed (m <sup>2</sup> )
Т	temperature (K)
WAB	T weighted average bed temperature (K)
WAR	T weighted average reactor temperature (K)
WHS	V weight hourly space velocity $(h^{-1})$
Greek	z Symbols
$\Delta H$	exotherm of reactions $(kJ/Nm^3 H_2)$
$ ho_{ m B}$	catalytic bed bulk density (kg/m <sup>3</sup> )
Subsc	ripts and superscripts

after after the quench point

- AR adiabatic reactor
- B adiabatic bed
- before before the quench point
- HC reaction of H<sub>2</sub> consumption
- HDS hydrodesulfurization reaction
- *i* index number
- in inlet
- out outlet
- IR isothermal reactor
- Q quench

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