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Hydrodesulfurization and hydrodemetallization of different origin vacuum residues: New modeling approach

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ABSTRACT

In order to be able to upgrade the heaviest part of the crude oil one needs to remove several impurities, such as sulfur or metals. Residue hydrotreatment in fixed beds, under high hydrogen pressure can achieve high removal performances, with an industrial catalysts optimized staging. Despite the recent improvements, petroleum residues remain very difficult to describe and characterize in detail. Several kinetic models have been developed, but mostly they are feed dependant and their predictions are not satisfying for residues of different origins. Based on a recent study comparing residue properties and the differentiating physical-chemical properties responsible for reactivity [1], the present work develops a

hydrotreatment kinetic model coupled with mass transfer in the catalyst which attempts to simulate the different residue performances. After estimation of kinetic parameters for a given residue, the model was validated for three other residues. This new model is able to take into account differences in residue characteristics and gives fairly good simulations of residues performances.

KEYWORDS : Vacuum residue, Diffusion, Kinetic Model, Hydrodesulfurization, Hydrodemetallization, reactor modeling

1. INTRODUCTION

Upgrading petroleum residue into lighter fractions is crucial to satisfy the increasing energetic demand. In addition, the available crude oils are becoming heavier and therefore the removal of impurities, as sulfur or metals is more necessary before converting. Residue upgrading processes produce either more distillates (low sulfur fuel oil) or residues suitable for the residue cracking units (RFCC). Among all residue upgrading processes, fixed bed hydrotreatment units are the most frequently used.

The residue fixed bed hydrotreatment process, HyvahlTM developed by IFPEN in 1982 [2], consists of several trickle bed reactors in series, subdivided into two different reaction sections with specific catalysts. In each one of them. The first section (HDM - hydrodemetallization) is intended to remove most of the metals and to disaggregate the large asphaltenes. The second section (HDS – hydrodesulfurization) allows, with a deeper desulfurization function, the required sulfur levels to be achieved. Both sections operate at high hydrogen pressure and high temperatures. The understanding of chemical and physical phenomena in these reactors is a major challenge.

The heaviest fraction of oil contains a large polydispersity of molecular structures, which is very difficult to characterize precisely. A typical way to start residue characterization is by fractionation. The heaviest fraction, called asphaltenes, is obtained by precipitation using a paraffin [3]. The nature of

asphaltenes is still a subject of much controversy [4-7]. It is nonetheless accepted that they are constituted of large size molecules and this phase possibly has a colloidal structure with an high concentration of impurities. Their hydrotreatment is then much more difficult than for lighter structures.

In parallel to the development of the process and understanding of the residue physical and chemical properties and reactivities, IFPEN has been working on the development of kinetic and catalyst deactivation models for both sections of the process [8-10]. These models give quite satisfying results, but were developed for specific Middle East residues and lack accuracy when tested to simulate residues of different origins. Alternative hydrotreatment models reported in the literature are based on heavy residues originating from other areas but are only tested for the specific residues for which they are developed and no general model is suggested [11-15].

The problem of such models is that their feed description is quite simple and that the model parameters such as kinetic constants, depend on the vacuum residue origin. To overcome such constraints, quite complex residue description models based on molecular reconstruction have been developed and can be found in the literature [16-18]. However, these models are so complex that, due to their computing time, they are almost never integrated in a complete kinetic model of residue hydrocracking and are of very difficult practical application.

In the present work, based on the experimental works of Ferreira et al. [1], we introduce a new heavy residue feed description and consequent kinetic network. The aim is that model parameters should be independent of vacuum residue origin whilst the model itself remains as simple as possible. This description is then introduced into the reactor/kinetic model which includes the two sections of the process. After parameter estimation with a Middle East residue, the model is validated with experimental results from three residues with different origins.

2. EXPERIMENTAL SECTION

Vacuum residues with quite different characteristics, i.e. densities, sulfur, metals and asphaltenes content were selected and tested: Arabian Light, Buzurgan (Iraqi residue), Djeno (African residue) and Ural (Russian residue).

The hydrotreating experiments were performed in an up-flow, isothermal fixed bed reactor unit (Figure1). The main equipment is a 500 cm³ reactor, which is loaded with commercial catalysts. A first set of experiments was carried out only with the HDM catalyst in order to obtain data on the HDM section. A second set of experiments was conducted with the association of HDM and HDS catalysts, both catalysts are present in a 50/50 volume ratio.

Figure 1 – Simplified pilot scheme.

Residue characterization and experiment details have been reported by Ferreira et al. [1].

3. MODEL

The model describes two plug flow reactors taking into account the mass transfer limitations in the catalyst. These last, for each reactor, are based on the Stefan-Maxwell model already described by Ferreira et al. [19]. However, the model has a new feed description and reaction network that, although still based on lumps, tries to improve the residues description.

3.1 Model assumptions

The reactor model assumptions are summarized below:

- Isothermal reactor;
- The extragranular phase is considered as a plug flow reactor;
- In the extragranular phase, the liquid phase does not exchange with the gas phase, the thermodynamic equilibrium is assumed at each position in space;

- The liquid mixture is ideal;
- Catalytic pellets are represented by spheres (HDM section) or by cylinders (HDS section) with average radius R_p ;
- The catalytic pellets are filled with liquid, the gas phase is considered only in the extragranular phase;
- The reactions occur only in the intragranular phase (catalyst), first order reactions are considered with respect to reactants;
- The chemical kinetics do not depend on hydrogen concentration, equilibrium being assumed.
- The molar volumes in the liquid and adsorbed phase are the same;
- Thermodynamic equilibrium is assumed between the fluid and adsorbed phases in catalyst pellets;
- All species have the same heat of adsorption (owing to the single-component dependence on temperature, this is a relatively good assumption);
- The adsorption equilibrium is represented by the generalized Langmuir model, assuming the same adsorption capacities for all adsorbates on the active sites;
- Mass transfer in the catalyst pore is described by the Stefan-Maxwell equations adapted to diffusion in a porous solid (Dusty Gas Model). Moreover the Stefan-Maxwell model considers the volume constraints by the Fornasiero formalism [20]. Considering the difference between molecular volumes, Fornasiero adapts the Stefan-Maxwell equations supposing the molecules collision occurs only between equivalent volumes. The number of segments is defined as follows: $n_{si} = \frac{\vartheta_i}{\vartheta^0}$ with ϑ_i the molar volume of component i and ϑ^0 the molar volume of the reference component, hydrogen (the smallest component). Resistance to mass transfer between extragranular and intragranular phases is represented by a linear driving force.

3.2 Material balances

The geometrical characteristics of the two reactors corresponding to the HDM and HDS sections are the same but the catalysts in the two sections are different. The main differences are the properties of the catalyst, such as initial porosity, pore radius and shape. The shape of catalyst differs according to the section; the catalyst is spherical for the HDM section and cylindrical for the HDS section. The mass

balances will also change slightly. For the balance in the bulk fluid, the specific surface area $a_s = \frac{S_c}{V_c}$

gives $a_s = \frac{3}{R_c}$ (case of spherical catalyst), and $a_s = \frac{2(R_c + L_c)}{R_c L_c}$ (case of cylindrical catalyst). In the latter

case, $L_c \gg R_c$, the specific surface area can be approximated to $a_s = \frac{2}{R_c}$.

The previous hypotheses lead to the following set of equations. ϕ designates the volume fractions, with subscripts corresponding to the species, and the superscript to the phase, **fluid** (extragranular phase), catalytic **pellet** (intragranular phase); nc designates the number of components. The relation between the concentrations in extragranular and intragranular phases and the respective volume fractions can be written as follows: $\phi_i^f = C_i^f n_{si} \vartheta^0$ for the extragranular phase and $\phi_i^p = C_i^p n_{si} \vartheta^0$ for the intragranular phase

In the extragranular phase (HDM and HDS)

$$\varepsilon_i v_o^f \frac{\partial \phi_i^f}{\partial z} = (1 - \varepsilon_i) \varepsilon_p a_s k_i^m (\phi_i^f - \phi_i^p) \quad i = 1, nc - 1 \quad (1)$$

The volume constraint associated with these equations is: $\sum_{j=1}^{nc} \phi_j^f = 1$

In the intragranular phase (catalyst pellet)

Considering that, for the cylindrical catalyst, the radial diffusion is more important than the axial diffusion ($L_c \gg R_c$) the same balances inside the catalyst can be written for both catalysts:

:

$$\varepsilon_p \frac{\partial \phi_i^p}{\partial t} = \mathcal{G}^0 \varepsilon_p \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \cdot N_i^0) + (1 - \varepsilon_p) \mathcal{G}^0 n_{si} S_{\text{catalyst}} r_i \quad i = 1, \text{nc}$$

With r_i is the global volumetric surface production rate of lump i ($\text{mol} \cdot \text{m}^{-3} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$), it defined by solid volume and by catalyst surface. N_i^0 is the flux defined as following $N_i^0 = n_{si} N_i$

The volume constraint associated with these equations is $\sum_{i=1}^{\text{nc}} \phi_i^p = 1$.

The associated boundaries conditions of this equation system for the intragranular phase are written as follows:

$$\begin{aligned} \forall t \quad \text{at } r = R_p, \quad N_i^0 &= \frac{k_i^m}{\mathcal{G}^0} (\phi_i^f - \phi_i^p) \\ \forall t \quad \text{at } r = 0, \quad N_i^0 &= 0 \end{aligned} \quad i = 1, \text{nc}$$

On the catalyst surface

The accumulation of metals and coke on catalyst surface are given by following mass balances:

$$\frac{d\phi_i^s}{dt} = \mathcal{G}^0 n_{si} S_{\text{catalyst}} r_i \quad \text{with } i = \text{Vanadium, Nickel ou coke}$$

The catalyst surface (S_{catalyst}) varies with the coke deposits according to the following expression:

$$S_{\text{catalyst}} = S_{\text{initially available}} - S_{\text{occupied, coke}}$$

The initially available surface is experimentally measured by the BET technique. A coke unit is assumed to be a sphere with diameter (R_{coke}) equivalent to average asphaltene diameter found in the

works of Tayakout et al. [21] . Its occupied surface ($S_{\text{occupied,coke}}$) is equivalent to the section surface of the sphere and can be written as follows:

$$S_{\text{occupied,coke}} = N_{\text{coke}} \pi R_{\text{coke}}^2 \quad \text{with} \quad N_{\text{coke}} = \frac{\phi_{\text{coke}}^S V_{\text{p,int ragranular phase}}}{\frac{4}{3} R_{\text{coke}}^3}.$$

The catalyst surface (S_{catalyst}) becomes:

$$S_{\text{catalyst}} = S_{\text{initially available}} - \frac{3\phi_{\text{coke}}^S V_{\text{p,int ragranular phase}}}{4R_{\text{coke}}}$$

Flux expression

The mass transfer is based on the Stefan-Maxwell equations and considers the volume constraints according to the Fornasiero formalism [20]. The mass transfer limitations need to be considered in the two sections. For the HDM section, despite using a macroporous catalyst it appears that the large size of residue molecules (especially asphaltenes) leads to specific steric hindrance constraints that must be added to the kinetic and thermodynamic models [22, 23].

The flux expression taking into account the Fornasiero formalism is written as follows:

$$\frac{\nabla \phi_i^p}{n_{\text{si}} \cdot \mathcal{G}^0} = \frac{1}{C_T} \frac{\sum_{j=1}^{n_c} \phi_j^p N_i^0 - \phi_i^p N_j^0}{D_{ij}^{\text{eff}}} \quad i = 1, n_c - 1$$

The model also considers that the reaction only occurs at the catalyst surface in the adsorbed phase, and the adsorption mechanism is described by a generalized Langmuir isotherm.

The effective diffusion coefficients of these residues have been described as follows [24] :

$$D_{ij}^{\text{eff}} = \frac{\varepsilon_p}{\tau_r} K_r K_p D_{i,j}$$

Where $D_{i,j}$ is calculated by correlations present in the literature. For the present model, a correlation valid for liquids was chosen, the Scheibel correlation. This last is based on molar volume and derived from Wilke-Chang correlation [25]:

$$D_{i,j} = \frac{A_s T}{\eta_j \vartheta_i^{1/3}} \left[1 + \left(\frac{3\vartheta_j}{\vartheta_i} \right)^{2/3} \right]$$

K_r and K_p are coefficients taking account respectively of reduction of the molecule mobility due to pore

wall and partitioning of the solute $\left(K_p = \frac{\phi_{\text{asph}}^p}{\phi_{\text{asph}}^f} \right)$.

Two expressions for K_p and K_r have been proposed in the literature [24], depending on the ratio $\lambda = R_h/r_0$ where R_h is the hydrodynamic radius of asphaltenes nano-aggregates considered as a sphere and r_0 the average pore radius:

$$K_p = (1 - \lambda)^2 \tag{14}$$

$$K_r = 1 - 2,104\lambda + 2,089\lambda^3 - 0,948\lambda^5$$

These correlations are accurate when $\lambda \leq 0.5$. To calculate the ratio λ , it is necessary to know the hydrodynamic radius of the molecules, and the pore radius variation with time.

The hydrodynamic radius R_h can be calculated through the Stokes-Einstein equation:

$$D_\infty = \frac{kT}{6\pi\eta R_h}$$

Where D_∞ is considered to be approximately equal to $D_{i,j}$. This is an approximation often used in the literature to have an order of magnitude for molecular radius.

Finally, the pore radius is related to the porosity. The porosity decreases due to coke and metal deposits, but also due to the adsorbed species. Consequently, the pore radius also decreases. A relationship is established by Tayakout et al. [21], between the porosity and the radius with the following assumptions:

- catalyst pores are supposed to be cylindrical
- the number of pores is constant with time

The relation can then be written as follows: $r_0(r, t) = r_0(r, 0) \cdot \sqrt{\frac{\varepsilon_p(r, t)}{\varepsilon_p(r, 0)}}$

To obtain the pore radius, the intragranular porosity at a given time is calculated through a volume

balance:
$$\varepsilon_p(r, t) = \varepsilon_p(r, t = 0) - \sum_{k=1}^{nd} \phi_k^p(r, t) - \sum_{k=1}^3 (1 - \varepsilon_p) \phi_k^s(r, t)$$

Given the variation of the pore radius and porosity with time and radial position in the catalyst, the effective diffusion coefficients will also vary with time and radial position in the catalyst.

3.3 Feed Description (Lumps)

Through the available analysis, the residue is considered as a mixture composed of fractions (SARA fractions). The goal is to have a different quantitative description for each residue, through its properties, and not through the kinetics or adsorption parameters. The most complex fractions are asphaltenes and resins. And previous works have shown that their behaviour is the hardest to describe [8-9, 12]. So the present model will focus on a more detailed description of both these fractions.

Usually, the asphaltenes and resins are each described by a single lump two lumps describe the asphaltenes and the resins but in this work, in order to take better account of their wide polydispersity, they have been divided into fractions depending on the type of metal present, their aliphaticity and their aromaticity.

Firstly, three main types of asphaltenes have been considered: simple asphaltenes, nickel asphaltenes and vanadium asphaltenes. Each of these three is divided into 4 sub-groups according to their aliphaticity (s1 for light aliphaticity and s2 for the stronger) and aromaticity (a1 for light aromaticity and a2 for the stronger) level. Thus we consider 4 sub-groups for describing asphaltenes : (a1s1, a1s2, a2s1, a2s2). The heaviest asphaltenes are noted Asp a2s2, and the lightest Asp a1s1. This asphaltenes representation is reported in Figure 2.

Figure 2 – Scheme of asphaltenes sub division

The sub-groups were then further divided into molecules containing sulfur, nitrogen or neither element, as shown in Figure 2. Each of the $4 \times 3 = 12$ asphaltenes presented are divided in three (with sulfur, with nitrogen or simple). For example, the Asp a2s1 (red in Figure 3) can contain sulfur, nitrogen, or neither.

Figure 3 - Scheme of asphaltenes inside of each sub division.

In conclusion, we will have $3 \times 4 \times 3 = 36$ different asphaltenes. For resins, the reasoning is exactly the same. We will also have 36 different resins.

The other SARA fractions are considered to be less complex, and so their description is simpler. Aromatics are described as two species, the aromatics and the sulfured aromatics. Saturates are lumped in a single species. The gases formed are described by two species (NH_3 and H_2S), with their chemical properties.

Finally, the model will have a total of 77 different lumped species (36 for asphaltenes + 36 for resins + 2 for aromatics + 1 for saturates + 2 for gas (NH_3 , H_2S)).

3.4 Kinetic Network in the both sections

The species defined previously have been used to build the kinetic network considering the referred reactions (HDM, HDS, cracking....) for the both sections, as shown in Figure 4.

Figure 4 – Scheme of asphaltenes with some of the possible reactions.

Since the number of lumps is rather large, the number of kinetic constants has been limited assuming the same rate constants for several related reactions, considering the following assumptions:

- For each metal, there is one kinetic constant for the asphaltenes, and another for the resins (total of 4 kinetic constants). After removing the metal, the asphaltene will have the same level of aromaticity and aliphaticity, as well as the quantity of sulfur and nitrogen. The metal removed will be a deposit in the catalyst;
- Two types of desulfurization reactions have been considered: with and without an alkyl chain removal. For all the asphaltenes only two kinetic constants are used, one for each type of desulfurization (the resins are treated in the same way);
- When the desulfurization removes an alkyl chain, the asphaltene aliphaticity changes ;
- The denitrogenation reactions are only possible in lumps free of metals. For both the asphaltenes and the resins, denitrogenation is represented by a single kinetic constant.
 - Two types of cracking reactions have been considered inside the 4 sub-fractions. The level of aromaticity and aliphaticity changes by removal of an aromatic or a saturate, respectively. Two kinetic constants for the asphaltenes and two others for the resins have been associated with these reactions;
- Only the lightest asphaltenes (Aspa1s1) can crack to give the heaviest resins (Resa2s2);
- The lightest resins (Resa1s1) can crack to give aromatics and saturates;
- For the aromatics, only the desulfurization of aromatics takes place;
- The coke formation is due to resins and asphaltenes, both without metals.

In total, 122 reactions can take place in the reactor, but the model uses only 17 different kinetic constants, as shown in the Table 1.

Table 1 – Reactions considered for the kinetic network

An apparent first order for all reactions has been assumed; except for demetallization and coke reactions where the apparent order is two, one for the lump concentration and one for the active site concentration. The active site concentration (q^{site}) decreases with the demetallization and the coke formation. The kinetic expressions can be written as follows:

- Demetallization and coke reactions: $r_i = k_i q_i q^{\text{site}}$ with k_i ($\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$) defined by m^2 of specific catalyst surface.

- Others reactions: $r_i = k_i q_i$ with k_i ($\text{m}^{-2} \cdot \text{s}^{-1}$) defined by m^2 of specific catalyst surface.

As mentioned before, the model considers that the reactions occur in the adsorbed phase, so adsorption coefficients must be considered for the Langmuir equations. The adsorbed concentrations q_i can be

expressed by the following relation: $q_i = \frac{q^{\text{site}} b_i C_i^{\text{p}}}{1 + \sum_{j=1}^{\text{nc}} b_j C_j^{\text{p}}}$ and the active site concentration (q^{site}) by the

following mass balance: $\frac{q^{\text{site}}}{q^{\text{max}}} = 1 - \phi_{\text{coke}}^{\text{S}} - \phi_{\text{Vanadium}}^{\text{S}} - \phi_{\text{Nickel}}^{\text{S}}$ with q^{max} the active site saturation concentration.

The kinetic expressions become:

- Demetallization and coke reactions: $r_i = k_i \frac{q^{\text{site}} b_i C_i^{\text{p}}}{1 + \sum_{j=1}^{\text{nc}} b_j C_j^{\text{p}}} q^{\text{site}}$

- Others reactions: $r_i = k_i \frac{q^{\text{site}} b_i C_i^{\text{p}}}{1 + \sum_{j=1}^{\text{nc}} b_j C_j^{\text{p}}}$

Since q^{max} (the maximum value for q^{site}) is not known, it is introduced in the apparent kinetic constants as follows:

- Demetallization and coke reactions: $r_i = k_i \frac{(1 - \phi_{\text{coke}}^{\text{S}} - \phi_{\text{Vanadium}}^{\text{S}} - \phi_{\text{Nickel}}^{\text{S}})^2}{1 + \sum_{j=1}^{\text{nc}} b_j C_j^{\text{p}}} C_i^{\text{p}}$

$$\text{- Others reactions: } r_i = k'_i \frac{(1 - \phi_{\text{coke}}^S - \phi_{\text{Vanadium}}^S - \phi_{\text{Nickel}}^S)}{1 + \sum_{j=1}^{nc} b_j C_j^p} C_i^p$$

with the kinetic constant for demetallization and coke reactions: $k'_i = k_i (q^{\max})^2 b_i$ and for other reactions $k'_i = k_i q^{\max} b_i$.

4. RESULTS AND DISCUSSION

The model describes the two sections corresponding to both the catalysts, the calculated result at exit of the first reactor (catalyst for HDM) has been used as the input to the second reactor (catalyst for HDS). In order to obtain the input of the first section, some parameters have to be calculated.

The fixed parameters are the catalysts properties. The catalysts and their properties are summarized in Table 2.

Table 2– Properties for both catalysts (HDM and HDS) used as model input.

4.1 Calculated parameters

Attribution of number of segments - n_{si}

To attribute the segment number (n_{si}) described in the Fornasiero formalism [20], the molar volume of each lump has to be known. This was calculated from the molecular weight and the density of each lump ($M_i = \rho_i \cdot n_{si} \cdot \mathcal{V}^0$). To have the order of magnitude of the molecular weight of each fraction, the values were chosen from an article [25] where the molecular weights presented were obtained experimentally using a vapour pressure osmometer for a Buzurgan residue. The values for densities were taken from the same article. It is also important to notice, that the only n_{si} attributed are for saturates and aromatics. The others are calculated through the kinetic network, in order to respect the

mass balance. For each residue GPC (Gas Permeation Chromatography) analysis was used to determine a ratio of molecular weights of saturates and aromatics compared to the Buzurgan residue. The segment numbers (n_{si}) for the other residues (Arabian Light, Ural and Djeno) were estimated from this. These GPC results were used for the comparison between the residues (through a ratio) and not to impose the molecular weights and the n_{si} . Indeed, the molecular weights can't be used because the GPC calibration method (based on equivalent to the polystyrene structure) means they are not measured absolutely used to calibrate the masses and not an absolute measure. The other molecular weights of Arabian, Ural and Djeno were calculated in the same way that for the Buzurgan residue, through the kinetic network, in order to respect the mass balance. The segment numbers n_{si} for aromatics and saturates are reported in Table 3.

Table 3 – Calculated n_{si} for aromatics and saturates of the different residues.

Repartition of asphaltenes, resins and heteroatoms in each sub-fraction

The asphaltenes and resins have been sub-divided into 4 fractions and each of these sub-fractions contains heteroatoms. From normalised GPC distributions [1], four mass intervals have been assumed. The GPC distribution of the lightest residue containing the smallest molecules (in the present case Ural) was taken as reference. The proportions of each sub-fraction relative to the entire fraction are given by the area of each interval for asphaltenes and resins of different vacuum residues respectively in Table 4 and Table 5.

Table 4 – Distribution of 4 sub-fractions of the asphaltenes for the 4 different vacuum residues.

Table 5 - Distribution of 4 sub-fractions of the resins for the 4 different vacuum residues.

The GPC signal shows the weight molecular distribution of asphaltenes and resins to be not directly proportional to the amount of asphaltenes or resins. In fact, the signal is the result of the coupling between aromaticity and quantity. In the Tables 4 and 5, it can be observed that for both resins and asphaltenes, the sub-fractions 2 and 3 are present in largest quantity. In particular, for asphaltenes sub-fraction 2 is the greatest, and for the resins the greatest quantity is in the sub-fraction 3.

Regarding the heteroatoms, little information is available relative to their distribution within the SARA fractions. Nonetheless, some work has been done recently, mainly relating to asphaltenes. The authors have considered each SARA fractions as an entire fraction, and not as 4 different distributions [26, 27]. Specifically for the evolution of asphaltenes in hydroprocessing [27], the sulfur conversion seemed to be quite similar in terms of aromaticity and polycondensation. Another work by Marques et al. [28] fractionated the asphaltenes of Safaniya (Middle-East heavy) vacuum residue into two fractions, and analyzed both these sub-fractions. The authors observed that the smaller asphaltenes had a lower Ni/V ratio than the bigger asphaltenes. In terms of reactivity, the smaller asphaltenes seemed to react faster, but this result could be due reduced mass transfer limitations for the smaller ones.. Despite these recent improvements, we do not have enough information to differentiate the residues. So, in a first approach, it is considered that the heteroatoms are distributed evenly in the different sub-fractions

4.2 Parameter Estimation

While the number of different species considered to be present in the reactor is 77, only six adsorption coefficients have been considered following the main lumps and gas: Asphaltenes, Resins, Aromatics, Saturates, NH_3 and H_2S . The number of reactions which might occur is 122 but only 17 apparent kinetic constants (k'_i) have been introduced to describe all reactions. In summary, 6 adsorption coefficients (b_i) and 17 apparent kinetic constants (k'_i) have been introduced in the kinetic networks, giving a total of 23 parameters for each section.

The kinetic and thermodynamic parameters were estimated for Buzurgan. Figure 5 shows the evolution profiles obtained by simulation of the model with the estimated parameters, and the experimental results. A good agreement is found between simulation and experimental results.

Figure 5 - Evolution profiles of the different species versus the residence time for the Buzurgan VR (simulation results). a) Evolution of the SARA fractions; b) Evolution of the heteroatoms (S, N, Ni, V).

Figure 6 shows the parity diagram between experimental and simulation results (all results for each lump are represented and not only the global ones, as in Figure 5). The parity diagram confirms the good agreement between experimental and model results. The model described the Buzurgan VR behaviour with good accuracy.

Figure 6 - Parity diagram between experimental and model results for the Buzurgan VR (the model parameters were estimated with the Buzurgan experimental results).

The estimated kinetic rates are given in Table 6. For the cracking, hydrodesulfuration and denitrogenation reactions, all kinetic constants vary between 1.10^{-3} and $1.4 \text{ m}^{-2}.\text{s}^{-1}$. For the demetallization and coke reactions all kinetic constants vary between 1.10^{-1} and $575 \text{ m}^{-2}.\text{s}^{-1}$ except for reaction 1) ($\text{AspNi} \rightarrow \text{Asp} + \text{Ni}$) in the HDS section. This last is practically equal to zero, probably due to the size of the corresponding asphaltenes, too large to have an access to sites. In general the apparent kinetic constants are higher in the HDS section than the HDM section. Also, the vanadium apparent kinetic constant is greater than the nickel one, both for asphaltenes and resins.

In comparison with the HDM section, the apparent kinetic constants of hydrodesulfurization are more or less the same in the HDS section for asphaltenes but are less important for resins and aromatics.

This model kinetic network can differentiate between the saturated or aromatic fraction removal cracking reactions,. However the kinetic constants for both cracking types have been found similar except for the asphaltenes in the HDS section. In these the apparent kinetic constants representative of cracking reactions are ten to twenty times greater than in HDM section.

Table 6– Estimated kinetic constants for the both sections.

Table 7 – Adsorption constants estimated in the model for the different lumps.

The estimated adsorption constants are given in 7. Stronger adsorption has been found for gas (H₂S and NH₃) and asphaltenes. The adsorption of saturates is lower. Also, the adsorption coefficients are higher for the HDM sections than the HDS section.

4.4 Other feeds simulation – model validation

The best way to validate the model is to simulate the behaviour of the other residues with the parameters estimated previously and compare them to experimental results. For these simulations the physical chemical properties that describe the residues have been changed through the SARA distribution and respective heteroatom content . The segment numbers n_{si} and the distributions of the asphaltenes and resins sub-fractions (see Table 1, Table 4 and Table 5) have been calculated. The heteroatom distributions have not been changed due to the lack of information.

Figure 7 represents the simulation results and comparison with experimental results for the Arabian Light residue. The results are in quite good agreement with the experimental ones. Both the SARA fractions evolution and heteroatom profiles are relatively well described.

Figure 7 - Evolution profiles of the different species versus the residence time for the Arabian Light VR (simulation results). a) Evolution of the SARA fractions; b) Evolution of the heteroatoms (S, N, Ni, V).

The Djeno residue behavior was also simulated and the results are presented in Figure 8. The simulation is less satisfactory than for the Arabian Light. These results were expected because the Djeno residue is unusual and rarely conforms to the behavior of other residues. In the HDS section, the resin conversion and the saturates and aromatics contents are overestimated. For heteroatoms some discrepancies can also be observed mainly for nickel and sulfur. The removal of nickel is always overestimated. However the removal of sulfur is underestimated in the HDM section and overestimated in the HDS section.

Figure 8 - Evolution profiles of the different species versus the residence time for the Djeno (simulation results). a) Evolution of the SARA fractions; b) Evolution of the heteroatoms (S, N, Ni, V).

In this work, the SARA sub-fractions repartition parameters were changed but not those of the heteroatoms. Since all sub-fractions have the same kinetic constants and adsorption coefficients most of the differences observed will be linked to mass transfer resistance in catalyst. So, in the case of Djeno a better fit may be gained by distributing most of the sulfur into the smallest sub-fractions (to better adjust the HDM section), and most metals in the largest subfractions.

Finally the Ural conversion simulation and the corresponding experimental results are shown in Figure 9. Quite good results for the SARA fractions and fairly good results for the heteroatom profiles can be observed. A discrepancy is observed for sulfur, for which conversion is overestimated.

Figure 9 - Evolution profiles of the different species versus the residence time for the Ural (simulation results). a) Evolution of the SARA fractions; b) Evolution of the heteroatoms (S, N, Ni, V).

CONCLUSIONS

In this work a preliminary model was developed in order to predict the hydrotreating performance for residues of different geographical origins. The simulation of the performance of two catalysts in sequence was achieved and the validation of the model is acceptable.

The differentiation of performance due to the change in crude was obtained through the introduction of some crucial aspects in the model description, i.e.: i) introducing the diffusion and size of the molecules into the model for both sections; ii) subdividing asphaltenes and resins which allowed an improvement in the prediction of evolution of SARA fractions ; iii) creating a kinetic dependency on the feed properties seems to give better simulation results .

To further improve the performance of the prediction obtained in the simulation, advances in characterization of the residue feeds are needed. For instance, in the present work it was proved that a better description of the molecules with heteroatoms (refer to Djeno case) could improve the ability to differentiate between the different residues and, consequently, to improve the simulation performance.

Also, the coupling of complex kinetic networks model with a molecular reconstructed feed could present quite interesting results, despite the required computing time.

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NOMENCLATURE

a_s : specific surface area of catalyst pellet ($\text{m}^2.\text{m}^{-3}$)

A_s : coefficient of the Scheibel correlation (-)

b_i : thermodynamic Langmuir coefficient of the specie i ($\text{m}^3.\text{mol}^{-1}$)

C_i^p : concentration of the family i in the fluid inside the pellet at equilibrium with the adsorbed phase (mol. m⁻³)

C_i^f : concentration of the family i in the extra granular fluid phase (mol. m⁻³)

C_T : total concentration (mol.m⁻³)

D_{ij}^{eff} : effective diffusion coefficient (m².s⁻¹)

D_{ij} : Stephan-Maxwell binary species (i,j) diffusion coefficient (m².s⁻¹)

D_{ij}^0 : Stephan-Maxwell binary segment (i,j) diffusion coefficient (m².s⁻¹)

D_{∞} : bulk phase diffusion coefficient or translational diffusion coefficient (m².s⁻¹)

k : Boltzmann constant (J.K⁻¹)

k_i : kinetic constant for the reaction (m⁻².s⁻¹ ou m³.mol⁻¹.m⁻².s⁻¹)

k_i' : apparent kinetic constant for the reaction (m⁻²s⁻¹)

k_i^m : mass transfer coefficient of the family i corresponding to the fluid phase (m.s⁻¹)

K_r : viscous drag coefficient of the considered lump (-)

K_p : solute partition coefficient (-)

L_c : length of the cylindrical pellet (m)

M_i : molecular weight of the specie i (kg.mol⁻¹)

nc : number of species (-)

nd : number of deposits (adsorbed lumps) (-)

N_i : molar flux of the family i (mol.m⁻².s⁻¹)

N_i^0 : molar flux of the segment i (mol.m⁻².s⁻¹)

N_{coke} : number of coke molecules (-)

n_{si} : number of segments of the specie i , comparing to the elementary volume (-)

q^{max} : active site saturation concentration (mol.m⁻³ of solid)

q^{site} : active site concentration (mol / m³ of solid)

q_i : concentration of the specie i in adsorbed phase (sites) (mol.m⁻³ of solid)

r_i : volumetric surface production rate of lump i (mol.m⁻³.m⁻².s⁻¹)

r_p : pore radius (m)

R : gas constant (J.mol⁻¹.K⁻¹)

R_c : catalyst pellet radius (m)

R_{coke} : coke molecules radius (m)

R_h : molecule hydrodynamic radius (m)

S_c : section of the catalyst pellet (m²)

S_{catalyst} : catalyst surface (m²)

$S_{\text{initially available}}$: initially available surface of catalyst (m²)

$S_{\text{occupied,coke}}$: occupied surface of catalyst (m²)

T : temperature (K)

V_c : catalyst volume (m^3)

$V_{p,\text{intra granular phase}}$: intra granular volume (m^3)

v_o^f : fluid velocity inside the reactor (m.s^{-1})

\mathfrak{V}_i : molecular volume of the specie i ($\text{m}^3.\text{mol}^{-1}$)

g^0 : molar volume of the elementary segment ($\text{m}^3.\text{mol}^{-1}$)

ε_i : extra granular porosity (-)

ε_p : intra granular porosity (-)

ϕ_i^p : volume fraction of the specie i in the intra granular solid phase (-)

ϕ_i^f : volume fraction of the specie i in the extra granular fluid phase (-)

ϕ_i^S : volume fraction of the coke, Vanadium or Nickel on the catalyst surface (-)

τ_R : catalyst tortuosity (-)

ρ_i : density (kg.m^3)

η : viscosity of the fluid phase (Pa.s)

λ : ratio between pore and molecule hydrodynamic radius (-)

REFERENCES

- [1] Ferreira C, Tayakout M, Guibard I, Lemos F, Toulhoat H, Ramôa Ribeiro F. Hydrodesulfuration and hydrodemetallization of different origin vacuum residues: Characterization and reactivity, *Fuel* 2012; 98: 218-228.;
- [2] Kressman S, Morel F, Kasztelan S. Recent developments in fixed-bed catalytic residue upgrading, *Catalysis Today* 1998; 43: 203-215.;
- [3] Speight JG. *The chemistry and technology of petroleum*, New York; 1999.
- [4] Murgich J. Molecular simulation and the aggregation of the heavy fractions in crude oils, *Molecular Simulation* 2003; 29: 451-461.;

- [5] Groezin H, Mullins OC. Molecular size and structure of asphaltenes from various sources, *Energy&Fuels* 2000; 14: 677-684.
- [6] Sheu EY. Petroleum asphaltene-properties, characterization and issues, *Energy&Fuels* 2002; 16: 74-82.
- [7] Fenistein D, Barré L, Broseta D, Espinat D, Livet A, Roux JN, Scarsella M. Viscoelastic and neutron scattering study of asphaltene aggregates in mixed toluene/heptane solvents, *Langmuir* 1998;14: 1013-1020.
- [8] Haulle FX, Kressmann S. Kinetic modeling of residue desulfurization: lumping approach on sulfur compounds in heavy oil fractions, *AIChE Spring Meeting 2002, New Orleans, 2002*.
- [9] Verstraete JJ, Leannic K, Guibard I. Modeling fixed-bed residue hydrotreating processes, *Chemical Engineering Science* 2007; 62: 5402-5408.
- [10] Toulhoat H, Hudebinec D, Raybaud P, Guillaume D, Kressmann S. THERMIDOR: A new model combined simulation of operations and optimization of catalysts in residues hydroprocessing units, *Catalysis Today* 2005; 109: 135-153 .
- [11] Sanchez S, Rodriguez MA, Ancheyta J. Kinetic model for moderate hydrocracking of heavy oils, *Industrial & Engineering Chemistry Research* 2005; 44: 9409-9413.
- [12] Alvarez A, Ancheyta J. Modeling residue hydroprocessing in multi-fixed-bed reactor system, *Applied Catalysis A – General* 2008; 351: 148-158,
- [13] Bellos GD, Kallinikos LE, Gounaris CE, Papayannakos NG. Modeling of performance of industrial HDS reactors using a hybrid neural network approach, *Chemical Engineering and Processing* 2005; 44: 505-515.

- [14] Jarullah AT, Mujtaba IM, Wood AS. Kinetic model development and simulation of simultaneous hydrodenitrogenation and hydrodemetallization of crude oil in trickle bed reactor, *Fuel* 2011; 90: 2165-2181,.
- [15] Jarullah AT, Mujtaba IM, Wood AS. Improving fuel quality by whole crude oil hydrotreating: A kinetic model for hydrodeasphaltenization in a trickle bed reactor, *Applied Energy* 2012; 94: 182-191.
- [16] Neurock M, Libanati C, Klein MT. Modeling asphaltenes reaction pathways: intrinsic chemistry, *AIChE Symposium series, Fundamentals of residue upgrading* 1989; 85- 273.
- [17] Jaffe SB, Freund H, Olmstead N. Extension of structure-oriented lumping to vacuum residue, *Industrial & Engineering Chemistry Research* 2005;, 44: 9840-9852.
- [18] Verstraete JJ. Molecular reconstruction of heavy petroleum residue fraction, *Chemical Engineering Science* 2008; 62: 5402-5408.
- [19] Ferreira C, Marques J, Tayakout M, Guibard I, Lemos F, Toulhoat H, Ramôa Ribeiro F. Modeling residue hydrotreating, *Chemical Engineering Science* 2009; 65, 322-329.
- [20] Fornasiero F, Prausnitz JM, Radke CJ. Multicomponent diffusion in highly asymmetric systems. An extended Maxwell-Stefan model for starkly different sized, segment accessible chain molecules, *Macromolecules* 2005; 38: 1364-1370.
- [21] Tayakout M, Ferreira C, Espinat D, Marques J, Picon SA, Sorbier L, Guillaume D, Guibard I. Diffusion of asphaltene molecules through the pore structure of hydroconversion catalysts, *Chemical Engineering Science* 2010; 65 (5): 1571-1583.
- [22] Jost K, Steuer W, Halasz I. Measurement of diffusion coefficients of oil residual fractions using porous membranes. *Chromatographia* 1985; 20: 700

- [23] Li J, Carr PW.. Accuracy of empirical correlations for estimating diffusion coefficients in aqueous organic mixtures. *Analytical Chemistry* 1997; 69: 2530–2536.
- [24] Deen W M. Hindered transport of large molecules in liquid-filled pores. *AIChE* 1987;33(9):1409–25.
- [25] Akbarzadeh K, Alboudwarej H, Svrcek WY, Yarraton HW. A generalized regular solution model for asphaltene precipitation from n-alkane diluted heavy oils and bitumens, *Fluid Phase Equilibria* 2005; 232: 159-170.
- [26] Hughey CA, Rodgers RP, Marshall AG, Qian K, Robbins WK. Identification of acidic NSO compounds in crude oils of different geochemical origins by negative ion electrospray Fourier transform ion cyclotron resonance mass spectrometry, *Organic Geochemistry* 2002; 33,:743-759.
- [27] Klein GC, Kim S, Rodgers RP, Marshall AG. Mass spectral analysis of asphaltenes, II Detailed compositional comparison of asphaltenes deposit to its crude oil counterpart for two geographically different crude oils by ESI FT-ICR MS, *Energy&Fuels* 2006; 20: 1973-1979.
- [28] Marques J, Merdrignac I, Baudot A, Barré L, Guillaume D, Espinat D Brunet S. Asphaltenes size polydispersity reduction by nano- and ultrafiltration separation methods - comparison with flocculation method, *Oil&Gas Science and Technology - Revue de l'Institut Français du Pétrole* 2008; 63: 139-149.