

Modeling of a fixed bed residue hydrotreating reactor

Improvements in the deactivation mechanism

Pedro Oliveira

Abstract

A simulation model for residue hydrotreating called THERMIDOR was developed over the last decade at IFP. It was implemented in FORTRAN and simulates a complete hydrotreating unit. The software consists of a kinetic model for residue hydrotreating based on 8 chemical families (gas, saturates, aromatics-, aromatics+, resins-, resins+, asphaltenes and metal deposits), which are further decomposed into sub-species to track the atomic composition (C, H, S, N, O, Ni, V) of each chemical lump. Between these various sub-species, a total of 87 reactions were taken into account. This kinetic model was integrated into a fixed bed reactor model that accounts for intraparticle transport by molecular, Knudsen and configurational diffusion. During this development, it was shown that, for these heavy petroleum feeds, significant intraparticle diffusion of heavy molecules needs to be explicitly accounted for.

The objective of the traineeship at IFP was to extend the process model by improving the representation of catalyst deactivation through coke laydown and metals deposition, while simultaneously incorporating their effects on catalyst activity and selectivity. The model contained a module that accounted for catalyst ageing, but its predicted effects did not correctly represent the observed phenomena, more specifically the initial rapid catalyst deactivation observed during the first two months after unit start-up.

Some modifications were successfully implemented in the code to improve it. The results obtained are more realistic and now the model predicts well the deactivation process. Other modifications were proposed with the objective of improving the program and to be used as an optimization tool.

Keywords: hydrotreatment, hydrodesulfurization, hydrodemetallization, residues, modeling

Introduction

In the last thirty years, the world petroleum market suffered big changes. The demand for heavy products has decreased and the need for lighter products (e.g. for transportation use) has gone in the opposite way ^[1]. Besides this, some countries approved regulations that restrict the content of metals, sulfur and nitrogen in fuels to reduce the pollutant emissions. To achieve these objectives, the flowsheets of refineries has been changed to reduce the production of heavy fuel oil and residues and to lower the contents of metals

and sulfur in the products. This was obtained with the introduction of new thermal and catalytic conversion such as *visbreaking*, *coking*, *catalytic cracking* (FCC, HDC) and *hydrotreating* (HDM, HDS, HDN...) that can convert a fraction of the atmospheric and vacuum residues into lighter and less polluted distillates. Since many of the conversion processes in a refinery are catalytic and contaminants like metals, sulfur and nitrogen deactivate the catalysts, *hydrotreating* has gained a considerable importance not only to improve the quality of the products but also to extend the life of the catalysts which permit longer runs of the

units resulting in economical benefits for the refiners.

The model

THERMIDOR is an acronym for THERmal Monitoring for Isoperformance Demetallization of Oil Residua. The program, written in FORTRAN 77 language, was first conceived as a simulator for hydrotreating catalyst ageing. Today, it simulates the entire HYVAHL process along the time on stream, taking into account the complex associations of guard bed materials and catalysts, each with their particle size, activity, pore size and shape grading. Another of THERMIDOR's important features is the realistic representation of the two main catalyst deactivation mechanisms in residue hydroprocessing: coke lay-down and metal deposition. The model also clearly illustrates the synergy between dedicated HDM and HDS catalysts [2].

Modifications to the model

Deactivation equation

In an industrial unit, the reactor temperature is raised to compensate for the deactivation of catalyst and to maintain the unit performances. The modeling of this deactivation will need to include the coke and metals deposits to reflect the initial and rapid temperature increase due to coke, and then the gradual and almost constant increase caused by metals. For this reason, the effect of metals deposits was added to the previous equation existent in the model which resulted in:

$$a_i(r) = \frac{1}{(1 + \alpha_i C_{Coke}(r))^n} \cdot \frac{1}{(1 + \beta_i C_{Metals}(r))^m} \quad (1)$$

Where α_i and β_i are coefficients for every subspecies (C, H, S, etc.), $C_{Coke}(r)$ and $C_{Metals}(r)$ are respectively the coke and metals concentration in the catalyst grain and n and m are parameters which allow to modulate the shape of the deactivation curve.

Although this is a valid approach and permits to obtain the desired results, it lacks from physical reality. Beside this, the equation has four parameters to manipulate and since there are not much deactivation data available, there are too many possibilities to the parameters values. To overcome this problem, and since THERMIDOR has implemented a very advanced model to describe the catalyst grains and the deposition of coke and metals on them, it is wise to use this possibility in the deactivation equation. According to this, the reduction in surface area due to coke and metals was re-introduced in equation (1) and resulted in:

$$a_i(r) = \frac{SS(C_{Coke}, C_{Metals})}{SS_0} \cdot \frac{1}{(1 + \alpha_i C_{Coke}(r))^n} \cdot \frac{1}{(1 + \beta_i C_{Metals}(r))^m} \quad (2)$$

Where $SS(C_{Coke}, C_{Metals})$ is the catalyst surface area available and depends on the amounts of coke and metals deposited, SS_0 is the surface area of the fresh catalyst.

This new equation predicts well the deactivation even with α_i and β_i equal to zero.

Since the parameters of the kinetic model were not obtained on a fresh catalyst but on a stabilized catalyst, it was decided to multiply the equation (2) by a parameter, a_0 , to correct the initial activity of the catalyst. Equation (3) was implemented in THERMIDOR.

$$a_i(r) = a_0 \cdot \frac{SS(C_{Coke}, C_{Metals})}{SS_0} \cdot \frac{1}{(1 + \alpha_i C_{Coke}(r))^n} \cdot \frac{1}{(1 + \beta_i C_{Metals}(r))^m} \quad (3)$$

Coke increases along the reactor

Experimental data show that in hydrotreatment processes, the coke increases along the reactor. To reproduce this observation in THERMIDOR, the coke formation has been only associated to asphaltenes and aromatics minus (< 520 °C). The association to these last ones was made just because they are the only spheres that increase along the reactor. With this approach, since the mass fraction of asphaltenes is inferior to the mass fraction of aromatic minus,

the kinetic constant for coke formed by aromatics minus need to be an order of magnitude higher when compared to the kinetic constant of asphaltenes. Moreover, it was considered that neither the resins plus and minus, aromatics plus and saturates produce coke [3]. These hypotheses do not have any reality as it is known that the coke build-up increases with the molecular weight and/or boiling range of the processed feed.

Some authors believed that coke is produced by precipitation of large molecular hydrocarbons such as asphaltenes when their solubility in oil is lowered [4,5]. An increase in the conversion of vacuum residues increases the aromaticity of the asphaltenes and decreases the aromaticity of the maltenes* [6]. Consequently, the solubility of the asphaltenes in the maltenes decreases. Absi-Halabi et al. propose that absorption of asphaltenes on the acidic sites of an alumina support is a major cause of the initial rapid coke deactivation, while a decrease in asphaltene solubility causes the following steady coke build-up [5]. This explains that the amount of coke increases from the entrance to the exit of the reactors as asphaltenes solubility decreases and that an increase in the residue conversion increases the amount of coke at the reactor exit [5]. Based on this information, a new function was added in THERMIDOR, which reflects the variation of aromaticity of asphaltenes and maltenes in coke formation, overcoming the lack of reality of the previous approach.

$$\Delta_{\text{aromaticity}}(L) = \left(\frac{\frac{[H]_{\text{maltenes}}(L)}{[H]_{\text{asphaltenes}}(L)}}{\frac{[H]_{\text{maltenes}}(\text{inlet})}{[H]_{\text{asphaltenes}}(\text{inlet})}} \right)^n \quad (4)$$

Where $[H]_X$ is the hydrogen content of compound X, n is the parameter to model the

* Maltenes are the sum of the entire feed compounds without asphaltenes.

aromaticity variation effect, L represents a generic position in the reactor bed and *inlet* corresponds to the reactor entrance.

As maltenes and asphaltenes become respectively less and more aromatic along the reactor, this results in an increase of hydrogen content for maltenes increases, while the hydrogen content of asphaltenes decreases. In this way, if n is positive, $\Delta_{\text{aromaticity}}(L)$ will always be bigger than 1 and increases along the reactor.

As the coking tendency increases when the aromaticity difference between asphaltenes and maltenes increases, the rate constants for the coking reactions were multiplied by the aromaticity function given in equation (4). Since the coking reactions are equilibrated reactions, this means that the equilibrium constant is now a function of temperature and of the aromaticity of asphaltenes.

Model results

Deactivation curve

Now that all the new parameters added to the deactivation mechanism are tuned and the existing coking parameters readjusted, a comparison was made between the new deactivation curve and the one from the previous THERMIDOR version [3] at the same operating conditions. Thus is illustrated in Figure 1.

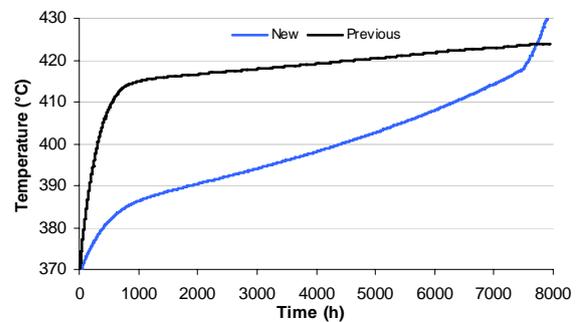


Figure 1 Comparison between the new deactivation curve and the previous one

By comparison of the new deactivation curve obtained with the one present by Tamm et al. [7] it is evident that the new curve, in opposition with the previous, has all the three stages well represented even without the use of empirical deactivation functions.

Since the model already obtains good results, a 12 month run simulation in isothermal mode was made to review all the results obtained such like the profiles of coke and metals along the reactor and into the grain for different reactor sections.

Grain profiles

Before showing the coke and metals profiles, it is important to understand the profiles of the families of compounds into the grain and their variation along the reactor, which are represented in Figure 2.

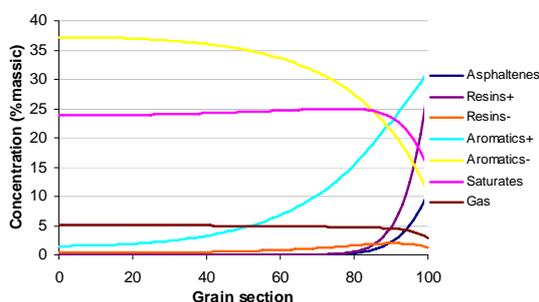


Figure 2 Profiles of the families of compounds in the grain for the first reactor section

As can be seen in the above figure, the size of the molecules influences a lot their concentration in the grain. The diffusion of the biggest molecules (asphaltenes and resins) is very limited and they do not reach the center of the grain. Otherwise, as the lighter molecules (gas, saturates) are formed inside the grain, their concentrations are higher in the center that at the surface of the grain.

The *Total deposits* were calculated as the sum of coke and metals deposits. The obtained results for the first reactor section after a 12 month run, illustrated in Figure 3, are similar to the ones obtained by Beuther et al. [8] and confirm that when the grain plugging occurs, its interior remains active, but inaccessible.

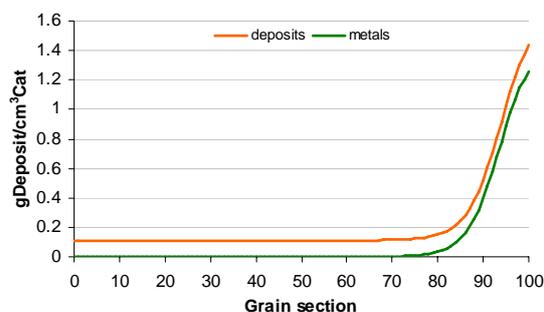


Figure 3 Representation of total deposits in the catalyst grain in the first reactor section for a 12 month simulation (plugged grain)

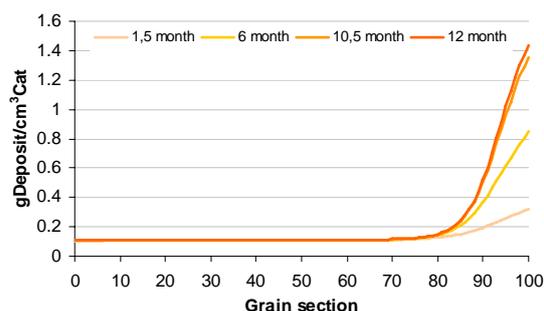


Figure 4 Evolution of deposit along the time in a grain on the first reactor section

Figure 4 shows the evolution of the deposits in the grains of the first reactor section. These deposits accumulation near the grain surface creates an extra resistance which significantly decreases the diffusion of the biggest molecules like resins and asphaltenes. This results in a smaller penetration into the grain, as shown in Figure 5.

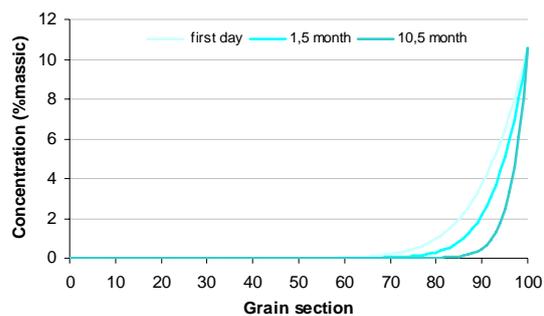


Figure 5 Decrease of the asphaltene diffusion into the catalyst grain along the run

Reactor profiles

Now that the grain profiles are understood, the reactor profiles for coke, metals and the families of compounds will now be shown.

The profiles of the families of compounds after 10.5 month of run, before the start of the percolation, are shown in Figure 6. It is possible to see that the lighter compounds such as gas, saturates and aromatics⁻ increase along the reactor by opposition to the heavier compounds (asphaltenes, resins⁺ and aromatics⁺) which decrease.

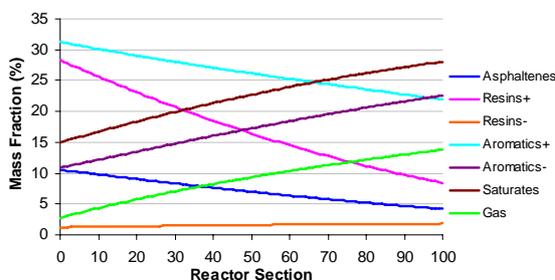


Figure 6 Profiles of the families of compounds along the reactor for a 10.5 month simulation (before percolation)

When pore plugging starts, the first sections of the reactor begin to die and the temperature increased to compensate the loss of catalyst which results in steeper profiles as shown in Figure 7. Notice that at the end of the run approximately 20% of the catalyst bed is no longer active.

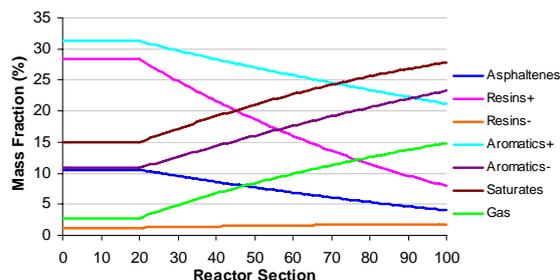


Figure 7 Profiles of the families of compounds along the reactor for a 12 month simulation (after the start of percolation)

In the first months of run, the deposits are almost constant along the reactor. This is because coke increases along the reactor but the metals go in the opposite direction as represented in Figure 8.

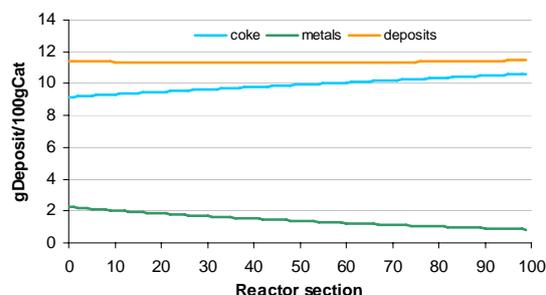


Figure 8 Representation of the deposits along the reactor for a 1.5 month run

During the run, coke remains almost constant but the metals begin to accumulate mostly in the entrance of the reactor which creates the steeper profiles presented in Figure 9. At the end of the run, the initial part of the reactor (20%) is dead but the rest is still active. Despite this, the run must be stopped because the temperature needed to maintain the performance is too high (over 430°C).

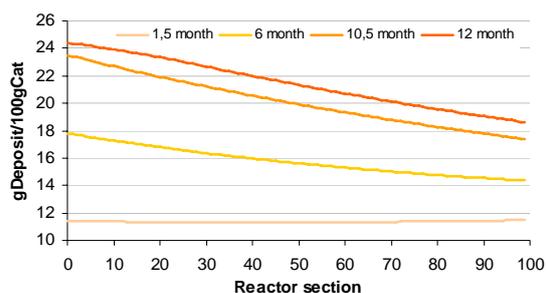


Figure 9 Variation of the deposits content in the reactor along the time

The aim of ARDS (atmospheric desulfurization) units is to get near 95% of conversion for HDM and near 90% for HDS. This is obtained with a reactor filled with two sections of catalyst, the first one with a HDM catalyst and the second with a HDS catalyst, as shown by Leprince [9]. In the present simulation, as only HDS catalyst was used in the reactor, the results will be somewhat different. It is clear from Figure 10 that HDS reaches the objective but HDM does not. At the end of the run, with near 20% of the catalyst dead, the HDS performance was maintained by the temperature increase but the rest of hydrotreatment reactions changed. These changes are due to the differences between the activation energies of the reactions.

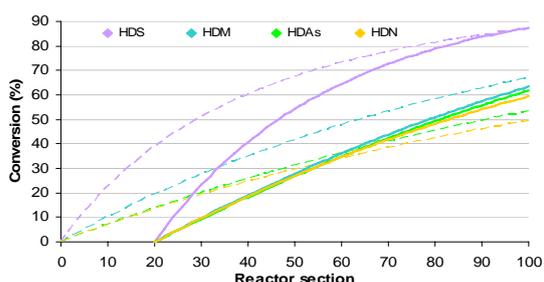


Figure 10 Variation in HDS, HDM, HDAs and HDN along the reactor bed. The dashed and full lines respectively correspond to the profiles at the begin and the end of a 12 month run

Since the objective chosen was to maintain a constant the HDS performance, as easily seen in the previous figure, the evolution of sulfur content in the various families of compounds was also followed and illustrated in Figure 11. The lighter

species such like aromatics and resins⁺ are almost completely desulfurized (the sulfur content becomes much lower than 0.5wt %). The heavier compounds as asphaltenes and resins⁺ are only partially desulfurized and remain with a sulfur content higher than 1wt %. They are effectively the most difficult to desulfurize. Moreover, their desulfurization is reduced along the run time.

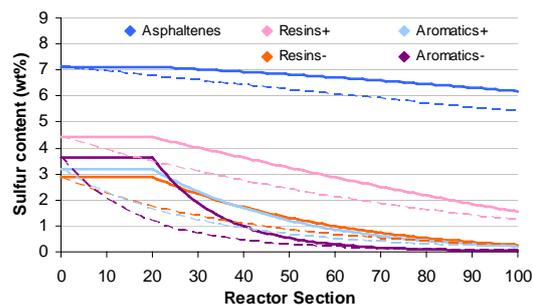


Figure 11 Evolution of the sulfur content in families of compounds along the reactor. The dashed and full lines respectively correspond to the profiles at the begin and the end of a 12 month run

Isothermal vs. Adiabatic

To understand the effect of a reactor temperature gradient on hydrotreatment reactions, a 12 month adiabatic simulation with the same feed, same catalyst and at the same operating conditions was made and compared to the one in isothermal mode.

The only difference between the adiabatic and the isothermal simulation is the temperature profiles inside the reactor, shown in Figure 12. Their influence will be discussed.

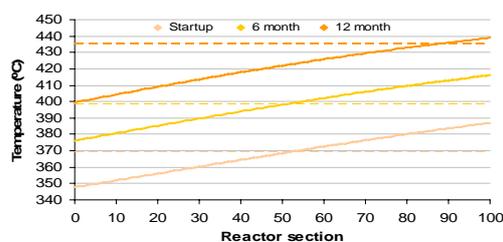


Figure 12 Temperature profiles along the reactor for different run times. The dashed and full lines respectively correspond to the profiles of isothermal and adiabatic modes

As can be seen in the first graph the temperature increases fairly linearly by approximately 40°C from the entrance to the exit of the reactor. This increase is due to the heat released by the hydrotreating reactions which are globally exothermic. Figure 12 also illustrates that the isothermal temperature is equal to the weight average bed temperature (WABT), which corresponds closely to the temperature in the middle of the reactor in adiabatic mode. This is no longer true however during the 12th month. This exception happens because in isothermal mode, after the 11th month, the reactor bed starts to percolate and in adiabatic mode there is no percolation observed. This is one of the most unexpected results in the adiabatic mode. From the Figure 13, this fact is easily understood since the deposits are more balanced along the reactor and not so concentrated in the inlet. This happens because the temperature gradient increases along the reactor which is also reflected in the kinetic parameters.

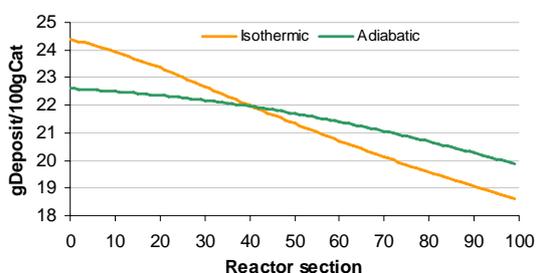


Figure 13 Comparison between the deposits profile in isothermal and adiabatic mode for a 12 months run

All the other profiles obtained in adiabatic mode are similar to the ones obtained in isothermal mode.

Conclusions

In agreement with the obtained results, it is now possible to say that the representation of the deactivation process is satisfactory for the HDS catalyst. The deactivation equation implemented

contains a physical part predicted by the model, the surface area reduction, and an empirical deactivation term. Since the results are acceptable only using the physical part, the empirical deactivation functions have not been used.

To take into account the increase of coke along the reactor, an "aromaticity" effect was implemented in the code. This effect reflects the variation of the asphaltenes and maltenes aromaticity across the reactor bed. The implementation of this effect has enabled the possibility to adjust the variation of coke along the reactor. When the catalyst starts to plug however, the aromaticity effect decreases resulting in a decline of the equilibrium coke. This result does not have any experimental validation at this moment. Hence, this effect could also be implemented in a different way.

Finally, after the modifications were implemented and some parameters tuned, the deactivation curve obtained was much more realistic than that of the previous version.

THERMIDOR also demonstrates well the existing difficulties to desulfurize the heaviest compounds such like asphaltenes and resins.

For the two modes of simulation in THERMIDOR, adiabatic and isothermal, it was concluded that in adiabatic mode the catalyst lasts longer. This is due to a more balanced deposition of the metals along the bed.

Reference:

- [1] LE PAGE, J.F.; CHATILA, S.G.; DAVIDSON, M., *Resid and Heavy Oil Processing*, Éditions TECHNIP, Paris, 1992
- [2] GONÇALVES, N., Modeling of a fixed bed hydrotreating reactor, Traineeship Report, Institut Français du Pétrole, 2006
- [3] BEECKMANS, J.L., *Modélisation de la Désactivation des Catalyseurs utilisés dans*

- l'hydrotraitement des résidus lourds*, Institut Français du Pétrole, 2006
- [4] WIEHE, I.A., *Industrial & Engineering Chemistry Research*, 32, pg. 2447, 1993
- [5] ABSI-HALABI, M.; STANISLAUS, A.; TRIM, D.L., *Applied Catalysis*, 72, pg. 193-215, 1991
- [6] TAKATSUKA, T.; WADA, Y.; HIROHAMA, S.; FUKUI, Y., *Journal of Chemical Engineering of Japan*, 22, pg. 298, 1986
- [7] TAMM, P.W.; HARNSBERGER, H.P.; BRIDGE, A.G., *Industrial Engineering Chemistry Process Design and Development*, 20, pg. 262, 1981
- [8] BEUTHER, H.; LARSON, O.A.; PERROTTA, A.J., *The mechanism of coke formation on catalysts*, *Catalyst Deactivation*, pg. 271, 1980
- [9] LEPRINCE, P., *Petroleum Refining - Conversion Processes*, Editions TECHNIP, Paris, 2001