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A hybrid model for the hydrotreatment of gasoil

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In this work neural networks are used to describe hydrogenation and hydrodesulfurization reactions in a gasoil hydrotreatment model. The resulting model has been called hybrid model, because it unifies first principle modeling (material balance in the reactor) and black box models (the neural network describing the kinetics). The proposed approach permits obtaining a simplified model of the hydroprocessing, which allows an accurate description of the system for a wide range of operating conditions and feed composition.

1. Introduction

The increasing demand for diesel fuel coupled with the tightening of environmental specifications is nowadays an important challenge for the oil industries. These introduce a new emphasis on the refining process optimization, especially for conversion and upgrading processes (hydrotreatment plants) in order to face a simultaneous increase of quality and quantity of gasoil considering the decreasing quality of crude oils available.
In this context many researchers have focused their research on the hydroprocessing of gasoil, which is the operation used to improve the quality of the product. The main objectives of the recent studies deal with the production of new and more efficient catalysts, and the continuous optimization of the process operation. The latter goal can be achieved by using an enough detailed model able to describe the industrial plant behavior in each situation (given catalyst and pressure) for all feeds, temperature, and LHSV allowing a reliable prediction of the most critical specifications.
Recently, a phenomenological model based on a detailed experimental analysis carried out on a pilot plant was proposed to predict the hydrogenation of aromatic compounds and the hydrodesulfurization of the refractive compounds during the gasoil hydroprocessing (Medde, 2008). The proposed model performs very well in several conditions, but in the perspective its phenomenological property, a deep knowledge of the real processes is required because the behavior of nineteen classes of aromatic compounds is described using detailed kinetic expressions. A so detailed description of the system requires a detailed characterization of the feed and the product of the hydroprocessing reactor for the calibration of the model and the calculation of the model inputs necessary for its implementation. Furthermore, the description of each

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reaction rate implies several parameters to be calibrated because in order to describe the conversion of aromatic, sulfur and nitrogen compounds accounting their competition in the adsorption on the typical hydroprocessing catalyst, the Langmuir-Hinshelwood kinetics is chosen. These requirements could be limiting for the model application because they imply the use of analytical procedure not generally developed in an industrial laboratory.

For this reason, the purpose of this work is to simplify the model proposed by Medde (2008) describing the kinetic rates by means of a neural model and, in the mean time, requiring a less detailed characterization of the feed and/or product. The results obtained with the proposed hybrid model are promising, in fact it is able to predict the composition of the hydroprocessing products in terms of aromatic compounds (i.e., diaromatics and triaromatics), and of total sulfur, which are important for the environmental specification. The formers have been recently suspected to have harmful effects on human health, while the latter is responsible for acid rain and particulate matter formation. Polyaromatic compounds are also important because they affect the cetane number of the gasoil (a measure of auto-ignition quality).

2. Experimental setup

Hydroprocessing experiments were carried out using a small scale pilot unit. The three-phase reactor (760 mm long, 19 mm ID) was loaded with a new generation commercial catalyst (trilobe $NiMo/Al_2O_3$) diluted with small inert particles (0.1 mm CSi), to avoid channeling and minimize back mixing. Hydrogen and gasoil are fed in co-current up-flow mode to ensure a good wetting of the catalyst particles (De Wind et al., 1988).

The reactor temperature profile, controlled by four independently heated furnaces, was monitored with a set of skin thermocouples and another set of four sensors, placed in a thermowell located at the center of the catalytic bed.

The hydrotreated product flowing out from the top of the reactor is sent to a high-pressure separator to remove the bulk of the gas from the liquid, and then to a low-pressure separator, to release the residual gas trapped into the liquid phase.

The experiments were carried out in isothermal conditions at different temperature levels (330°C÷365°C) with different feeds of straight run gasoil (SRGO), in the pressure range of 30-90 bars and the LHSV between 1.5 and 2 h^{-1}. All the reactions were carried out in a hydrogen excess atmosphere, in order to neglect the gas-liquid mass transfer resistance and to reduce the variations in hydrogen partial pressure associated with the H_2S produced by the desulfurization reaction.

Samples taken downstream of the low pressure separator were analyzed in terms of boiling point distribution (ASTM D 2887), aromatic classes (EN12916), total nitrogen (ASTM D 4629) and total sulfur (ASTM 5453, ultraviolet fluorescence).

3. Model formulation

The idea of the present work is to propose a model for hydroprocessing unit, which may be implemented on line in an industrial plant. The model was hence constructed to give the most important information, in an industrial framework, on the quality of gasoils: the concentration of polyaromatic compounds and the content of sulfur.

The proposed model describes the hydrogenation of each macro-classes of aromatic compounds, distinct by a different number of aromatic rings, and desulfurization reactions. Considering that the boiling point distribution of gasoil is comprised between 230 and 365ºC, only molecular structures with no more than three rings can be present in the mixture. For this reason the following reaction scheme were considered for the hydrogenation reactions:

$$Triaromatic + H_2 \longleftrightarrow Diaromatic$$

$$Diaromatic + 2H_2 \longleftrightarrow Monoaromatic$$

$$Monoaromatic + 3H_2 \longleftrightarrow Saturated$$

Even if previous studies demonstrated the different reactivity of compounds within the macro-classes (Korre et al. (1994, 1995)), this description of the system does not require a detailed characterization of feed and product, and the necessary analysis can be easily performed in an industrial laboratory.

Sulfur is present in gasoils as labile and refractory compounds. The former do not determine the sulfur content in the hydrotreated gasoil, because they immediately reacts, and may be included in the previous scheme, depending on the number of rings. Conversely, the concentration of refractory compounds is very low, but their conversion can allow achieving the very low limit of 10 wppm that the new environmental EU regulation imposes. Their conversion does not affect the hydrogenation of total aromatic compounds, but they are important in term of hydrodelfurization. The reactivity of refractory compounds varies from mild to strong refractory (Medde, 2008; Ma et al., 1994), but again it is preferable to avoid deep characterization of gasoil, and only a single macro-class of the refractory sulfur was considered in the model.

Summarizing, the proposed model describes the mass balances of the three main classes of aromatic compounds present in gasoil and the refractory sulfur compounds, hence it includes hydrogenation of monoaromatic, diaromatic and triaromatic compounds and the hydrodesulfurization of the refractive compounds during the gasoil hydroprocessing. The kinetics were, in this case, described by means of a black-box model (neural network), which was inserted in the plug flow model with axial dispersion describing the fluid dynamics of the experimental reactor (cf., Medde, 2008).

3.1 The neural network model

The kinetics of the considered classes were described by means of a three layer feedforward neural network (Haykin, 1994) with six neurons in the input layer, one neuron in the hidden layer and four neurons in the output layer, i.e. the four reaction rates for the considered macro-classes. It was assumed that each calculated reaction rate is the sum of the direct and inverse reaction rate.

The selection of the neural model inputs was easily accomplished by considering the variables that affect the hydrogenation and hydrodesulfurization processes: they are the concentration of the four classes, the reactor temperature and the reactor pressure (Melis et al., 2004; Erby et al., 2005).

The selection of the number of the hidden neurons is not aided by rules, but it is in general preferred to have a parsimonious model. Starting from the simplest model, which had one hidden neuron, and observing that the addition of one more neuron did

not change significantly the model performance, the number of hidden neuron was fixed equal to one. Hidden and output neurons were activated by a sigmoidal function:

$$f(x) = \frac{1}{1+e^{-x}} \tag{1}$$

where x represents the weighted sum of the signal inputs to the neuron. The input and hidden layers were augmented with an extra neuron, the bias, which provides a constant output signal equal to one.

The training of the network was developed by means of the Levenberg-Marquardt optimization algorithm. Because of the unavailability of reaction rate experimental values, the parameter estimation was based on the error between the experimental and calculated concentration at the reactor exit. Those states are obtained as results of the integration of the reactor model, assuming that the error between the experimental and calculated concentration is exclusively due to reaction rates. In particular, the following objective function $\Phi(\mathbf{w})$ was used:

$$\Phi(\mathbf{w}) = \sum_{i=1}^{N_c}\sum_{j=1}^{N_e}\left[\frac{\left(c_{ij}^{e} - c_{ij}^{c}\right)}{c_{ij}^{e}}\right]^2 \tag{2}$$

where $\mathbf{w}$ represents the weights (parameters) of the neural model, c^e and c^c are respectively the experimental and calculated concentration at reactor exit, N_c is the number of macro-classes and N_e the number of experimental data.

Because of the limited amount of experimental data, training and validation/test of the neural model were conducted by means of the Leave-One-Out Method (Haykin, 1994), which consisted of selecting all data for the training but one, repeating the procedure until all data were processed. The selected neural network is that with the minimum error for training and test.

4. Results and discussion

The experimental data used to calibrate and test the proposed model and the properties of the feed are reported, respectively, in Tables 1 and 2.

Table 1. Experimental data for model calibration and test

	Feed and modality	Temperature (ºC)	Pressure (bar)	LHSV (h^{-1})
Set 1	SRGO HT	330	30 – 45 – 75 – 90	1.5 – 2
Set 2	SRGO HT	330 – 365	75	2
Set 3	SRGO HT	330 – 365	60 – 90	1.5

Table 2. Properties of the mixture SRGO HT

	Density (kg/m^3)	Sulfur (wppm)	Monoaromatics (%w)	Diaromatics (%w)	Triaromatics (%w)
Set 1	866.4	10018	16.7	10.8	2.0
Set 2	864.6	10577	16.6	10.4	1.8
Set 3	874.5	9166	18.7	10.5	2.0

As shown in the Tables, a wide range of operating conditions is considered, being the main objective of the present work to possibly obtain a simple but accurate model, capable to describe the industrial plant behavior in each situation (temperature, pressure and LHSV) and for all feeds. In such a way, the model can be utilized to guarantee the full respect of both diesel demand and environmental specifications.

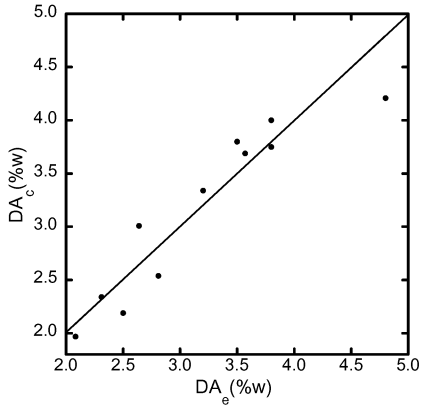

Figure 1. Calculated diaromatic concentration versus experimental one.

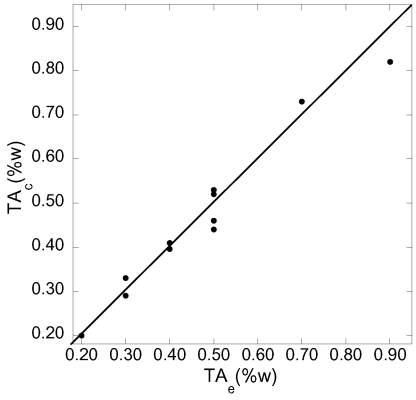

Figure 2. Calculated triaromatic concentration versus experimental one.

Figures 1 and 2 represent the results obtained for the polyaromatic classes and show the calculated concentration (DA_c and TA_c) at the reactor exit versus the experimental one (DA_e and TA_e). The model performance is rather good, in fact it is able to describe, within the experimental error, the system in the several conditions investigated.

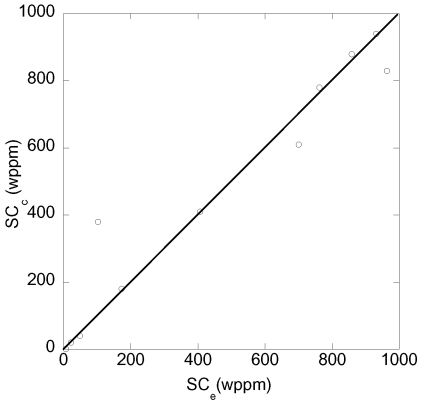

Figure 3. Calculated sulfur content versus experimental one.

The capability to estimate sulfur content is reported in Figure 3, where the calculated sulfur content (SC_c) is reported against the experimental one (SC_e). The agreement between experimental and calculated data evidences the ability of the simplified model to describe with accuracy also the hydrodesulfurization reactions. It is worth noting that a unique class of refractory compounds is considered, grouping molecules having different grade of reactivity. Furthermore, the model is able to describe the system at low and high values of sulfur concentration, hence it can be used in very different situations.

5. Conclusions

A hybrid model obtained introducing a neural network in a first principle model was developed in order to reconstruct the behavior of aromatic and sulfur compounds in a hydroprocessing unit. The proposed model is a good compromise between simplicity and ability to estimate, with typical industrial accuracy, the concentration of the considered classes of compounds for different operating conditions and feeds. Such qualities suggest an on-line implementation of the model to obtain important information, useful for the conduction of hydroprocessing plant. It is worth noting that compared to more detailed and accurate models the absence of complex kinetics law makes it more appealing to an industrial environment.

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