Modeling nitrogen effect on the hydrodesulfurization process

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Progressive tightening of environmental specifications imposes the production of ultra low sulfur diesel that requires a deep knowledge on the governing phenomena.
In particular, in this work the kinetic behavior of nitrogen compounds, with particular attention to their cross-effect on the hydrodesulfurization of sulfur compounds is investigated. The proposed model is able to satisfactorily predict the total sulfur content and the distribution of the refractory compounds in the hydrotreated products.

1. Introduction

In order to satisfy the new environmental regulations that impose the production of ultra low sulfur diesel (under 10 ppm from 2009), worldwide refineries are required to adopt the latest technological innovations, both in terms of hydroprocessing catalysts and reactor internals, and to optimize the hydrodesulphurization (HDS) process conditions as a function of feed properties.

Hundreds of sulfur compounds are present in gasoil but most of them can be easily desulphurized under typical hydrotreating operating conditions. On the other hand the removal of refractory alkyldibenzothiophenes results much more difficult, mainly due to their steric configuration and represents the major problem associated to the production of ultra low sulfur diesel. This situation is further complicated by the presence of nitrogen compounds that strongly inhibit the hydrodesulphurization through competitive adsorption on the catalyst active sites.

In this work we investigated the kinetic behavior of nitrogen compounds, with particular attention to their cross-effect on the hydrodesulphurization of sulfur compounds. This was done comparing the results obtained through dedicated pilot unit experiments with by different feeds and operating conditions with the predictions of a recently developed hydroprocessing model (Melis et al., 2004; Erby et al., 2005), suitably revised to account for the nitrogen inhibition. In agreement with the previous model, we applied the lumped approach for the characterization of the feed accounting for 10 lumps for the aromatic hydrocarbons, 1 lump for the saturate compounds, 2 lumps for the labile sulfur species (Melis et al., 2004), 4 lumps for the refractory sulfur (Erby et al., 2005) and adding 3 lumps for the nitrogen compounds (c.f., Sun et al., 2005). The resulting model is able to satisfactorily predict the total sulfur content and the distribution of the refractory compounds in the hydrotreated products.

2. Experimental

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 hydroprocessed 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 bar 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 desulphurization 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). Further, the samples were analyzed in terms of sulfur species distribution using an own-developed analytical method running on a Gas Chromatograph equipped with a PTV injector and a Pulsed Flame Photometric Detector (PFPD).

3. Model Formulation

Gasoil generally contains low levels of organic nitrogen compounds (typically ranging from 50 to 300 ppm) that however strongly affect the performance of hydroprocessing reactors. Nitrogen species can be divided into three different groups, depending on their reactivity and polarity. First group is constituted of basic compounds, where the nitrogen atom belongs to a six member aromatic ring (for example quinoline and acridine). According to the literature, nitrogen species belonging to this group amount to 1/3 of total nitrogen. Second group is made up by refractory neutral compounds, where the nitrogen atom is included into a five member aromatic ring (for example carbazole) and amounts to half of the total nitrogen. Finally, there are neutral labile species, where the nitrogen atom does not belong to an aromatic ring (i.e., amines and aniline).

Nitrogen molecules of the third group are characterized by a very fast kinetics, while those belonging to the first and second group are rather difficult to remove as they require a preliminary hydrogenation before denitrification. Further, basic nitrogen is characterized by a great affinity for the hydrogenation sites of the catalyst that hence are not available for other reactions, with particular reference to the indirect desulphurization (via preliminary hydrogenation) of the most refractory sulfur species.

Similarly to the case of hydrodesulphurization and hydrogenation reaction (Erby et al., 2005; Melis et al., 2004) we selected a Langmuir-Hinshelwood kinetics also for the hydrodenitrification reactions. According also to Nagai and Kabe (1983), the following expressions were applied for the neutral and basic nitrogen:

$$r_{HDN}^{N} = \frac{k_{HDN}^{N} P^{3} \omega_{N_2}^{N}}{(1+K_{H_2}P)^{2}(1+K_{sat}\omega_{sat}+K_{mono}\omega_{mono}+K_{di}\omega_{di}+K_{tri}\omega_{tri}+K_{N_2}^{N}\omega_{N_2}^{N}+K_{N_2}^{B}\omega_{N_2}^{B})} \qquad (1)$$

$$r_{HDN}^{B} = \frac{k_{HDN}^{:B} P^{3} \omega_{N_2}^{B}}{(1+K_{H_2}P)^{3}(1+K_{sat}\omega_{sat}+K_{mono}\omega_{mono}+K_{di}\omega_{di}+K_{tri}\omega_{tri}+K_{N_2}^{N}\omega_{N_2}^{N}+K_{N_2}^{B}\omega_{N_2}^{B})} \qquad (2)$$

where $r^{N}{}_{HDN}$ and $r^{B}{}_{HDN}$ are reaction rate, $k^{N}{}_{HDN}$ and $k^{B}{}_{HDN}$ rate constants, K_{H2} the hydrogen adsorption constant, P_{H2} the hydrogen partial pressure, $\omega^{N}{}_{N2}$ and $\omega^{B}{}_{N2}$ are the weight fractions for nitrogen compounds, K_j the j-th class aromatics adsorption constants and of course ω_j the j-th lump weight fractions.

For the description of hydrodesulphurization, we focused the attention on refractory sulfur species. Detailed sulfur analyses showed that approximately 50 species are typically detected in the ultra low sulfur diesel, all belonging to the dibenzothiophene class. In agreement with Ma et al. (1994) and with our previous work (Erby et al., 2005) such species can be grouped into four lumps each including species characterized by the same conversion and where the two most refractory lumps are characterized by the same kinetic behavior of the 4 methyl-DBT and the 4, 6 dimethyl-DBT, respectively.

According to the Gates and Topsøe (1997), the alkyldibenzothiophenes conversion was described through a parallel reaction scheme consisting of a hydrogenolysis (direct desulphurization, DDS route) yielding biphenyl, and a hydrogenation followed by desulphurization (HYD route) yielding first tetrahydrodibenzothiophene (THDBT) and then cyclohexylbenzene.

Direct desulphurization occurs on the vacancies of the MoS_2 structure of the catalyst (Erby et al. (2005)) so that is not affected by the competition by nitrogen and aromatic molecules. Accordingly, the following kinetic expression is used for the DDS mechanism of each sulfur lump:

$$r_{iDDS} = \frac{k_{iDDS}\omega_i P_{H_2}^{2}}{\left(K_{di}\left(\omega_1+\omega_2+\omega_3+\omega_4\right)\right)\left(1+K_{H_2}P_{H_2}\right)^{2}} \qquad (3)$$

where ri_{DDS} is DDS reaction rate of i-th class, k_{iDDS} is the rate constant, ω_i is the weight fractions for the i-th sulphur class, K_{di} the adsorption constants of diaromatic compounds.

On the other hand, desulphurization after hydrogenation occurs on the hydrogenation sites where also aromatic and nitrogen molecules are adsorbed. While the different alkylic structure of the various sulfur species (for example the alkylic groups of 4-methyl and 4,6-dimethyldibenzothiophene) strongly affect the adsorption on DDS sites so that individual kinetics apply to each lump, this is not the case for the hydrogenation route, where it is assumed that all sulfur lumps react with the same rate. Under the hypothesis above, the kinetic expression for the HYD route of the desulphurization reaction can be described by the following expression:

$$r_{iHYD} = \frac{k_{HYD}\omega_i P_{H_2}^2}{(K_{sat}\omega_{sat} + K_{mono}\omega_{mono} + K_{di}\omega_{di} + K_{tri}\omega_{tri} + K_{N_2}^N\omega_{N_2}^N + K_{N_2}^B\omega_{N_2}^B)\cdot\left(1 + K_{H_2}P_{H_2}\right)^2} \qquad (4)$$

where k_{HDY} is the reaction rate constant and ω_i is the sulfur weight fraction of the *i*-th lump.

A detailed description of the kinetics for the saturation of the aromatic species is reported in Melis et al. (2004).

4. Results and Discussion

Hydrodenitrification and hydrodesulphurization kinetic expressions reported previously can be used to interpret the results obtained with a commercial NiMo/Al_2O_3 catalyst for the different feeds considered in this work.

We considered three types of straight run gasoils, each characterized by different polyaromatic, sulfur and nitrogen contents and we carried out tests at different operating conditions in terms of pressure, temperature and LHSV. Denitrification parameters were estimated on the basis of all three tests and resulted in an adsorption constant of non-basic compounds negligible so the only nitrogen lump that is really present in the Langmuir-Hinshelwood denominator is that of basic nitrogen compounds.

The results, shown in Figure 1a for the first two feeds at low temperature (i.e. 330 °C), and in Figure 1b for the third feed in the entire temperature range, demonstrate that the model correctly fits the all the experimental data.

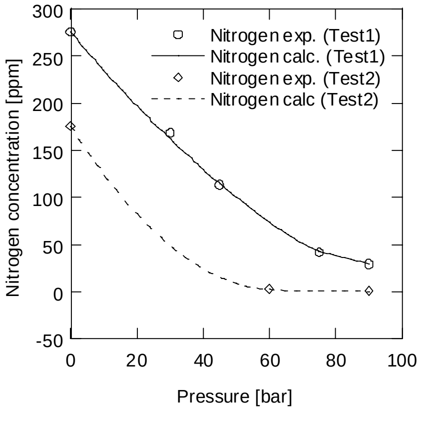

Fig.1a Comparison between experimental data and model fit for total nitrogen at 330 °C for Tests 1 and 2

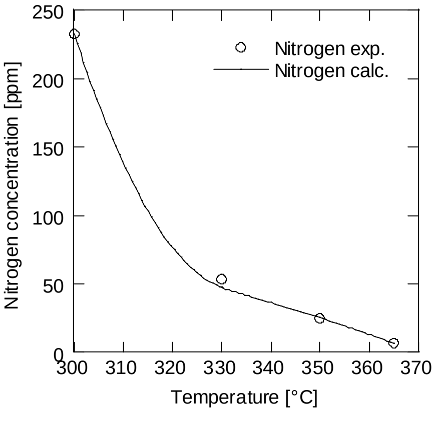

Fig.1b Comparison between experimental data and model fit for total nitrogen as a function of temperature for Test 3

Desulphurization parameters were estimated fitting the experimental data originated from Test 1 (330 °C) and from Test 3 (at varying temperature), while results of Test 2 were used for model validation (i.e. without any parameter adjustment).

The results at 330 °C are shown in Figures 2a and 2b, where it can be seen that model satisfactorily reproduce the experimental behavior in all tested conditions, while those at varying temperature for Test 3 are displayed in Figure 2c, showing a satisfactory agreement also in this case.

A further demonstration of model reliability is finally given in Table 1, where the experimental data at 350 °C for Tests 1 and 2 are compared with model prediction in terms of total sulfur .

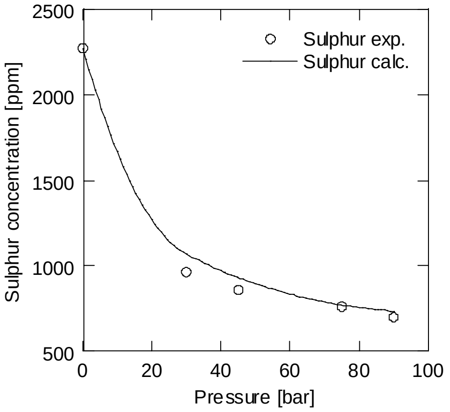

Fig. 2a Comparison between experimental data and model fit for total sulfur at 330°C for Test 1.

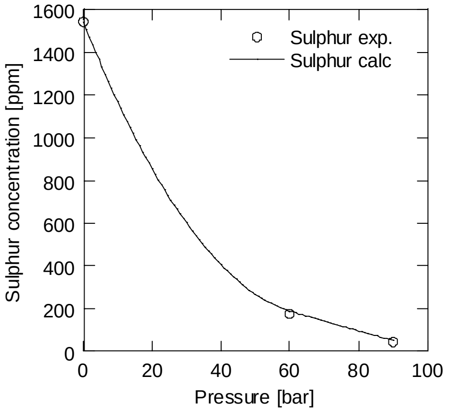

Fig. 2b Comparison between experimental data and model prediction for total sulfur at 330°C for Test 2.

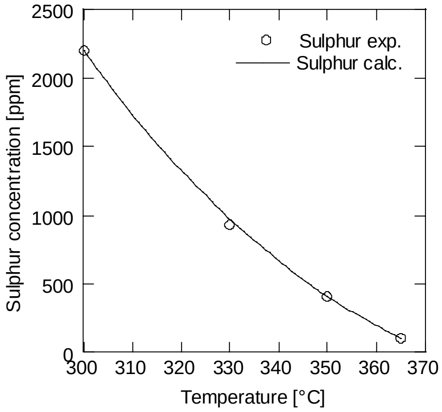

Fig.2c Comparison between experimental data and model results for total sulfur as a function of temperature for Test 3.

It is worth noting that ultra low sulfur diesel can be obtained only when the nitrogen content of the product is extremely low (in the 1 ppm range). In fact, the DDS contribution to the hydrodesulphurization of most refractory species (independent of nitrogen inhibition) is typically small since these species are hardly adsorbed on desulphurization active sites. On the other hand, owing to the exceptionally high adsorption constant of the basic nitrogen species (three order of magnitude larger than aromatic species), the kinetics for the desulphurization via HYD route is effective only when most of the nitrogen has been removed, as even few ppm of basic nitrogen can reduce its rate by several times.

	Sulfur exp. [ppm]	Sulfur calc. [ppm]
Test 1 (350°C- 90 bar)	50	54.06
Test 2 (350°C- 60 bar)	13	9.15

Tab.1. Comparison between experimental data and model fit for total sulfur content Test1 and Test2.

5. Concluding Remarks

In this work a kinetic mechanism to predict the nitrogen content of hydrotreated gasoil and to correctly describe its inhibitive effect on hydrodesulphurization has been presented. A lumped approach was considered and the total nitrogen content was distributed in basic, neutral-refractory and neutral-labile nitrogen species. The inhibitive effect was introduced in the hydrodesulphurization kinetic described by two mechanisms (DDS and HYD) considered for the four lumps of refractory sulfur compounds. Such approach allows us to interpret the various experimental trends observed with different feeds. The reliability of the model was verified through the comparison with experimental data, from a hydroprocessing pilot unit, and in all cases a satisfactory agreement was obtained.

Acknowledgement

The authors gratefully acknowledge the MIUR for the financial support (grant 13491/297 AD).

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