Ex situ monitoring of the state of Hydrodesulfurization catalysts: an effective method for obtaining clean diesel

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***Abstract*:**

For just over a decade, the energy transition has been initiated around the world. This has led to an increase in the consumption of renewable energies without, however, causing a considerable decrease in the consumption of fossil fuels. The use of petroleum and its derivatives is still relevant. In this context, the efforts undertaken for the effective implementation of renewable energies must be combined with those aimed to reduce the environmental impact of petroleum derivatives coming from petroleum refining. For example, the presence of sulfur in diesel oil is an important source of pollution. Reducing the content of sulfur in diesel oil therefore remains a major challenge for petroleum refining units. The current means to overcome this challenge are few and expensive. The most common way is to improve existing infrastructures. However, rigorous monitoring of hydrodesulfurization catalysts could be a simple and efficient way to obtain a clean diesel. Taking the "Société Ivoirienne de Raffinage (SIR)" which is the Ivorian refining company as an example, the implementation of this approach is analyzed in the present work.

***Keywords*:** Gasoline, Hydrodesulfurization, Hydrocracking, Catalyst, Coke.

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1. Introduction

Consequences of burning fossil fuel are many: melting glaciers, rising seas, increasing global temperature averages, etc. [1]. Recently, it has been shown that air pollution from fossil fuels is responsible for nearly one in every five deaths worldwide [2]. Then energy transition involving the use of renewable energies is an emergency and a challenge [3]. Because the fossil energies are still used, it is important to minimize or why not to overcome environmental pollution that they provoked especially the petroleum derivatives coming from refinement process. Diesel which is one of these derivatives is a great source of pollution especially when it is dirty. Among factors which can alter the quality of diesel is its high content of sulfur. According to international specifications, the sulfur content in diesel must be around 10 ppm [4]. Since 2016, following the "Dirty Diesel" report [5], the Ivorian government as well as many African countries have aimed to lower sulfur content in fuels in agreement with international specifications. Indeed, the Partnership for Clean Fuels and Vehicles (PCFV) [6] launched at the World Summit on Sustainable Development (WSSD) in Johannesburg in September 2002, has shown in a short document that the sulfur content in diesel in Côte d'Ivoire is above international standards. Likewise, it has been demonstrated that the cost of upgrading the refinery in Côte d'Ivoire is approximately $ 130

million, with an investment of about $ 4,500 per barrel of additional low-sulfur fuel.

As a contribution of the search of simple and less costly methods to obtain clean diesel, this work was undertaken. The present work is devoted to the study of the state of hydrodesulfurization catalysts at the Ivorian refining society named "Société Ivoirienne de Raffinage (SIR)". The different ways of ensuring the longevity of these catalysts are also reviewed.

2. Literature review

2.1. Hydrodesulfurization

Hydrotreatment is the process for treating petroleum cuts under hydrogen pressure to remove heteroatoms contained in organic molecules such as sulfur (hydrodesulfurization or HDS), nitrogen (hydrodenitrogenation or HDN), oxygen (hydrodeoxygenation or HDO) and metals, in particular nickel and vanadium (hydrometallation). Hydrodesulfurization makes it possible to extract sulfur molecules such as: benzothiophene (BT), dibenzothiophene (DBT) [7] or alkyldibenzothiophenes including 4,6-dimethyldibenzothiophene (4,6-DMDBT). These latter compounds are recognized as the most refractory to HDS. According to Houalla et al. [8] and Singhal et al. [9], the two main pathways of the hydrodesulfurization (HDS) of DBT are DSD and HYD. DSD leads to BiPhenyl (BPh) and HYD gives DiCycloHexyl (DCH) as showed in figure 1.

Hydrodesulfurization history has started with bulk of molybdenum sulfide, the stoichiometry of which is close to two atoms of sulfur for one atom of molybdenum (MoS_2) [10]. Molybdenum sulfide crystallizes in the hexagonal system with Mo^{2+} cations at the center of a trigonal prism formed by 6 sulfur atoms S^{2-}. These geometric units by assembling give rise to a structure in sheets of the SMoSSMoS type. The hexagonal-shaped MoS_2 sheets then interact only through Van der Waals forces. When adding

nickel or cobalt, a gain in catalytic activity is observed. This synergy effect is maximum for a promoter / (promoter + molybdenum) molar ratio of the order of 0.3 to 0.4. Figure 2 shows the promoter effect of Ni or Co in HDS of dibenzothiophene. For NiMo, NiW and CoMo, the maximum ratios are around 0.4, 0.6 and 0.3, respectively. This information is very important for the synthesis of the catalyst supported on an inert solid.
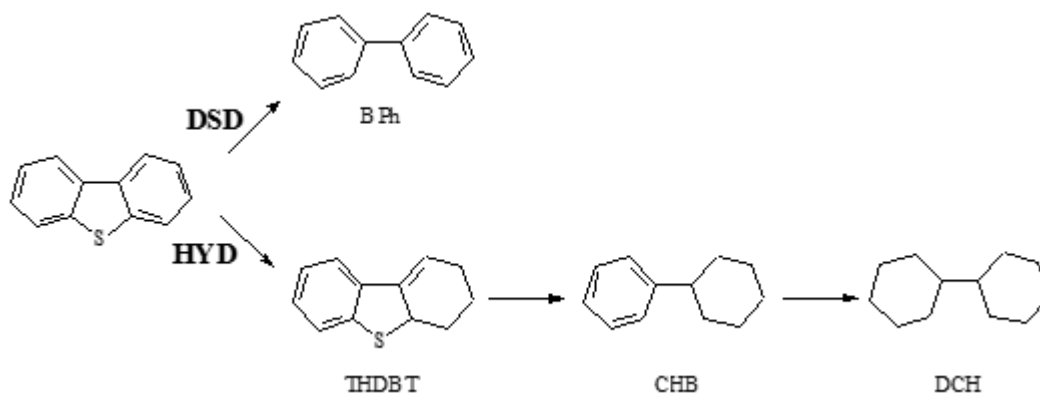

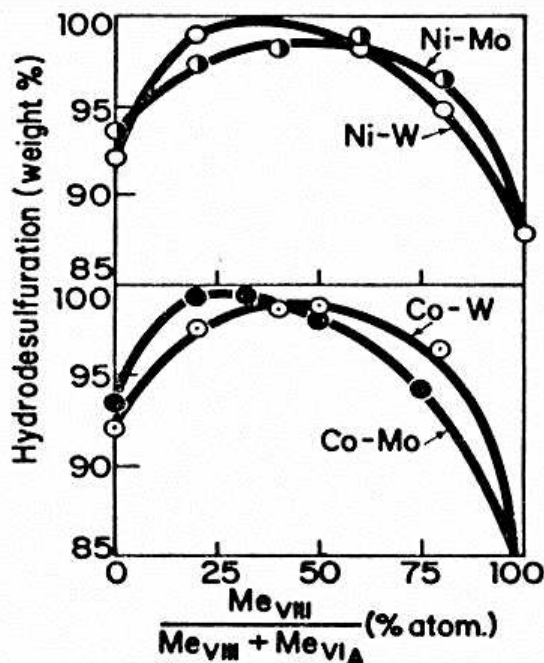**Fig. 1.** Dibenzothiophene hydrodesulfurization reaction scheme [8, 9].

Fig. 2. Promoting effect of Ni or Co in hydrodesulfurization of dibenzothiophene [11].

2.2. Modeling of catalytic activity

Modeling of catalytic activity started with the pioneer works of Delmond et al. [12], who proposed a "contact synergy" model. This model assumes the coexistence of crystallites of MoS_2 and Co_9S_8 on the support. These crystallites must be close enough for the hydrogen activated on Co_9S_8 to be transferred to MoS_2 where the catalytic act takes place: this is a "spill-over" phenomenon. Later, Topsøe and Clausen [13] developed the "Co-Mo-S mixed phase" model. Nowadays, this model seems to be the most widely accepted. They describe the active species as MoS_2 sheets with cobalt located in the extension of the sheets support. Figure 3 gives an overview of the structure proposed by Topsøe and Clausen [13]. Supported catalysts are produced for several reasons. One of them is that by supporting precious metals it is possible to reduce the amount needed to obtain the same catalytic effect; simply because the metal is maintained in a dispersed state. Often, there are additional benefits of supporting a catalytically active phase. The catalytic activity and/or selectivity may be improved as a result of the interaction with the support. In addition, supported catalysts may be more stable than bulk catalysts; they may sinter more slowly (as a result of altered solid-state chemistry) and may be less prone to poisoning.

Alumina (Al_2O_3) is a very good catalyst support because of its ability to disperse the supported phase, its high thermal stability (depending on the crystal phase), and its moderate price. The ability to disperse is associated with the acid–basic character of Al_2O_3 surfaces. The impregnation or deposition of the active phase, or of its precursor, onto the support surface is a true chemical reaction. Alumina, with its very stable surface OH groups, its Lewis acidity, and the very high polarity of the surface acid–base pairs, provides specific sites for anchoring cationic, anionic, and metallic species. There are indications that supported species are located at specific sites on the alumina surface. Surface defects, corners, and edges are likely playing an important role for the dispersion of active species during the various preparation steps, including impregnation and deposition, subsequent drying and calcination, and reduction in the case of metal catalysts, or sulfidation in the case of supported sulfide catalysts. The presence of additional species during the contact of the precursor of the active phase with the support may also be a relevant factor [14].

It is worthy to notice that deactivation of the catalysts is inevitable. The deactivation rate increases with the complexity of the loads treated and the severity of the operating conditions [15]. Moreover, in recent years, research has shown that the main cause of catalyst deactivation is due to coke [16-20].
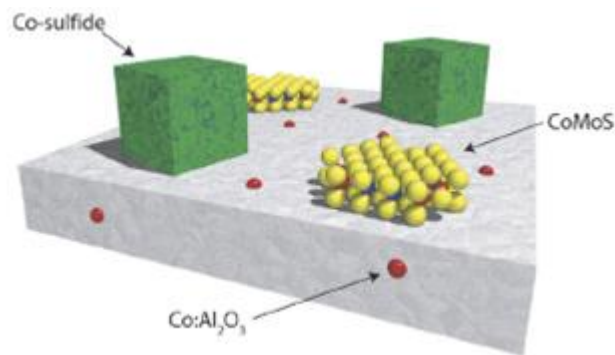
Fig. 3. Structural model proposed by Topsøe and Clausen [13].

2.3. Hydrocracking process

Hydrocracking is a process by which the hydrocarbon molecules of petroleum are broken into simpler molecules, as of gasoline or kerosene, by the addition of hydrogen under high pressure and in the presence of a catalyst. This process employs hydrogen gas to improve the hydrogen-carbon ratio in the cracked molecules and to arrive at a broader range of end products. The major products from hydrocracking are jet fuel and diesel, but low-sulfur naphtha fractions and Liquefied Petroleum Gas (LPG) are also produced. All these products have a very low content of sulfur and other contaminants.

Hydrocracking catalysts have a cracking function and a hydrogenation–dehydrogenation function (Figure 4). The cracking function is provided by an acidic support, whereas the hydrogenation–dehydrogenation function is provided by active metals. The acidic support can be (a) amorphous oxides (e.g. silica–alumina), (b) a crystalline zeolite (mostly modified Y zeolite) plus binder (e.g. alumina) or (c) a mixture of crystalline zeolite and amorphous oxides. Cracking and isomerization reactions take place on the acidic support [21].

The metals providing the hydrogenation–dehydrogenation function can be noble metals (palladium, platinum) or non-noble metal sulphides from Group VI.A (molybdenum, tungsten) and group VIII.A (cobalt, nickel). These metals catalyze the hydrogenation of the feedstock, making it more reactive for cracking and heteroatom removal and reducing the coking rate. They also initiate the cracking by forming a reactive olefin intermediate via dehydrogenation. The ratio between the catalyst's cracking function and hydrogenation function can be adjusted to optimize activity and selectivity. The relative strength of different hydrogenation components and cracking (acid) components in hydrocracking catalysts are shown in Table 1.
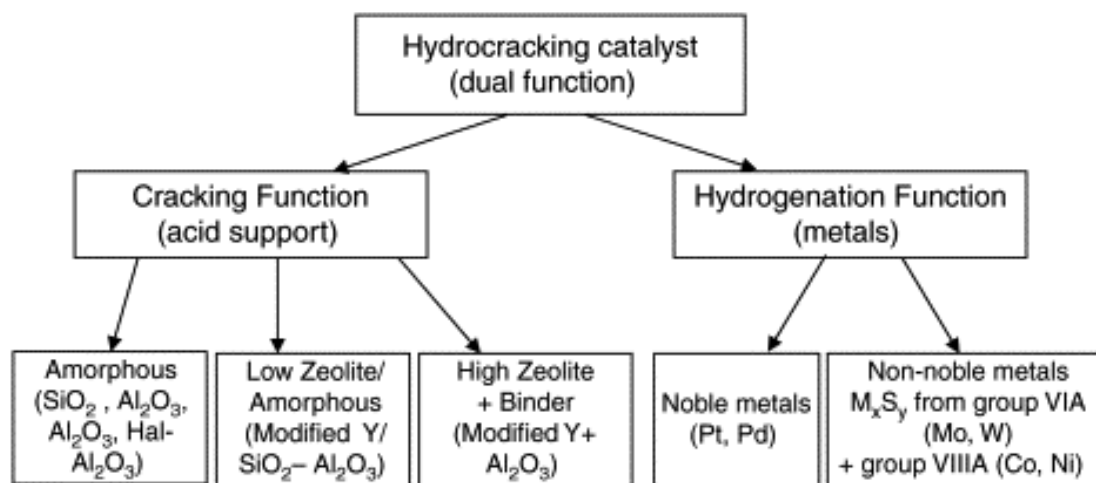
Fig. 4. Classification of hydrocracking catalysts [21].

Table 1
Bifunctional catalyst strength for hydrogenation and cracking [22]

Hydrogenation function	Co/Mo	Ni/Mo	Ni/W	Pt(Pd)
	x	xx	xxx	xxxx
Cracking function	Al_2O_3	Al_2O_3–Hal	SiO_3–Al_2O_3	Zeolite
	x	xx	xxx	xxxx

3. Case of "Société Ivoirienne de Raffinage (SIR)"

3.1. Quick overview

SIR (Société Ivoirienne de Raffinage) is the only oil refinery in Côte d'Ivoire. It was created on October 3, 1962 by the Ivorian government with the assistance of international oil groups. It ensures the refining of crude oil and the distribution of petroleum products in Côte d'Ivoire and in some countries. Equipped with two atmospheric distillation units of 75,000 barrels/day and an 18,000 barrels/day hydrocracker, today processes 3.8 million tons per year. The Diesel produced at SIR comes from atmospheric distillation then it is treated at the hydrocracking unit made up of two reactors: 87R01 reactor (see Figure 5) dedicated to hydrotreatment (Hydrodesulfurization), and 87R02 reactor (see Figure 6) where cracking reactions take place, but also little hydrotreatment reactions. The process is as follows: the distillate which come from the distillation tower arrive at 87R01 reactor. After being hydrotreated, then it goes within 87R02 reactor where it is craked, to obtain small molecules. Hydrodesulfurization is obtained by the catalyst $NiMo/Al_2O_3$ (catalyst supported); the active phase on this catalyst is CoMoS. At the bottom of 87R01 reactor there are little layers of zeolite and a lot of $NiMo/Al_2O_3$. In contrast, in the 87R02 reactor, there are little layers of

NiMo/Al₂O₃ and a lot of zeolites. This latest catalyst lead to cracking reactions. Hydrodesulfurization is important for the cracking process, because it purifies distillate from poison of zeolite catalyst, such as sulphur, and other metals. So, if hydrotreatment in 87R01 reactor is not effective, the quality of gasoil will be bad. Therefore, hydrodesulfurization is one of important stages considered at SIR. Figure 7 summarizes the hydrocracking process at SIR.
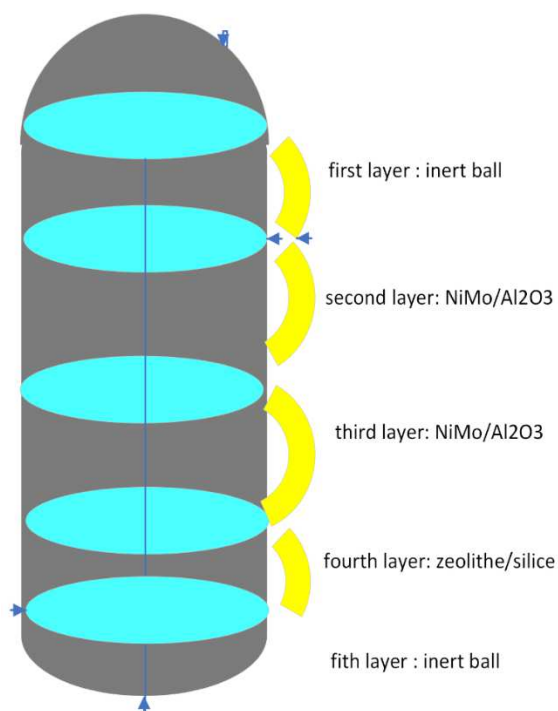

first layer : inert ball

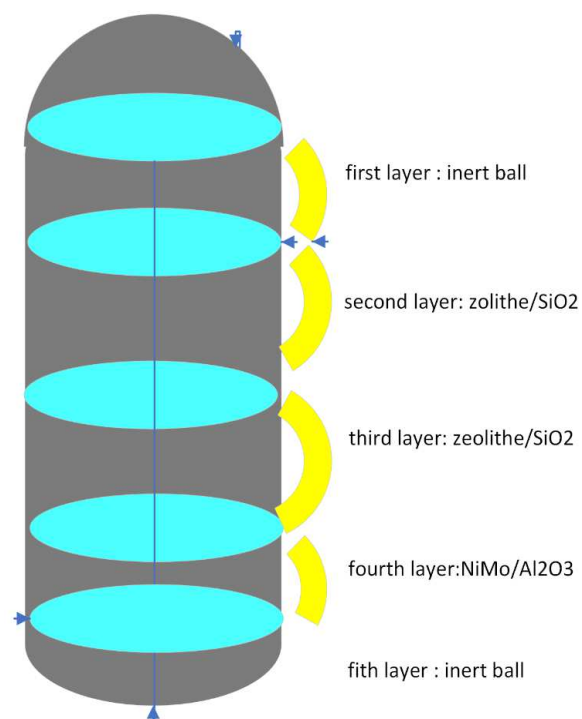second layer: NiMo/Al2O3

third layer: NiMo/Al2O3

fourth layer: zeolithe/silice

fith layer : inert ball

Fig. 5. Scheme of 87R01 reactor.

first layer : inert ball

second layer: zolithe/SiO2

third layer: zeolithe/SiO2

fourth layer:NiMo/Al2O3

fith layer : inert ball

Fig. 6. Scheme of 87R02 reactor.

Fluid from distillation (distillate)

Gasoline
Kerosene
Diesel

87R01 Hydrotreatment of distillate

87R02 Cracking of big molecules

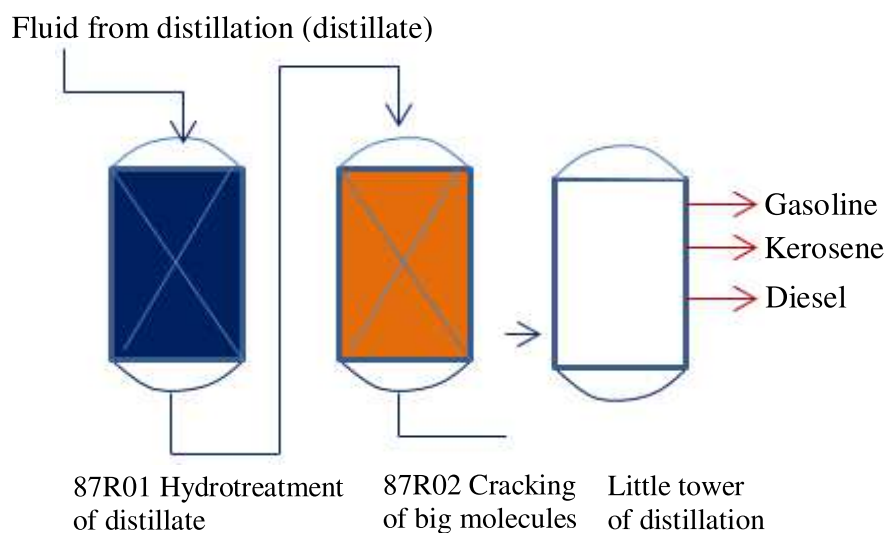Little tower of distillation

Fig. 7. Hydrocracking scheme at SIR.

3.2. Catalysts and coke

3.2.1. NiMo/Al$_2$O$_3$ catalyst

The hydrotreatment catalyst which is used at SIR initially looks like what we see on the Figure 8; its color is green-yellow, which correspond to the oxided state. Then, the refinery asks an experienced company to collect the catalyst inside the reactor. To do this, technician, enter inside the reactor dressed in specific suit: as a matter of fact during the shutdown, the reactor is swept by inert gas, nitrogen.

Fig. 8. Oxyded form of the catalyst NiMo/Al$_2$O$_3$.

3.2.2. Coke in the hydrocracking reactor

After a shutdown at SIR (in 2016), a large quantity of black deposit in the internals of the reactor has been observed (Figs. 9-12).

Fig. 9. Black deposit on the inert catalyst.

Fig. 10. Black deposit inside the internal reactor tubing.

Fig. 11. Black deposit on catalytic bed of the reactor.

Fig. 12. Graded bed fouling.

The black deposit observed is linked to petroleum coke. Indeed, Kraus [23] and Lebreton [24] showed that the phenomenon of coking could occur at a high contact time or too high temperature. The formation of coke on metal catalyst could have various origins [19]. Carbon may be chemisorbed strongly as a monolayer or

physically adsorbed in multilayers and in either case block access of reactants to metal surface sites. On the other hand, in extreme cases, strong carbon filaments may build-up in pores to the extent that they stress and fracture the support material, ultimately causing disintegration of catalyst pellets and plugging of reactor voids (Fig.13).
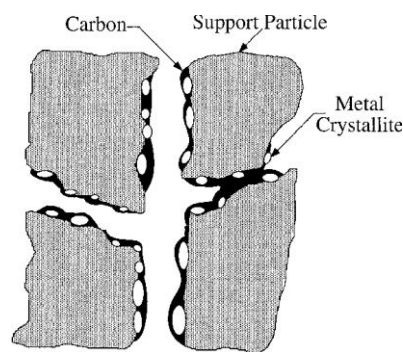
Mechanisms of carbon deposition and coke formation on metal catalysts from carbon monoxide and hydrocarbons [25–30] are illustrated in figure 14. This theory has been recognized by several authors [31-33] According to the work of Bartolomew [19], it can be conclude that the rapid deactivation of $NiMo/Al_2O_3$ catalysts in the 87R01 reactor is coke.

Fig. 13. Conceptual model of fouling, crystallite encapsulation and pore plugging of a supported metal catalyst due to carbon deposition [19].
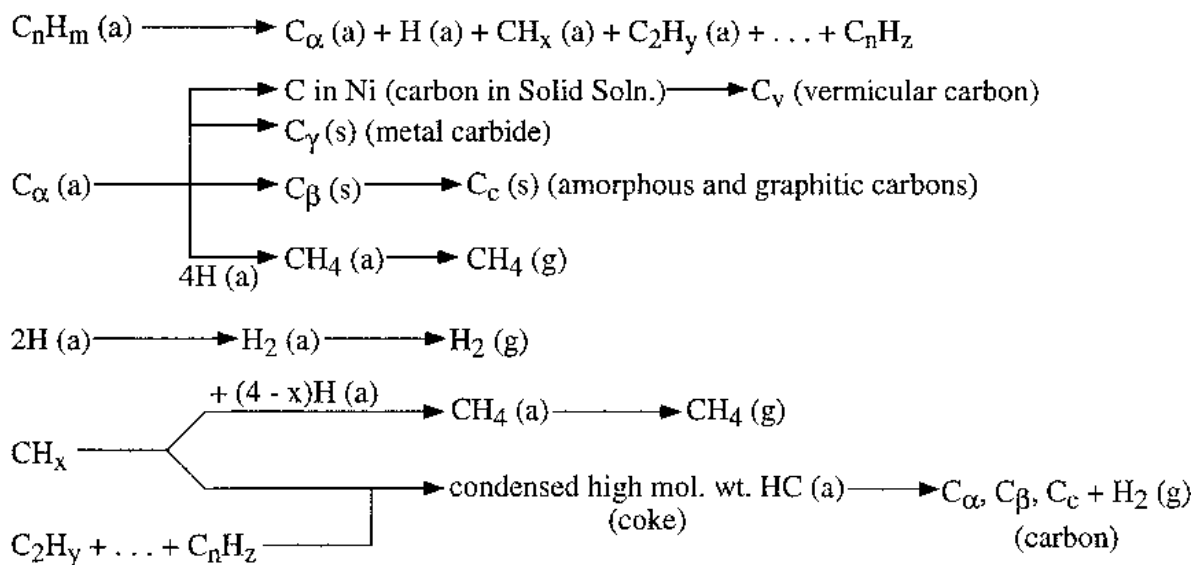

Fig. 14. Formation and transformation of coke on metal surfaces (a, g, s refer to adsorbed, gaseous and solid states, respectively); gas phase reactions are not considered [19].

3.3. Proposals to obtain clean diesel

3.3.1. The use of pilot test

The first and most efficient method, which can provide lasting solutions without much effort, would be to carry out a pilot test before using any catalyst.

The use of a pilot test could be very useful to reduce coke (which is a real poison for hydrotreatment catalysts $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$) from one part and improve the process in general. Swoboda et al. [34] showed that the better way to improve catalytic process in FCC (Fluid Catalytic Cracking) is pilot plant where it is possible to change parameters and obtain the desire results. In the same way, Akimoto et al. [35] have been able to improve catalytic hydrotreating of heavy residua by using pilot plant.

In the case of SIR, this pilot test may be composed of drivers for working under all types of gas: corrosive, toxic, and flammable (H_2S, CO_2, CO, H_2, C_2, H_2, 1, 3-butadiene, CH_4, light olefins, etc.). It is possible to work under "Batch" reactors and milli-reactors (25 mL to 3 L) with wide range of temperatures and pressures (up to 800 °C and from P = 1 bar to P > 100 bars). In addition, the pilot test offers the advantage of testing different types of catalysts. Thereupon, Zeuthen et al. [36] developed a new generation of hydrotreatment catalysts for the hydrocracker pretreatment reactor (dedicated to the hydrotreatment of gasoline): the TK 6001. A sulfur content of 70.2 ppm is obtained at the

reactor outlet while the initial value was around 195 ppm.

In practice, the distillate (Diesel cut of the distillation tower) at the inlet of the 87R01 reactor, can be passed through the pilot, gradually changing the parameters and/or the hydrotreatment catalysts. In this regard it can still be a $NiMo/Al_2O_3$ but the formula is more elaborate.

3.3.2. Fuel sampling inlet and outlet of the U87 unit

Starting from the same procedure as that used for the pilot, it is possible to take the distillate at the inlet of the 87R01 reactor and at the outlet of the 87R02 reactor. These two liquid samples will be analyzed using an ICP. This instrument enables analysis of 70 elements in solution; it has a detection limit of 0.1 mg for most elements. So, it is possible to give the amount of sulfur at the entrance and on the output of the two reactors. With these values, the desulfurization rate (τ) can be calculated using the following formula [37]:

$$\tau = (S_0 - S_t)/S_0 \qquad (1)$$

S_0 = initial sulfur weight% (87R01 reactor)
S_t = final sulfur weight% (87R02 reactor)

3.2.3. Catalyst sampling from the 87R01 reactor

3.2.3.1. Catalyst characterization

This path consists in withdrawing sample in 87R01 reactor. This can be done by qualitative and quantitative analysis of the sulfur species by chemical and textural characterization. For this

action, it is possible to use the EMIA-320V2 Analyzer which provides information on the catalyst constitution of carbon and sulfur.

This method has been already used by Pessanha et al. [38] on four generations of spent NiMo/Al$_2$O$_3$ catalysts covering 32 years. These catalysts worked in the sulfided form in the same hydrotreater of a Brazilian refinery. This unit is designed for HDS crude diesel fractions obtained after processing various crude oil. Elemental analysis were run using a 2400 Perkin Elmer elemental Analyzer. The result of this analysis according to the work of these authors, shows that the elemental analysis of the carbon content on NiMo/γ-Al$_2$O$_3$ catalysts before and after use varies from 13% to 8.2% depending on the generation of catalysts considered (Table 2), and it decreases more and more from the first to the fourth generation. This shows that before the catalyst is used, the carbon content is non-existent and it becomes high when the reactor is running. This study also shows that the new generation of catalysts is a little more effective against coke but does not eliminate it. The fourth generation continues to be used in many countries including Côte d'Ivoire. So this technic could be apply at SIR.

BET surface study can be used for the textural analysis. ASAP 2020 OF MICROMETRICS is an appropriate material to study the mesoporosity of solids (2 nm <Ø <200 nm). This study permits to see the coking of catalyst. Another technic to find the weight percentage of carbon on catalyst could be the Transmission Electronic Microscopy (TEM) coupled with the EDX. This type of microscope allows both high resolution images to be viewed and chemical composition to be determined. An example with NiMo/γ-Al$_2$O$_3$ catalyst is shown by Wang et al. [39]. The images from TEM coupled with EDX chemical analysis obtained by Wang et al. [39] are presented in figure 15 and table 3, respectively. Wang et al's results [39] show that the amount of coke deposited is greater than 21.4% (weight). The immediate consequence is a drastic reduction in the specific surface area and the pore volume of the catalyst. TEM analysis provides valuable elements for understanding the deactivation of the NiMo/γ-Al$_2$O$_3$ catalyst due to coke. Indeed, a low specific surface area means a low activity and therefore a poor performance of the catalyst which cannot hydrotreat correctly the charge.

Table 2
Chemical analysis (C dry weight) on NiMo/γ-Al$_2$O$_3$ catalyst before and after use [38]

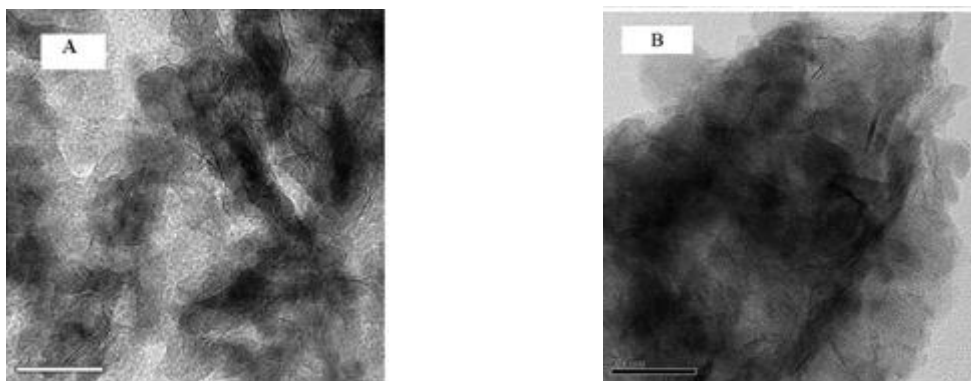|	I		II		III		IV	
Generation	1979 -1986		1993 -1998		2003 -2008		2008 -2011	
State of catalyst	Fresh	spent	Fresh	spent	Fresh	spent	Fresh	spent
% C	Absent	13	Absent	12,5	Absent	10,2	Absent	8,2

Fig. 15. Transmission Electron Microscope image of a new sulfided (A) and used (B) NiMo/γ-Al₂O₃ catalyst [39] (Scale in each figure is 20 nm).

Table 3
Textural property of a new sulphide and spent NiMo/γ-Al₂O₃ catalyst [39]

	NiMo/γ-Al₂O₃ new sulfided	NiMo/γ-Al₂O₃ used
Pore volume (mL g⁻¹)	0.69	0.17
Surface area (m² g⁻¹)	264	79
Average pore size (nm)	10.5	8.7
Average length of slabs (nm)	5.1	5.7
Average number of layers	1.5	1.7
Carbon content (wt%)	na	21.4

*na : not available

According to Wang et al's work [39], XRD analysis is not suitable for this kind of study. They showed the diffractograms of the fresh and the used NiMo/γ-Al₂O₃ catalyst (figure 16). The γ-Al₂O₃ diffraction peak is found on the two diffractograms. The analysis shows that the NiMo/γ-Al₂O₃ catalyst has a largely amorphous structure with species widely dispersed on its surface. Thus, with this technique, it will be difficult to detect the C found in coke.
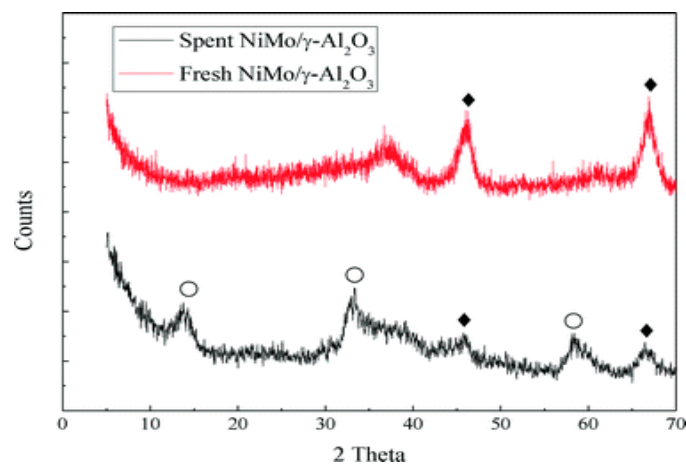
○ − MoS₂; ♦ − Al₂O₃.

Fig. 16. Diffractograms of the NiMo/γ-Al₂O₃ catalyst before and after use [39].

On the other hand, Raman spectroscopy is a very efficient method of characterizing the coke at the surface of the catalyst. From this method, Digne et al. [40], showed that the nature of the coke deposited on the surface of the $NiMo/\gamma-Al_2O_3$ depends on the charge used. It is possible to determine the bands characterizing the coke present in the form of carbon; they are located in two distinct places. The first corresponding to wavelengths between 1550 cm^{-1} and 1650 cm^{-1}; this high intensity band is visible for all samples (a), (b), (c), (d).

The second one corresponding to wavelengths between 1250 cm^{-1} and 1450 cm^{-1}; this low intensity band is visible only for samples (a), (c), (d).
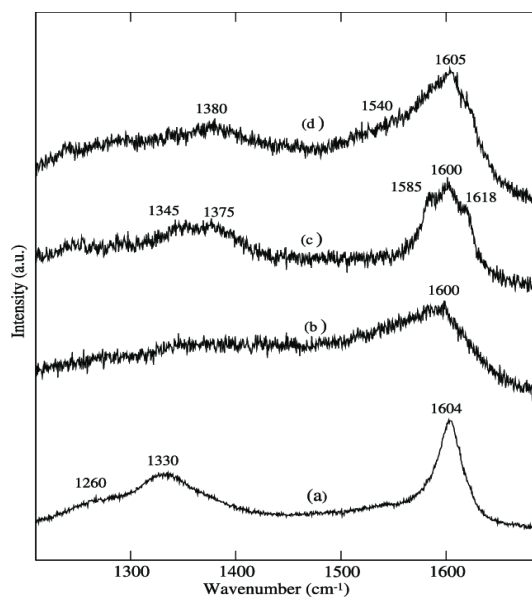
Another efficient method to characterize the coke on the surface of the catalysts is the thermal analysis using the "Programmed Oxidation Temperature (TPO)". Oxidation profile temperature of spent $NiMo/\gamma-Al_2O_3$ is shown in figure 18 [39]. It can be noticed that the consumption of O_2 coincides with the formation of CO and CO_2, according to equations (2) and (3):

$$C + 1/2O_2 \rightarrow CO \qquad (2)$$
$$CO + 1/2O_2 \rightarrow CO_2 \qquad (3)$$

The spectra of CO and CO_2 are identical. The presence of the H_2O peak before CO and CO_2 shows that the carbonaceous species that have burned are poor in hydrogen. This proves the presence of coke by referring to the equation in Figure 14.
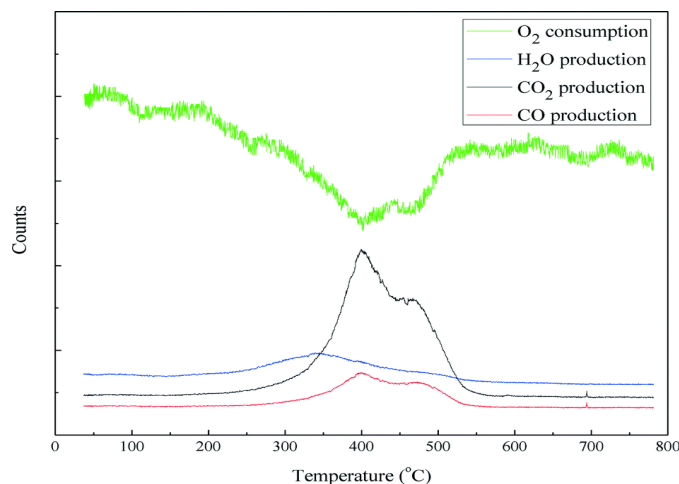

Fig. 17. Raman spectrum of a new sulphide and spent $NiMo/\gamma-Al_2O_3$ catalyst [40].
(a) $NiMo/\gamma-Al_2O_3$ from an industrial unit;
(b) $NiMo/\gamma-Al_2O_3$ in a pilot-charge: standard diesel; (c) $NiMo/\gamma-Al_2O_3$ in a pilot - charge: gas oil from distillate; (d) $NiMo/\gamma-Al_2O_3$ in a pilot-load: gas oil from a residue from a conversion unit.

Fig. 18. Oxidation profile temperature of spent $NiMo/\gamma-Al_2O_3$ [39].

2.2.3.2. Catalyst regeneration

After the characterization of catalyst it is important to consider its regeneration.

Many authors have worked on the deactivation and regeneration of hydrotreatment catalysts. Thus, Gomez [41] studied the regeneration of $CoMo/Al_2O_3$ catalysts (hydrotreating catalyst such as $NiMo/Al_2O_3$). He showed that the regeneration of the catalyst had to be done at a temperature below 773 K (calcination under nitrogen) in order to approach the initial activity of the catalyst. Likewise, Buduvka [42] explained that the regeneration of hydrotreatment catalysts is an important topic to consider. He cited many suppliers who have developed a new generation of catalysts specially designed to be regenerated *in situ*: REACT TM [43], ReFRESH TM [44], and PHOENIX TM (Advanced Refining Technologies LLC) [45]. Gardner [46], of the Phillips Petroleum Company, obtained a patent for an efficient method of hydrotreatment catalyst regeneration.

2.3.4. Simulator

IFP Energies Nouvelles [47] has developed a hydrocracking process simulator which offer the better compromise between performance, production costs and environmental impact. The new So'Crack simulator makes it possible to predict the performance of a hydrocracking process with a view to proposing the best possible catalyst chain. The marked improvement in performance predictions, making it possible to ramp up the implementation of the process and propose innovative catalyst chains that fully exploit the synergies of the different catalytic functions. The constant effort in the fields of advanced analysis, process modeling and applied mathematics is of a very great contribution [47] and deserves to be encouraged.

3. Conclusion

The crudes (petroleum) used at the "Société Ivoirienne de Raffinage" have low content of sulfur. Thus, there is a possibility of improving the sulfur level at the outlet of the hydrocracker. This involves lowering the rate of coke in the reactor. In the perspective of Research and Development, the present work, shows that various techniques can be used as sustainable solution, in particular by improving the life and performance of hydrotreatment catalysts. Thus, it has been shown that the optimization of operating conditions via pilot or simulator tests is possible by working directly on the catalysts or the hydrocracker inlet and outlet fluids. The ultimate method would be to use new generations of catalysts. More than ever, research is found at all levels of a process. In this context, collaborations between research laboratories and "Société Ivoirienne de Raffinage (SIR)" are welcome.

Acknowledgement

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