

Effective use of catalysts through catalyst regeneration

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ABSTRACT

The refining industry is currently undergoing its most serious challenge in recent times, since cleaner fuels are gradually introduced in many markets. Middle East countries still have less history than Europe, Japan or the USA when it comes to clean fuels, but the trend is there, which will eventually increase the demand for hydroprocessing catalysts. On the other hand, more sophisticated catalysts are being introduced in refining and petrochemicals applications, with increased catalytic performances.

A good way for a refinery to reduce the global catalyst expenses is to maximize the catalyst multiple uses, which is possible for a number of applications. The technique of ex situ regeneration gives the best chance to recover the maximum performance, with the lowest chance for pressure drop build up in the reactor beds as well as improper liquid distribution.

This paper illustrates a number of cases of successful regeneration in the various fields of oil refining and petrochemical applications. The limits to regeneration often come from catalysts poisoning by various contaminants such as Vanadium, Arsenic or Silicon. This impact can be minimized by a careful management of the three actions “Sample, Analyze, Segregate”. This effort allows to maximize the quantity of catalyst recovery with the best possible quality insurance. Non contaminated regenerated catalysts can recover activities rather similar to fresh ones as assessed by a statistical study performed at Eurecat over several years.

The handling and transport of spent catalysts to an off site regeneration facility is currently performed, but requires some precaution as the material is classified as self heating, type UN3190.

Changing hydroprocessing environment

World is changing rapidly on many aspects and especially in the oil refining and petrochemical industries, and it is our task to adapt to this moving environment. The most clear change relates to the specifications of fuels, gasoline and diesel, as well as some other petroleum cuts, which is putting a strong pressure on refiners of various countries who have to adapt their processing modes to meet these new targets. It is good to recall that the production in Europe of the new Ultra Low Sulfur fuel (ULSF) is a real technical challenge, as the today's specification of 350 wt ppm Sulfur has to go down to 50 ppm in 2005 and 10 ppm in 2009. This decrease in Sulfur outlet in a diesel hydrotreating unit would correspond to a necessary activity increase of a factor of 2.5 and nearly 5 respectively compared to the base case. In other words, if no technical progress were made on the hydroprocessing process and catalyst sides, the necessary capacity increase for diesel hydrotreating units would have been roughly a factor of around 5 between 2000 and 2009. Fortunately a lot of progress has been made on processes and catalysts, which then limit the amount of those new investments in Europe. One can guess that globally in this zone the necessary capacity increase for HDT units will be less than a factor of 2 during that period, thanks to the progress in different areas and mainly: (1) Improvement of liquid distribution (better trays and better loading), (2) Improvement of Hydrogen purity, (3) Catalysts of new generation.

Situation in Middle East is somehow different in terms of fuels Sulfur content. Nevertheless, there is a significant trend towards sulfur reduction in the 2005-2010 time frame, to reach a 750 ppm average sulfur content. It is also worth to note that there could still be at that stage significant differences in terms of product quality requirements between Middle East local markets and other industrialized countries where ULSF are mandated.

Hydrotreating catalysts have been steadily improved over the last years. Typically their intrinsic activity has been multiplied by a factor of around 4 over the last two decades (1985-2005), which by the way has been insufficient for following the activity needed by the environmental regulations. Catalysts have thus become more and more sophisticated and one indirect consequence is that they need more careful procedures for regeneration than in the past. This point will be discussed later.

Another change in our industry as in others comes from a greater need of productivity and improved economics. This leads at managing the refining and petrochemical units differently. Three immediate consequences of this statement is that the major refining companies (1) are

largely practicing catalyst reuse, (2) have abandoned in situ regeneration for different reasons, one being that it took too much downtime without production, (3) are encouraging actions which minimize shut down time.

Basics of deactivation and regeneration

Most of the catalysts used in refining or petrochemical applications deactivate more or less quickly with time. Fixed bed applications are designed as a function of catalyst deactivation kinetics so that the catalyst life be minimum 6 months and usually 1 to 3 years. It is generally admitted that there are three causes of catalyst deactivation, the main one being by far coke formation. Coke is the term used for these large molecules often containing polyaromatic rings and which partially covers the active sites, as well as may block the catalyst porosity. As shown in Table 1, this statement is true for a majority of catalytic processes used in refineries, whether it is for hydrotreating, hydrocracking, naphtha reforming and Isomerization, selective hydrogenation...and even FCC where this coke lay out occurs in a matter of seconds. The second cause may be the damage of active phase structure and dispersion, while the third one is contamination by various chemicals which adsorb on the active sites.

Catalytic process	Catalyst	Causes of deactivation		
		Coke deposit	Sintering of active phase	Contamination
Diesel Hydrodesulfurization	CoMo / Al ₂ O ₃	+++	++	+
Resid hydrotreatment	NiMo–CoMo / Al ₂ O ₃	+++	+	+++
VGO Hydrocracking	NiMo–NiW / Silica alumina zeolite	+++	+	+
Naphtha Reforming	Pt Re Cl / Al ₂ O ₃	+++	++	+(1)
Pygas, olefins, Selective Hydrogenation	Pd – Ni / Al ₂ O ₃	++	+	++
Alkylation Aromatics/olefins	Zeolite + binder	+++	-	+(2)

(1) Contamination by sulphur for instance can occur

(2) In some cases, contamination of the acidic zeolite by some nitrogen containing molecules

TABLE 1: Examples of oil refining and petrochemical catalytic processes showing main causes of catalyst deactivation

Regeneration can restore activity in some cases. By using an oxidizing atmosphere at a temperature of around 500°C, it is possible to eliminate the coke lay out by burning the carbonaceous species. Regeneration has the benefit of eliminating the 1st cause of deactivation, coke deposit, but it can do more, as illustrated in Table 2. For example, in the case of hydroprocessing, regeneration converts the sulfide phase back to an oxide phase quite similar to the original one of the fresh catalyst.

Catalytic process	Activity recovery by regeneration			Predominant regeneration practise
	Coke removal	Redispersion	Contaminants removal	
Diesel HDS	Yes	Yes	No (1)	Ex situ
Resid hydrotreatment	Yes	Yes	No (1)	Almost no regeneration (2)
VGO hydrocracking	Yes	Yes	Yes/no (3)	Ex situ
Naphtha reforming	Yes	Yes/no (4)	Yes/no (5)	In situ
Pygas, olefins Selective Hydro.	Yes	No	Yes/no (6)	In situ/ Ex situ(7)
Alkylation Aromatics/olefins (zeolite)	Yes	-	Yes (8)	Ex situ

(1) Contaminants such as V, Si, As, Fe, Si, cannot be removed by regeneration.

(2) Resid catalysts are not regenerated, except in some special cases, such as the last reactor/ beds which are less contaminated by metals.

(3) Metals contamination at top of 1st reactor is irreversible. But deactivation of acidic function of hydrocracking catalyst by heavy nitrogen containing molecules is reversible.

(4) The carbon burn-off operation does not restore the platinum phase dispersion. This is achieved by the subsequent operation of oxychlorination.

(5) A partial sulfur removal is possible with a specific procedure.

(6) Contamination is usually not removed. However its effect can be attenuated, e.g. in the case of Arsenic with a Palladium catalyst, where As migrates from the metallic to the support phase.

(7) Some units have 2 reactors in parallel. In this configuration in situ regeneration is still used.

(8) Regeneration can eventually remove adsorbed basic molecules from the acidic sites.

TABLE 2: Examples of catalytic processes showing the possibilities of activity recovery by regeneration

Regeneration best practices

Until the mid 1970s, all regenerations of hydroprocessing catalysts were conducted in-situ in the unit reactors, but ex situ regeneration has gradually become the industry standard in the western world. Other parts of the world are rapidly increasing their use of off-site regeneration services. This technique is preferred to in-situ regeneration for many reasons including corrosion issues, safety, time considerations, and better activity recovery. As said above, the higher degree of sophistication of the most recent catalysts, whether in the field of hydrotreating or

hydrocracking, push even more in favour of off site regeneration for getting good performance for the 2nd cycle. There are other examples, such as the reaction of alkylation of olefins with benzene for making ethyl benzene or cumene, where the zeolite catalyst can only be regenerate safely ex situ.

Eurecat process

The industrial regeneration process most employed by Eurecat is based on the use of a Roto-louvre oven technology, which enables an excellent contact between gas and solids (Figure 1). A high degree of homogeneity and excellent temperature control are achieved from the contact between hot air, passing through the spaces between the louvres, and the thin layer of catalyst rotating slowly inside this conical inner shell.

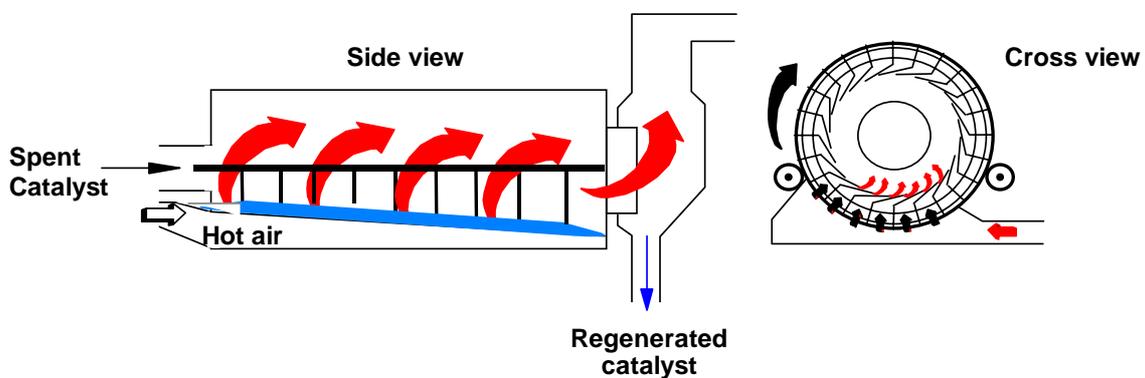


Figure 1 - Side & Cross view of a roto-louvre oven

Unloading and handling of spent catalyst

Spent catalysts are characterized by some particular features. As an example, spent hydroprocessing catalysts show the presence of coke up to 30 wt%, and typically between 5 and 15 wt%, the presence of hydrocarbons or other volatiles, typically up to 15 wt%, as well as adsorbed metallic contaminants, such as vanadium, iron, arsenic, silica, sodium...

Hazards associated with spent hydroprocessing catalysts, from the standpoint of Health, Safety and Environmental aspects, are essentially associated with their self-heating behaviour. A material is declared self-heating if it undergoes spontaneous heating in the presence of air at a certain temperature with a certain amount of material. The UN self-heating test is a rather simple laboratory procedure, summarized in Table 3.

Laboratory procedure for UN self-heating test:

1. Heat a sample at 140°C for 24h.
If the sample temperature > 200 °C
the material is self-heating.
2. Heat a sample at 140° for 24h.
If the sample temperature > 200°C
the material is self-heating group II.
If the sample temperature < 200°C
the material is self-heating group III.

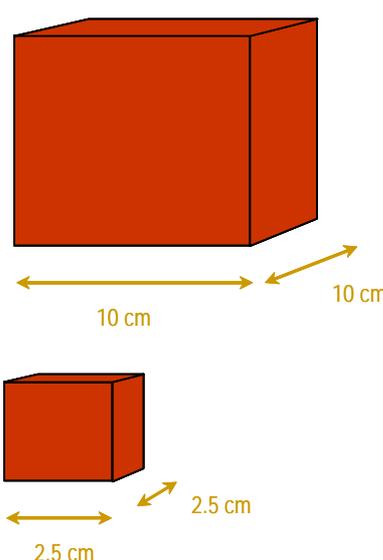


Table 3 – UN Self-heating test

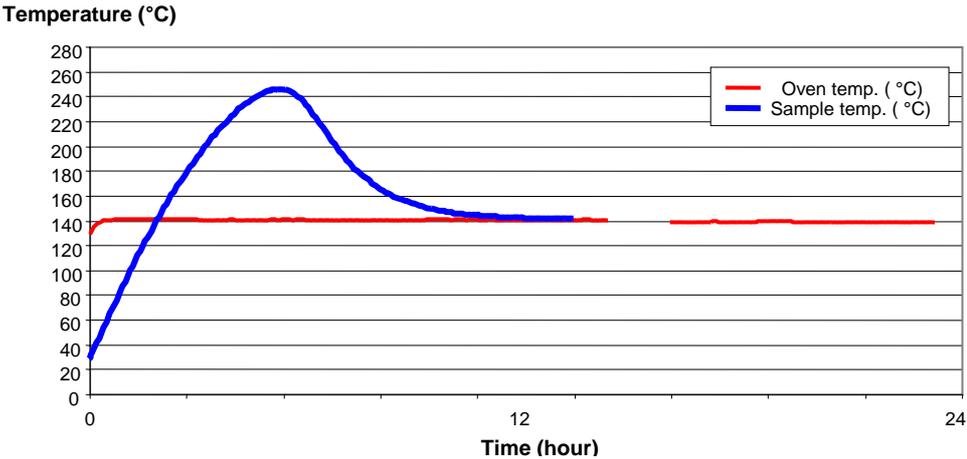


Figure 2 – Self-heating test results for a typical spent CoMo catalyst

Most spent hydroprocessing catalysts fall under that category of self heating substances as shown in Figure 2, and are classified under the class 4.2., UN N° 3190 category, as “inorganic,

self-heating substances, n.o.s”. Consequently, solidness and air-tightness are requirements for the UN certification of the packaging (drums or containers) used to store or transport such materials (for drums: UN 1A2/Y/...and for containers: UN 11A/Y/...).

Benefits of “Sample, Analyze, Segregate” service

Extensive analytical programs are needed in order to verify the properties of the spent catalysts and their suitability for reuse after regeneration. In many cases, there is a significant amount of contaminants on the catalyst and the detailed analysis of a global representative sample is not sufficient and can lead to a waste of potentially good product. In order to get the best possible activity recovery of the regenerated catalyst, as well as the maximum recovery yield, the contamination issue has to be considered already before reactor shutdown as it can affect significantly the shutdown strategy. One has to predict the possible contamination profile, and choose the best unloading method: in case of severe contamination prediction by poisons such as Fe, As, Na, Si, V, vacuum unloading can be a good choice to separate properly layers of contaminated catalysts. Before unloading the catalyst from the reactor, it is also possible to take samples from the reactor top layers with e.g. the Probatcat technique, available from Petroval. It can be used to either determine a metals contamination vertical profile, or also to identify preferential paths within the reactor bed.

In any case, it is of primary importance to have a good quality labelling and sampling of drums or containers of unloaded catalyst for being able subsequently to analyse and segregate properly good material from contaminated one. This can be done at the foot of the reactor or in the regeneration company’s yard. Then the company laboratory can analyze quickly some selected samples for helping the refiner to take the good decisions for catalyst reutilization. He can decide of the segregation strategy of the whole catalyst batch in several lots of various qualities, which then can be either reloaded in the same unit or in another one of similar service, or cascaded to a less severe service or sent for metals reclaiming.

We describe here below one example of unloading where the benefits of this service of “Sample, Analyze, Segregate” has been very clear. An FCC pre-treatment reactor has been gravity unloading in containers which were well labelled and sampled. Figure 3 shows that the 1st containers are not contaminated by Vanadium, corresponding to catalyst situated in the reactor

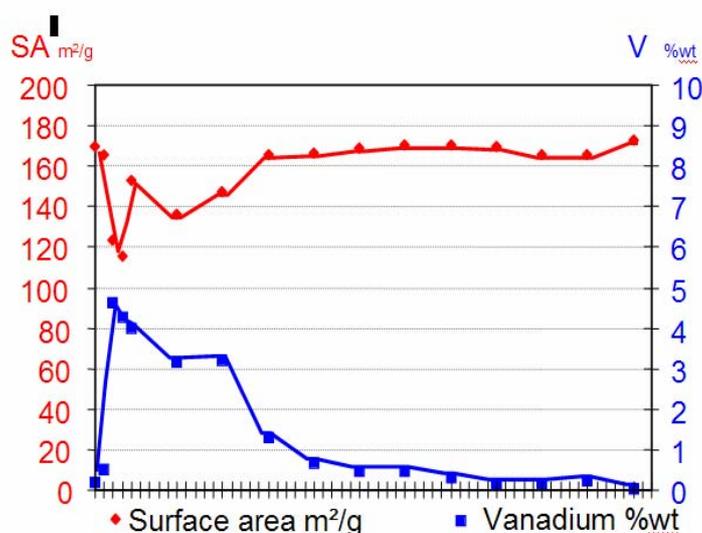


Figure 3: Evolution of Vanadium content and Surface Area of a spent catalyst versus the number of containers after a gravity unloading of a FCC pretreatment reactor.

bottom; then a sharp peak of Vanadium content appears at more than 4 %, corresponding to the top of the reactor (the well known “chimney effect”), finally decreasing to less than 1% after around 1/3 of the total quantity. This analytical study coupled with a well mastered unloading and labelling allowed to save and reuse roughly 2/3 of the whole batch, when the analysis of an average sample only would have imposed to send the whole batch for metals reclaiming.

Activity recovery for diesel hydrotreating catalysts

It is common practice to qualify the performance of HDT catalyst by BET Surface Area (SA) measurement. This works rather well so far on alumina based hydrotreating catalysts. Nevertheless, this correlation can be foul when poisoning is observed and activity testing remains the ultimate tool to qualify the catalyst quality. Eurecat has now a 7 years experience of HDS testing and Surface Area measurement. We can thus well correlate the average loss of HDS activity after regeneration after the 1st cycle with the average loss of Surface Area on a large number of products.

A series of regenerated CoMo catalysts, KF752 and KF756 used in Atmospheric Gas Oil units, were evaluated versus their fresh counterpart. Some of them were regenerated more than once. The two correlations for SA and HDS RWA are:

$$\checkmark SA_{IND} = 94\% SA_{FRESH} \pm 6\%$$

$$\checkmark RWA_{IND} = 89\% RWA_{FRESH} \pm 11\%$$

✓

So the relative loss of Surface Area is around 6%, which corresponds to a relative loss of 11% in activity. This HDS debit of 11% would correspond roughly to a maximum of 3°C in start of run temperature compared to the first cycle with a fresh catalyst. Again this assumption is valid for non poisoned catalysts. This clearly shows that regenerated catalysts show excellent performances, not very different than fresh, and that in many cases they can make another cycle with a performance debit very easily compensated by a temperature increase too small to affect the potential cycle length.

Conclusion

From the three typical causes of deactivation, coke, sintering and contamination, at least the two first can be eliminated by regeneration in the case of hydroprocessing catalysts, the ex situ method being much more preferred nowadays for a better quality assessment. The limits to regeneration often come from catalysts poisoning. Its impact can be minimized by a careful management of the three actions “Sample, Analyze, Segregate”, which then allows to maximize the catalyst recovery yield with the best possible quality insurance. Non contaminated regenerated catalysts can recover activities rather similar to fresh ones as assessed by a statistical study performed at Eurecat over several years on non contaminated CoMo catalysts. The handling and transport of spent catalysts to an off site regeneration facility is currently performed, but requires some precaution as the material is classified as self heating, type UN3190.