

New life cycle options for hydroprocessing catalysts: best ways to maximize operating profit and minimize environmental impact?

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Abstract

Oil refining and petrochemical plants are facing many challenges from technical or economical or environmental point of view. In the field of hydroprocessing, there is potential for a high reuse of spent catalysts after off-site regeneration, as there is now ample knowledge that such a well managed catalyst off-site regeneration does restore activity.

By reusing regenerated catalyst, not only unit performance requirements are met, but this also allows a reduction of catalyst procurement expenses as well as being a way to limit the generation of chemical waste. Relying on physical parameters of regenerated catalyst as this was common practice in the past is not acceptable any more in an environment where performance and reliability are critical elements. Systematic activity testing and pressure drop analysis are nowadays a must to assess reusability of catalyst.

Furthermore, a new concept has been recently introduced by Eurecat, called «Sampling, Analysis, Segregation» (SAS) which allows to isolate non contaminated material for possible reuse, while maximizing unit performance.

These techniques and additional tools described in this paper are available to the refiners to maximize the use of regenerated catalyst. Case studies are presented in this article.

Introduction

Oil refining and petrochemical plants are currently undergoing serious challenges from a technical and economical point of view, as well as from an environmental point of view. The volume of installed capacity of hydroprocessing catalyst is increasing in order to cope with the development of nearly sulphur free clean fuels and the need for deeper heavy ends conversion. In the same time, low refining margins are driving industry to cost optimization, while environmental regulations are getting tougher.

In addition to the growing fresh hydroprocessing catalyst market (hydrodesulfurization, hydrocracking), regenerated catalyst usage is also increasing with an estimated worldwide consumption of roughly 30000 t/y. This additional tonnage of regenerated catalysts is extremely useful for refineries hoping to reduce their procurement expenses as well as to limit their generation of chemical waste. Unfortunately, the ratio between the regenerated and the fresh catalyst market in distillates hydroprocessing is below 50 %, meaning that not all spent catalysts are regenerated at least once. This low reuse rate can certainly be increased by a careful evaluation of the spent catalyst.

Discussion

Regeneration of hydroprocessing catalysts restores activity

The end-of-cycle for hydroprocessing units is usually determined by: (i) a scheduled unit shutdown; (ii) a unit upset, such as too high pressure drop, compressor failure, and so on; (iii) a catalyst activity too low for meeting product specifications. In this last case, activity decrease is mainly due to partial blockage of the active sites by coke and sometimes contaminants. Carbon content on spent HDS catalysts largely varies from 5 to 25 wt%, with an average for diesel units of 8-15 wt%. It is common knowledge now that regeneration of spent hydroprocessing catalysts does restore activity, and this is confirmed by our experience over the past years, as shown on **Figure 1**. By using an oxidizing atmosphere at a temperature of 450-550°C, carbonaceous species can be removed from the catalyst. Regeneration has

the benefit of eliminating the first cause of deactivation, i.e. coke deposit. But it does more by converting the sulphide phase, which may have become partially sintered, back to an oxide phase similar to the fresh catalyst. This works well for conventional catalysts while the latest generation catalysts may need an additional treatment to achieve better recovery of activity.

How are hydroprocessing catalysts contaminated?

Various contaminants are found on spent hydroprocessing catalysts at the end of cycle. They originate either from the feed (vanadium, nickel, arsenic, sodium), or from additives used during transport or refining operations (silicon, lead, phosphorous), or from corrosion (iron). Their effects are quite different:

Ni + V

The Ni and V containing molecules present in the heavier fraction of vacuum gas oil and resid feeds are readily decomposed to Ni and V sulphides on the catalyst surface. After regeneration, the sulphides are converted back to oxides, also promoting some alumina sulphatation. Depending on the hydrotreating application, it is usually not advised to reuse catalysts containing more than 1.0 to 3.0wt% V (often expressed as Ni+V, as these 2 metals generally exist together, even if nickel is not itself considered a poison).

As

Organoarsenic compounds contained in some crudes are extremely reactive under hydroprocessing conditions and are thus readily decomposed and adsorbed on the catalyst surface. Therefore, a very steep As gradient is always observed between the top and the bottom of the reactor. Arsenic is considered a severe poison for HDS activity as a quantity of 0.2 to 0.4 wt% can prevent catalyst reuse.

Na

Sodium is usually not present in the various hydroprocessing feeds in normal operation. However, it could be present on the catalyst due to desalter malfunction, because of various upsets leading to upstream introduction of caustic soda (for instance, upsets of Merox units), or when sea water is introduced to the unit via heat exchanger leakage. Sodium then adsorbs on the catalyst surface and has a significant deactivation effect which is usually more noticeable after regeneration. The maximum tolerated poison level for Na is typically between 0.1 and 0.2 wt%.

Si

Silicon originates essentially from lighter fractions of coker or visbreaker operations where polydimethylsiloxanes are used as anti-foaming agents. Silicon could also originate from silicon based chemicals injected into pipelines for reduction of pressure drop. Silicon is not a very strong poison during the cycle and deactivation seems higher after regeneration.

Pb, P

Lead is no longer seen in spent catalysts in many countries, due to the general phase down of tetraethyl lead as an octane booster. Poisoning by phosphorous may be seen sometimes, but not often as phosphorous containing additives are not so common yet.

Fe

In distillate HDS units, iron contamination comes from corrosion of upstream equipment. As such, iron scale or fine particles usually do not penetrate deeply into the catalyst pores and do not have any strong poisoning effect. Its contribution to pressure drop build up is more problematic, as Fe particles may accumulate at the top of the bed or in the interstices between catalyst granules.

How to maximize the quantity of reusable regenerated catalyst? Sorting is a solution.

Catalyst regeneration will not cure anything as regards deactivation by contaminants, which remain adsorbed after thermal treatment. This does not mean that a contaminated batch cannot be regenerated. What is necessary is to implement a sorting technique, as there is always a concentration gradient observed in fixed bed reactors, in case of metals contamination.

SAS service (sampling, analysis, segregation) can save a great deal of good catalyst

When catalyst is contaminated, the analysis of a global representative sample does not tell us anything regarding the concentration gradients throughout the reactor bed and is thus not sufficient; it could even be counter productive as it could lead to wrong decisions such as sending the whole batch for metals reclaim, when a clever sorting would have saved a great deal of good catalyst.

Contamination issues must be considered before any reactor shutdown. The sorting strategy simply starts by good quality labeling of the drums or containers of unloaded catalyst, during the unloading operation at the foot of the reactor. This will later enable accurate interpretation of the analysis of each container by drawing the contaminant profile and then deciding on the subsequent segregation of good product from contaminated material. The catalyst owner may decide on a segregation strategy: the entire catalyst batch is divided into several lots of varying quality, which can be either reloaded in the same unit, used in another unit of similar service, cascaded down to a less severe service, or sent for metals reclamation.

Case Study 1: Recovery and regeneration of 75% of the catalyst batch (equivalent to 1,3 MM\$ savings as fresh catalyst) by SAS technique

The following is an interesting example of Eurecat's SAS service which resulted in considerable savings for the refiner. A reactor containing 96 tons of catalyst was gravity unloaded in well labeled containers. Upon arrival at the Eurecat site, the lot was sampled in the standard way and a representative sample of the whole reactor was analyzed and tested. Contaminant levels were pretty high: 0.11wt% As; 0.35wt% Na; 0.5wt% Si. Moreover the HDS activity was found to be 83% that of fresh catalyst. With these results in hand, the customer's initial decision was to send the entire 96 tons batch for metals reclamation.

Eurecat then proposed to examine the lot in more details and perform a complete analysis on every third container to determine the contamination profile. **Figure 2** shows the contamination profile with a rather clear cut between clean and contaminated fractions.

The high level of contaminants in the first containers illustrates the so-called "chimney effect" where top layers come first just after the very bottom part.

A composite sample of containers 1 to 3 and 24 to 74 was obtained, analyzed and tested. In these composites, the level of contaminants is low (0.02wt% As; 0.05wt% Na; 0.1wt% Si) and the HDS activity came back at 96% that of fresh catalyst. This detailed contamination analysis coupled with HDS testing made the customer's decision much easier: recycle the contaminated fraction of only 22 tons and regenerate the remaining 74 tons of good material.

Case Study 2: 65% of the catalyst lot was found good for reuse (0,9 MM\$ savings)

The SAS procedure was applied on another case of a 75 tons reactor where silicon and arsenic contamination was suspected. The arsenic concentration of the whole batch is 0.11 wt%, not high enough to decide to eliminate all of the batch, but still preventing the batch from performing at the ideal level for an activity sensitive unit. The labelling, sampling, analysis procedure resulted in a very regular contamination profile.

The cut was decided that way: 49 tons were recovered with an arsenic level below 0.05 wt%, and 26 tons with 0.21 wt% As and 0.51 wt% Si were sent for metals reclaim. HDS Activity has been upgraded from 89% to 94% RVA versus fresh catalyst (**Figure 3**).

Activity test is necessary for assessing catalyst reuse

Up to a couple of years back, contaminant and Surface Area analysis were sufficient for assessing a safe reuse. Eurecat has numerous statistical data showing the correlation between Surface Area and HDS Activity. Often, general belief is that for conventional catalysts SA recovery of more than 90%-95% (versus fresh catalyst) would guarantee a 90% activity recovery. This corresponds to a delta start of run temperature of around 3°C in a commercial unit.

However the situation has drastically changed in a couple of years with the progressive replacement of conventional catalysts by the new generation catalysts. Then, even if SA is still an important parameter for catalyst characterization, it is not any more perfectly related to Activity. In other words, there are cases where surface is high enough and Activity below the limit of reuse, 85 or 90%; but the reverse also exists, where SA is surprisingly lower than 80% versus fresh and activity above 90%.

This is demonstrated on **Figure 4** for various CoMo catalysts of the new generation. Some points are clearly outside a direct correlation. Using the only criterion of surface recovery would have lead to mistakes of two types: accept some batches with low activity recovery and discard some good batches despite their too low surface.

This shows that a true catalytic testing is absolutely necessary for assessing a safe regenerated catalyst reuse. Eurecat has an in-house capacity of up to 80 tests per month, which guarantees quick results to its customers.

Assessing catalyst reuse by pressure drop evaluation

Catalyst reuse can be achieved safely as soon as two criteria are met: activity recovery and mechanical properties. The first of these is assessed by the contamination studies followed by sorting as previously discussed and activity testing is performed on the segregated clean catalyst component. With this in place, catalyst activity is well defined for safe reuse. As regards the second requirement concerning mechanical properties: these are evaluated by various analyses, such as strength (bulk crushing or side crushing), average length and particle size distribution, attrition level and content of various sizes of fines. All of this helps to answer the question: can this be reused without any risk of pressure drop? A complementary way to look at the question is to measure directly the pressure drop of a representative sample at the laboratory scale. Eurecat has developed and implemented such equipment in order to better assess catalyst reusability.

Figure 5a shows how fines content influences the pressure drop of a catalyst batch. A catalyst lot has been selected with fines content of less than 1mm of 2.0, 5.0 and 10.0wt%. Pressure drop increases by about 60% and 130% respectively for a fines content of 5.0 and 10.0wt%. **Figure 5b** shows a typical particle size distribution of a catalyst containing 10% fines below 1 mm.

Recycling spent non-reusable catalyst

Used catalyst has to be recycled when its performance cannot be brought back to the desired level or if the catalyst particles are too damaged for reuse, being either too weak or too short for safe reuse, the risk being excess pressure drop in the reactor. They are then considered to be chemical waste.

Metals prices fluctuate a lot, and are nowadays high enough to give spent catalysts a positive value. Thus the debate between landfilling and reclaiming has ended and all spent hydroprocessing catalysts can now be sent to metallurgical recovery plants.

Two main routes are used for metals reclamation: hydrometallurgy and pyrometallurgy. Eurecat has developed a pyrometallurgical route with its partner Eramet Valdi, which operates with full transparency and highest environmental standards. In addition, this process brings value to all of the catalyst components: Mo, Co and Ni are used to produce specialty steels, while the recovered alumina is used in the production of rock wool material.

Conclusion

Sound regeneration practice can greatly contribute to an overall reduction in hydroprocessing catalyst costs. Careful analysis of spent catalyst allows to cherry-pick the best quality material for re-use. An assessment of catalyst quality needs to be done by direct measurement of activity using pilot plant testing. Finally, beyond all the necessary analyses related to mechanical properties, a direct measure of bed pressure drop is a guarantee of totally safe reuse of catalyst.

Figure 1: HDS Activity (RVA) from regenerated catalysts

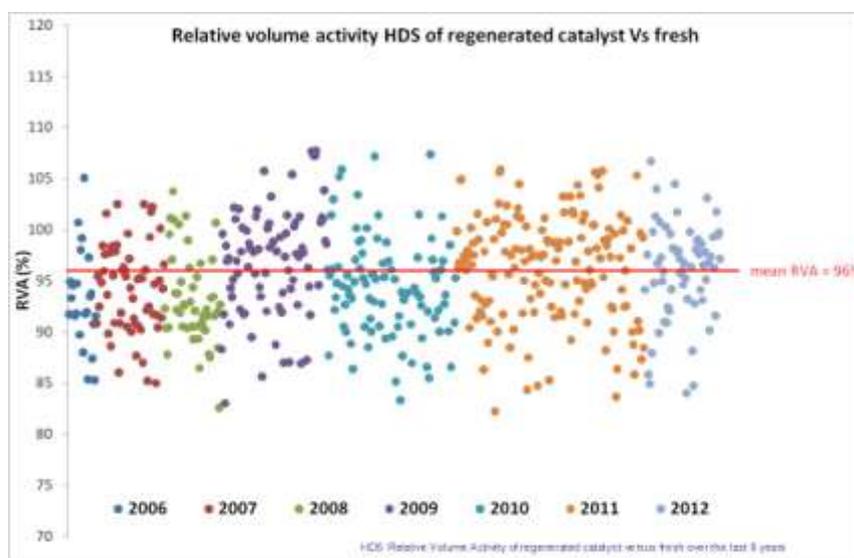


Figure 2: SAS service. Contaminants analysis (Sodium, Arsenic, Silicon) vs. bin number on a load of spent HDS catalyst

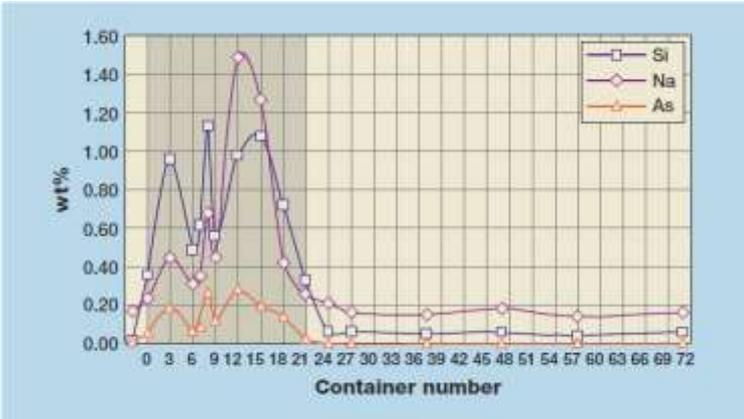


Figure 3: SAS service. Contaminants analysis (Iron, Arsenic, Silicon, Sodium) vs. bin number on a load of spent HDS catalyst

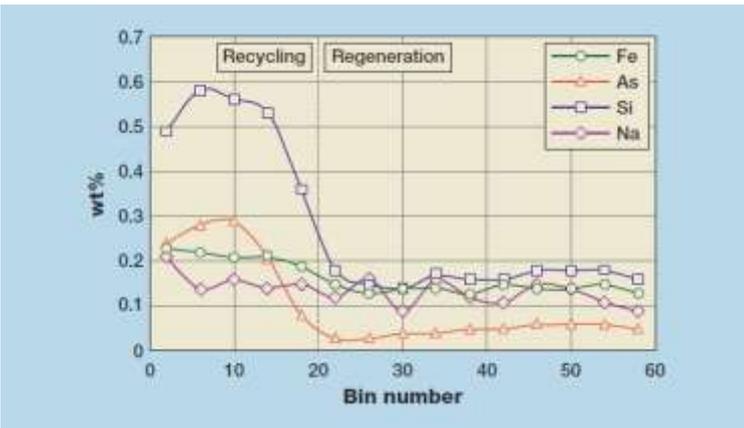


Figure 4: Variation of Surface Area (SA) and HDS Activity (RWA) for various regenerated batches of a new generation CoMo

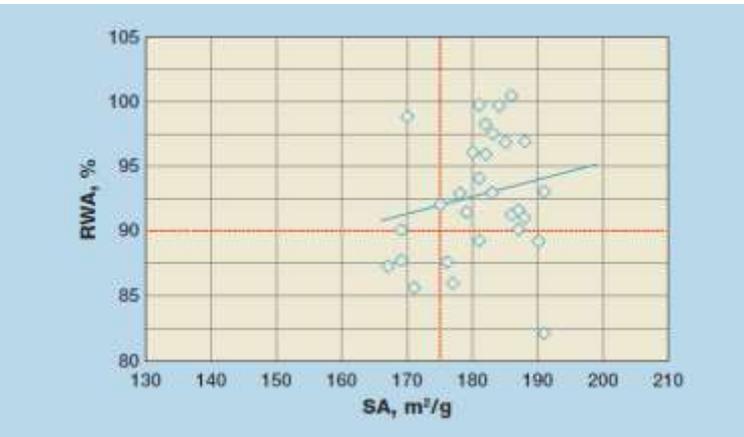


Figure 5a: Effect of fines of less than 1 mm up to 2, 5 and 10 wt% on pressure drop generation

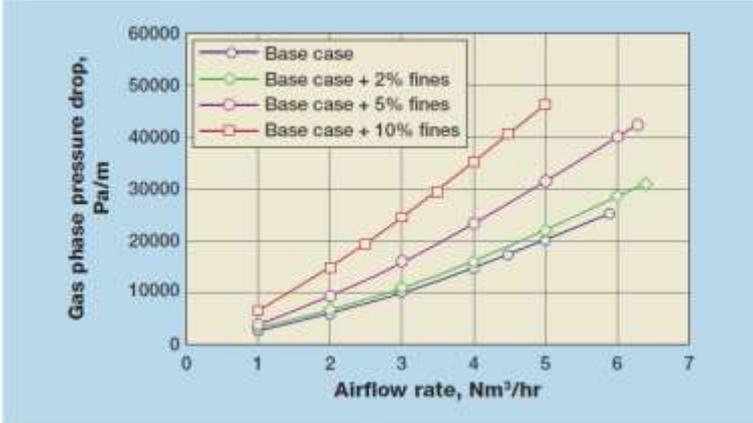


Figure 5b: Particle Size Distribution of a catalyst containing 10% fines below 1 mm

