OPTIMAL MANAGEMENT OF YOUR CATALYTIC OPERATION NOW MADE POSSIBLE

Frédéric Girardier

Eurecat SA, La Voulte-sur-Rhône, France

Eric Gaillard

Petroval SA, Les Trois Pierres, France

ABSTRACT

The increasing importance of the HDS units in the refinery, the greater sophistication of their catalysts, the need for maximum performance and more and more stringent environmental regulations have first led in the late 1970's to the development of the off-site regeneration as a new service.

More recently, other catalyst services have become available to assist the refiners with the management of their increasingly complicated catalytic operations.

On one hand, off-site processing of spent or fresh catalyst (regeneration, preconditioning, recycling and associated services) is becoming the rule adopted widely all over the world. On the other hand, a series of on site services have been developed to insure the refiner gets the maximum yield out of its unit : catalyst sampling, handling, dense loading, reactor expertise.

The availability of those services has allowed a change of thinking regarding catalyst management.

This paper presents the technical and financial advantages brought by these services.

I INTRODUCTION

Until the seventies, catalysts used in the oil refining and petrochemical industries had a very simple life cycle: they were either used for one production cycle until exhaustion of their catalytic properties, or otherwise they were used for a few cycles, with some in-situ regeneration between cycles. Disposal, in a more or less acceptable environmental way was the last step. Under those conditions, there was a rather limited need for off-site services.

The situation has changed drastically, more recently, as off-site regeneration of many catalysts and particularly hydroprocessing catalysts has become widely accepted and preferred by the industry. This is due to a number of reasons, including safety and time considerations and better catalyst activity recovery.

Together with off-site regeneration, other services such as off-site presulfiding, other preconditioning processes and catalyst handling have become available to help the refiners manage their unit shutdowns and start-ups. Furthermore, spent catalyst disposal is evolving towards more environmentally acceptable recycling schemes.

The growth of catalyst services is the result of more severe catalyst requirements due to more stringent product specifications or performance needs. Handling activities are now also becoming critical to meet those needs, and dedicated technologies and reactor expertise are now available to assist the operator with its turnaround activities.

In addition, the availability of catalyst services enables plant operators to look at their catalytic units in a more global and optimized way, best suited for their needs. At present, catalyst management has become a reality.

II RECENT IMPROVEMENTS

The increasing catalyst inventories and the need to reduce operating costs is the strong development of off-site catalyst regeneration.

Its efficiency in terms of time saving and activity recovery is now nearly universally recognised and there is no more dispute about its advantages as compared to the in-situ procedure. Today, in the western world, about 90 % of the HDS catalysts regeneration are done off-site, and this trend is also spreading to other parts of the world (Middle East, Far East) as regeneration plants are available in these areas.

To meet the refiner’s requirement in terms of quality and cost efficiency, regeneration companies have significantly modified their processes in order to provide a regenerated catalyst whose characteristics are as close as possible to the fresh ones, while recovering as much product as possible.

Catalyst characterisation

Before proceeding with the industrial regeneration, it is essential to perfectly characterise the raw material (spent catalyst) sent by the refiner. Upon arrival at the regenerator’s facility, catalyst is sampled, regenerated in the laboratory under very mild conditions, which will restore its properties to the best possible level.

After this step, various parameters are looked at, such as : residual carbon, residual sulfur (a high residual sulfur is often an indication of metals poisoning), surface area (to be compared to either the fresh catalyst or to the value obtained after a previous regeneration), mechanical strength, length distribution, contaminants level.

Metal contamination

During the production cycle, catalyst may indeed be contaminated by various poisons such as nickel, vanadium (for example when VGO, Atmospheric or Vacuum Resids are processed), silica when antifoaming agents are used in the refinery. Originally, silica was found in Coker Naphtha units but it is increasingly found in Diesel cuts as well. Less frequent are poisoning by arsenic, sodium or lead.

Typically these poisons are trapped by the upper layers of catalyst bed and it becomes necessary to segregate the contaminated material from the “reusable” one.

Depending on the technique used for unloading, this separation can be done either on site or at the regenerator’s facility.

If catalyst is unloaded by gravity, the chimney effect will result in top and bottom material being thoroughly mixed. Extra sampling is then required : instead of one representative sample for the whole batch of catalyst, Eurecat takes samples with a much higher frequency, typically one for every tonne of catalyst. For a standard VGO hydrotreater this may result in 80 or 100 samples for the reactor load. These samples are regenerated in the laboratory and analysed for the specific poisons, whose level is then plotted against surface area. Figure 1 shows the results of this procedure, in the case of vanadium poisoning.

A cut-off point is then chosen to determine which part of the catalyst will be disposed of and which part will be saved. The main advantage of this method is to minimise the unloading time while allowing to recover a good part of the uncontaminated material.

Another way to separate both materials is to take samples inside the reactors upon opening via the Probacat technology offered by Petroval. Completed with an on-site metals analysis, it allows to determine the thickness of the contaminated layer before unloading the reactor. The handling contractor can then safely unload the poisoned catalyst by vacuum, the "good" material being then unloaded by gravity.

This solution allows a very clear separation and avoids transporting non regenerable material to the regenerator's facility. It may require however longer handling time in some particular cases.

Improved activity recovery

Catalysts have improved drastically over the last ten years in order to help refiners meet the required specifications, and we may expect to witness even higher improvements in the coming years.

For CoMo catalysts the gain of activity was often related to a much higher metal content thus making the catalyst more sensitive especially to regeneration conditions. This higher degree of sophistication has obliged the regeneration company to constantly improve their processes in order to keep the activity recovery to the required level.

There are several technologies available for catalyst regeneration : rotating kiln, belt oven or fluidised bed. For its industrial process, Eurecat uses a Roto-Louvre oven which enables an excellent contact between gas and solid (Figure 2).

Over the years, the main process concept has remained largely the same, but continuous improvements have been implemented to cope with the higher sensitivity of the more recent catalysts : internal design changes, better temperature control and monitoring, catalyst flow rate control, air or other gas media distribution.

Eurecat has also developed analytical tools to better control the industrial process. In addition to the surface area measurement which remains the key parameter to evaluate catalyst quality, Eurecat is also using Dynamic Oxygen Chemisorption (DOC) especially for the high metal content catalysts. This measurement is however rather sensitive to metals poisoning and the results require careful interpretation.

Activity testing after regeneration is also more and more frequently used as a tool to guarantee the performance of the regenerated catalyst. Thanks to the improvements brought to the regeneration procedure, Eurecat is able to deliver a product with characteristics quite close to the fresh catalyst Figure 3 shows a plot of surface area recovery vs activity (relative RWA) after regeneration. Catalyst is a recent CoMo catalyst used in deep HDS units.

These data confirm the excellent results obtained by Eurecat with the Roto-Louvre technique. Surface area recovery is close to 95 % of the fresh value and activity recovery, while showing more variation than expected, remain high.

Physical properties

One of the answers given by the refiners to the new specifications requirements was to build much bigger units with larger catalytic inventories. Because of their size, these units are more sensitive to pressure drop and catalyst length properties (average length and particle size distribution). Today, many units require tight specifications for these parameters.

To insure that catalyst will meet these specifications, care must be taken from the very beginning, i.e. the catalyst unloading operation.

Especially when unloading by vacuum is used, it is important that particle size distribution be monitored throughout the handling operation in order to adjust the operating parameters and to avoid excessive breakage of the catalyst. Petroval has developed a quick and reliable on site length measurement method, and thanks to its know-how in reactor monitoring, shutdown activities can provide an expertise independent from the handling contractors.

In some cases, although catalyst still shows a good activity, it does not meet the requirements in terms of particle size distribution. In some cases, it is possible to restore the catalyst batch qualities to an acceptable level by carrying a length grading after regeneration. This naturally induce a reduction of the “reusable” catalyst, but also eliminates all risks of pressure drop. Figure 4 shows an example of what can be achieved.

Catalyst recycling

In the early 90’s legislation about waste disposal or transborder transfer became stricter, and catalyst recycling became an important issue. Refiners had to develop a “legal” expertise and to find alternative solutions to the disposal.

Another solution was to ask another party to take care of the exhausted catalyst and an obvious partner was the catalyst manufacturer who was providing the product in the first place.
Proposals for fresh catalyst started to include recycling options, the manufacturer taking the commitment to find a solution for its own batch. This turned out as however not very practical, at least in Europe, since catalyst very often undergoes several regenerations before being disposed of, and that several years might have gone by between the purchase and the disposal of any given batch. During this period the economical and legal situation might have changed quite drastically, making the initial agreement meaningless. Other alternatives had to be developed, as will be described later on.

Sock and dense loading

Catalyst loading is a critical factor for maximizing catalyst performance. Drums, bins or bags are-used, depending on the refiner’s choice and safety considerations. Minimization of catalyst breakage and uniform catalyst distribution in the reactor are critical to the success of this operation. *Sock loading* may not maximize a reactor’s capacity due to its tendency to create void spaces, and does not guarantee an homogeneous loading of the reactor which may give way to channeling and a non optimal use of the catalyst batch.

Dense-loading techniques are very popular to achieve an improved catalyst orientation and uniform void spacing and to maximize bed density (high activity and bed stability).

Among them, the most successful and reference for quality is *Densicat*, the technology originally developed by Total and proposed by Petroval or its certified loading operators. The *Densicat* technology allows a predictable guaranteed loading density, a perfectly homogenous loading, the highest speed and flexibility to accomodate many types of reactors, some examples of particular reactor configurations being shown in *Figure 5.*

III CATALYST MANAGEMENT

The desire of many operators to subcontract more and more of their tasks, which are not strictly part of their day-to-day activities, and the availability of various innovative catalyst services has resulted in a change of thinking regarding the management of all catalyst related operations.

One of the clear changes has been the growing interest towards multi-cycle operations using the same catalyst batch, with off-site regenerations in between production cycles. For example, Eurecat's experience shows that many refiners now routinely run 2 or 3 cycles with any of the state-of-the-art HDS catalysts, either in the same unit, or through cascading the regenerated catalyst to a less severe unit.

The use of various catalyst services is now an integral part of catalyst management, since all catalyst batches may undergo extensive service lives (« life cycles »), as described in *Figure 6*.

Typical costs associated with some off-site services, relative to the cost of fresh catalyst, for a GO-HDS unit are given in *Figure 7.*

Of particular significance is the low cost of off-site regeneration relative to fresh catalyst, whereas the catalytic performance of regenerated catalyst remains close to that of the fresh catalyst.

It is also interesting to note that as the use of regenerated catalysts increases relative to fresh catalyst, the total expense (fresh catalyst + services) is reduced significantly.

Because of the new product specifications, larger HDS units were built in the recent years and catalyst inventories increased. It become necessary for the refiners to imagine ways of limiting the financial burden linked to these developments. There is also the need to cope with other regulations (environmental ones for example) for which the refiners do not always possess the necessary expertise and have to rely on specialised contractors.

All this led to the set-up of catalyst management schemes which can be defined as action taken to control the various steps of the catalyst life cycle as described in Figure 6.

It must be stressed however that if catalyst cycle is basically the same for the various hydrotreating units, each refinery configuration is rather unique and consequently catalyst management scheme will differ significantly from one case to another.

Solutions will be different depending on several factors:

- Single refinery operation or group of refineries,

- Existence of a refiner’s research center
- Management scheme applied to all units/catalysts within the refinery or to a single type of units/catalyst
- Proximity to a regenerator’s facility
- Local legislation for disposal of waste
- Etc…

Each scheme must derive from a discussion between the various partners : refiner, catalyst manufacturer, regenerator, handling company and must be adapted to each specific situation. As demonstrated by the examples given hereafter catalyst management might be as simple as finding a solution to recycle some spent catalyst or far more sophisticated as in the case of a catalyst pool involving several refineries spread all over Europe.

Catalyst down grading or cascading

Even after a successful regeneration, unit requirements can very so that the regenerated catalyst is no longer suitable. This can be the case after a second regeneration or for very high severity units or for strategically important ones, where only fresh catalysts are used. Various options can be then be considered :

<u>Multi application cascading :</u> a catalyst not suitable any more for a rather severe operation, can be used in a less demanding application.

Typically cascading will be from gas oil hydrotreater to naphtha hydrotreater to kero hydrotreater. It can be done within the refinery itself or within a group of refineries. Eurecat helps the refiner by storing the regenerated catalyst and by its knowledge of the other units requirements. This type of cascading, although useful, does however have some limitations :

- Types of catalyst may differ for different units (often, CoMo for gasoil hydrotreaters and, NiMo for naphtha).

- Larger inventories for severe applications (e.g gasoil HDS) and longer cycle length on other units (e.g naphtha) may quickly lead to an unbalance and demand for regenerated catalyst.

<u>Single application cascading or “catalyst shifting</u>”.

Units built to meet the low sulfur requirements are very often large multi bed reactors or even multi reactors system (typically a small guard vessel in front of a larger vessel downstream). In the case of a major oil company, several identical units were built in its various refineries. In these cases, it is often possible to shift a regenerated catalyst upstream (from the main reactor to the guard vessel for example). After a few cycles, catalyst situation is typically as shown in Figure 8.

This solution is to be considered especially when metals poisoning (even at low a level) is the reason for catalyst deactivation. Using a regenerated catalyst upstream will provide sufficient HDS/HDN activity whilst not poisoning the fresh catalyst. Shorter cycle length of the guard reactor compared to the downstream reactor will often allow the use of most of the regenerated catalyst.

Savings compared to the use of only fresh or only once regenerated catalyst are quite large especially if batches can be rotated amongst several refineries.

<u>Catalyst resale</u>

If no solution can be found internally, a batch of catalyst can be proposed as second hand material for another refiner. For example this can be done with the help of Eurecat who will process the spent material, eliminate the low quality portion in order to offer a good quality material. An activity test can be required, which can be performed either by the refinery or by Eurecat.

Catalyst pools

In order to cope with the large inventories of catalyst, some refiners have studied the possibility to operate catalyst pools. Typically this pool will regroup catalyst used by several refineries of a given geographical area (USA, Europe, Middle East) for a single application (e.g. : GO HDS) or for all applications.

This main purpose of a pool is to have a spare batch available at any given moment, so even in case of emergency shut down, unit change out is limited to the handling operations.

Eurecat is involved in two main pool management schemes operated by two refiners, with two different philosophy although the same type of units (G.O hydrotreaters) are concerned.

In the first case, when a batch is unloaded from one of the units, sampling is done at the refinery. Catalyst is fully analysed by the refiner research center (including activity test), and if the batch is deemed reusable, it is transferred to Eurecat's facility for regeneration and presulfiding. Immediately after processing, the batch is shipped back to one of the refineries where it is stored until requested by the next user.

In the second case, the batch is transferred immediately to Eurecat's premises after being unloaded. Sampling and quality control are taken care of, and results transferred to the refiner's pool manager who will decide whether the batch may remain in the pool, used for another application or disposed of. Discussions between the pool manager and Eurecat's technical-service staff will help to decide upon segregation of any part of the batch and/or length grading requirements. Catalyst will then be processed and stored until the pool manager decides to dispatch it to one or the other refineries of the group.
Although the two operating modes are quite different as well as the use of the service company capabilities, the two schemes show similar requirements : first of all, the technical and quality aspects of the regeneration must be agreed upon first internally between the different users and then discussed with the service company. This is not always an easy task. Also, the initial reluctance of a user to get somebody's else catalyst needs to be overcome.

A good set of technical specifications, a systematic activity test and the collaboration with Eurecat and high quality standards were the answers.

CONCLUSION

The increased severity and economical constraints of all hydroprocessing unit operations put added demand on the catalyst performance. Such performance must therefore be monitored and optimized at all stages of the catalyst life cycle. Various off-site services are available to achieve these objectives, including regeneration and presulfiding.

On site services, and especially reactor expertise are also playing a key role to help the refiner minimize the shut-down associated costs, insure he will get the best performance out of his catalyst and improve the overall economics of the HDS unit.

Petroval and Eurecat are able, together or separately, to offer a wide range of the services required to achieve these goals.

FIGURES

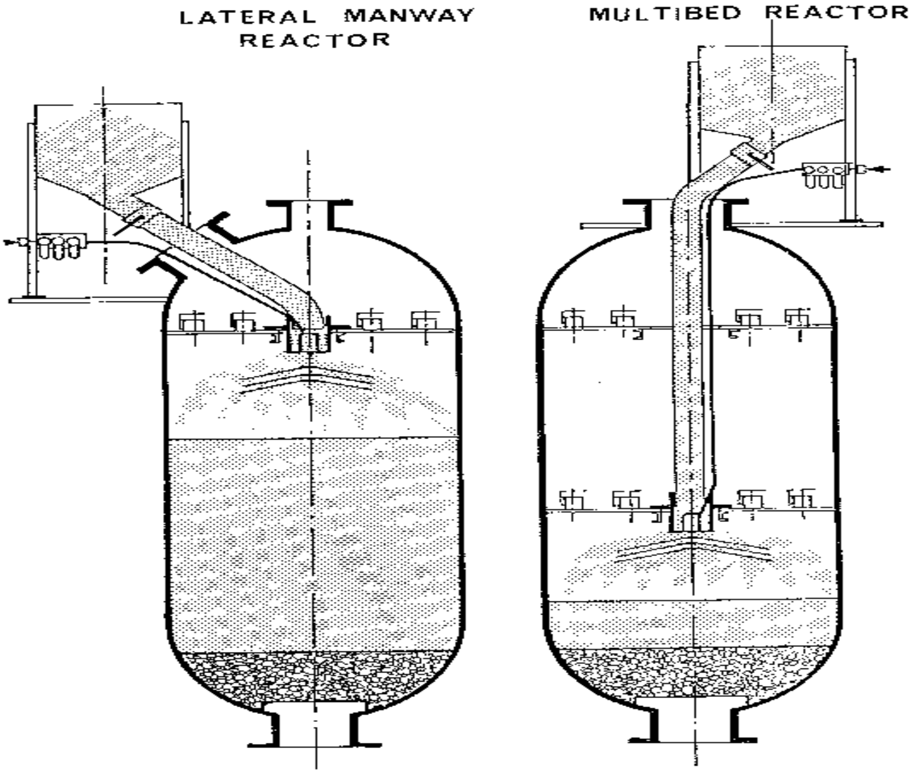

Figure 5 : Application of Densicat to particular reactor types

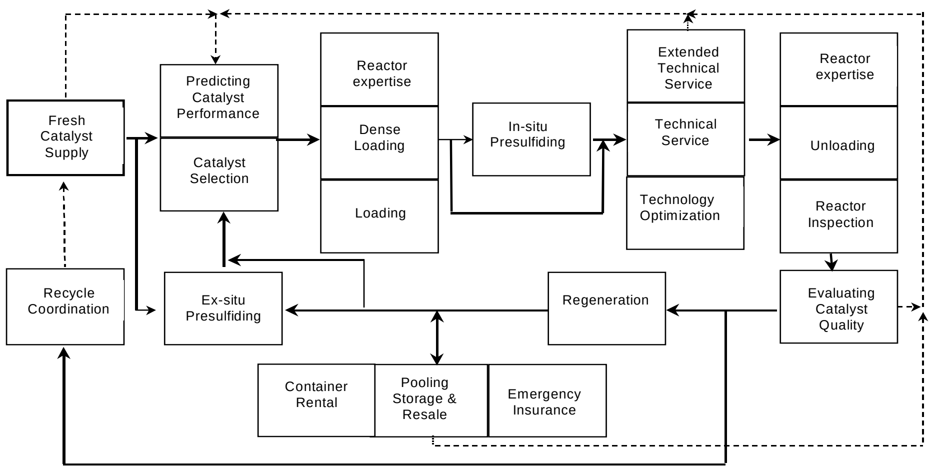

Figure 6 : Catalyst Life Cycle

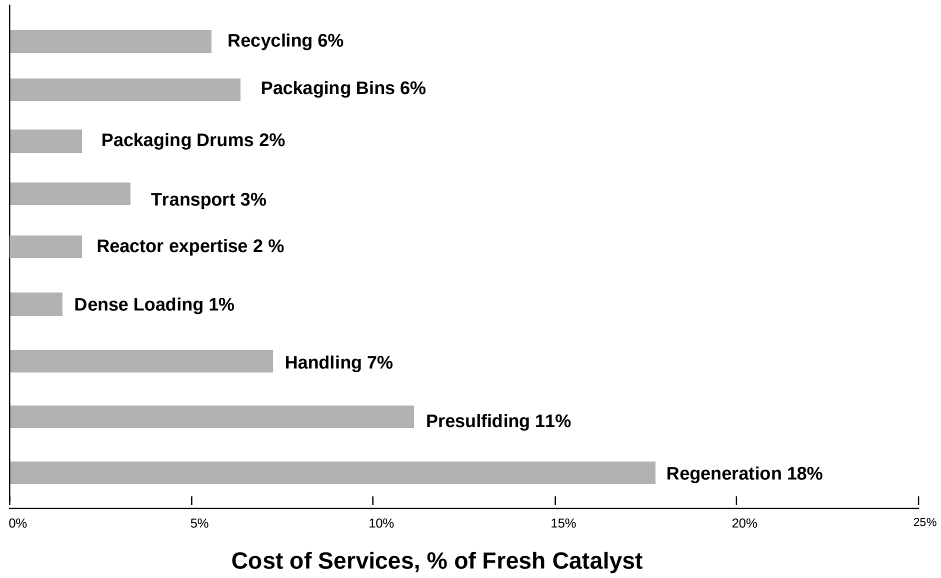

Figure 7 : Cost of off-site services vs fresh catalyst