TOOLS AND EXPERTISE FOR SOUND CATALYST SERVICES AND MANAGEMENT

Francis Valeri, Frédéric Girardier

Eurecat SA, La Voulte-sur-Rhône, France

Yvon Haquet, Eric Gaillard

Petroval SA, Les Trois Pierres, France

ABSTRACT

Specialized companies are now available to provide ex-situ or on site services to oil refineries and petrochemical plants, in relation to their catalyst operations, such as off-site regeneration, off-site presulfiding, sampling, dense loading and other handling or expert services, and recycling options.

The growth of catalyst services relates to the fact that catalyst requirements for many industrial units are becoming more severe, due to more stringent product specifications or unit severity requirements. In some cases, use of increased catalyst volumes and/or reduced cycle lengths are observed.

This paper presents the financial and technical advantages brought by the availability of such tools and expertise.

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. 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.

Catalyst management possibilities exist for a single refinery unit operation or for more complex operation involving more units or more sites. Managing catalyst operations becomes increasingly complicated and partnership with a specialized service and technology company (such as Eurecat) provides key benefits to the refiner.

II CATALYST AGING PROCESS

During a catalytic operation, various factors can cause a temporary or permanent aging of the catalyst. As an example, let us illustrate the case of hydroprocessing catalysts :

Deactivation

Depending on the type of service and unit severity, the cycle length of a hydroprocessing unit is typically between 6 months to 4 years. In fixed bed units catalyst deactivation during the run is compensated by a progressive increase in bed temperature, up to a certain value dictated by metallurgical constraints or product qualities. The end-of-cycle is usually determined by a level of activity too low to meet product specifications, but it also can be due to a unit upset (high pressure drop, compressor failure, hydrogen shortage), or to a scheduled unit shutdown. This is confirmed by the carbon content on spent HDS catalysts before regeneration.

Deactivation is due to three main causes: carbon (or coke) laydown, active phase sintering, and metal poisoning. The detrimental effects of coke are a reduction of support porosity, leading to diffusional limitations, and blocked access to active sites. During off-site regeneration, good success is achieved with carbon elimination as well as active phase redispersion.

Metal contamination

Metal contamination by nickel or vanadium is observed in units running with feedstocks such as VGO, atmospheric resids, or vacuum resids. The V/Ni weight ratio depends on the type of crude, and is usually in the range of 2:1 to 4:1. As nickel is not a poison for catalyst activity, being itself an active metal for hydroprocessing reactions, the criterion for reuse of a regenerated catalyst is generally based on the vanadium content.

Depending on the type of service, catalysts containing more than 2 to 4 wt% vanadium are usually considered unsuitable for regeneration and reuse. Vanadium concentration has been found to vary with bed depth, but may also vary radially in case of flow maldistribution. *Figure 1* shows one example of vanadium contamination observed on a catalyst coming from a VGO unit.

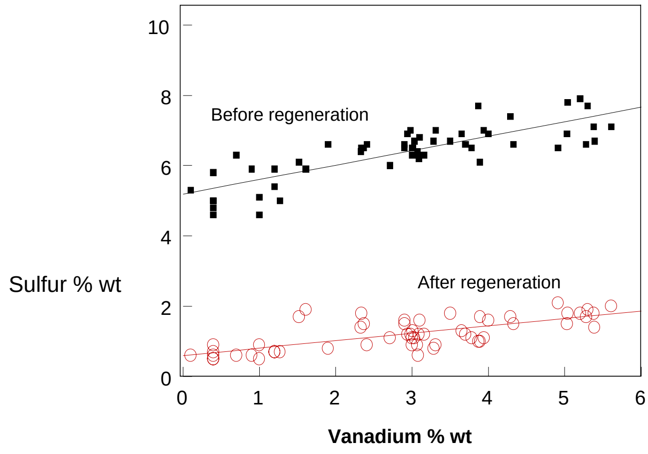


Figure 1 : Vanadium & Sulfur content on Catalyst

Traces amounts of arsenic are found on some spent catalysts, and they remain on the catalyst after regeneration. Arsenic is probably stabilized by forming an inter-metallic compound with the catalyst metals or as a mixed oxide with the support.

When arsenic is present, levels of 500 to 2000 wt ppm are often found on the spent catalyst. It is generally observed that there is a very steep arsenic gradient from the top to the bottom of the bed under hydroprocessing conditions. Vacuum unloading of the top catalyst layers is advised to permit catalyst segregation and analysis whenever arsenic contamination is suspected. In most cases, when arsenic contents exceed 1000 wt ppm on the catalyst, catalytic activity starts to be seriously affected.

Iron, sodium are other metal contaminants often found in the spent catalysts. Iron has a rather low catalyst deactivating effect and comes essentially from corrosion of upstream equipment, and is generally found in low quantities. Sodium is encountered in cases of unit upsets, such as desalter malfunctioning, contamination by caustic soda, or sea water heat exchanger leakage.

Silicon contamination is also quite common for naphta HDS units running on coker naphta, due to use of silicon-based anti-foaming agents, but it is increasingly found in diesel cuts as well.

III OFF SITE CATALYST SERVICES

The availability of various catalyst services has gradually increased since the late 1970s, initiated by the rapid spread of off-site regeneration, offering alternative or new ways for refiners to more precisely evaluate catalyst aspects of their hydroprocessing or other process unit operation.

Regeneration

Until the mid 1970s, all regenerations were conducted in-situ in the unit reactors, but off-site regeneration has gradually become the industry standard in the western world, as illustrated in *Figure 2.* Other parts of the world are rapidly increasing their use of off-site regeneration services. This technique is preferred to the in-situ regeneration for many reasons including safety, time considerations, and better activity recovery.

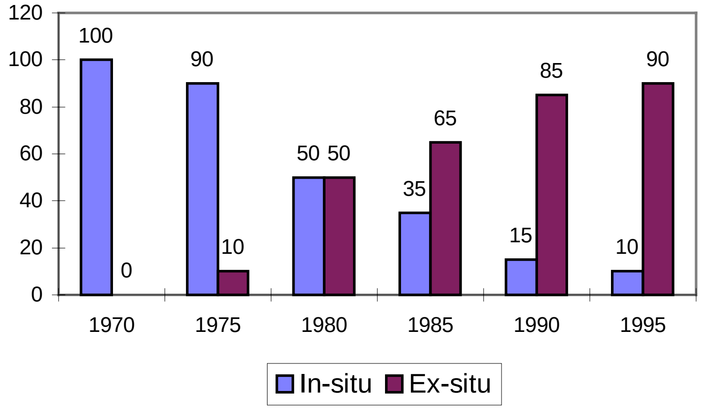


Figure 2 : Trends in Off-Site Regeneration in Europe

Different technologies are available in the industry to carry out off-site regeneration : rotating kiln, belt oven or fluidized bed oven.The *industrial regeneration process* employed by Eurecat is based on the use of a *Roto-Louvre* oven technology, which enables an excellent contact between gas and solids (*Figure 3).* 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.

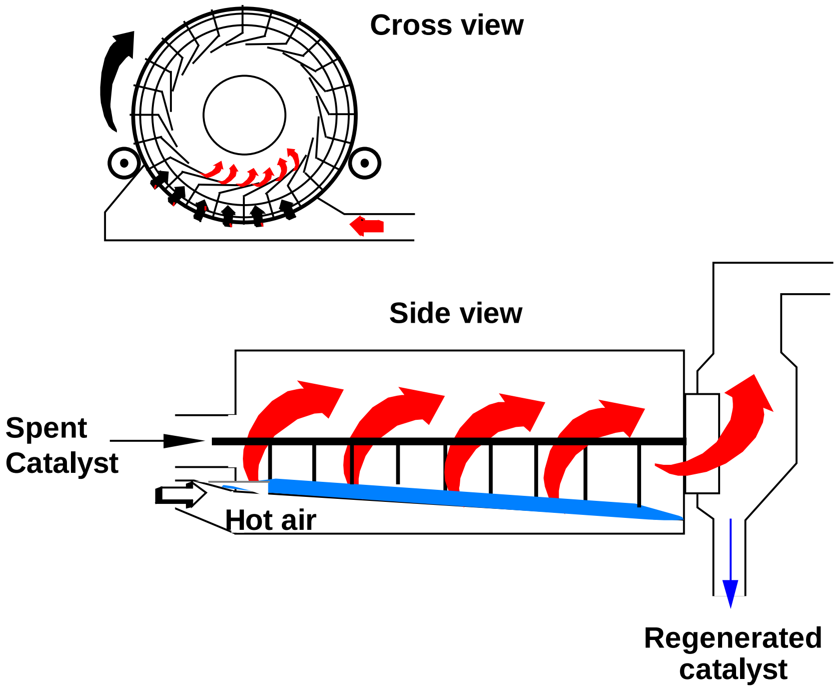


Figure 3 : Side & Cross view of a roto-louvre oven

Catalyst quality and *performance tests* are a critical part of all regeneration jobs performed by Eurecat in order to assess the regenerability or interest for reuse of a given lot of spent catalyst, and to ensure optimal quality control during the industrial process.

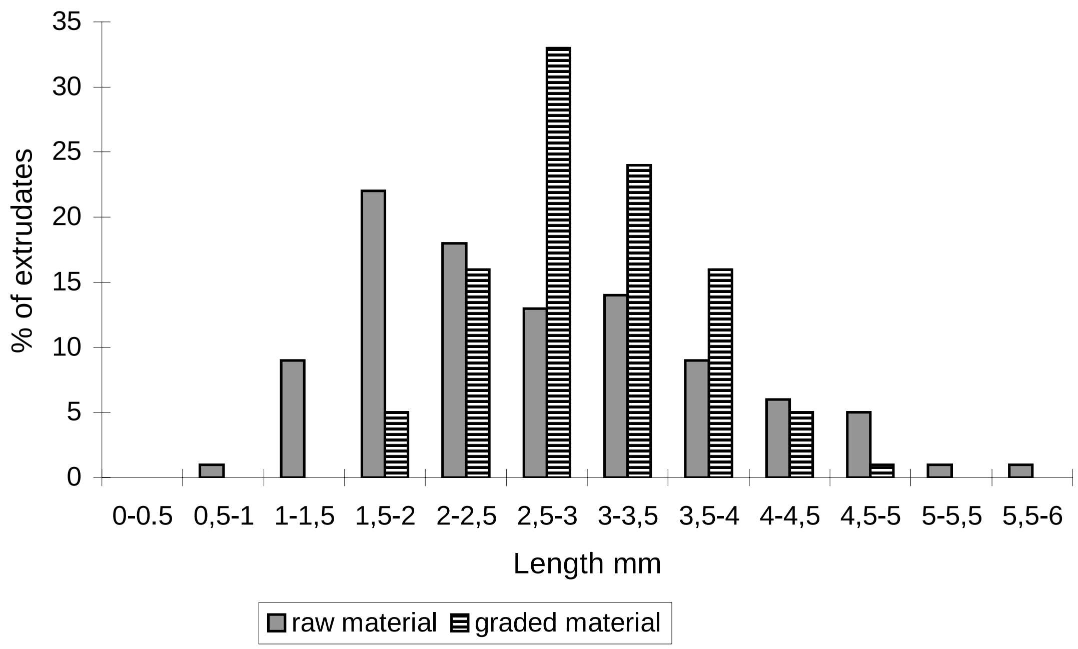
First, physical properties of the catalyst, such as mechanical strength (BCS or SPCS) and length distribution must be monitored. Comparing the surface area of the regenerated catalyst to that of the fresh catalyst provides an excellent indication of the catalyst's quality. Carbon and sulfur analyses are also key factors and elemental metal analyses are necessary to identify metal contamination. The presence of metal contamination is not always linked with a loss in surface area.

Dynamic Oxygen Chemisorption (DOC) is a good complementary tool to evaluate active phase sintering for some special catalysts. Sensitivity to metal poisoning and the difficult analytical techniques involved in the DOC procedure require careful interpretation of the DOC test results.

The most reliable tool to evaluate the global performance of a hydroprocessing catalyst is clearly an activity test, and Eurecat has various equipment for that purpose.

Catalyst Physical Separation

Various *grading or physical separation equipment* are used by Eurecat to address all kinds of individual needs or situations : length grading, separation of components from catalyst mixtures, separation of ceramic balls of various sizes, etc. An example of *length grading* is shown in *Figure 4* .



Customer requirements : - average length > 2.6 mm
- extrudates < 2 mm less than 10%

Figure 4 : Particle size distribution : raw and graded material

Presulfiding and other Preconditioning

In order to be "active", all hydroprocessing catalysts containing molybdenum, nickel or cobalt must be sulfided. Thus, the metal oxides must be converted to the sulfided form.

Ten years ago, all sulfiding operations were carried out in-situ, i.e. after the fresh or regenerated catalyst had been loaded into the unit reactors. Various methods were used, the most efficient one being the use of a sulfur containing agent, such as dimethyl disulfide. Drawbacks to the in-situ method include: the handling of a toxic, environmentally unfriendly sulfur compound ; risk of non-homogeneous sulfiding; and the lost production time required for sulfiding.

Since 1986, Eurecat has pioneered the use of *Sulficat*, a new technology for off-site presulfiding (or presulfurization) of hydroprocessing and other catalysts. It provides the refiner with a stable non-toxic catalyst, homogeneously presulfided with each catalyst grain containing the correct amount of sulfur. This technique simplifies of the unit start-up procedure and reduces start-up time considerably.

Innovation by Eurecat continues to take place with the introduction of *Totsucat*, a technology designed to provide complete catalyst activation off-site and to skin-passivate the catalyst as needed to allow its safe handling. As a result, the catalyst will be ready for use, and the start-up procedure will be reduced to a bare minimum, i.e., the heating of the unit to oil-in temperature.

Other preconditioning processes have been developed by Eurecat, that provide oil refiners and petrochemical plants some new options for the utilization of their catalysts, as shown on *Table 1.*

Table 1: Preconditioning Processes

Active Catalyst Phase	Application	Sulfiding	Reduction/ Sulfiding	Reduction	Chlorination
CoMo, NiMo	Hydrotreating	XX			
NiW	Hydrotreating	XX			
NiMo (CoMo) zeolite	Hydrocracking	XX			
NiW zeolite	Hydrocracking	XX			
Nickel	Hydrogenation		XX	XX	
Palladium	Hydrogenation			XX	
Platinum	Hydrogenation			XX	XX
Platinum	C_5-C_6 isom			XX	XX
Platinum	Reforming		XX	XX	XX
Custom catalysts	Various	XX	XX	XX	XX

Eurecat is practicing commercially an off-site chlorination procedure (*Chloricat*), as part of a complete off-site regeneration procedure developed for platinum-based reforming catalysts. Excellent results are achieved in terms of platinum dispersion, as shown in *Table 2*.

Table 2: Platinum Dispersion of a Pt/Sn Reforming Catalyst

Catalyst	Fresh	In Operation	Spent	Chloricat Regenerated
Pt dispersion, %	91	100	47	97

Catalyst Resale

Each individual refinery or unit determines its catalyst requirements and the most economical way to achieve them. As a consequence, refiners have from time to time surplus amounts of regenerable catalyst. Eurecat, through a catalyst resale program, assists refiners in finding an outlet for their material, and acts as a source point for those seeking to employ available regenerated catalyst.

Recycling

Although landfilling is still widely practiced, increasingly restrictive environmental regulations regarding hazardous wastes and risks of future liabilities are inducing most refiners to turn to more environmentally sound options.

The non-availability of a “universal” recycling company, capable of handling all types of spent catalysts found in refineries and petrochemical plants, makes it sometimes difficult for the user to find the appropriate outlet for the spent materials. In addition, legislation and transportation regulations often vary between geographical regions and countries. The presence of many brokers or other intermediators does not always guarantee a safe and environmentally acceptable recycling process. Many plants prefer to deal with a well established company such as Eurecat which has, over the years, developed its own hydrometallurgical process, a unique expertise and a network of partner companies to assist the user in finding the optimal recycling solutions appropriate to his need.

Noble metal catalysts containing platinum (Pt) or paladium (Pd) are sent to specialized metal reclamation companies. For spent hydroprocessing catalysts, pyrometallurgy or a combination of hydrometallurgy and pyrometallurgy are available options.

Transportation and storage

Regenerated catalyst can be transported or stored by means identical to those used for fresh catalyst, typically in drums, bins or bags.

Same as presulfided catalysts, spent catalysts are normally classified as self-heating substances ; therefore, drums or bins are required. Other national or regional restrictions for shipping may apply in various parts of the world.

Specialized bins from rental companies are now available, which provide a safe and efficient means to transport spent, regenerated, and presulfided catalyst. This mode of transportation is particularly attractive for turnaround operation, since the number of rental days is limited. In other cases, the cost of rental for a long period may be uneconomical.

IV ON SITE CATALYST SERVICES

During unit turnaround, catalyst handling takes place, together with various inspection, maintenance or other activities.

Such operations are very critical for the plant operators, in terms of quality of the work performed (unit performance after start-up), expenses (respect of the budget) and planning (respect of the schedule).

Following is a description of some of the critical services which can be outsourced by the refineries or petrochemical plants during their turnaround operations.

Sampling

Before unloading the catalyst from the reactor, it is possible to take samples with the *Probacat* technology offered by Petroval. It can be used to either determine a metals contamination vertical profile, or to identify preferential paths within the reactor bed.

Unloading

Spent catalysts due for unloading from a reactor are most of the time highly reactive materials, owing to their sulfided form. As such, they can react spontaneously when exposed to oxygen or air and require special handling, storage and transportation procedures. The presence of pyrophoric iron sulfide in spent catalyst, compounds the problem even more.

Various precautions, including unloading under inert atmosphere, either by gravity or by vacuum, are recommended by specialized handling service companies for safety reasons. Catalyst passivation methods also exist to render the spent catalyst less hazardous, but they exhibit various degrees of success.

Depending on the shutdown procedure used, the quantity of hydrocarbons adsorbed in the spent catalyst porosity may vary considerably. A film of hydrocarbons makes the catalyst less sensitive to oxidation, but this requires an additional stripping step prior to regeneration.

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. *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.

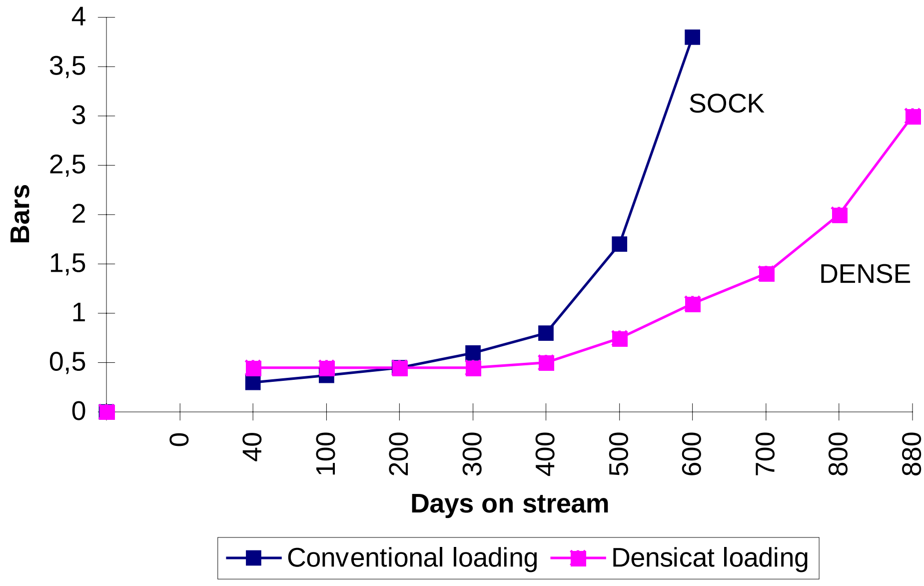


Figure 5 : Typical Pressure Drop Variation

Reactor Expertise

The best way that the plant's maintenance or shutdown crew has to insure that all catalyst and mechanical operations are successfully done with a quality work is to have an expert « right arm », independent from the contractor(s) who do the job. Such unique « reactor expertise » service, aiming at continuously monitoring the progress of the shutdown activities and the quality of the performed work, is offered by Petroval. To-date, it has been very effective at obtaining successful turnaround operations for different oil companies all around the world.

V THE CRITICAL ROLE OF CATALYST SERVICES

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*.

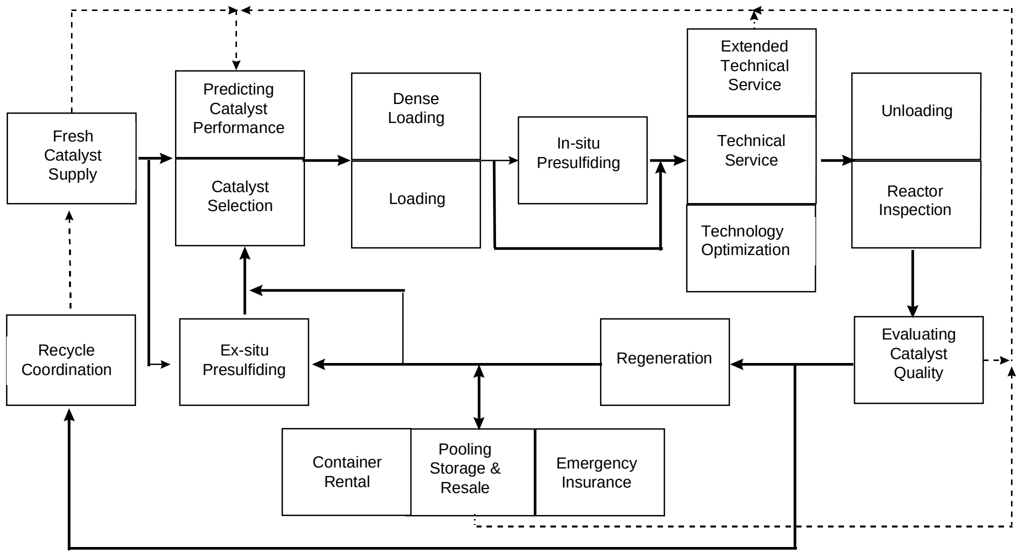


Figure 6 : Catalyst Life Cycle

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.*

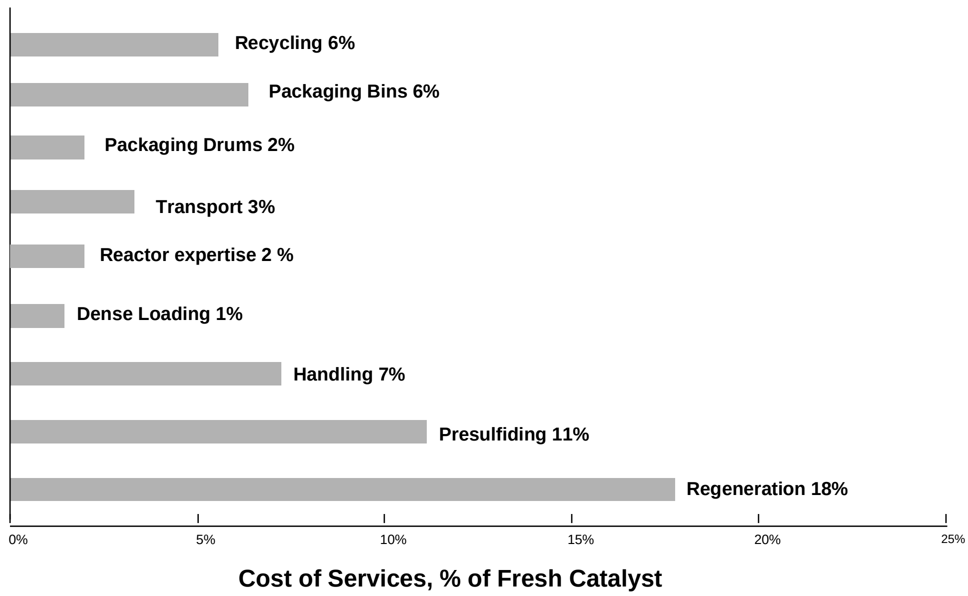


Figure 7 : Cost of off-site services vs fresh catalyst

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, as shown in *Figure 8.*

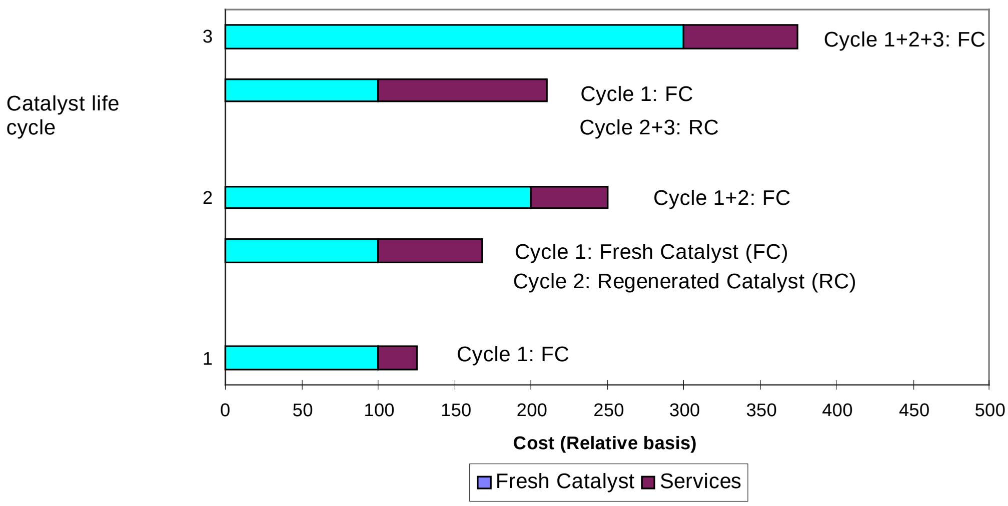


Figure 8 : Fresh Catalyst and Services Costs

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.

In addition to providing such services, companies like Eurecat are now involved in partnerships with refiners who are implementing a catalyst management program to satisfy their particular needs, with emphasis on product tracing and performance control. This offers operating companies access to minimized overall operating expenses and maximized profitability from their units.