MINIMIZING CATALYST COSTS BY SOUND CATALYST MANAGEMENT

Francis Valeri, Frédéric Girardier
Eurecat SA - La Voulte-sur-Rhône - France

Dr. Saleh Abotteen
Al-Bilad Catalyst Co. - Jubail - Saudi Arabia

ABSTRACT

Specialized companies are now available to provide services to oil refineries and petrochemical plants, in relation to their catalyst operations, such as off-site regeneration, off-site presulfiding or other catalyst preconditioning, handling and recycling services.

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 those catalyst services, together with the various options now offered to the refiner to manage its catalytic units. Various scenarios are described, applicable either to a simple refinery scheme, or to a more complex multi-sites and/or multi-units operation.

Each operator can now adapt the various catalyst management options to its particular needs, in order to minimize catalyst costs and maximize units profitability.

An active partnership with a local specialized service company is a key element to ensure maximum success of such programs.

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.

1. 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 :

1.1. 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.

Deactivation is due to three main causes: carbon (or coke) laydown, active phase sintering, and metal poisoning. During off-site regeneration, good success is achieved with carbon elimination as well as active phase redispersion.

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.

The detrimental effects of coke are a reduction of support porosity, leading to diffusional limitations, and blocked access to active sites.

1.2. Metal contamination

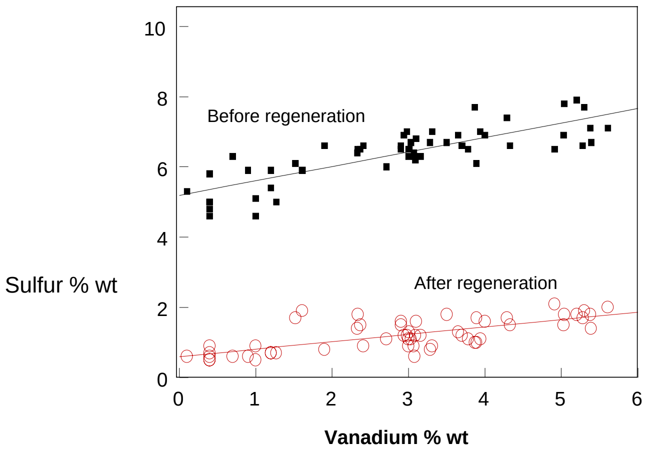
Metal contamination by nickel or vanadium is observed in units running with feedstocks such as VGO, atmospheric resids, or vacuum resids. The V :Ni weight ratio depends on the type of crude, and is usually in the range of 2:1 to 4:1. As nickel is not a poison for catalyst activity, being itself an active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

We observe a 0.41 slope relating sulfur content to vanadium, for spent catalyst, whereas 0.94 corresponds to stoichiometry for vanadium sulfide V_2S_3. After regeneration, a 0.21 slope is observed, significantly lower than the 0.63 ratio for vanadyl sulfate $VOSO_4$. This shows that vanadium is probably present in the regenerated catalyst as vanadium oxide, and that the remaining sulfur is present as aluminium sulfate.

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 and silica 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.

2. 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.

2.1 Regeneration

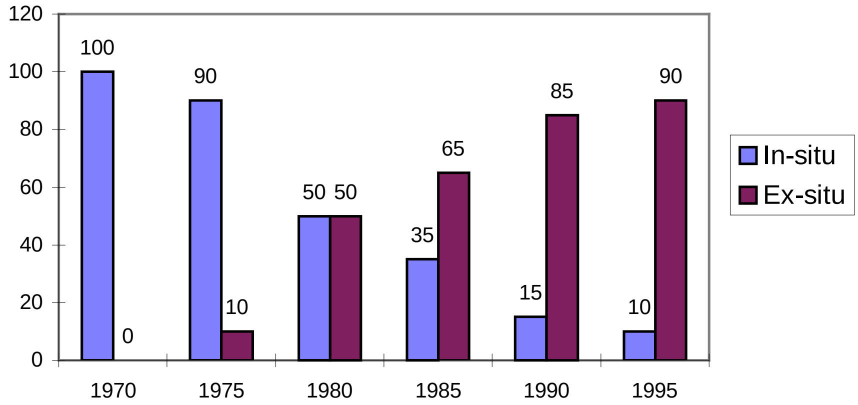
Until the mid 1970s, all regenerations were conducted in-situ in the unit reactors, but off-site regeneration has gradually become the industry standard in the western world, as illustrated in *Figure 2.* The other parts of the world are rapidly increasing their use of off-site regeneration services.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

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 (Bulk Crushing Strength or Side Crushing Strength), average length 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.

Figure 2

Trends in Off-Site Regeneration in Europe



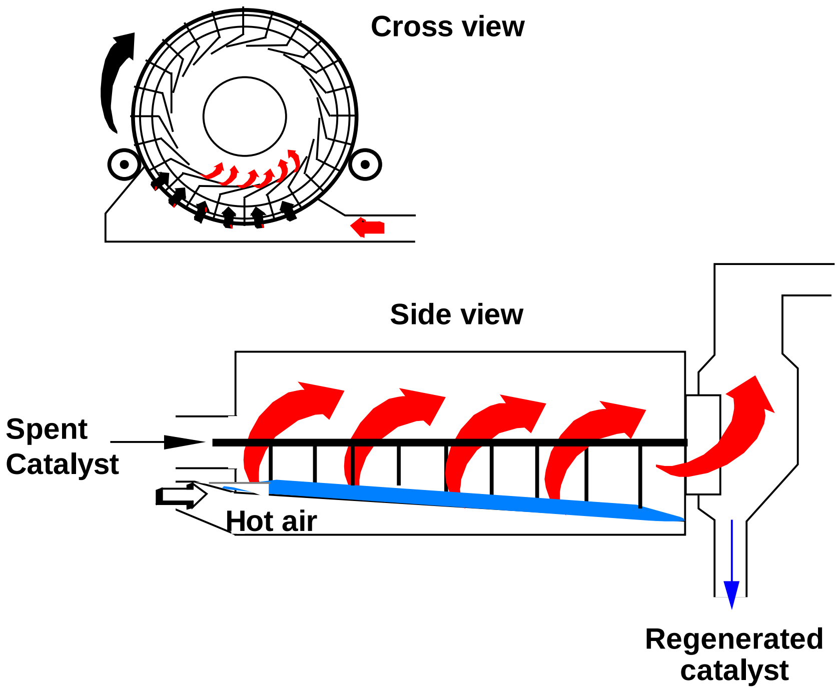
Dynamic Oxygen Chemisorption (DOC) is a good complementary tool to evaluate active phase sintering for some special catalysts. Sensitivity to metal poisoning and the difficult analytical techniques involved in the DOC procedure require careful interpretation of the DOC test results.

The most reliable tool to evaluate the global performance of a hydroprocessing catalyst is clearly an activity test.

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



2.2. Catalyst Physical Separation

Various *grading or physical separation equipment* are required 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. Quite often, grading requirements are connected with an off-site regeneration.

2.3. 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, our company has pioneered the use of a new technology for off-site presulfiding (or presulfurization) of hydroprocessing and other catalysts followed more recently by other companies. 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 continues to take place with the introduction of technologies designed to provide complete catalyst activation off-site and to skin-passivate the catalyst 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, 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

2.4. 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.

2.5. Catalyst Handling

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.

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. *Dense-loading* techniques are very popular to achieve an improved catalyst orientation and uniform void spacing and maximize bed density.

Supervision of the catalyst unloading and loading by a competent expert company provides additional help or insurance for the plant operator : it mainly aims at having a permanent “process” look, in addition to the conventional shutdown maintenance activities.

2.6. Recycling

Various possibilities are offered to refineries and petrochemical plants to dispose of their spent catalysts, depending on factors such as catalyst type and contaminant metals.

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 catalysts or other 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 well established companies who can provide 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 platinium (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. Although landfilling is still widely practiced, increasingly restrictive environmental regulations regarding hazardous wastes and risks of future liabilities are inducing most refiners turn to more environmentally sound options.

2.7. 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.

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.

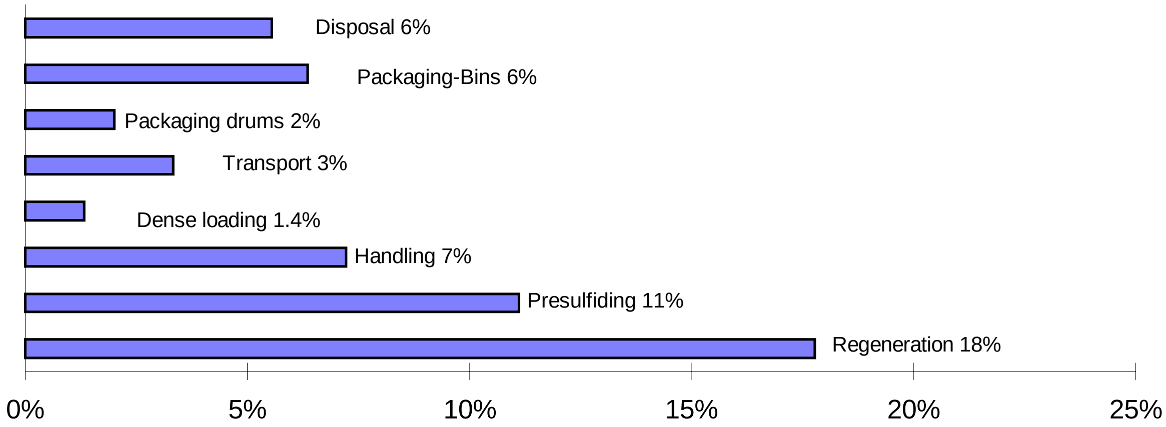
3. ECONOMICS OF CATALYST SERVICES

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.

Typical costs associated with some off-site services, relative to the cost of fresh catalyst, for a GO-HDS unit are given in *Figure 4.* 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.

Figure 4

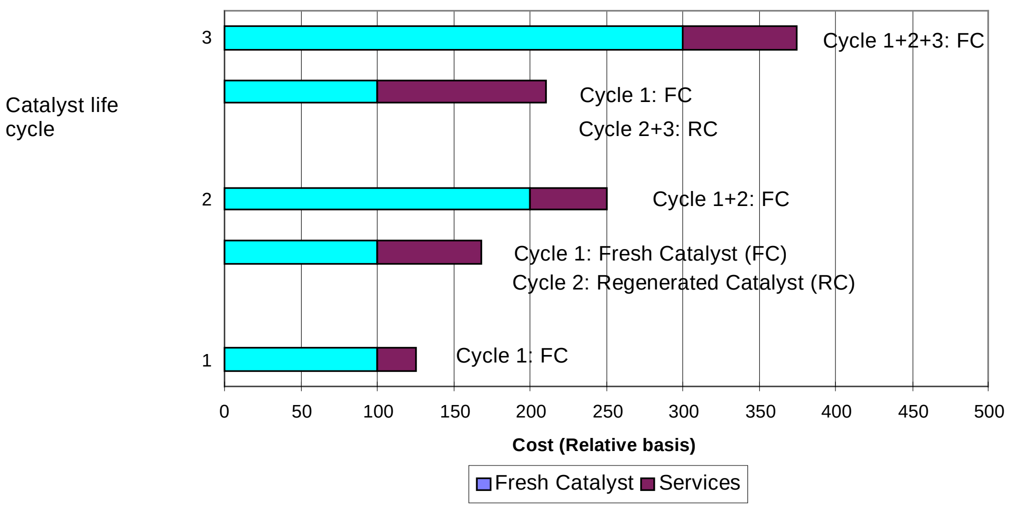
COST OF OFF-SITE SERVICES VS FRESH CATALYST



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 *Figure5.*

Figure 5

Fresh Catalyst and Services Costs



4. CATALYST MANAGEMENT

Total Catalyst Management can be defined as the actions taken to control all events involving the catalyst during its service life, from purchase of the fresh catalyst to its disposal in an environmentally sound way.

As indicated previously, the use of various catalyst services are now an integral part of catalyst management. We would like to describe here different particular cases :

4.1. Single refinery operation

Although having ensured the best activity recovery through ex-situ regeneration, the refiners requirements may be such that even after only one cycle, it is not possible to reuse the catalyst in the same service. This is typically the case for very high severity units, or units of strategic importance. The refiner then faces various options depending on the refinery lay out:

- multi-application cascading,
- single application cascading,
- resale.

4.1.1. Multi-application cascading

If not reusable in the original unit, catalyst might still be suitable in less severe applications. Typically cascading could be gasoil hydrotreater ⇒ naphta hydrotreater ⇒ kerosene hydrotreater. This type of cascading, although useful, does however have some limitations :

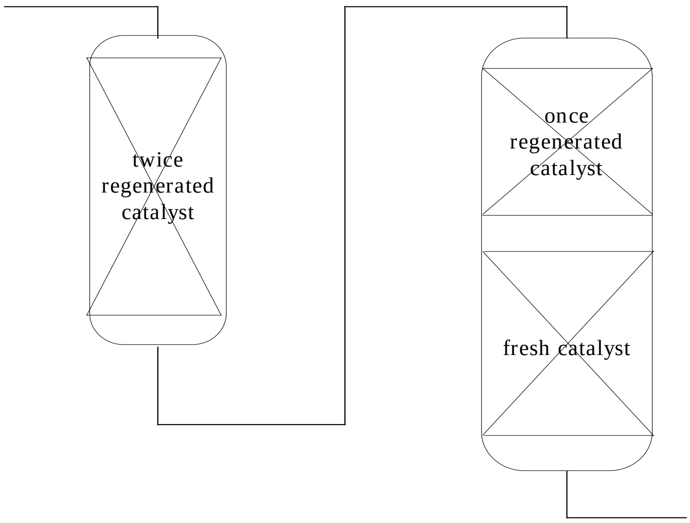
- type of catalyst may differ for different units (CoMo for gasoil HDS/NiMo for naphta).
- larger inventories for severe applications (e.g. gasoil HDS), and longer cycle length on other units (e.g. naphta), may quickly lead an unbalance between supply and demand for regenerated catalyst.

4.1.2. Catalyst shifting

Units built to meet the low sulfhur requirements are very often large multi-bed reactors, or even multi-reactor systems (typically a small guard reactor and a larger vessel downstream). VGO hydrotreaters are also often multi-reactor units. In these cases, it is often possible to shift a regenerated catalyst upstream (from the main vessel to the guard reactor for example).

This solution is to be considered especially when metals poisoning, even at low levels, is the reason for catalyst deactivation. Using a regenerated catalyst upstream will provide sufficient HDS/HDN activity whilst not sacrificing the fresh catalyst to metals poisoning. Shorter cycle length of the guard reactor compared to the downstream reactor will often allow use of most of the regenerated catalyst, as shown on *Figure 6.*

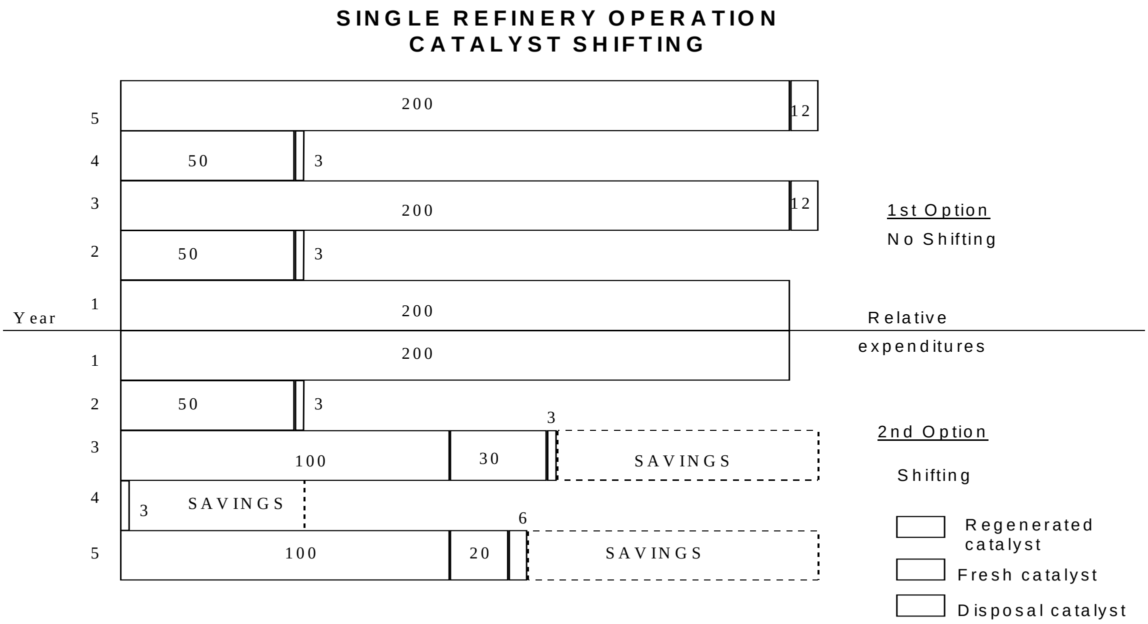
Figure 6. Catalyst shifting



Protection of the HDS/HDN catalyst will be improved by using a demetallisation catalyst as top layer. These top layer demetallisation catalysts are usually not regenerable.

Figure 7 illustrates, as an example, the economical benefits of the above described operation, resulting in a 30% savings over a 5-year period.

Figure 7.



Since metals poisoning is a concern, special attention needs to be given to the analyses performed before and after regeneration. If metal breakthrough is suspected, segregation of the potentially contaminated area may be possible during unloading (e.g. by vacuum unloading). Regeneration companies, through their analytical capabilities and experience will be able to advise when reusability of any given batch is questioned.

4.1.3. Catalyst resale

If not reusable internally, or not needed in the short/medium term by the refiner, catalyst might be of a sufficient quality for another refiner's requirements, and resale is an option. This requires close collaboration between the refiner and the service company. The catalyst needs to be to fully characterised, those parts which are not reusable need to be segregated, and the quality catalyst proposed to the market (world-wide).

4.2. Multi-refinery operation

To reduce downtime to a minimum, allow stricter control of both fresh and regenerated catalyst quality, and also protect against emergency catalyst requirements, spare batch operation is becoming the norm. As a result larger and larger catalyst inventories are observed.

To reduce total cost, companies which operate several refineries in a specific geographical zone, are looking increasingly at setting-up pools of catalyst, dedicated to a specific application. This is being done in close collaboration with catalyst manufacturers and service companies such as Eurecat.

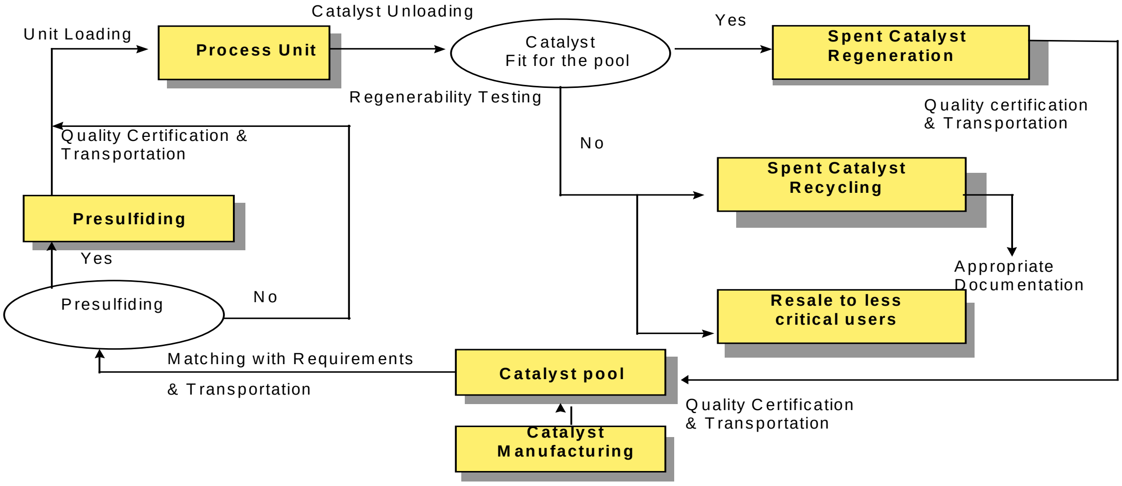
The key element for a pool of catalyst is to have, at any time, a batch of quality catalyst ready for use. The size of this batch is typically equivalent to the capacity of the largest unit in the pool.

4.2.1. Pool operation

A catalyst pool, consisting of regenerated and fresh catalysts, which can be used by any of the hydroprocessing units which are part of this program. Any catalyst lot which is part of the pool can be subject to various services, contracted by the client company.

Figure 8

Catalyst Life Cycle



Obviously, operation of such a pool requires a full partnership between the refiner and the service company, initially to set up the quality requirements for the catalyst, and then at each step of the decision-making cycle. Collaboration is also necessary to decide how catalyst rejected from the pool can best be used: cascading, shifting, resale, or disposal.

4.2.2. Pool quality requirements

For the pool to function effectively the refiners must be sure that the catalyst will have the required activity. It is therefore vital to have only top quality catalyst, and to quantify this.

A means of quantifying and/or testing activity is necessary, both to determine whether catalyst is regenerable or not prior to regeneration, and also to determine whether catalyst is acceptable for the pool.

But other parameters are also critical in order to establish the quality of the catalyst, such as the average length. Large units are particularly sensitive to pressure drop, and catalyst particle length distribution must be studied closely before reloading any given batch. In many cases length grading will be necessary in order to obtain an acceptable product.

4.2.3. Pool management requirements

Pool management requires a designated catalyst co-ordinator within the group, responsible for:

- incorporation (or rejection) of a regenerated catalyst into the pool,
- catalyst mixing from various batches of regenerated and fresh catalyst to meet the end users' requirements,
- dispatching of given batch to the end users.

End users requirements need to be clearly stated as far as batch size, activity and cycle length are concerned.

The service company will support the pool manager with analysis of each batch and keeping an up-to-date inventory available, but cannot replace him for key decisions concerning reuse of catalyst.

In total, many services are provided by the service company, such as :

- catalyst quality/performance tests,
- regeneration,
- presulfiding or other preconditioning processes,
- catalyst grading/separation
- resale,
- spent catalyst recycling (possibly through an external partnership),
- handling/reactor loading expertise (possibly through an external partnership)
- logistics,
- segregated storage,
- metallic containers/bins rental.

4.2.4. Economical incentives of pool management

Implementation of a pool of catalyst presents various economical incentives, besides improving the overall catalyst quality, which alone would justify its existence:

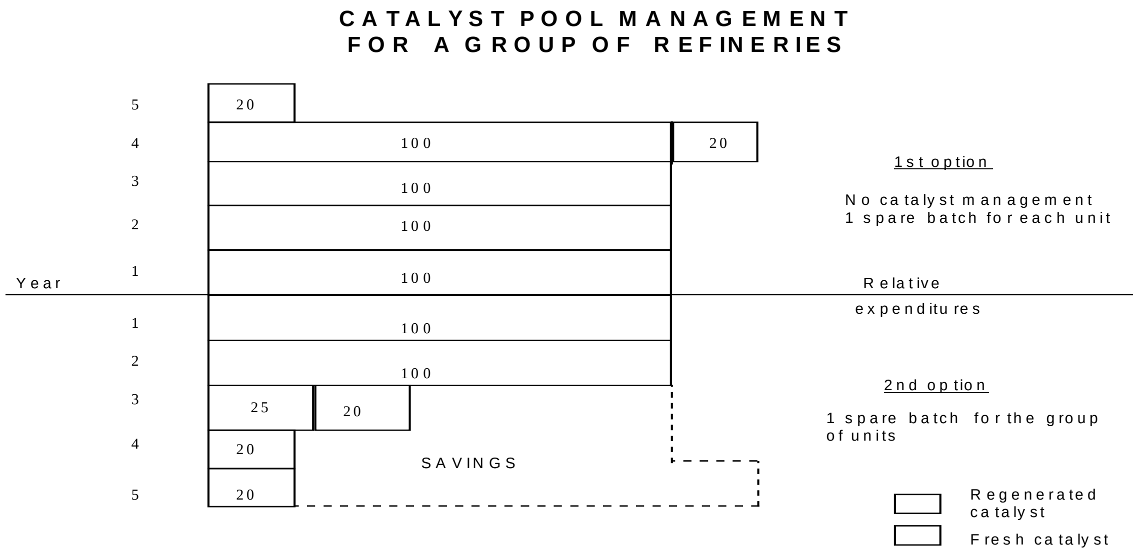
- The existence of a spare charge guarantees that unit shutdown will be limited to the strict minimum (catalyst handling and unit inspection if required).

- Accurate planning of expected cycle length is possible through catalyst quality controls : in fact, catalyst quality and performance is known and certified at key steps of its life cycle.

- One spare charge is necessary for the whole group, instead of one per unit/refinery, substantially reducing the catalyst inventory, and therefore overall catalyst expenditures.

As an example, Figure 9 describes the economical benefits of a catalyst pool operation. In this case a 35% savings is achieved over a 5-year.

Figure 9.



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.

Figure 1

Vanadium & Sulfur content on Catalyst

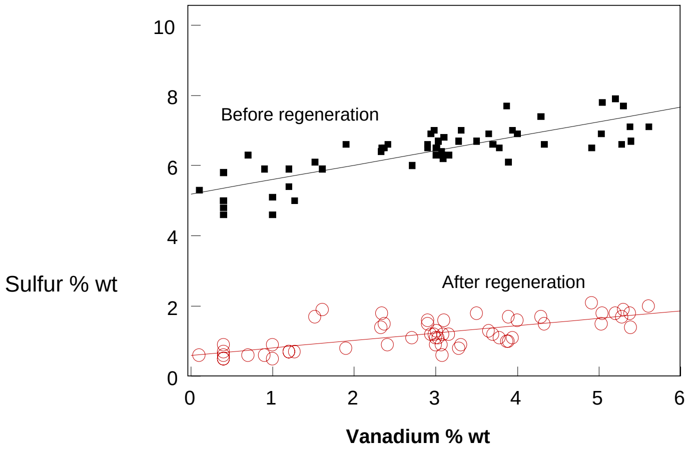


Figure 2

Trends in Off-Site Regeneration in Europe

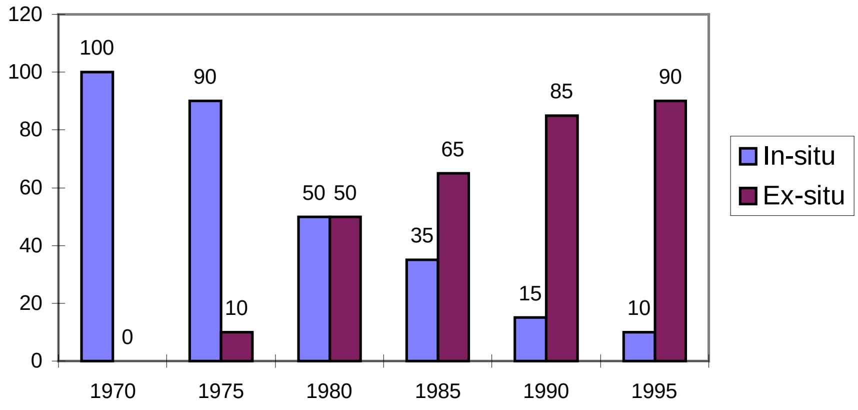


Figure 3

Side & Cross view of a roto-louvre oven

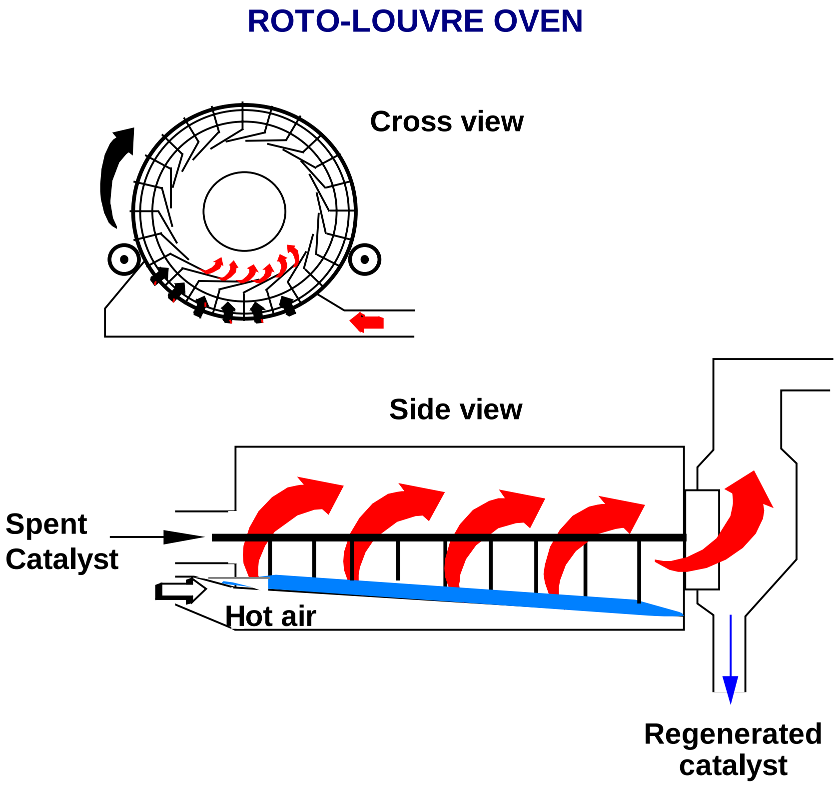


Figure 4

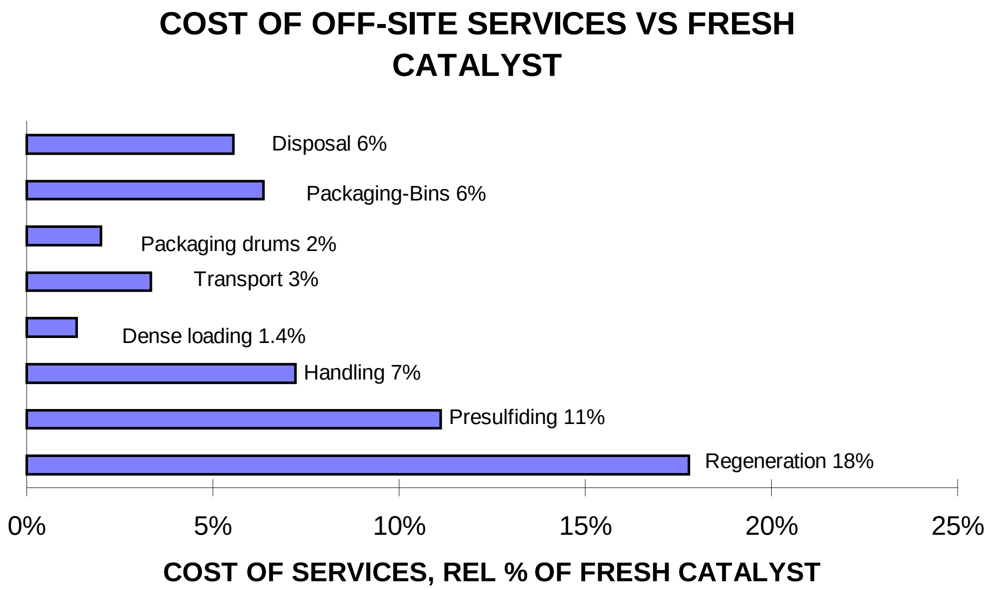

COST OF OFF-SITE SERVICES VS FRESH CATALYST
Disposal 6%
Packaging-Bins 6%
Packaging drums 2%
Transport 3%
Dense loading 1.4%
Handling 7%
Presulfiding 11%
Regeneration 18%
0%
5%
10%
15%
20%
25%
COST OF SERVICES, REL % OF FRESH CATALYST

Figure 5
Fresh Catalyst and Services Costs

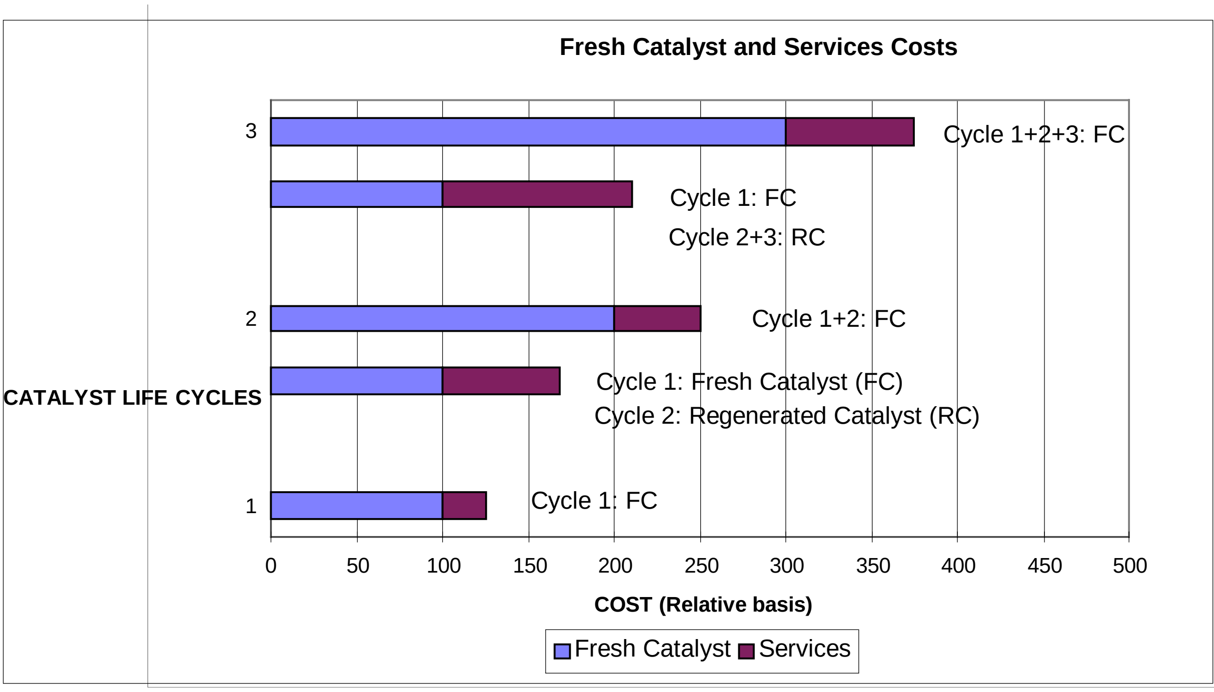


Figure 6

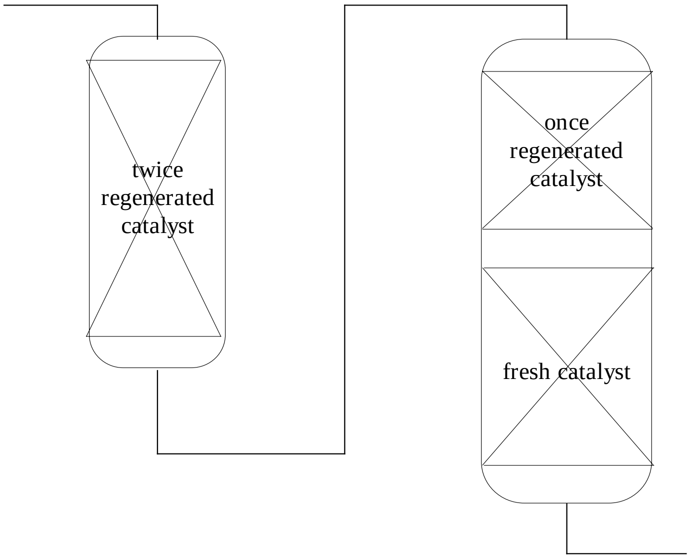

twice regenerated catalyst
once regenerated catalyst
fresh catalyst

Figure 7

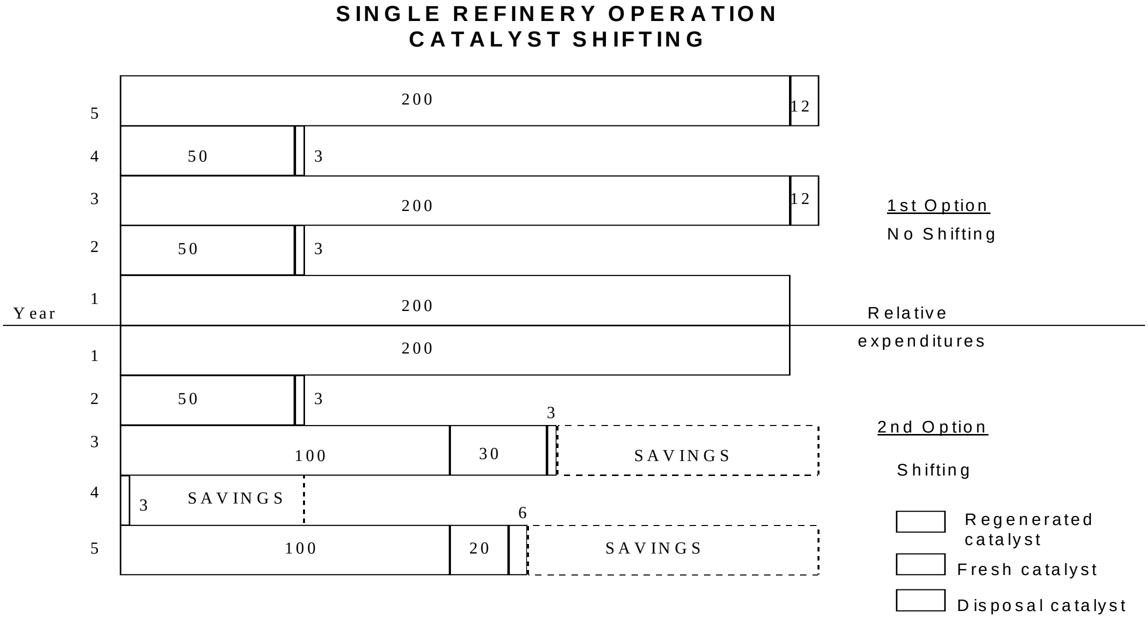

SINGLE REFINERY OPERATION
CATALYST SHIFTING
200
12
50
3
200
12
50
3
200
200
50
3
100
30
3
SAVINGS
3
SAVINGS
100
20
6
SAVINGS
5
4
3
2
1
Year
1
2
3
4
5
1st Option
No Shifting
Relative
expenditures
2nd Option
Shifting
Regenerated catalyst
Fresh catalyst
Disposal catalyst

Figure 8
Catalyst Life Cycle

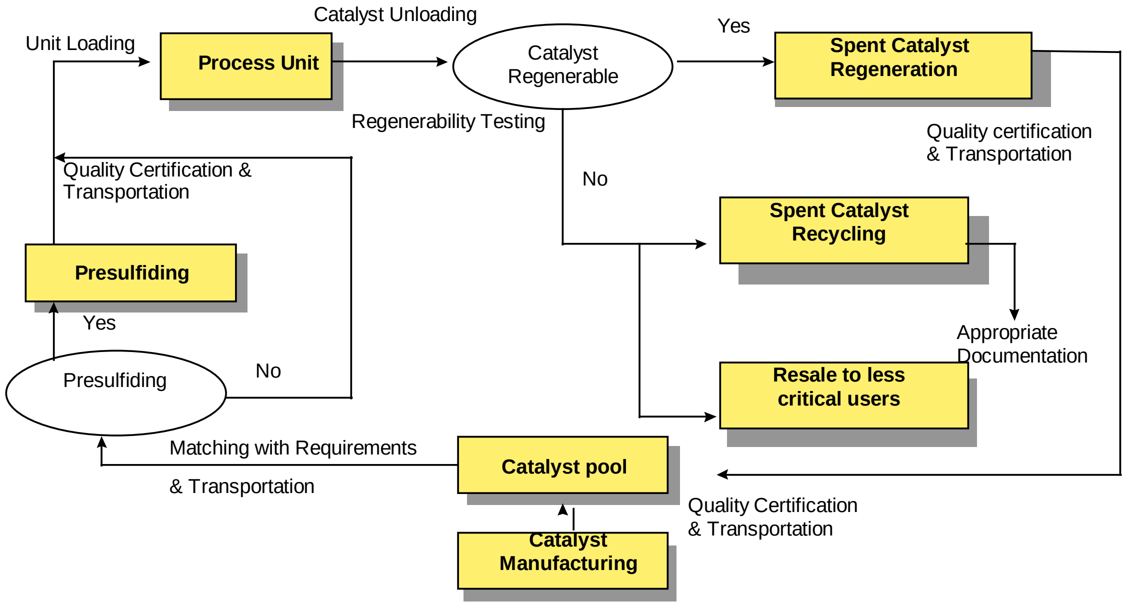
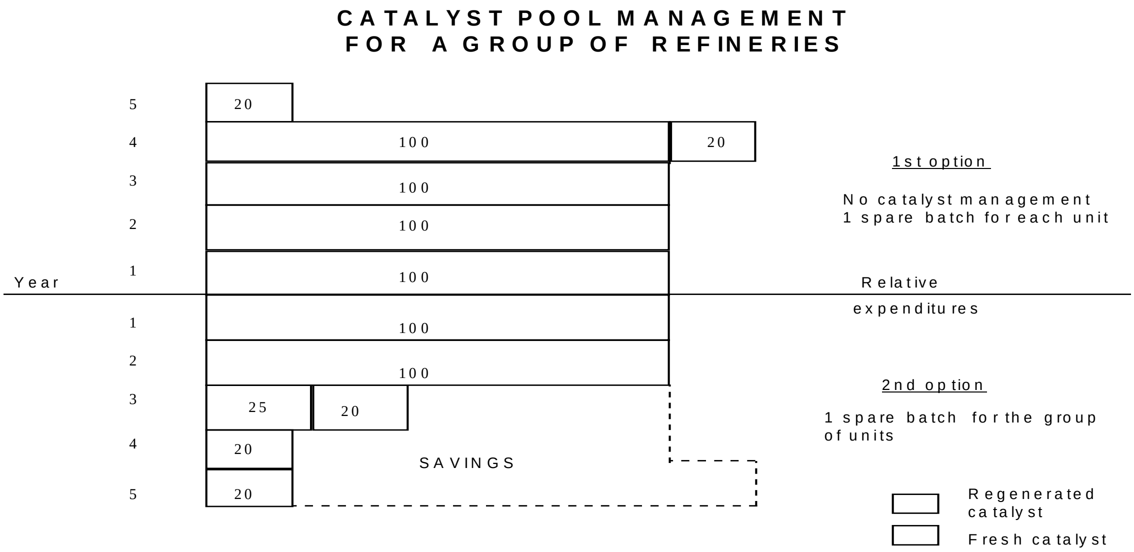


Figure 9


CATALYST POOL MANAGEMENT
FOR A GROUP OF REFINERIES
5
20
4
100
20
1st option
3
100
No catalyst management
1 spare batch for each unit
2
100
Year
1
100
Relative
expenditures
1
100
2
100
2nd option
3
25
20
1 spare batch for the group of units
4
20
SAVINGS
5
20
Regenerated catalyst
Fresh catalyst