

REACTOR MANAGEMENT SERVICES :

EXPERIENCES IN THE PETROCHEMICAL, CHEMICAL & REFINING INDUSTRIES

By :

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INTRODUCTION

During the last decade, the petrochemical and refining industries have faced new economical, technical and environmental constraints. In order to survive, most of the plants had to find solutions to improve their competitiveness and profitability, as for example in the case of new gasoline and diesel specifications.

It has now become very important for the plant operators to maximize the performance of the catalysts in use and to maintain as long as possible those reactors in operation. Also, any reduction of the shutdown duration and costs is highly desirable.

This paper presents the Reactor Management Services (RMS) concept that Eurecat and Petroval have developed together, combining both off-site and on-site services and technologies, in order to match the new needs of those industries. Some examples are described in order to illustrate the concept and highlight its advantages/benefits.

OFF-SITE SERVICES

Off-site services and expertise are offered by Eurecat all around the world, and include:

- Regeneration:
 - Transition metals (CoMo, NiMo, NiW, Ni, Cu, Fe,...) containing catalysts
 - Noble metals (Pt, Pd,...) containing catalysts
 - Zeolites, Aluminas & Molecular Sieves
 - Customized treatments

- Reactivation:
 - Selective hydrogenation Pd containing catalysts – **New**
 - Hydrogenation Ni and Pd containing catalysts – **New**

- Regeneration (coke removal and platinum redispersion) of naphtha reforming catalysts
- Regeneration of isomerization catalysts
- (Chemical) regeneration of ion exchange resin catalysts – **New**
 - Etherification (MTBE/ETBE/TAME)
 - Esterification
 - Phenol alkylation & purification
- Presulfiding of hydroprocessing (CoMo/NiMo/NiW) catalysts
 - Sulficat[®]
 - Totsucat[®] - **New**
- Preconditioning:
 - Reducat[®] (reduction)
 - Chloricat[®] (oxy- and hydro-chlorination)
 - (Pre)reduction & (pre)sulfiding of pygas selective hydrogenation catalysts, including the Resucat[®] technology
 - Selectivation
 - Customised treatments
- Resale of second hand catalysts:
 - Hydroprocessing (CoMo/NiMo/NiW) catalysts
 - Specialty catalysts
 - Molecular sieves
- Recycling of spent non reusable catalysts, zeolites, aluminas, molecular sieves, activated carbons and metal containing sludges.
- Carbon burn-off of noble containing catalysts.
- Associated services:
 - Advice on classification, packaging, labeling and transport document preparation
 - Packaging (UN drums supply and UN metallic container rental)
 - Transportation
 - Catalyst evaluation: characterization, laboratory regenerability or reactivation studies, activity tests, self-heating tests, length grading, density grading and catalyst segregation,...
 - Technical assistance for (pre)sulfided and preconditioned catalyst start-up: start-up procedure review, guidelines for safe and optimum start-up, on-site presence during start-up, storage
 - Catalyst pool management.

ON-SITE SERVICES

Petroval's **on-site** services and expertise are both catalyst and reactor orientated. They are carried out by professional technicians in order to ensure the highest possible quality standard, and they can be summarized as follows:

- Catalyst sampling in reactor beds by Probacat[®] process
- Fixed bed reactor catalyst loading:
 - Inert loading
 - Sock loading
 - Dense loading: Densicat[®], the most successful and widely used technology in the industry; Catapac[®], the IFP technology now available to Petroval - **New**
- Loading of primary reformer tubes – Norsk Hydro's Unidense[®] process
- Reactor expertise, including auditor supervision activities such as:
 - (a) Visual inspection of the top reactor section before catalyst unloading (cleanliness of the distributor plates, presence of gaskets and proper fasteners, functionality of liquid holes and overflows, levelness of distributor trays,...)
 - (b) Visual inspection of the top bed catalyst before unloading (disturbance of the catalyst bed surface, fouling of the top layer, deposits in the baskets, levelness of the baskets, slump of catalyst bed,...)
 - (c) Control and optimization of the unloading procedure to minimize catalyst breakage (granulometric analysis, determination of particle length distribution,...)
 - (d) Control of the reactor internals before catalyst loading (collectors, quenches, distributor trays, baskets, grids, splash trays,...)
 - (e) Inert ceramic balls and catalyst loading (expected loading density measurement, loading procedure preparation, control and optimization,...)
 - (f) Data collection from inside reactor
 - (g) Reporting of the full operation

REACTOR MANAGEMENT SERVICES

The Eurecat and Petroval's Reactor Management Services (RMS) concept is unique. It consists in offering to any catalyst user both **off-site** and **on-site** services and catalyst and reactor expertise during any shutdown/turnaround operation, with the objective to guarantee:

- 1) optimum coordination
- 2) time and cost savings
- 3) quality insurance

Eurecat and Petroval are familiar with all the various disciplines needed to manage all the shutdown/turnaround operations to be carried out in the industries using catalysts. They are, without any doubt, a reliable partner to manage such operations and their services and expertise are totally integrated to match the client's needs.

All operations, from full reactor to full reactor, can be handled in such a RMS scheme.

EXAMPLES

Three examples are described below in order to illustrate how clients can benefit from the implementation of the RMS concept developed by EURECAT and PETROVAL.

Example 1: Pyrolysis gasoline unit

The pyrolysis gasoline unit consisted in 2 reactors loaded with a Ni containing catalyst (first stage) and CoMo catalyst (second stage).

For this job, a combination of unique services and technologies were used:

- Packaging rental (UN approved metallic containers)
- Sampling (Probacat[®])
- Unloading by gravity/vacuum and under inert atmosphere
- Truck loading & transport document preparation
- Transportation
- Reactor inspection
- Internals replacement
- Regeneration, (pre)reduction and (pre)sulfiding of Ni containing catalyst
- Regeneration and sulfiding (Totsucat[®]) of CoMo catalyst
- Supply of second hand CoMo (as make-up)
- Inert balls sieving and separation
- Recycling of dusts, fines and broken inert balls
- Return transportation
- Truck unloading
- Dense loading (Densicat[®])
- Co-ordination of all sub-contractants (handling company, scaffolding, crane,...)
- Video recording of all on-site activities
- Reporting of all on-site and off-site activities

Let's describe in more details some of those specific services:

(Pre)reduction and (pre)sulfiding of Ni containing catalysts

Catalyst manufacturers are developing new pygas selective hydrogenation Ni containing catalysts. In order to improve their performances compared to palladium containing catalysts, they contain more nickel. In order to avoid runaway reactions

during start-up, it is mandatory for those catalysts to be (pre)reduced and (pre)sulfided before loading. This is valid for both fresh and regenerated catalysts. The Eurecat treatment allows a quick and safe start-up of the pyrolysis gasoline hydrogenation unit. It is quite clear that this specific pretreatment must be adapted and optimized according to the catalyst type & formulation.

Totsucat[®]

Eurecat have recently introduced its new Totsucat[®] off-site **TOTAL SUL**fiding process of **CAT**alysts to the market. The sulfided catalyst is already activated and is ready for use. The treatment is applicable to all hydroprocessing catalysts whatever the application (naphtha, diesel, VGO, tail gas units, H₂ plants, petrochemical processes,...). The sulfided catalyst is self-heating (class 4.2. UN 3190) like Sulficat[®] presulfided catalyst. Totsucat[®] gives quick and simple start-up and no risk of failure.

Totsucat[®] catalyst exhibits a relative volume activity (RVA) equivalent to oxide in-situ sulfided, and better in some cases.

Resale

Eurecat markets only premium quality fresh or regenerated, or (pre)sulfided or not, hydrotreating/hydrocracking catalysts for resale. Resale catalysts are offered to refineries around the world through all the Eurecat locations (Europe, USA, Japan, Saudi Arabia). The Eurecat resale catalyst inventory is available on our website (<http://www.eurecat.fr>). For each resale catalyst, the following information are given : catalyst type, tonnage, location, packaging, chemical/physical properties,...

Densicat[®]

Petroval and licensed operators load worldwide more than 17000 metric tons of catalyst per year with the Densicat[®] dense loading process. Those loadings are made either by Petroval technicians, or by external operators fully trained and certified by Petroval.

The benefits of a good dense loading are summarized below:

- ◆ Maximum catalyst density: higher activity, longer cycle length, bed stability
- ◆ Catalyst bed homogeneity (uniform void fraction): no channeling
- ◆ Horizontal orientation of grains: better contact between reactive phases
- ◆ No significant attrition
- ◆ Typical gain in density compared to sock loading

Beads	9 to 13 %
Extrudates	15 to 20 %
Multilobes	16 to 22 %

- ◆ Parameters which affect the gain in density: shape and size of the particles, sliding friction coefficient of the particles

The benefits of the Densicat[®] process over competition are summarized as follows:

- Densicat[®] achieves THE optimum density (regardless of the characteristics of the catalyst)
- Typically density increase:
 - Densicat[®] versus Competitor 1: +1.5 % to +6 %
 - Densicat[®] versus Competitor 2: +1.5 % to +3 %
- Pressure drop: despite the slight higher density, pressure drop can be minimized thanks to better homogeneity of loading (no preferential paths)

Example 2: Front-End C₂ selective hydrogenation unit

The Front-End C₂ selective hydrogenation unit consisted in a reactor with two beds loaded with a Pd/Ag containing catalyst.

Job description:

- Packaging supply (drums)
- Unloading by gravity
- Truck loading & transport document preparation, transportation
- Reactor & internals inspection
- Catalyst reactivation
- Inert balls sieving and separation
- Recycling of dusts, fines and broken inert balls
- Return transportation, truck unloading
- Dense loading (Densicat[®])
- Reporting of all on-site and off-site activities

The benefits of the reactivation are detailed below:

Reactivation

Eurecat has developed a new regeneration process to recover high activity and selectivity of palladium containing catalyst used in Front-End C₂ selective hydrogenation. This proprietary process is called **reactivation**. This service gives better performances than the standard regeneration. For this kind of application, it is very important to maintain the clean-up temperature (T₁) as low as possible and have the largest operating window (Delta T). The clean-up temperature is the temperature needed to remove the acetylene traces while the operating window is the temperature range where there is no risk to convert ethylene to ethane and to face a runaway. In this specific case, standard regeneration at laboratory scale showed poor activity/selectivity recovery, whereas reactivation allows to reuse the catalyst with performances even better than fresh.

Fresh Pd/Ag catalyst	T_1	ΔT
Regenerated catalyst	T_1+3	$\Delta T-2$
Reactivated catalyst	T_1-8	$\Delta T+16$

(Temperatures are expressed in °F)

This new reactivation technology avoids palladium sintering and promotes some contaminants removal.

Reactivation is also applicable on low palladium containing catalysts used in Back End C₂ and Gas Phase C₃ selective hydrogenation applications and results are similar.

Example 3: Cumene/phenol plant

The cumene/phenol plant consisted in 3 reactors loaded with alkylation/transalkylation zeolite based catalyst (cumene unit) and palladium containing catalyst to hydrogenate alpha methylstyrene back to cumene (phenol unit). The plant also included two heat-exchangers which had to be cleaned up every two or three weeks due to severe fouling problems.

Job description:

- Packaging rental (UN approved metallic containers)
- Unloading by gravity and under inert atmosphere
- Truck loading & transport document preparation, transportation
- Reactor & internals inspection
- Installation of anti-fouling devices sold by Petroval (Turbotal[®])
- Regeneration of zeolite based catalyst
- Reactivation of Pd containing catalyst
- Inert balls sieving and separation
- Recycling of dusts, fines and broken inert balls
- Return transportation, truck unloading
- Dense loading (Catapac[®])
- Co-ordination of all sub-contractants (handling company, scaffolding,...)
- Reporting of all on-site and off-site activities

The most important services or technologies are described hereafter:

Reactivation

Reactivation is also applicable on high palladium contained catalyst. For such catalyst, palladium dispersion measured by dynamic chemisorption of carbon monoxide (DCOC) gives a good indication of the residual activity. On the reactivated catalyst, a DCOC value of 87% (relative to fresh catalyst) was obtained, which is better than for standard regeneration (DCOC at 74 %).

Heat exchanger inserts

Turbotal[®] devices consist of rigid helicoïdal insert elements held at the upstream end of the exchanger tubes by a system allowing their rotation around their axis under the fluid drag. This rotating movement slows down fouling and enhances heat transfer. The efficiency of this technology has been demonstrated in various services in chemical and petroleum refining industries. In some cases, the cycle length between two cleanings has been extended by a factor of 5 or more. On top of the gains resulting from fouling mitigation, Turbotal[®] provides a significant energy saving due to tube side heat transfer enhancement.

Turbotal[®] devices are easy and quick to install and do not require any specific tools. Some care has to be taken in handling the inserts, especially when removing them from the shipment boxes so as not to entangle them. This installation is typically done by the Petroval experts.

Turbotal[®] was originally developed for crude distillation preheat trains in refineries. Following the good results obtained in this field, it has been applied successfully in others services, such as :

- Coolers with scaling or brackish water
- Sugar plants with vertical tubes
- Gasolines
- Furfural, lubricants
- Hydroquinone
- Ethylbenzene
- Phenol
- Various chemicals.

In general, this technology is potentially beneficial whenever fouling takes place inside the tubes. So far, more than 450 000 devices have been installed world-wide, and Turbotal[®] inserts are currently used in 20 process units.

Spirelf[®] is similar to Turbotal[®]. However, instead to rotate, the helicoïdal wire is fixed at its two extremities and vibrates under the flow energy of the fluid. It accepts therefore higher fluid velocities. More than 150 000 devices are also installed world-wide in similar applications

Catapac[®]

Petroval is now the exclusive licensee from IFP for all Catapac[®] dense loadings.

REFERENCES

Eurecat and Petroval have already implemented the RMS concept for various clients, including Air Liquide, Agip Petroli, Atofina, Basf, Knpc, Rhodia and TotalFinaElf.

The latest shutdown / turnaround operation included 19 reactors and the replacement of approximately 650 metric tons of catalyst.

CONCLUSION

Eurecat and Petroval can be considered as a reliable partner to manage any shutdown/turnaround operation to be carried out in the petroleum refining, petrochemical and chemical industries and involving catalyst replacements.

Eurecat supplies many off-site services and is very innovative in this field, while Petroval has a lot of expertise in catalyst and reactor. Together, they have the right people and expertise to provide the necessary co-ordination of all tasks, for the preparation and for the successful execution of the work.