

# **Off Site Regeneration of UOP Ebz-500 Catalyst: Laboratory Studies and Commercial Experience**

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### **Abstract**

A batch of spent UOP EBZ-500 catalyst, originating from a European petrochemical site, has been successfully regenerated by Eurecat at its site in La Voulte, France. The catalyst was deactivated by coke as well as nearly 0.2 wt-% Nitrogen which inhibited the zeolite acidic function. The oxidative treatment completed C and N removal without any zeolite structure damage, as shown by Surface Area results.

Commercially regenerated catalyst performance in the customer unit is as good as fresh after six months of operation.

Also, mechanical strength of EBZ-500 catalyst and smoothness of the Eurecat industrial equipment avoided the formation of large quantity of fines during processing. In addition to some product fines generated during handling operations, a low 0.5 wt-% fines generation occurred during regeneration, resulting in a satisfactory final average length of the regenerated catalyst.

### **1-Production of ethyl benzene with EBZ-500 catalyst**

In the early 1990s the Lummus/UOP Liquid Phase EB process used UOC-4120 catalyst in both the alkylation and transalkylation sections. The catalyst in both reaction sections deactivated primarily by coking. A regeneration procedure was developed to remove the carbon. UOC-4120 catalyst has been successfully regenerated by both ex-situ and in-situ procedures.

In the mid-1990s UOP introduced a new generation of catalysts that offered improved stability and selectivity. EBZ-500 catalyst was developed for the alkylation reaction section. It has substantial EB yield and stability benefits compared to UOC-4120. In the transalkylation section, UOC-4120 catalyst was replaced with higher-activity EBZ-100 catalyst.

Both EBZ-500 and EBZ-100 catalysts have been successfully regenerated by in-situ and ex-situ regeneration techniques. This paper describes the Eurecat experience with ex-situ regeneration of a EBZ-500 catalyst batch used in a European petrochemical plant.

## 2-EB catalyst deactivation and regeneration

Catalysts used for refining or petrochemicals applications usually deactivate continuously throughout an operating cycle. This is due to a continuous and slow build-up of various contaminants at the catalyst surface as well as a modification of the nature of the active sites. The most common contaminants are the highly condensed hydrocarbon molecules called “coke”, formed by a series of side reactions, but in specific cases other components may come with the feed, such as Sulfur, Nitrogen or Metals containing molecules, and poison the catalyst.

Conventional regeneration typically consists of a thermal treatment conducted in oxidizing conditions, whether it is performed in the reactor or “off site”. This treatment can remove carbon deposits, as well as other types of contaminants, while metals deposited cannot typically be removed. However, to achieve satisfactory regenerated product, some specific catalysts may require more sophisticated treatments than just a simple controlled heat-up under an oxygen containing gas.

Off-site regeneration techniques have been widely accepted over the last twenty years by the petroleum refining and petrochemical industry. A majority of units have abandoned the conventional in-situ technique for a number of reasons including safety, time considerations and better activity recovery. The high quality achieved by off site regeneration often makes more than one cycle possible, depending on catalyst contamination, severity of operation and unit duty. In addition to this economical incentive for regeneration, more and more stringent environmental regulations for disposal of spent catalysts encourage their re-use.

Historically the industrial regeneration process employed by Eurecat is based on the use of the rotolouvre technology <sup>(1)</sup>. However Eurecat companies also have in their plants other hardware that can cater for different treatment techniques employed in catalyst regeneration or other conditioning <sup>(2)</sup>.

For UOP’s EB catalysts, a relatively simple oxidation treatment is adequate to remove carbon, nitrogen, and most other contaminants. Catalyst that has been poisoned by metals cannot be regenerated and must be replaced. Both ex-situ and in-situ regeneration methods successfully restore catalyst activity. It is usually site-specific situations that determine which method is used. Some of the key factors that influence this decision are:

- Capital Investment – Additional equipment must be purchased for in-situ regeneration. This equipment is used infrequently and may not be a cost-effective use of capital.
- Location of Ex-Situ Facility – Is there a regeneration facility nearby?
- Time Required – In-situ regeneration takes about two weeks. Ex-situ regeneration time depends on the time required to regenerate and transportation time to/from site. In most cases, the catalyst can be regenerated and returned to site within the turnaround schedule. If the regeneration timing is not compatible with the turnaround schedule, then a spare load of catalyst is needed.

- Catalyst Losses – Handling losses are typically 1-5%. Makeup catalyst will be required for each ex-situ regeneration. Since catalyst is not removed for the in-situ case, no make-up catalyst is required.

Most EB plant designs do not include in-situ regeneration capabilities. At the design basis phase of the project, the owners usually decide that ex-situ regeneration is the most cost-effective option for them.

### 3-Laboratory study

In November 1998, Eurecat received two samples of commercially spent EBZ-500 catalyst, one from composite of bed inlet and the other from middle of bed. Regeneration has been performed at lab scale at various temperatures in order to follow-up Carbon content and Surface Area. As shown on Table 1, the optimal temperature is a compromise between sufficient carbon elimination and the zeolite structure preservation. Temperature “T3” offers the most carbon removal while maintaining high catalyst surface area.

	Treatment Temp. (°C)	LOI @ 500°C (wt-%)	Carbon (wt-%)	Surface Area (% of base)	BCS (MPa)	Length (mm)
Bed middle	Coked	7.8	4.7			2.7
T199013	T1		0.1	100		
T199014	T2		0.1	99		
T199004	T3		0.1	99	1.4	
T199015	T4		<0.1	95		
T199016	T5		<0.1	94		

	Treatment Temp. (°C)	LOI @ 500°C (wt-%)	Carbon (wt-%)	Surface Area (% of base)	BCS (MPa)	Length (mm)
Bed inlet	Coked	11.9	7.9			2.4
T199010	T1		0.3	99		
T199011	T2		0.2	99		
T199003	T3		0.1	100	1.6	
T199012	T4		0.1	96		
T199013	T5		0.1	95		

Table 1: Characterization of spent EBZ-500 as such and after regeneration at laboratory scale at various temperatures.

### 4-Commercial experience

#### 4.1 Classification and packaging

According to European legislation, a spent catalyst is considered as hazardous when it contains more than 3-ppm benzene. The limit was 5 ppm before June 2000 and should become 1 ppm in 2003<sup>(3)</sup>. It is

the responsibility of the product owner to select its classification. The Eurecat recommendations for European Ethyl Benzene or Cumene producers are typically the following: (1) Use the most efficient stripping procedure of the catalyst bed during the shutdown procedure in order to remove all traces of benzene and thus avoid classification as dangerous goods. (2) In case of doubt, be on the safe side and classify spent EBZ-500 as dangerous product, more precisely class 6.1 65°C, danger group 60, UN number 3288, toxic inorganic solid, n.o.s. This classification results in some packaging constraints: 1 or 2 m<sup>3</sup> metallic containers cannot be used anymore (IMDG and ADR regulations limit weight of class 6.1 product to 400 kg net per container) and drums have to be UN approved. These UN approved drums are just slightly more expensive than standard drums.

#### 4.2 Regeneration at Eurecat

A batch of spent EBZ-500 catalyst was received at the Eurecat location in France from a European petrochemical site. In this particular case, the customer purchased UN approved drums. When the unloaded catalyst analysis revealed no traces of benzene, the customer decided not to classify the product as dangerous.

Upon arrival at Eurecat, product is always sampled by dedicated personnel according to a very strict procedure for making a representative sample of the lot. In this case, one sample was made per catalyst bed. The product did not need any stripping operation prior to regeneration, as the shutdown procedure was performed correctly for removing traces of light hydrocarbons. The inert balls and the particles below 1 mm are separated before the treatment.

The material was unloaded by gravity from a two-bed reactor. Table 2 shows the amount of catalyst breakage for unloading and regeneration. A surprising fact is the breakage that has been generated by this unloading operation, only 0.3 wt % for the top bed, but 4 wt-% for the bottom bed. The fines generated by the processing itself are on the low side with an average of 0.5 wt %, due to high product strength and the smooth Eurecat process.

Percent of Catalyst	Unregenerated Dust (< 1 mm)	Regenerated Catalyst	Regenerated Fines (< 1 mm)
Top Bed	0.3	99.3	0.4
Bottom Bed	4.1	95.2	0.7

Table 2: Mass balance of the commercial regeneration of the two-bed reactor of EBZ-500 catalyst unloaded from a European unit.

The analysis shown on Table 3 stresses the good quality of the material obtained after the off site regeneration, especially in terms of Surface Area recovery and average length. This catalyst is rather strong as indicated by the high Bulk Crush Strength value of 1.2 MPa.

The nitrogen content of the spent catalyst shows that in this particular case, catalyst deactivation occurred primarily from adsorption of basic species on the zeolite acidic sites. This level of nitrogen may explain why End of Run activity was reached only after one and a half years on stream. Nitrogen contamination may come from either the ethylene or benzene feedstocks. However, it is more common for the nitrogen poisons to enter with the fresh benzene. There may be several sources of nitrogen introduced from benzene feeds: amines used as corrosion inhibitors in fractionation columns, nitrogen containing compounds used as solvents for liquid extraction, or contamination of pipelines or shipping vessels used to transport benzene. Anyway the good point is that nitrogen is totally removable in these regeneration conditions.

UOP <b>EBZ-500</b> Catalyst Average top/Bottom Bed	Spent	Laboratory Regeneration	Specifications	Industrial Regeneration
Carbon, %wt	4.3	0.1	< 0.3	0.1
Sulfur, %wt	< 0.1	< 0.1		< 0.1
Nitrogen (Kjeldahl), ppm	1922	< 100		< 100
Surface area, % of base		100	> 95	99
Bulk Crush Strength, MPa		1.2	> 1.1	1.2
Average Length, mm		2.9		3.1
Aspect	Grey	White		White

Table 3: Analysis of spent, laboratory and industrially regenerated catalyst

## 5-Regenerated catalyst performance

The performance of the regenerated catalyst has been carefully followed by UOP in the customer unit in order to compare fresh and regenerated catalyst performance. As shown in Table 4, six months after loading of regenerated material, the second cycle looks identical to the first one. Activity of both beds 1 and 2 are as good as in the 1<sup>st</sup> cycle and the selectivity is also fine as the Ethyl Benzene yields remain above 99 %.

Cycle	1		2	
	1	2	1	2
Bed	1	2	1	2
Time on Stream, months	6	End	6	6
% Active Bed	87	0	88	93
Typical EB yields	99.3 – 99.5	99.3 – 99.5	99.2 – 99.5	99.3 – 99.5

Table 4: Performance of fresh and regenerated EBZ-500 in the commercial unit

## 6-Conclusion

The off site regeneration of the UOP EBZ-500 zeolite catalyst has been commercially proven at Eurecat with excellent performance of the industrial unit. It is cost effective and may be performed either on a turn around basis, or with a spare catalyst batch. This last option allows taking less risk for unit operation, as the spare batch is always available on site or stored at regenerator location. For helping customers to manage their shutdowns and start-up operations, Eurecat can also provide a total on site supervision of these operations, with the assistance of Petroval company, the world leader expert for reactor dense loading, which is now part of the Eurecat group.

## References

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