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**NOVEL EBULLATED BED CATALYST REGENERATION TECHNOLOGY  
IMPROVES REGENERATED CATALYST QUALITY**

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## **ABSTRACT**

Regeneration of spent hydroprocessing catalysts has long been practiced by the refining industry. With increased pressures on refiners to reduce catalyst expenditures and waste generation, refiners are more frequently reusing spent hydroprocessing catalysts after ex-situ regeneration to restore catalytic activity. By reusing regenerated catalyst for at least two cycles, the refiner reduces catalyst waste by at least one-half. As environmental laws become more restrictive, spent hydroprocessing catalyst is more likely to be classified as hazardous waste. Disposal of spent catalyst, which was previously accomplished by landfilling, now requires more expensive reclamation techniques.

TRICAT has introduced the TRICAT Regeneration Process (TRP), a novel ebullated bed regeneration plant, to improve the catalyst regeneration process. The ebullated bed design allows for better control of heat release during the regeneration process. As a result, the regeneration can be accomplished in a single-pass, with improved catalyst activity retention. Catalyst losses are also minimized due to reduced catalyst handling.

Commercial results from the TRP have demonstrated successful scale-up of the technology from pilot scale. The plant has achieved complete recovery of the available catalyst activity with little or no losses in catalyst yield or extrudate length. The flexibility of the TRP to process a variety of catalysts is also discussed.

## **INTRODUCTION**

### **Use of Regenerated Catalysts**

Hydroprocessing capacity and hydroprocessing catalyst usage

has been increasing dramatically in the U.S. and worldwide.<sup>1</sup> Two major factors contributing to the increase are restrictions on the sulfur content of gasoline, diesel and other fuels; and increasing demand for lighter products. The recently imposed limit of 0.05 wt% sulfur for diesel fuels in U.S. has led to the construction of many "low sulfur diesel" hydrotreaters. It has also resulted in higher severity operation and shorter cycles in existing units.

Increased light products demand has led to a dramatic increase in hydrocracking capacity, and has also led to an increase in FCC feed hydrotreating capacity. Both of these units tend to employ large volumes of catalysts due to relatively low space velocities.

Hydroprocessing catalyst deactivates during a typical operating cycle, mainly due to the deposition of carbon and contaminant metals. The contaminant metals, predominantly nickel and vanadium (from the heavier crude oil fractions) and silicon (which is normally associated with anti-foamants employed in delayed cokers), cannot be removed by oxidative regeneration.

Oxidative regeneration of spent hydroprocessing catalyst in order to restore catalyst activity has been widely practiced by the refining industry for many years. The original motivation for reusing catalyst was purely economic. Refiners were able to reuse the catalyst for an additional cycle at a cost equal to a small fraction of the fresh catalyst price.

Often the catalyst is returned to the same application for a second (and less frequently a third) cycle after regeneration.

As the number of hydroprocessing units in a refinery increases, so do the variety of techniques used by refiners to reuse regenerated catalyst. Among those discussed in the literature are:<sup>2,3</sup>

- **Cascading to less severe service.** After regeneration, catalyst from a severe hydrotreating service (e.g., gas oil) is returned to a less severe service (e.g., naphtha or straight run distillate).
- **Cascading to high metals service.** After regeneration, the catalyst is placed in a hydrotreater which treats a feed containing high levels of contaminant metals. Often the catalyst is used in a guard bed or in the first bed of a multi-bed operation. In this application, the regenerated catalyst is used as a metals trap to protect higher activity (typically fresh) catalyst in subsequent reactors or reactor beds.
- **Cascading to a high silicon service.** In this

application, silicon contamination (from the anti-foamant employed in a delayed coker) overwhelms catalyst deactivation due to carbon deposition. As a result, cycle length is shortened due to silicon breakthrough, or by high pressure drop across the reactor. Refiners would rather employ a relatively low priced regenerated catalyst than fresh catalyst which is not fully utilized.

- **Make-up catalyst after a reactor skim.** Many units require frequent skims to alleviate pressure drop buildup in the top of the bed. Rather than employ fresh catalyst (which will be removed if pressure drop problems reoccur), refiners cascade regenerated catalyst from other service.

Examples of these applications are discussed in a later section.

### **Environmental Issues**

Reducing waste, especially hazardous waste, from the refinery now provides a stronger motivation for reusing the catalyst. Spent hydroprocessing catalysts are frequently characterized as RCRA hazardous waste, mainly due to the tight limit on leachable benzene from the catalyst (0.5 mg benzene per liter of catalyst). The disposal of hazardous waste from the refinery is typically much more expensive than non-hazardous waste. The potential liability associated with the improper disposal of spent catalysts is also of paramount concern to the refiner.

Until recently, landfilling spent catalyst has been the predominant means of catalyst disposal. At a cost of only a few cents per pound plus shipping, the price for landfilling was quite attractive. Many refiners continue to landfill spent catalyst, although the amount of catalyst landfilled is decreasing and the costs are increasing. For hazardous catalysts, landfilling is frequently not an option.

Most spent catalysts are now sent for metals reclamation, where the metals (including contaminant metals) are recovered, and the alumina base is recycled. This option is more expensive than landfilling (even after taking "credits" for the recovered metals), but the reclaimer will issue a "Certificate of Destruction" for the hazardous material. For refiners concerned about potential liability for improper disposal of hazardous waste, this certificate is well worth the additional cost.

As these costs increase, refiners become more interested in reusing the catalyst for a second or third cycle. Using a

catalyst for a second cycle effectively reduces the volume of this waste stream by one-half.

### **Catalyst Regeneration: In-situ versus Ex-situ**

Carbon removal by oxidative regeneration can be very successful in restoring the activity of spent catalysts. Prior to the mid-1970's, regeneration was performed in the same reactor employed for hydroprocessing (i.e., in-situ). In-situ regeneration, however, can be problematic.<sup>4,5</sup> Among the problems that can be encountered are temperature excursions and regeneration gas channelling. Temperature excursions will lead to irreversible catalyst activity loss due to sintering and metals agglomeration. Channelling will cause incomplete regeneration and poor activity recovery.

Another important consideration governing in-situ regeneration is the control of SO<sub>x</sub> emissions generated from the combustion of sulfur compounds deposited on the spent catalyst. While this may not have been an important consideration 20 years ago, concerns about SO<sub>x</sub> emissions are enough to explain why in-situ regeneration of spent hydroprocessing catalysts is rarely undertaken in refineries today.

An additional benefit provided by ex-situ regeneration is the ability to screen catalyst, and return the catalyst to hydroprocessing service free of fines and chips. Smaller catalyst particles can contribute to pressure drop problems in the hydroprocessing unit.

In the late 1970's, two companies, CRI and Catco, introduced the concept of ex-situ regeneration to the refining industry.

CRI's moving grate, and Catco's roto-louvre designs perform the regeneration in air with improved temperature control over in-situ regeneration. Both processes require multiple regeneration passes to completely regenerate the catalyst. For highly coked catalysts, regeneration residence times of up to 24 hours are not uncommon in these designs.

TRICAT was founded in 1992. In 1993, TRICAT commercialized a new regeneration process which substantially improves on the techniques developed in the early 1970's for ex-situ regeneration. The proprietary TRICAT Regeneration Process (TRP) utilizes fluid bed technology to improve air/catalyst mixing. The new technology was initially demonstrated in a 50 pound per day pilot unit. The pilot unit proved the concept that a fluid bed process would achieve complete regeneration of the catalyst in a single pass. This paper describes the technology employed in the commercial design of the TRP, and

discusses the results achieved in the TRP to date.

## THE TRICAT REGENERATION PROCESS (TRP)

### Process Description

A simplified flow schematic of the TRP is shown in Figure 1. Spent catalyst is initially screened in the vibrating feed screener to remove support and catalyst fines before entering the regenerator. Support can be washed, reclassified and reused. Fines are typically sent for metals reclamation.

Most reclaimers do not require carbon removal in order to reclaim metals, so fines are typically not processed in the TRP. One exception is precious metals catalyst fines. Precious metals reclaimers typically impose a surcharge on the reclamation of catalyst containing greater than 2% carbon. Thus when regenerating precious metals-containing catalysts; fines are not removed in the feed screener, and are regenerated with the extrudate (or spheres) in the TRP. The older moving grate regenerator design cannot regenerate catalyst fines as they cannot be held on the grate.

Screened catalyst enters the first of two ebullated bed regeneration reactors. A schematic of the reactors is shown in Figure 2. The fluidization medium is the regeneration air, which is fed through distributor plates at the bottom of each reactor. Air is supplied to each reactor independently. Temperature control is achieved through a number of independent variables. Among the key variables used to control reactor temperature are:

- **Catalyst feed rate:** Carbon on the catalyst is the "fuel" for the regeneration process. At constant conditions, increasing catalyst feed rate will raise regenerator temperature.
- **Air temperature:** The air supplied to the regenerator is heated in natural gas-fired burners. At start-up, the air temperature is typically above 800°F. At steady state operation, ambient air is typically employed in the first reactor.
- **Cooling coils:** Both reactors contain water-filled cooling coils. Increasing the flow of water through the coils also removes heat from the reactors.

- **Regenerator catalyst level:** The catalyst level can be varied by moving the height of the regenerated catalyst outlet tubes. Catalyst height is determined through visual inspection. Increasing catalyst level will increase regeneration residence time and temperature. Highly coked catalysts are typically regenerated at higher catalyst bed levels.

Regenerator temperature is typically maintained between 850 and 950°F. At these temperatures, complete regeneration of the catalyst is achieved in a single pass through the TRP. By contrast, the older designs require as many as five passes to regenerate highly coked catalysts. The differences arise due to improved air/catalyst mixing achieved in the fluidized (ebullated) bed reactors, as well as the more effective heat removal achieved in this new design.

Catalyst particle temperatures are difficult to ascertain. However, it is likely that the fluidized bed design maintains particle temperatures well below those experienced in both the moving grate and roto-louvre designs wherein a several inch thick bed of catalyst extrudates passes through the burning zone.

In the TRP, regenerated catalyst passes through a water-jacketed cooler before product screening and packaging. Since the support is already removed, the screener can be used to separate a mix of extrudate sizes. It is common for refiners to load larger size extrudate on the top (and occasionally the bottom) of a reactor containing predominantly 1/16 or 1/20" extrudate.

Regeneration flue gas is cooled before passing through a bag house to remove catalyst dust. A significant quantity of dust is usually generated in the refiner's reactor during normal operation and catalyst removal. This dust tends to "stick" to the unregenerated catalyst, but is efficiently separated in the regenerator. Dust-free flue gas is then scrubbed to remove SO<sub>x</sub> from the flue gas. SO<sub>x</sub> is generated from the combustion of the sulfur compounds on the spent catalyst. Scrubbed flue gas is exhausted to the atmosphere. The scrubber solution is neutralized and then discharged.

Prior to regeneration, spent catalyst may be pre-treated in TRICAT's "inert gas stripper." In the stripper (Figure 3), a stream of heated inert gas (mainly nitrogen and carbon dioxide) passes across a downflowing stream of catalyst. Excess hydrocarbons and water are removed from the catalyst in the stripper. The stripping step provides several major advantages which are realized upon regeneration:

- Removing any hydrocarbons from the catalyst surface

reduces the amount of "fuel" to the regenerator, thus permitting higher regeneration rates and reduced residence time. The hydrocarbons also tend to burn quickly and at higher temperatures than the more highly condensed coke on the catalyst. The high temperatures may contribute to catalyst surface area loss and active metals agglomeration.

- Excessive hydrocarbons on the catalyst often arise due to uneven stripping in the reactor at the refinery. Inconsistent levels of hydrocarbons on the catalyst can cause erratic regeneration performance with poor temperature control. Stripping the catalyst prior to regeneration improves regenerator temperature control.
- Excessive hydrocarbons and/or water on the catalyst make it cohesive. Stripping improves the fluid properties of the catalyst, which is particularly beneficial when screening the spent catalyst to remove fines prior to regeneration.

The decision to strip catalyst prior to regeneration is made after analyzing a representative composite sample of a catalyst lot.

### **Commercial Data**

Since commissioning the TRP in April 1993, TRICAT has processed over 60 separate lots of catalyst, including nickel-molybdenum (NiMo) and cobalt-molybdenum (CoMo) hydrotreating catalysts; platinum-based reforming and isomerization catalysts; and zeolitic hydrocracking catalysts.

In evaluating an ex-situ catalyst regeneration, three main factors are generally considered: regenerated catalyst activity, its physical quality, and the yield of regenerated product. During regeneration, composite samples of spent and regenerated catalysts are gathered for analysis. Several grams of spent catalyst are regenerated in a single layer in a muffle furnace at 850°F for 4 hours to burn the catalyst clean. Typically, the lab regenerated carbon level is reduced to less than 0.1 wt%. "Available" surface area on the spent catalyst is determined from this lab regenerated sample.

The relative activity of regenerated catalysts are typically estimated from their surface area. The surface area of commercially regenerated product is compared to a fresh sample of the catalyst, as well as the sample of spent catalyst regenerated in the laboratory under controlled conditions. Occasionally, major refiners may choose to evaluate the activity of regenerated catalyst in a pilot plant, and compare



the performance with the fresh catalyst.

The most critical physical properties of the regenerated catalyst are length-to-diameter ratio (L/D) and fines content of the regenerated product. Both of these properties impact the potential for flow maldistribution and excessive pressure drop in the hydroprocessing reactor. L/D is compared with both fresh catalyst and the spent material prior to regeneration. Average length and diameter are measured on representative samples of the spent and regenerated catalyst using microprocessor-equipped calipers. Fines content is determined by screening the regenerated product.

The results from three illustrative regenerations are detailed below.

### **Case Study 1 - "Typical" NiMo Catalyst Regeneration**

The catalyst presented here is a widely used NiMo catalyst. The catalyst was employed for a single cycle for about 15 months hydrotreating FCC light cycle oil. Table 1 and Figure 4 present the results for this regeneration. The catalyst was not stripped prior to regeneration due to low levels of moisture and unstripped hydrocarbons on the spent catalyst.

The catalyst was completely regenerated in the TRP in a single pass. Quality of the regenerated catalyst is uniformly excellent. Regenerated carbon and sulfur levels are very low.

The commercially regenerated catalyst retains all of the available surface area. In addition, the available surface area is 94% of the surface area of fresh catalyst. L/D of the regenerated catalyst is essentially equal to that of the spent catalyst. In addition, the fines content of the regenerated product is negligible. All of these properties indicate that this catalyst is an excellent candidate for a second hydrotreating cycle. In fact, the catalyst was successfully returned to service in a naphtha hydrotreater (catalytic reformer pretreater) at the same refinery.

The material balance for the regeneration indicates that all of the catalyst and support provided to the plant was accounted for in the products. Fines and dust yield were just over 12% of the regenerated product yield. Nearly all of the fines and dust recovered were present in the catalyst supplied to the plant. Less than 2% of the regenerated product was recovered as fines after regeneration. Because the TRP regenerates catalyst in a single pass, catalyst handling is minimized; and the potential for catalyst breakage is reduced.

### **Case Study 2 - High Carbon, High Hydrocarbon NiMo Catalyst Regeneration**

The catalyst presented here is another NiMo catalyst. The catalyst was employed in a vacuum gas oil hydrotreater for a single cycle. The unit was shut down due to pressure drop problems and a portion of the inventory was removed by vacuuming. The hydrocarbon content of the spent catalyst was quite high due to poor gas distribution in the reactor during shutdown.

An attempt was made to regenerate a portion of this catalyst lot in a roto-louvre type ex-situ regeneration unit. The roto-louvre was unable to control regeneration temperature due to the high levels of volatile hydrocarbons on the catalyst, and the run was aborted. TRICAT was able to regenerate this catalyst after stripping the catalyst in TRICAT's inert gas stripper. The stripper results are presented in Figure 5. Stripping removes nearly 15% of the carbon and volatiles from the catalyst prior to regeneration. It is interesting to note the difficulty encountered in screening this oily catalyst. Nearly half the fines present in this lot of catalyst were carried over into the stripper.

The catalyst was regenerated in a single pass in the TRP after stripping. The results for this catalyst (Table 2 and Figure 5) are very similar to those obtained for more typically coked spent catalyst discussed in Case 1. Again, essentially all of the available surface area and catalyst L/D are retained from the spent catalyst. Fines content of the regenerated product is again reduced to very low levels despite the high fines content of the spent catalyst received.

The regenerated product was tested for activity and physical quality in the refiner's laboratory. Pilot plant testing indicate that the regenerated catalyst's activity is within 5°F. of fresh catalyst. The refiner intends to return this catalyst to the first bed of the same process unit from which it was removed.

### **Case Study 3 - Platinum-Rhenium (Pt-Re) Reforming Catalyst Regeneration**

Reforming catalysts are still typically regenerated in-situ by refiners. Since these catalysts generally have little or no sulfur on them, SO<sub>x</sub> emissions are negligible. However, when the catalyst must be dumped and screened, refiners often choose to utilize ex-situ regeneration services.

Recently, TRICAT performed an ex-situ regeneration of a Platinum-Rhenium-based reforming catalyst. Due to the large volume of catalyst requiring regeneration and the time constraints imposed by the refiner's turnaround schedule, the regeneration of the catalyst was divided between the TRP and an older regeneration unit employing the roto-louvre design.

Both units were able to reduce the carbon content of the catalyst from each of the four reforming reactors to a few tenths of a percent. Table 3 shows the results for the regeneration of catalyst in the fourth reactor, which contained the largest catalyst volume and most highly coked catalyst. The TRP accomplished the regeneration of this catalyst in a single pass without stripping. The roto-louvre required four passes, at a residence time five times longer than the TRP. Regeneration temperature was comparable in both units. Both the TRP and the roto-louvre unit retained nearly 100% of the available catalyst surface area.

## **CONCLUSIONS**

Ex-situ regeneration of spent hydroprocessing catalysts is an effective means of restoring catalyst activity. By reusing the catalyst, the refiner reduces waste disposal and catalyst expenditures.

TRICAT has successfully demonstrated the performance of an ebullated bed process for the regeneration of hydroprocessing catalysts as well as other refining catalysts. The TRICAT Regeneration Process is quite flexible. Catalysts of various sizes are regenerated in a single pass, even at carbon levels above 30%. Regenerated carbon and sulfur levels are typically well below 1%, and nearly 100% recovery of the available surface area and catalyst length are achieved.

The use of an inert gas stripper to remove excess hydrocarbons and water has also been successfully demonstrated. Pre-treating the catalyst in the stripper prior to regeneration has eliminated the potential for temperature excursions. Catalysts containing up to 40% volatile matter are now regenerated in a single pass by first pre-treating the catalyst in the stripper.

The TRP technology, successfully commercialized at TRICAT's McAlester, Oklahoma plant, will also be utilized at TRICAT Europe's new facility in Germany. The new plant will start up in 1995.

## REFERENCES

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4. Martin, Joseph, "Regeneration of Hydrotreating Catalysts," Ketjen Catalyst Symposium, 1981.
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Table 1

**NiMo CATALYST REGENERATION  
Material Balance**

<b>Regeneration Temperature, °F</b>	<b>930</b>
<b>Regeneration Residence Time, hrs</b>	<b>3.5</b>
<b>By-Products, wt% of Finished Product</b>	
- Support Material	<b>37.0</b>
- Volatile Matter	<b>15.5</b>
- Non-Regenerated Fines	<b>3.0</b>
- Regenerated Fines	<b>1.5</b>
- Dust Catch	<b>6.1</b>
<b>Total Product Recovery, wt%</b>	<b>99.96</b>

Table 2

**Criterion Catalyst Stripping/Regeneration  
Material Balance**

<b>Stripping Temperature (max.), °F</b>	<b>750</b>
<b>Stripping Residence Time, hrs</b>	<b>4</b>
<b>Regeneration Temperature, °F</b>	<b>930</b>
<b>Regeneration Residence Time, hrs</b>	<b>6.75</b>

**By-Products, wt% of Finished Product**

<b>- Support Material</b>	<b>0.3</b>
<b>- Volatile Matter</b>	<b>63.1</b>
<b>- Non-Regenerated Fines</b>	<b>39.6</b>
<b>- Regenerated Fines</b>	<b>12.5</b>
<b>- Dust Catch</b>	<b>6.1</b>
<b>Total Product Recovery, wt%</b>	<b>99.91</b>

Table 3

**Pt-Re Catalyst Regeneration  
Comparison of TRP and Roto-louvre Results**

<b>Regeneration Unit</b>	<b>TRP</b>	<b>Roto-louvre</b>
<b>Carbon on Catalyst, wt.%</b>		
<b>Spent</b>	<b>12.6</b>	<b>12.2</b>
<b>Regenerated</b>	<b>0.33</b>	<b>0.48</b>
<b>Maximum Regeneration Temperature, °F</b>	<b>950</b>	<b>975</b>
<b>Number of Regeneration Passes</b>	<b>1</b>	<b>4</b>
<b>Regeneration Residence Time, hrs</b>	<b>4</b>	<b>20</b>
<b>By-Products, wt% of Finished Product</b>	<b>+1</b>	<b>-2</b>

**Note 1 – Commercially regenerated catalyst compared to lab-regenerate sample of spent catalyst**

Figure 1

# TRICAT REGENERATION PROCESS (TRP)

## Flow Diagram

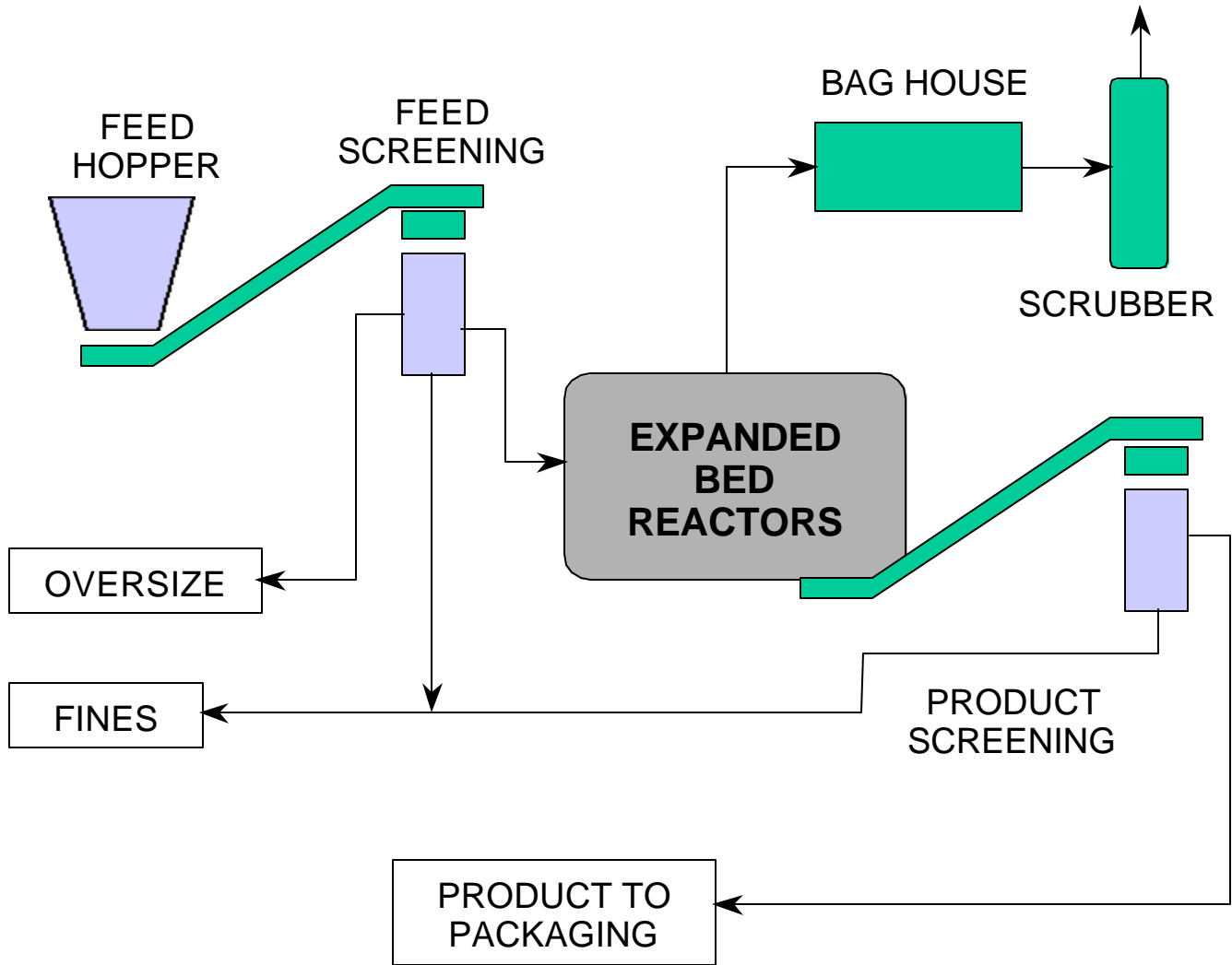




Figure 2

# TRICAT REGENERATION PROCESS (TRP)

## Regeneration Reactors

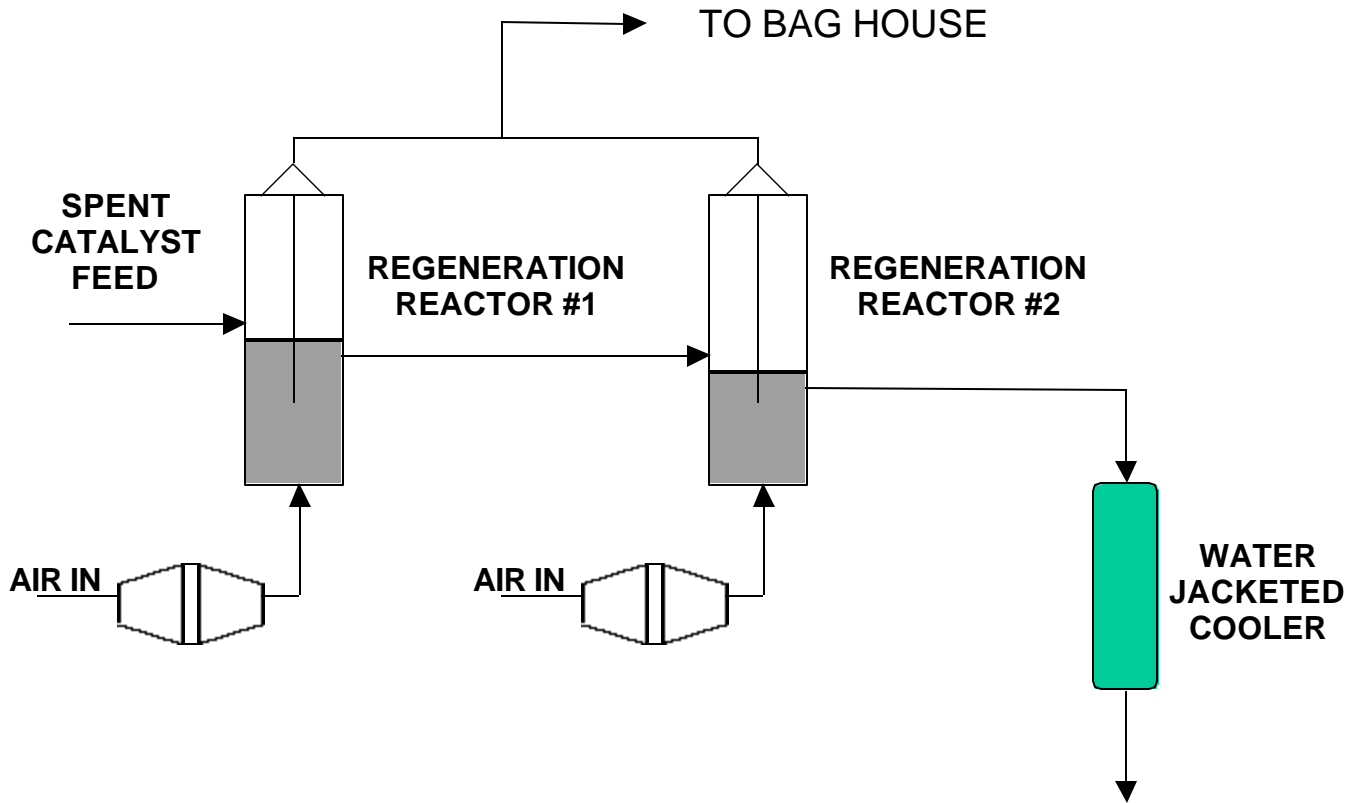


Figure 3

# TRICAT INERT GAS STRIPPER

## Flow Diagram

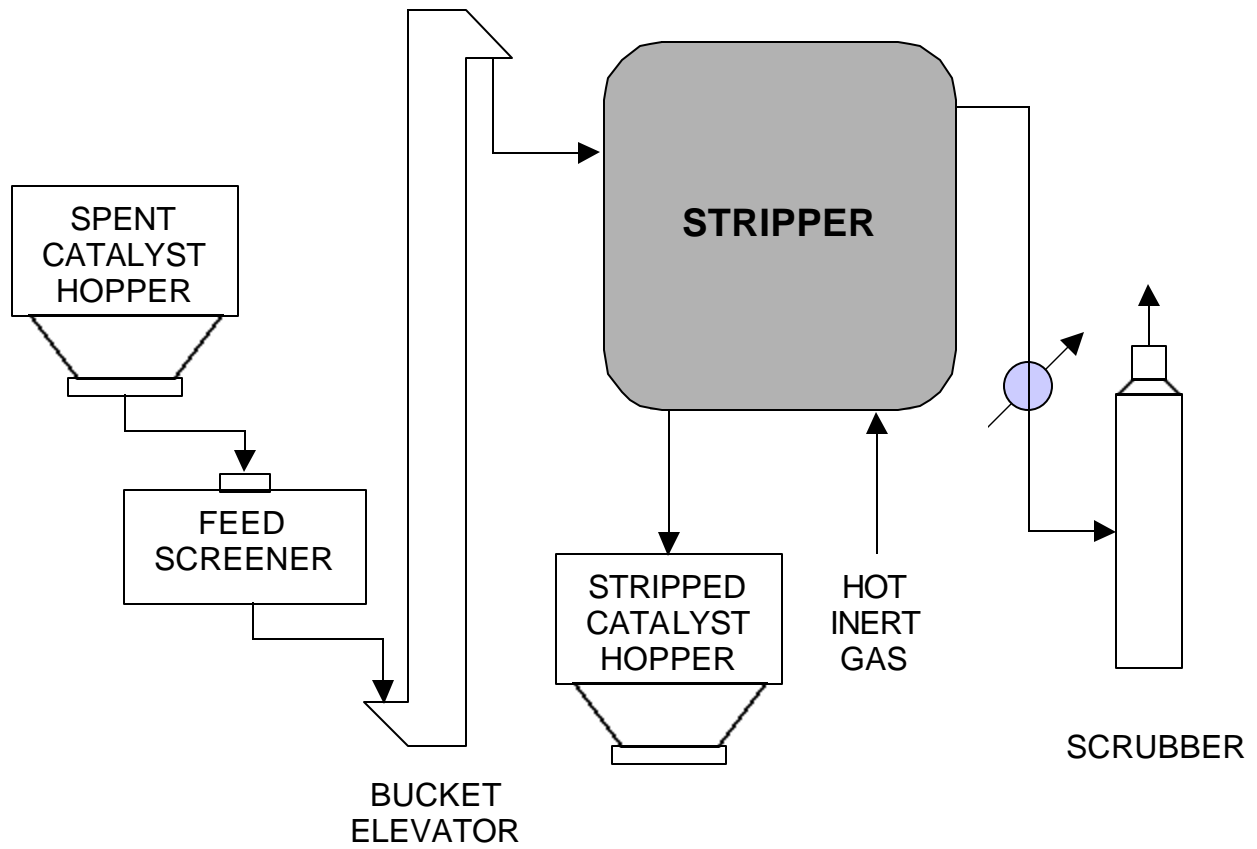


Figure 4

# NiMo CATALYST REGENERATION Product Quality

TRICAT REGENERATION PROCESS

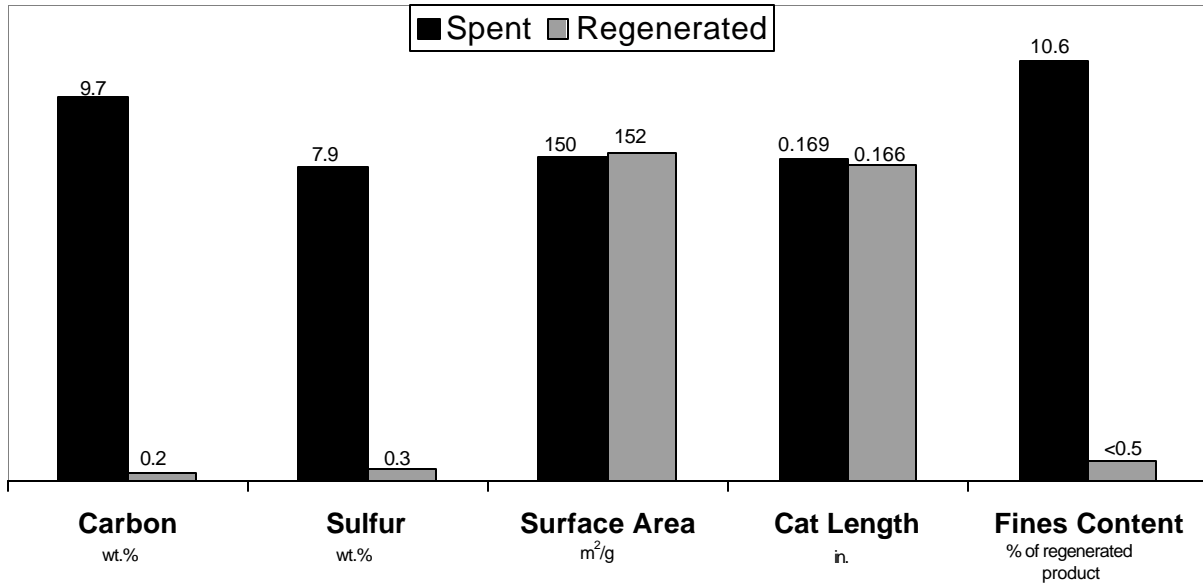


Figure 5

# NiMo CATALYST STRIPPING Stripper Performance

TRICAT INERT GAS STRIPPER

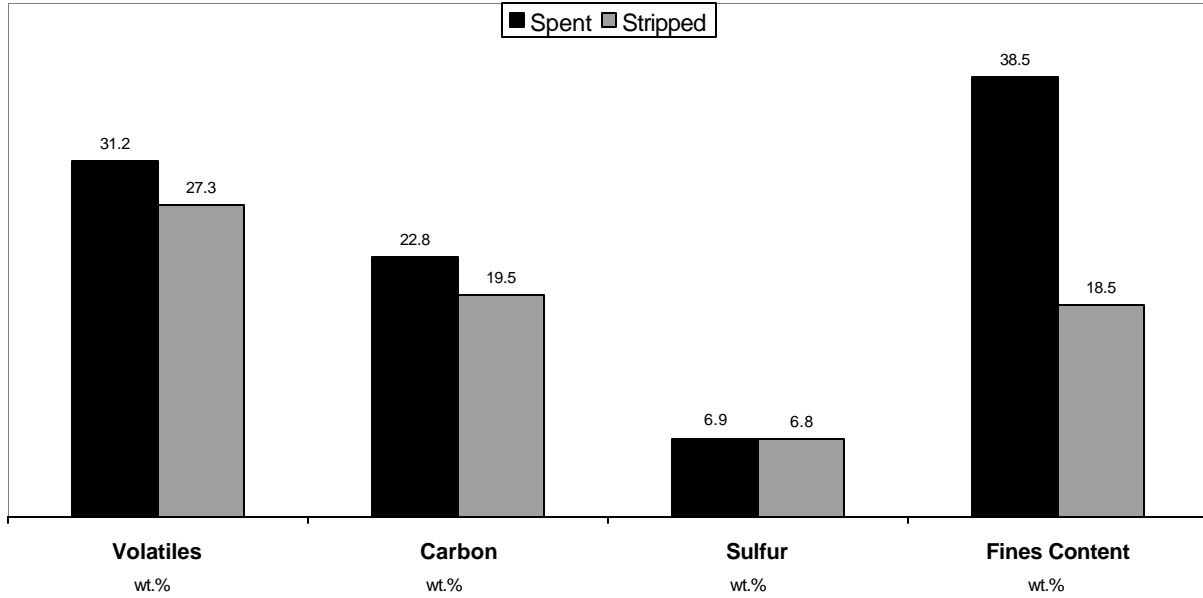


Figure 6

# STRIPPED NiMo CATALYST REGENERATION Product Quality

TRICAT REGENERATION PROCESS

