

THE MANAGEMENT OF SPENT CATALYST OF HYDROCONVERSION PROCESSES IN ASEAN REFINERIES

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1. INTRODUCTION

Catalytic processing is a keystone of today's petroleum refining. The catalytic processes applied in the petroleum industry are generally large scale.

In today's operating climate of increased attentiveness toward environmental and safety issues, spent catalyst management options have become an important consideration for refiners.

A catalyst deactivation determines how it can be handled after it is discharged from the processing unit. The type of the catalyst and its condition (whether it is considered hazardous) often determines the disposal route selected. Because of the self-heating and leaching problems associated with spent hydrotreating catalyst, it is recommended that refiners ship their spent catalysts to what is called "true recycles".

The U.S. Environmental Protection Agency (EPA), for example, is in the process of reevaluating the designation of spent hydroprocessing catalyst as an hazardous waste.

Out of 3,837 MBPSD total crude oil currently processed in ASEAN (Brunei Darussalam, Indonesia, Malaysia, Philippines, Singapore, Thailand, not including Vietnam, Laos and Myanmar) around 61 percent volume is passed through catalytic processes (included hydroconversion processes 58 vol.%) to produce various fuel components such as gasoline and diesel oil. These hydroconversion processes use about 3,279 tons of catalyst with about 28 tons per day of spent catalyst.

The present paper discusses briefly a survey on the management of spent catalyst of hydroconversion processes in ASEAN refineries and some aspects of

catalyst poisoning of major hydroconversion processes in petroleum refinery.

A survey on the management of spent catalyst from hydroconversion processes in ASEAN refineries is described in this paper.

II. HYDROCONVERSION PROCESSES

Out of 3,837 MBPSD total crude oil currently processed in 26 units of refineries, as much as 61 vol.% of this total crude is passed through catalytic processes in ASEAN refineries (Table 1)

Hydroconversion processes can be used for a very wide range of duties, from the improvement of petroleum products.

The metal sites of the hydroconversion catalysts are a couple of metals of groups VIA and VIII such as Co-Mo, Ni-Mo, Ni-W and Co-W. No matter which support and pair of active sulfides are used, and no matter what

Table 1
Hydroconversion Processes in ASEAN Refineries

No.	Type of Processes	Total Units	Total Capacity MBPSD
1	No. of Refineries	26	
2	Atmospheric Distillation	45	3,873.9
3	Catalytic Hydrocracking Processes	13	271.08
4	Hydrotreating Processes	55	1,330.98
4.1	Naptha Hydrotreating	26	574.88
4.2	Kerosene Hydrotreating	4	49.20
4.3	Distillate Hydrotreating	24	648.90
4.4	Residue Hydrotreating	1	58.00

the reaction is, the atomatic ration remains between 0.25 and 0.40 at the optimum conversion. These optimal area evidence of the synergistic effect exercised by sulfides of the metals of group VIII (Co_8S_9 , MoS_2 and Ni_2S_3).

Over 1,543 MBPSD total capacity is available in 54 units of hydroconversion processes (i.e. hydrotreating hydrocracking processes) where about 3,279 tons of catalyts. Metal content of hydroconversion catalysts are given in Figure 1. Surface area, pore volume vs bulk density of hydroconversion processes are given in Figure 2 and 3.

The reaction severity selected depends upon the properties of the charge stock as well as the improvement desired. The least severe conditions for cracked distilates, heavy oils, and waxes. The principal proces variables are hydrogen partial pressure, space velocity or contact time, and temperature.

A. Hydrotreating processes

Hydrotreating is a proces to catalytically stabilize petroleum product and/or remove objectionable elements from products or feedstocks by reacting them with hydrogen. Hydrotreating is applied to a wide range of feedstocks ranging from naphtha to residue.

The catalysts employed for hydrotreating are mono-functional. Catalyst supports are alumines with large surface area and high pore volume. A large variety of catalysts can be employed for catalytic hydrotreating using hydrogen, but the type commonly used is mixed metal sulfides of Co-Mo supported on Al_2O_3 . The operating conditions depend on the type of feedstocks and the desired product quality, and area as follows: hydrogen partial pressures: 5-40 bar, temperatures: 330-400 °C and space velocities: 1-8. Catalyst life and consumption are 1-5 years and 0,001-0,007 lb per barrel feed, respectively.

Over 1,330 MBPSD total capacity is available in 56 units of hydrotreating processes in ASEAN refineries with a total of about 2,052 tons of catalysts (Co-Mo/ Al_2O_3). These hydrotrating processe treated the following feedstock: naphtha 43.19 vol.%, middle distilates 52.45 vol.% and residues 4.36 vol.%. Total spent catalyst from these hydrotreating processed is estimated at about 24.8 tons per day. There metal contents are as follows: Co from 1.5 to 5.2 wt.% and Mo from 9.9 to 20.0 wt.% on catalyst.

1. Naptha Hydrotreating

Naptha hydrotreating for preparation of catalytic reformer and catalytic isomerization feedstocks is aimed eliminating sulfur, nitrogen, oxygenated compounds, and

organo-metallic impurities (Pb, As, P) that may poison the platinum catalysts. The selective hydrogenation of thermal cracked naphthas removes sulfur selectively without cracking or polimerization, and saturates essentially all conjugated dienes with a moderate degree of monoolefins hydrogenations. This selective hydrgenation produces a low sulfur, low gum content product with retention of moderarte high reseach octane number.

There are 26 units of naphtha hydrotreating processes with about 574 MBPSD of the total capacity (i.e. straight-run and thermal cracked naphthas) in ASEAN refineries. Over 416 tons of catalyst consumption or about 5.2 tons per day of spent catalyst.

2. Middle Distillate Hydrotreating

The hydrotreating of middle distillates is currently the larger application of this type of hydro processing. The primary objective in hydrotreating of kerosene, stve oil, jet fuel, gas oil, and heting oil is to enhance their quality by a reduction in sulfur and trace improvement in burning characteristics, color stability, and resistance to sludging and to saturate aromatics.

About 628 MBPSD total capacity (i.e. straight-run and thermal, and catalytic cracked middle disstillates) is operating in 30 units of hydrotreating processes with over 1,552 tons of catalysts. With average about 0.06 lb per bbl feed, the spent catalyst produced is about 19.1 tons per day.

3. Residue Hydrotreating

The increased refinery runs of heavy high sulfur stocks have forced many petroleum refiners to to apply hydrotreating to process streams to orders to maintain product quality. How over, the increased yield of residual fuels from low grade stocks and the reduced percentage demand for these heavy residual fuels have spotlighted the essential incentive for hyrotreating the conversion of low grade crudes and residuals into disstillates. The residuals contain asphaltene components that readily deposit on the catalyst as coke, or from materials that deposit as coke which deactivates catalysts.

There is one unit of of hydrodemellization of reduced crude in ASEAN with about 58 MBPSD capacity to produce cat. Cracked feedstock. Over 84 tons catalyst is used with about 6 months of the catalyst life, or about 0.5 ton per day of the spent catalyst.

4. Hydrocracking Processes

Hydrocracking of petroleum fractions to produce lighter distillates is generally carried out over dual-func-

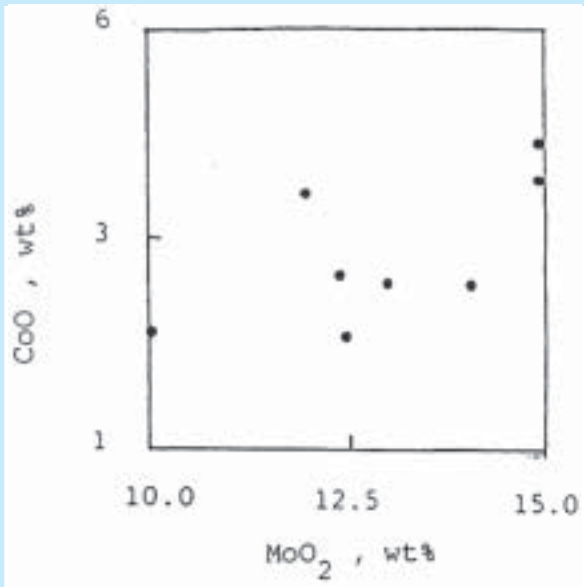


Figure 1
Metal content of hydroconversion catalyst

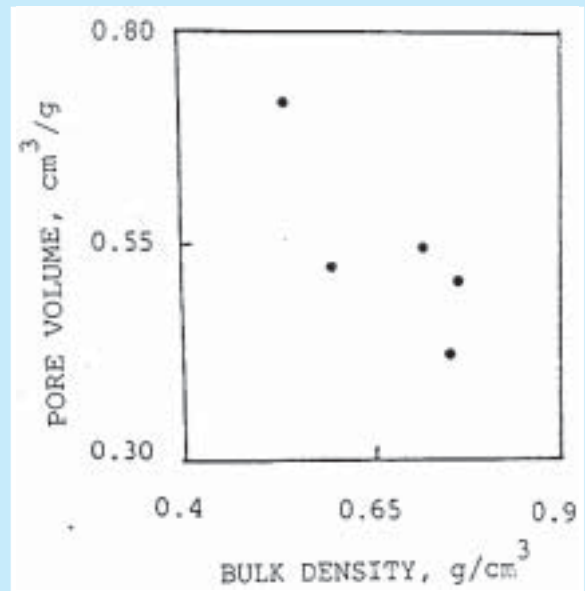


Figure 3
Relation between bulk density and pore volume of hydrotreating catalyst

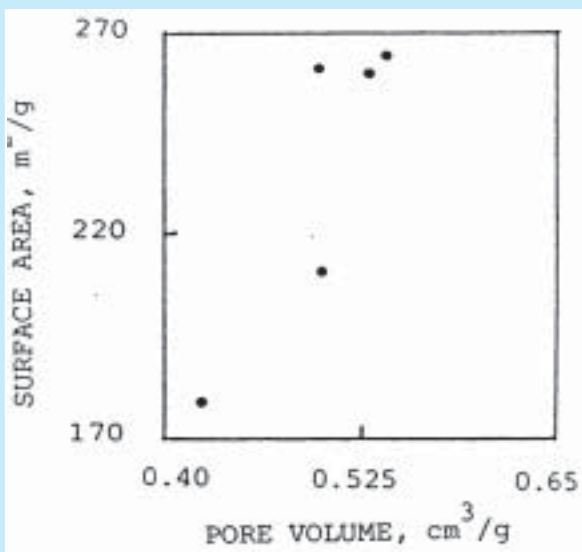


Figure 2
Relation between surface area and pore volume of hydrotreating catalyst

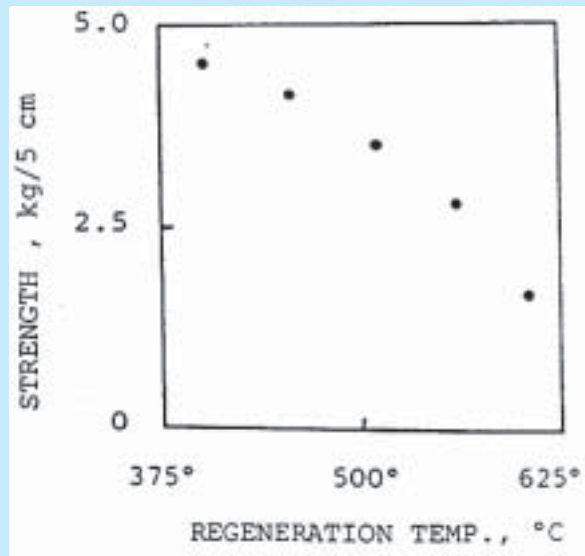


Figure 4
Effect of regeneration temperature on the mechanical strength of hydrotreating catalyst

tion catalyst. The function serve to: (a) crack higher-molecular-weight hydrocarbons, and (b) activate molecular hydrogen and hydrogenate unsaturated compounds present in the feed or formed during the cracking processes. The acid cracking function is usually provided by an amorphous silica-alumina (similar to the catalyst in cat. Cracking), acristalline aluminosicate (zeolite). The major hydrogenation compounds are Ni-Mo or Ni-W.

Over 280 MBPSD total capacity is operating in 13 units of hydrocracking process to produce middle disstillate in ASEAN with a total catalyst (Ni-Mo and Ni-W supported on $Al_2O_3-SiO_2$) of 1,227 tons. With average catalyst is estimated at about 3.0 tons. Metal content of hydrocracking catalysts are as follows : Ni from 3.2 to 4.2 wt.% and from 13.0 to 15.0 wt.% and Won catalyst.

III. DEACTIVATION OF HYDROCONVERSION CATALYSTS

Deactivation of the hydroconversion catalysts, which may occur by physical transformation (such as sintering), coking or poisoning, is there fore to be minimized as much as it is feasible. Some aspects of catalyst poisoning, defined as the deactivation caused by strong,irreversible adsorption of feed contaminants and the reaction severity selected in major refining processes employing heterogenous catalysts.

A. Presulfiding of catalyst

The unsaturated hydrocarbons of the feedstock could impose additional high risk of cokeformation on the fresh catalyst because of the olefinic and polynuclear-aromatic (PNA) components. A special start-up procedure is there fore recommended to improve presulfiding presulfiding without excessive coke formation on the fresh catalyst. A diesel-range hydrotreated gas oil is used for presulfiding,thus eliminating the risk of coke formation caused by olefins and PNA's in the untreated gas oils. The use hydrotreated gas oil feedstock must be continued for 24 hr after completion of presulfiding before introducing coker gas oil feedstocks into the unit.

When the presulfiding temperature of catalyst activation is reached, the temperature is steady untill the conversion of the catalyst metal oxides to metal sulfides is completed. This procedure is good for achieving rapid start-up, but the reactions are highly exothermic. In extreme casses, the exotherms can give heat enough to reduce the metal oxides to base metal. If this happens, the catalyst will not achieve its optimum activity level. The new technology utilizes a model organic matrix to

form a complex with the sulfur and metal oxide on the catalyst. Catalysts presulfided in this manner contain a range of metal sulfides which are converted to sulfides over a wide temperature range, thus eliminating sharp exotherms.

B. Impurities of Feedstock

1. Sulfur Components

The sensitivity of the hydrogenation functions is,of course, dependent upon the choice of the metal. As very high hydrogenation activity is not necessary or even desirable, metal sulfides such as mixed sulfides of the Co-Mo, Ni-Mo or Ni-W types can be employed for hydroconversion processes. This type of hydrogenation component is,of course, quite tolerant to sulfur and will even have to be operated with some sulfur to maintain to sulfided state (Co_8S_9 , MoS_2 , Ni_3Si_2 , and WS_2). However, with some high sulfur content of feedstocks it is frequently desirable to scrub the recycle gas to prevent the accumulation of hydrogn sulfide as a potential catalyst poison. In some instances it may be necessary to enrich the recycle gas by absorption or blending of some hydrogen lean gas from the high pressur separator and changing hydrogen rich make-up gas.

The overall effect of hydrogen partial pressure is made up of the combined effects of total pressure, hydrogen concnertration of the recycle gas, and the hydrogen to hydrocarbon ratio. Rotal pressure in commercial units varies from 100 to 1,000 psig, hydrogen content of the recycle gas should be above 60% vol. And preferably 80-90% vol. The recycle gas ratio is usually maintained in the range 500-4,000 scf per barrel of charge.

2. Nitrogen Component

The majority of crudes contain only small amounts of total nitrogen consiting of basic and non-basic nitrogen compounds, of the order of 0.1 wt.% or less. Some Californian and South American crudes, however, are known to contain appreciable amounts of the order between 0.1 to 0.9 wt.%.

The fact that asphaltic crudes tend to contain relatively higher proportion of nitrogen,concetrated mainly in the heavier fractions and residues. High carbon residue is paralleled by a high total nitrogen content. The ratio of basic nitrogen to total nitrogen content is almost constant (varying between 0.25 and 0.35),and that although the amount of basic nitrogen (pyridine, pyrrole, quinoline, isoquoniline, indole and carbazole) increases with boiling point, the ratio reins constant.

The acid function of hydrocracking catalyst is sen-

sitive to poisoning by nitrogen bases in the feedstock. Cracking catalysts based in crystalline aluminosilicate can stand some nitrogen and may actually prepare a certain nitrogen concentration for stable operation. The effect the nitrogen content of feedstock on the reaction temperature required to maintain a constant catalyst activity is higher for amorph support than that for zeolite support.

3. Asphaltene Component

Coke is thought to be produced by the precipitation of large-molecular hydrocarbons, such as asphaltenes, when their solubility in oil is decreased. An increase in the conversion of vacuum residue increases the aromaticity of asphaltenes and decreases the aromaticity of malthenes. Consequently, the solubility of the asphaltenes in malthenes decreases.

It was also proposed that a decrease in asphaltenes solubility is partly responsible for the steady build-up of coke in the catalyst, subsequent to the initial rapid coke deposition caused by the absorption of asphaltenes on the acidic sites of an alumina support. This may explain why an increase in residue conversion increases the amount of coke in the reactor exit.

If the unit has to be shut down, not because of catalyst deactivation of coke, but due to pressure drops caused by carbon deposits and scales of iron sulfide at the top of the bed, the catalyst must be drawn off wholly or in part, depending on the design of the reactor and screened.

4. Metal Organic Component

Particular problems for hydroprocessing of the heavy end of crude oil are posed by the presence of metal (V, Ni and Fe) and polyaromatics, heteroatom-rich materials called asphaltenes. Concentrations of vanadium (the main metal contaminant) range between 50 and 100 ppmw. Residual feedstock from some crudes are much richer in metals, vanadium content being sometimes as high as about 1,000 ppmw. Vanadium and nickel (and Cu, at smaller extent iron and cobalt) occur as very stable, oil-soluble nitrogen complexes in the form of phosphyrins. Phosphirins (and associated dihydro and tetrahydro) are well defined group of compounds with a wide range of molecular weight, according to the varying types and number of alkyl, carbonyl and carboxyl substituents they contain. The metal content of crude appears in the distillation residues, associated with asphaltic fraction.

One of the chief problems with processing of residues is the deposition of the metals. Vanadium is the depos-

ited in the form of a film in the outside of the grain (uniform pore poisoning or homogenous pore poisoning). Heterogenous pore poisoning gives lower pore effectiveness than does the homogenous pore poisoning⁽¹⁾.

If deactivation is due to metal deposits, the catalyst cannot be completely restored by combustion, which does not remove the deposited metals progressively, from one cycle to the next; and the catalyst must be changed before this front reaches the bottom of the catalytic bed, even if the hydrodesulfurization performance is still acceptable.

The retention of mechanical strength after in-situ regeneration in the presence of steam or flue gas is necessary for long catalyst life (Figura 4). Multiple beds may be required to reduce the pressure on the bottom layer of catalyst which generally rests on a layer alumina balls.

Pressure drop through the catalyst bed, which is the function of low conditions and catalyst particle size, is important because it determines the power requirement for make-up and recycle hydrogen compression. Consideration must be given to the mechanical strength of the catalyst and method of packing it to avoid crushing.

C. Operating Conditions

1. Temperature

Catalyst coke formation is markedly temperature dependent, and therefore the temperature should be maintained as low as possible at all times, consistent with desired product quality, so that the rate of catalyst fouling is minimized. The temperature is normally maintained between 500 and 775°C. When substantial hydrocracking reactions become predominant.

2. Space Velocity

The effect of an increase in liquid hourly space velocity or reciprocal contact time in vapor phase operations is to decrease formation of coke on the catalyst. Commercial operations utilize space velocities in the range of 1–10 volumes of feed per volume of catalyst per hour.

D. Regeneration of Catalyst

Catalyst deactivated by coke can be regenerated by combustion. The operation releases a very large amount of heat due to the combustion of the coke and to the oxidation of the sulfides. The liberated heat tends to provoke rises in the temperature that must be carefully con-

trolled at all points through the catalyst bed. Even short periods with hot spot can damage the catalyst. Above 550°C, molybdenum oxide vaporises, and the specific area as well as the mechanical resistance of some catalyst can begin to decrease (Figure 4). Therefore the rise in temperature is monitored by operating the combustion at low air partial pressure which is diluted with a heat carrier such as steam or nitrogen.

Each of the inert diluent gases, steam or nitrogen, has its advantages and disadvantages. Combustion in the presence of steam is simple and easy to conduct, but under some conditions of temperatures, prolonged treatment with steam can cause a change in the crystallized phase of alumina support. The results are a loss of surface, a reduction in activity of the catalyst, and a deterioration of the catalyst mechanical properties, in the case of well-run operations, however, catalysts can withstand five to ten regenerations of this type.

Combustion with nitrogen also involved operating under pressure, with nitrogen recirculation. Water from the combustion is condensed, then neutralized. This operation requires more care and is probably more expensive than the regeneration with steam, but it's better for the catalyst and poses fewer pollution problems.

IV. MANAGEMENT OF THE SPENT CATALYST

In today's operating climate of increased attentiveness toward environmental and safety issues, catalyst management options have become an important consideration for refiners.

A catalyst's deactivation mechanism determines how it can be handled after it is discharged from the processing unit.

The three basic deactivation mechanisms for refining catalyst are:

- coke or carbon formation (plugging of pores, coverage of active sites)
- Aging (metal agglomerations)
- Poisoning (feed contaminations).

In most cases, catalyst, deactivated by coking is suitable for regeneration and reuse. Often, regenerated catalysts can be reloaded into the same unit. "In severe duty units, only fresh catalyst will give the desired performance and the regenerated can be cascaded to less severe service.

A recent development in the regeneration and reuse

of catalyst is what it calls management of regenerated catalyst for groups of refiners.

The U.S. Environmental Protection Agency (EPA) considers spent hydrotreating and hydrorefining catalysts a hazardous waste only if they exhibit certain hazardous characteristics, such as pyroforicity, or fail the Toxicity Characteristic Leachate Procedure (TCLP). Catalysts that fail the TCLP test usually do so because of arsenic and benzene. The EPA, however, is in the process of deciding whether to classify all

hydrotreating and hydrorefining catalysts as a listed hazardous waste, regardless of their characteristics.

In recent years, a select number of refiners have been shipping a greater portion of their spent hydrotreating catalysts to landfills.

When EPA restricts a hazardous waste from disposal in landfills, it must set methods or levels of treatment. In the case of hydrotreating catalysts, this means high-temperature metals recovery, followed by stabilization.

The management of spent catalyst in hydroconversion units and metallic by-products has become increasingly more complex over the last couple of years, due to tightening environmental concern. Spent hydroconversion catalyst are also reused as an alternate raw material in the making of stainless steels where spent nickel, for example, is used; further, in the manufacture of metal salts and chemicals. This recycling process keeps thousands of tons of usable materials from being dumped into landfill. Spent catalysts may sometimes have a negative value and cost to be reclaimed. This results from low metal content (compared to spent catalyst of hydroconversion processes), low metal values, and high extraction costs or metal losses. However, the end result is reclamation and recovery which eliminates or reduces landfill.

The micronutrient industry is an example of such an end market. The production of micronutrients involves a simple process where metal oxides are blended together, acidulated with sulfuric acid to yield primary metals, granulated, sized and shipped to fertilizer manufacturer. The micronutrients are then blended with other fertilizer ingredients to correct for regional soil deficiencies.

In Indonesia and the Philippines, spent hydroconversion catalysts are disposed to landfill. Leach test was performed for spent catalyst prior to landfill. In Thailand, most refineries used the method of recycle by sending the spent catalyst back to the country of origin to do the process of recycle.

To maximize the reclamation of spent hydroconversion catalyst both economically and environmentally, five factors should be addressed: (1) proper planning and physical handling; (2) transportation of spent catalysts; (3) environmental concerns; (4) end uses of spent catalyst; and (5) choosing the proper safe reclamation "homes" for the full range of spent catalysts and other metallic by-products. Proper classification of spent catalyst is required prior to reclamation and recycling. Test should be performed on these spent catalyst to find out whether or not their materials are hazardous wastes such as toxic characteristic leaching procedure (TCLP). This test determines the leachable hazardous characteristics of a spent catalyst and its metals content. Further, a full chemical analysis should be performed to verify the spent catalyst and its actual content, as well as to determine whether or not a spent catalyst is classified as a non hazardous or hazardous material, or as a RCA hazardous waste.

V. CONCLUSION

Out of 3,837 MBPSD total crude oil currently processed in 26 units of refineries, as much as 2,581 MBPSD of its fractions (or 67 vol.%) of this total crude is passed through catalytic processes in ASEAN refineries.

Hydroconversion processes can be used in a very wide range of duties, from the improvement petroleum products to the conversion heavy fraction into lighter products.

Over 1,611 MBPSD in total capacity is processed in 54 units of hydroconversion processes i.e. hydrotreating and hydrocracking with about 3,279 tons of catalysts which consist of 2,052 tons of hydrotreating catalyst (Co-Mo/A1203) and of 1,227 tons of hydrocracking catalyst (Ni-Mo or Ni-W supported on $\text{Al}_2\text{O}_3\text{-SiO}_2$) to produce about 28.0 tons of spent catalyst per day.

In Indonesia and the Philippines, spent catalysts are disposed to landfill, while Thailand uses the method of recycle by sending the spent catalyst back to the country of origin to do the processes of recycle.

The management of spent catalyst and metallic by-product has become increasingly more complex over the last couple of years, due to lightening environmental concern.

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