



## Review

## A review of metal recovery from spent petroleum catalysts and ash

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## ABSTRACT

With the increase in environmental awareness, the disposal of any form of hazardous waste has become a great concern for the industrial sector. Spent catalysts contribute to a significant amount of the solid waste generated by the petrochemical and petroleum refining industry. Hydro-cracking and hydrodesulfurization (HDS) catalysts are extensively used in the petroleum refining and petrochemical industries. The catalysts used in the refining processes lose their effectiveness over time. When the activity of catalysts decline below the acceptable level, they are usually regenerated and reused but regeneration is not possible every time. Recycling of some industrial waste containing base metals (such as V, Ni, Co, Mo) is estimated as an economical opportunity in the exploitation of these wastes. Alkali roasted catalysts can be leached in water to get the Mo and V in solution (in which temperature plays an important role during leaching). Several techniques are possible to separate the different metals, among those selective precipitation and solvent extraction are the most used. Pyrometallurgical treatment and bio-hydrometallurgical leaching were also proposed in the scientific literature but up to now they did not have any industrial application. An overview on patented and commercial processes was also presented.

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## 1. Introduction

Catalysis undoubtedly played a very important part during the second half of the 20th century in the development of refining and petrochemical industries. The main categories of catalysts mostly

belong to heterogeneous catalysis, which involves acid, metal, sulfur, and bifunctional catalysts and, to a lesser degree, oxide phases (other than supports) (Marcilly, 2003). Catalysts are indispensable in the conventional production of gasoline, diesel fuel, jet fuel, heavy hydrocarbons, petrochemicals and plastics in the petroleum distillation and petrochemicals industry.

Because the technology for the regeneration and reactivation of the catalysts that are deactivated by metal fouling is not available

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to refiners, the spent catalysts are discarded as solid waste (Marafi and Stanislaus, 2008a,b; Macaskie et al., 2010). Although spent refinery catalysts correspond to about 4 wt.% of the overall refinery waste (Liu et al., 2004), they are classified as one of the most hazardous wastes generated in petroleum refineries. Spent catalysts are managed through the following approaches: (1) chemical or microbial treatment for recovery of valuable metals for different applications, (2) regeneration and reuse and (3) landfilling. Beside the serious environmental threat, hydroprocessing catalyst is also identified as one of the important potential sources of base and critical metals such as Ni, Co, Mo, W, V, Cr, Cu and Zn. Considering all these facts, the treatment of spent refinery catalysts for metal recovery is becoming potentially viable (Marafi and Stanislaus, 2008a,b; Santhiya and Ting, 2006).

Recently, an increasing demand for clean chemical process technologies in engineering can be observed, especially for removal of pollutants. It is very well known that the sulfur and nitrogen impurities present in fuels are an important source of air pollution, acid rain and they also affect pollution control devices. In order to decrease pollution, new specifications for sulfur in diesel have been established in many countries (Zepeda et al., 2012; Liu et al., 2012; Baeza et al., 2012). Conventional hydrotreating (HDT) methods are effective for removing many sulfur and nitrogen compounds. However, they are less competent for removing heterocyclic sulfur or nitrogen compounds such as dibenzothiophenes and quinolines, which are abundant especially in diesel (Song and Ma, 2003; Liu et al., 2008; Guimaraes et al., 2008). Other processes have been studied in order to remove refractory HDS compounds.

The largest petrochemical industries are located in the USA and Western Europe; however, major growth in new production capacity is in the Middle East and Asia (Cefic, 2011). Currently, there are few companies with the ability to perform this process within the economical and environmentally acceptable boundaries. Energy savings and environmental benefits are also important in these recycling processes. Refineries are facing a difficult challenge to reduce the sulfur content in their products, because of low quality petroleum with high sulfur content. Technically, it is possible to remove sulfur from products during separation, but in terms of the main process modifications, the economic impact can be significant. As waste disposal is no longer considered to be the best choice, disposing catalyst waste has become a significant environmental issue. In many cases, spent catalysts are considered to be hazardous wastes and are subject to strict legislations. The amount of hydro-processed catalyst wastes that are considered as solid wastes in the petrochemical industry has increased to meet demand for low-sulfur fuels that have rapidly increased in terms of hydroprocessing capacity (Marafi and Stanislaus, 2007).

Raw petroleum is a complex mixture that has the texture between water and tar. A typical raw petroleum is comprised of 84% carbon, 14% hydrogen, 1–3% sulfur and >1% nitrogen, oxygen, metals and salts. Raw petroleum can be classified as paraffinic, naphthenic or aromatic, based on the dominant ratio of hydrocarbons. Metals like nickel, iron and vanadium are found in low amounts in petroleum and are removed during the separation processes. Trace amounts of arsenic, vanadium and nickel can poison and clog the porous structure of catalysts and this affects the catalytic activity negatively. Catalytic hydroprocessing is a hydrogenation process that is used to remove 90% of pollutants such as nitrogen, sulfur, oxygen and metals in petroleum fractions. If these pollutants are not removed from petroleum fractions, they will move along the processing units and negatively affect the downstream equipment, catalysts and the quality of finished products. Generally, hydroprocessing is applied before processes such as catalytic regeneration to prevent pollution of catalysts by the raw products. Hydroprocessing is also used to decrease the sulfur content before cracking and to increase the product yield.

Catalytic cracking is similar to thermal cracking, except that catalysts ease the transformation of heavy molecules into lighter products. Use of catalytic cracking increases the quality product yield under easier conditions compared to thermal cracking. Typical temperatures range between 454 and 482 °C at 0.7–1.4 atm. Catalysts used in catalytic cracking are generally in solid form (zeolite, aluminum, hydro silicate, processed bentonite clay, bauxite, silica-alumina) and are shaped like dust, marble, particle or other various shapes (Gupta, 2003).

Production of renewable fuels and waste disposal are two of the major concerns facing the world today, because both environmental concerns and energy derived from petroleum-based fuels will define the future economic potential (Jopert et al., 2015). Throughout the world, much research is being conducted on the use of waste materials (Van Jaarsveld et al., 1998) in order to either avert an increasing toxic threat to the environment or to streamline present waste disposal techniques by making them more affordable. It, therefore, follows logically that an economically viable solution to this problem should include utilization of waste materials in new products for other applications rather than disposal in a landfill.

When the precious metal content is considered, petrochemical wastes can be considered as significant secondary resources. These solid wastes contain a high amount of metal oxide/sulfur. The oxides and sulfur, which can easily be oxidized, react with the environment by self-leaching when it comes in contact with the external atmosphere, and pollutes the environment (Furimsky, 1996). For this reason, storing petroleum catalyst waste is never an appropriate option. The only option is to determine metal recovery methods that are environmentally friendly and economical.

Hydroprocessed catalyst wastes require a strict adherence to environmental regulations due to their hazardous structure and toxic chemical content. The importance of the amount of hydroprocessed catalyst waste has increased due to the following reasons (Marafi and Stanislaus, 2008a,b):

- Increase in distilled hydroprocess capacity to meet the demand for fuels with ultra-low sulfur content,
- decreased recovery time in diesel hydroprocessing's heavier processes,
- constant increase in heavy raw materials with high sulfur and metal content (heavy crude oil even from non-conventional resources like tight and shale oil).

The volume of installed capacity of hydroprocessing catalyst is increasing in order to cope with the increasing demand for the development of nearly sulfur free clean fuels and the need for deeper heavy ends conversion. Similarly, low refining margins are driving industry to cost optimization, while environmental regulations are getting tougher. In addition to the growing fresh hydroprocessing catalyst market (hydrodesulfurization, hydrocracking), regenerated catalyst usage is also increasing with an estimated worldwide consumption of roughly 30,000 t/y. This additional tonnage of regenerated catalysts is extremely useful for refineries hoping to reduce their procurement expenses as well as to limit their generation of chemical waste. Unfortunately, the ratio between the regenerated and the fresh catalyst market in distillates hydroprocessing is below 50%, meaning that not all spent catalysts are regenerated at least once. This low reuse rate can certainly be increased by a careful evaluation of the spent catalyst (Saha et al., 2012).

Spent hydroprocessing catalysts have been classified by the U.S. Environment Protection Agency (EPA) as hazardous wastes. EPA has added hydroprocessing catalyst (K171) and hydro-separation catalyst (K172) in August 1998 due to their self-heating property and the toxic chemical content (Federal Register, August 6, 1998).

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