Waste Management of Spent Petroleum Refinery Catalyst: Mechanism Review

Isam Al-Zubaidi and Congning Yang

Abstract—Petroleum refinery uses many catalysts such as hydroprocessing catalyst HPC, fluid catalytic cracking catalyst FCCC, reforming catalyst RC, etc. During the refining processes, the catalysts are deactivated; the spent catalysts are regarded as hazardous toxic materials due to heavy metals, coke, other poisonous compounds, and hydrocarbons. Huge amount of spent catalysts SC is generated which is expected to increase with expansion capacities of available refineries processes. This paper is reviewing the mechanisms of refining catalyst and the deactivation processes and focusing on spent catalysts management. Management of spent catalyst includes four main options; select the catalysts which reduce the generation of SC by switching to more environment friendly, longer lifetime and less toxic catalyst during the refining process; regenerate the SC; and precious metal recovery should be explored and reuse for other applications. The selection can be based on many factors such as safety, environment, mobility, etc.

Index Terms—Management, Petroleum Refinery, Spent Catalyst.

I. INTRODUCTION

Catalysts play an important role in petroleum refining processes and especially during heavy crude processing. Catalyst allows crude oil products to meet the quality and environmental requirements by changing the molecular structure, removing of sulfur, metals and other heteroatoms and also adding hydrogen during catalytic processes. Hydrocarbons can be converted into desirable and acceptable products. Three main processes use catalysts: HP, FCC, and RC. In 2018, catalyst market in North America was 893.47x106 $ and it may reach 1048.4x106 $ by 2023, at Compound annual growth rate (CAGR) of 3.25% during the forecast period from 2018 to 2023 [1]. Catalysts market is increasing with an increasing demand of energy. Fig. 1 shows the Middle East and Worldwide catalyst consumption in petroleum refineries [2]. However, there is a significant loss in catalyst activity over time and reach to the point that the activity is not accepted (spent catalyst) and action need to be taken either to regenerate or replace it. Since environmental regulations on spent catalyst are very strict, great attention need to be taken on the development of regeneration and utilization on other applications. It is known that some SC has economic value through recovery due to their unique properties. This paper will focus mainly on spent catalyst management.

Refinery HP includes hydrocracking HC and hydrotreating processes HTP to convert conventional petroleum to commercial fuels through adding hydrogen while reducing sulfur, nitrogen and aromatics. Typical HPC is used to optimize the yield of high-quality light oil fraction from heavy crude oil containing high impurities. Spent HPCs are hazardous solid wastes due to the presence of hazardous materials including, heavy metals, metal oxides, and metal sulphides [3]. These catalysts have very high porosity and surface areas. The deactivation is due to the coke deposition. Spent HPC is shown in Fig. 2.

The catalytic hydrogenation and hydrocracking processes help to converts high molecular weight feedstock into low molecular weight products. Impurities in the feed such as sulfur, nitrogen and metals are removed by hydrogenation. Then cracking breaks bonds to produce unsaturated stable products (diesel fuel, lubricating oils, jet fuel, low sulfur fuel oil, kerosene, etc.). The hydrocracking catalyst has two functions: cracking and hydrogenation /dehydrogenation. The cracking function is served as acidic support, which can be amorphous oxide (e.g. silica-alumina), crystalline zeolite (e.g. modified Y zeolite) plus binder (e.g. alumina) or mixture of crystalline zeolite and amorphous oxides. Hydrogenation function is served by metals, which are noble metals (e.g. palladium, platinum) or non-noble metal sulphides (e.g. Co, Ni, Mo, W). These metals make feedstock more reactive for removing heteroatom and cracking and decreasing coking rate. Activity and selectivity of hydrocracking catalyst can be improved by adjusting the ratio of cracking and hydrogenation function. The composition of hydrocracking
Catalyst is related to the final product requirements and process types [5-6]. Hydrocracking is pretreatment process of removing harmful impurities such as sulfur, nitrogen and metals by reacting with hydrogen before hydrocracking process. Catalyst is used to meet the final product specification of kerosene; light naphtha and low sulfur fuel oils. Catalyst selection is based on activity and desired products. Co-Mo catalyst can apply for desulphurization of straight run petroleum fractions while Ni-Mo hydrotreating catalyst is used for saturation of poly-nuclear aromatic compounds with higher activity and removing nitrogen compounds. Ni-W is used for high activity aromatic saturation. The life period of typical hydrotreating catalyst is about one year depending on operating condition and process. Recently, the use of hydrotreating catalyst had been increasing due to the strict regulations on sulfur-free or ultra-low sulfur contents in diesel and jet fuels. The maximum sulfur content in on-road diesel fuel is 10-15 ppm [7-8].

B. FCC Catalysts

FCC is the heart of refinery process due to its applicability, flexibility and good economic feasibility, which is able to converts high boiling, high molecular weight and straight-chain alkane hydrocarbon fractions into high valuable and high-octane gasoline, olefinic gases and other products. Carbon is deposit as coke on the active sites of the catalyst. FCC catalysts are in fine powder form with a bulk density of 0.80 to 0.96 g/cm3 and average particle size of 75 mm and average surface area of 800 m²/g [9]. Typical catalyst has two major parts, crystalline zeolite and matrix. Crystalline structure of alumino-silicates of Y-Zeolite is the main active component (solid acid), which represents 15%-40% of most commercial catalysts. It is the major contributor to the catalytic activity and selectivity. The alumina matrix part increases the body of catalyst and optimizes properties of catalyst. There are three substances in the alumina matrix: binder, filler and additives. Binder and filler provide physical properties of catalyst. Binder is usually silica sol, which provides cohesion for zeolite particles. Filler is usually clay, which contributes the body and physical integrity of catalyst. The addition of additives to the catalyst is to improve the combustion of CO and CO₂ in the regenerater. As an example, the addition of metallic oxides can help to fix SO₂ on the catalyst so that sulfur will be recovered as H₂S in the ractor and helps to promote octane number of gasoline and catalyst metal resistance, boost CO oxidation and reduce SO₂ emission. FCC catalyst is good to crack and produce branched hydrocarbons, even a small amount of metal deposits catalyzes coke disposal that can reduce yield and change the composition of the oil. So, desirable chemical and physical properties of typical catalyst should be considered through high activity, large pore sizes, good stability under high temperature, good resistance to attrition and low coke disposition. FCC catalyst contamination with vanadium (V), nickel (Ni), iron (Fe) and sodium (Na) has a bad effect and can affect the structure and performance of the catalyst while the effect of nitrogen and sulfur are less harmful. The pore blockage by coking effect the sulfur and acid sites neutralization by nitrogen are caused serious problems [10].

C. Reforming Catalysts

Catalytic reforming process is highly endothermic process that converts C7-C10 hydrocarbons with low octane numbers into high-octane reformat products. Low octane naphtha is converted into iso-paraffins and cyclic naphthenes. Part of iso-paraffins and cyclic naphthenes are dehydrogenated to produce high-octane aromatic hydrocarbons. Hydrogen gas is by product from the dehydrogenation, is fed into other process such as hydrocracking. RC is bi-functional catalyst, which contains platinum (Pt) or rhenium (Re) on gamma alumina support base [11]. Pt or Re acts as catalytic sites for the dehydrogenation and chlorinate alumina provides the acid site to increase structure changes such as isomerization, cyclization and hydrocracking reactions. RC should be chlorinated before using otherwise hydrogen will restore Pt/Re to metallic state in the vapor phase. It should pay more attention while chlorinated, otherwise excess chlorination can reduce the activity of the catalyst. Iridium (Ir) and Tin (Sn) can be added to optimize activity and yield at low pressures of catalyst respectively [12]. The activity of the catalyst in semi-regenerative catalytic reformer is related to coke deposition and chloride loss. Impurities such as coke, sulfur, nitrogen, metals and water can deactivate the RC. In semi-regenerative catalytic reformer, the activity of RC can be restored by in-situ high temperature oxidation of the carbon followed by chlorination for every 6-24 months. This process is semi-regenerative. Normally RC can be regenerated in situ at least three or four times. After that the manufacture will collect spent reforming catalysts for reclamation of the valuable Pt and/or Re content.

II. CATALYST DEACTIVATION

Catalyst deactivation is referred to the loss of activity and selectivity [13]. It is the most concerning problem that causes a negative impact on the behavior of the process, which affects economic performance through catalyst replacement, research and process shutdown. Catalyst deactivation can be poisoned by one of the contaminants existing in the feed. During cracking or condensation reaction, carbon filaments and coke can plug its surface, pores and void and damage its pellets. Oxygen or chlorine in the feed gas can make the presence of volatile oxides or chlorides of the active phase, then it is transported from the reactor. Deactivation is generally dependent on catalyst structure, operating conditions, and the feedstock characterization [8]. Catalyst deactivation can classify to: Poisoning; fouling; thermal degradation; vapor compound formation accompanied by transport; vapor-solid and/or solid-solid reactions, and attrition/crushing [14]. Table I represent the deactivation reasons and their significant on the catalyst deactivation for three refinery processes [15].

| TABLE I: EFFECTS OF COKE AND METALS DEPOSITION ON DEACTIVATION OF HPC [15] |
|---------------------------------|----------------|----------------|
| Refinery process               | Relative effect | Metal deposit  |
| Hydrodesulfurization           | Moderate       | Strong         |
| Hydrogenation                  | Weak           | Strong         |
| Hydrocracking                  | Weak           | Very strong    |

Three major mechanisms of catalyst deactivation will be summarized here as follows:

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A. Poisoning

Poisoning refers to the strong chemisorption of contaminants from the reacting substances or reaction products on the catalyst active sites. It decreases the number of active catalytic sites or the fraction of the total surface area, which has the capability of optimizing reaction. Moreover, it increases the average distance for a reactant molecule diffuses through the pore structure before reaction [16]. If the rate of poisoning is smaller than the rate of diffusion, the catalyst will be distributed by the poison which known as homogeneous poisoning. However, if the rate of poisoning is larger than the rate of diffusion, the pore-mouth poisoning occurs as exterior layers of the catalyst, which is covered by a poisoned shell. In both situations, poisoned sites will be blocked for further catalytic reaction. Although catalyst poisoning is bad and undesirable, it can promote selectivity of reactions by isolating selective intermediates. Two types classify poisoning: temporary and permanent poisoning. In temporary poisoning (or reversible poisoning), poisons (or inhibitors) can be removed so that catalyst activity and selectivity can largely recover. Common temporary poisons are sulfur, organic nitrogen, water, oxygenated organics, halogens, etc. [17]. Catalyst deactivation by sulfur is due to the formation of strong metal sulfur bonds. Sulfur chemisorbs on the surface of catalyst reacts with the active site in order to stop products [18]. Organic nitrogen poisoned hydrocracking and reforming catalysts and reacts to form ammonia. Ammonia will neutralize the acid functions of the catalyst metal sites [19]. FCC feedstock consist of vacuum gas oil which contain 25-30% of the nitrogen in crude oil and vacuum residue which contain 70-75 % of the nitrogen in crude oil. Basic nitrogen compounds are mainly present in the light fractions of crude oil and non-basic are predominant in heavier fractions of crude oil [20]. Nitrogen deactivates FCC catalyst by interacting with the acid sites, which is responsible for the cracking reaction and resulted in deactivating the catalyst. The higher the proton affinity of nitrogen base, stronger catalyst activation will occur [21]. Water as temporary poisoning has an impact on catalysts by dissolving partial soluble components of the catalyst. Water can dissolve chlorides of reforming catalyst so that, the acid site activity is reduced on the catalyst surface. This will reduce the ability of catalyst in isomerization reaction and water leads to hydrothermal aging, which causes crystal growth and activity lost permanently. Residue water in catalyst had a bad effect and can form high-pressure steam, which breaks the support structure of catalyst. In permanent poisoning (or irreversible poisoning), poisons cannot be removed because they are strongly adsorbed, and the loss of catalyst activity and selectivity cannot be restored. Heavy metals such as arsenic, lead copper, iron, nickel, chromium, mercury, sodium, potassium cause permanent poisoning. Arsenic and mercury are particularly toxic because they react with the active metals to form inactive surface. This can reduce the surface area for reactivity. Nickel deposits are formed on the catalyst surface in FCC processes. They can increase carbon deposition as a strong dehydrogenation catalyst. Nickel does not have an impact on catalyst activity, but it has a negative effect on selectivity [19]. It increases the coke selectivity. Unlike nickel, sodium on the catalyst surface has mobility because it first interacts with alumina phase and then moves to the fresh particles. Sodium is the reason for zeolite structure permanent damage under high temperature.

B. Fouling/Coking

Fouling is the physical deposition from fluid phased and covers the catalyst surface. It not only plugs the active sites and pores of the catalyst to cause activity loss, but cause disintegration of catalyst particles and blocking of the reactor voids [13]. Coke deposits may represent 15%-20% (w/w) of the catalyst and this deposit deactivates the catalyst by covering the active sites or pore blocking. The main difference between coke and carbon is arbitrary; carbon can be considered as a product of CO disproportionation (2CO→C+ CO₂), while coke is the product of decomposition (cracking) or condensation of hydrocarbons [22]. The most common example of fouling is coke formation by carbon deposition. Gerber (1999) suggests that there are three different forms of coke formation; the first form is built by strongly and reversibly bound aromatic hydrocarbons such as benzene, naphthalene, and poly-nuclear aromatics which produced by polymerization of benzene and naphthalene; the second form consists of thermal decoupling of asphaltic clusters and subsequent binding onto a catalyst surface sulfur side; and the third form is produced by poly-nuclear aromatic meso-phase crystals formed ilom the asphahenes [19,23]. Coke formation is complex because it depends on catalyst and reaction types, and reaction conditions such as partial pressure of hydrogen. Polymerization or condensation and dehydrogenation reactions can all form coke. Coke on HP catalysts is deposited very slowly due to high hydrogen partial pressure. However, it will form more easily on FCC catalysts because of the absence of high hydrogen partial pressure. In this circumstance, contaminants such as nickel and vanadium can further catalyze coke deposition to motivate dehydrogenation reactions in few seconds and catalyst deactivation occurs quickly. Many authors showed the mechanisms of carbon deposit and coke formation on metal catalysts [24-29].

C. Thermal Degradation/Sintering

Thermal degradation or sintering is caused by the loss of catalytic active surface area and the loss of support area due to the crystallite growth of catalytic phase and support collapse and due to pore collapse on crystallites of the active phase. Understanding sintering kinetics and the associated mechanisms is an important goal to be able to limit and control catalyst sintering rationally [30]. The crystallite growth and support collapse are referred to sintering. This occurs at high reaction temperatures over 500°C and accelerated by the presences of water vapor. The impact of temperature on sintering of metal is related to the dissociation and diffusion of surface atoms. The surface atom vibration increases with the rising temperature. Then less strongly bound surface atom dissociates and diffuses over the surface until a desired temperature achieved. As reaching to the Tamman temperature, the atoms can move freely through bulk catalyst to increase surface activity or to reduce it because of the uneven crystallite size and growth [16, 29]. The sintering process has three phases; phase 1 involves rapid loss in catalyst activity (surface area). Phase 2 when sintering slowly down, and phase 3 if the catalyst reaches stable...
performance [31].

III. PREVENTION OF CATALYST DEACTIVATION

Poisoning is due to the strong chemisorption of contaminants from the reacting substances or products of the reaction on the catalyst active sites; it is very difficult to regenerate poisoned catalysts. The best way to prevent poisoning is by removing impurities from the feed to the catalyst [31]. These authors showed that the strongly basic compounds such as ammonia, amines and pyridines could be removed from the feed during the hydrosacrifying reaction for oxide catalysts. Other methods for minimization the poisoning are; using guard bed to adsorb poison; using additives that selectively adsorb poison; select lower adsorption strength reaction conditions; reduce poison on active sites by promote pore structure and mass transfer regimes; and use coating that prevent diffusion. Coke formation is very complex because it relates to catalyst types, reaction types and reaction conditions. The methods of preventing fouling/coking are varying with different mechanisms. Coke formation on the catalyst surface can be reduced by selecting reaction conditions or by using gasifying agents. If coke deposition on some oxide or sulfide catalysts, it can be minimized by reducing the acidity of the support to extend catalysts life. Specific reactor bed or catalyst geometries can be used to decrease coke on pore plugging. It is very important to select the reaction conditions and catalyst properties to prevent thermal degradation or sintering because this process is irreversible. The selection of lower reaction temperature than the melting point of metal can effectively avoid sintering. The minimizing water vapor is very important because water vapor will motivate the crystallization and structural modification of oxide supports. In addition, adding thermal stabilizers such as higher melting noble metals can lower the rate of sintering on the catalyst [32].

IV. SPENT CATALYST MANAGEMENT

During Catalytic processing, there will be a significant loss in catalytic activity and/or selectivity, and the process will not meet the requirement of the quality of products with the set operating variables due to poisoning, thermal degradation, fouling and other physical and chemical losses. The catalyst is completing their life cycle need to withdraw from the process. Dufresne, 2007, showed that worldwide-generated spent catalysts are in the range of 150,000 to 170,000 tons per year [33]. Therefore, with 5% annual increase in catalyst consumption, the generation of spent hydrosacrifying catalysts predicted to be 250,000 tons annually. Significant increase of spent hydrosacrifying catalysts volumes are mainly attributed to rapid growth in the distillate hydrotreating capacity to meet the increasing demand for ultra-low sulfur transportation fuels, reduced cycle times due to in increased severity operations to meet stringent fuel specifications and demand of processing sour crudes based on economic criteria. The deactivated catalyst is known as equilibrium catalyst or spent catalyst. In HP or RP, the spent catalysts can be replaced with fresh catalysts. In FCC processing, the spent catalysts is a mixture of fresh catalysts and regenerated catalysts. Some relative less active spent catalysts are replaced with same amount of fresh catalysts, mixing with other regenerated or aged catalysts, then they continue to circulate in the FCC riser. Spent FCC catalysts have lower flammability and toxicity than that spent HP and RC. Refineries pay more attention on spent catalyst management based on high expensive active fresh catalysts and environmental concerns.

A. Spent Catalyst Properties and Mechanisms

When operating HPC for long time, many hazardous components such as heavy metals (Al, V, Mo, Co, Ni, As, Fe) and nonmetallic elements (C, S) are built up on the HPC. These contaminants plug pores and become potentially dangerous to the environment. Some of heavy metals are very valuable to recovery as secondary raw materials. Al Sheeha.H (2014) collected HP spent catalysts from Kuwait National Petroleum Company and examined by X-ray analysis (SEM-EDX). The results showed that the spent catalysts contained high deposition of C, Al, V, Ni, P and Mo. These heavy metals destroy the structure of the catalyst with irregular shapes. The V is mostly remained at the entrance of catalyst pore and Ni is remained in the interior of the catalyst [36-38]. The comparison between fresh hydrosacrifying catalyst and spent hydrosacrifying catalyst is shown in Fig. 3.

The SEM images of fresh and spent hydrosacrifying catalysts.

The decrease in specific surface area and total pore volume of the spent catalyst is related to heavy metal deposits and fouling coke. FCC catalyst deactivation takes place by several mechanisms. During the first hot cycle, there are some permanent deactivations because of steam migration of silica in the zeolite [18]. After FCC catalysts move to the vessel outside the riser, there is some loss of porosity of the

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amorphous silica-alumina and this can destroy part of zeolite structure. Therefore, the spent FCC catalysts result from the reducing of surface area and pore volume. For spent FCC catalysts, both amount of coke formation and flammability of the spent FCC catalyst are lower than those of hydrotreating catalyst. The distribution of coke deposition is evenly on the FCC catalyst surface, so it is easily oxidized. The composition of fresh and spent FCC catalysts is shown in Table II.

### TABLE II: COMPOSITION OF FRESH AND SPENT FCC CATALYSTS BY XRF IN PPM [39]

<table>
<thead>
<tr>
<th>Element</th>
<th>Fresh Catalyst</th>
<th>Spent Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>141,100</td>
<td>161,467</td>
</tr>
<tr>
<td>Silicon</td>
<td>260,000</td>
<td>322,000</td>
</tr>
<tr>
<td>Vanadium</td>
<td>&lt;33</td>
<td>1,455</td>
</tr>
<tr>
<td>Nickel</td>
<td>31</td>
<td>3,930</td>
</tr>
<tr>
<td>Iron</td>
<td>3,880</td>
<td>6,500</td>
</tr>
<tr>
<td>Titanium</td>
<td>3,980</td>
<td>6,430</td>
</tr>
<tr>
<td>Barium</td>
<td>1,684</td>
<td>93</td>
</tr>
<tr>
<td>Antimony</td>
<td>&lt;1.9</td>
<td>1,326</td>
</tr>
<tr>
<td>Lanthanum</td>
<td>2,700</td>
<td>3,490</td>
</tr>
<tr>
<td>Cerium</td>
<td>3,470</td>
<td>4,077</td>
</tr>
<tr>
<td>Sulfur</td>
<td>3,440</td>
<td>1,100</td>
</tr>
</tbody>
</table>

Spent reforming catalyst properties are very similar to spent hydrotreating catalysts. Catalyst activity is reduced by coke deposition and chloride loss. Therefore, the spent reforming catalysts contain impurities such as coke, sulfur, nitrogen metals and water.

### B. Options for Spent Refinery Catalysts Management

There are many post treatment methods for spent catalyst such as regeneration, rejuvenation, reuse, and utilization as raw materials to handle them before final disposal.

1) **Regeneration and Rejuvenation: Metal Recovery**

The concept of regeneration and rejuvenation of spent refinery catalysts is to de-coke and recover the valuable metals by oxygen to burn carbon and sulfur with control temperature and gas flow rate if the concentrations of metal contaminants on the catalysts surface are low. First, it is required to identify the renderability of spent catalysts. If the concentration of metal contaminants is high on the catalysts surface, then the catalysts are very easily affected to irreversible deactivation by adsorption of metal contaminants. This will lead to pore plugging and diffusion limitations. The rejuvenation process for spent residue HPC is shown in Fig. 5.

2) **Leaching**

Leaching is extracting material from a solid by dissolving them is liquid. This process can achieve by acidic leaching, basic leaching, alkali leaching, bioleaching and supercritical fluid leaching.

**a) Acidic Leaching**

Acidic leaching is an extraction process, which can achieve by acidic agents to ground and de-coke spent hydrotreating catalysts in order to recover metals. Two acidic agents are available; organic and inorganic acids. Citric acid, oxalic acid, and Ethylene-diaminetetraacetic acid (EDTA) are regarded as organic acids while sulfuric acid (H2SO4) and nitric acid (HNO3) are considered as inorganic acids. The leaching efficiency of recovery metals reached to 95% as shown in Table III [39].

### TABLE III: ACIDIC LEACHING OF SPENT HP FINE POWDER CATALYST [39]

<table>
<thead>
<tr>
<th>Leaching Agents</th>
<th>Aeric Acid</th>
<th>Oxalic Acid</th>
<th>Nitric Acid</th>
<th>Sulfuric Acid</th>
<th>Citric Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal Recovery</td>
<td>V&lt;77%</td>
<td>V&lt;75%</td>
<td>V&lt;78%</td>
<td>V&lt;96%</td>
<td>V&lt;94%</td>
</tr>
<tr>
<td>Recovery from</td>
<td>Mo&lt;98%</td>
<td>Mo&lt;98%</td>
<td>Mo&lt;98%</td>
<td>Mo&lt;85%</td>
<td>Mo&lt;82%</td>
</tr>
<tr>
<td>Aquous Acids</td>
<td>Ni&lt;27%</td>
<td>Ni&lt;28%</td>
<td>Ni&lt;30%</td>
<td>Ni&lt;88%</td>
<td>Ni&lt;83%</td>
</tr>
<tr>
<td>Solution</td>
<td>AI&lt;3.5%</td>
<td>AI&lt;2.6%</td>
<td>AI&lt;0.3%</td>
<td>AI&lt;3.5%</td>
<td>AI&lt;0.3%</td>
</tr>
</tbody>
</table>

H2SO4 is used for improving leaching process for spent HPC [41]. Spent HPC contained Mo, V, Co in an alumina carrier were first roasted at temperature between 400 and 1000°C, followed by reduction dissolution by dissolving the roasted product with H2SO4. Large amount of Al can be separated and recovered as (NH4)2Al(SO4)2 from the solution. Iron can be removed from the solution by solvent extraction to extract Mo as MoO2. Then V can be extracted as VO3 through solvent extraction. Then finally recovering Ni and Co from the residual solution [42-47]. Dewi Purnama, 2018, concluded that citric acid process has higher ability to extract valuable metals as high as organic acid [48]. The surface metal on the spent hydrotreating catalysts can effectively extracted from basic leaching agents such as ammonia and ammonium salt solutions, which have weakly basic and slightly acidic characters. Different metal extraction had been reported in Table IV by using different basic leaching agents [39, 42, 44].

### TABLE IV: BASIC LEACHING OF FINE SPENT HPC POWDER [39]

<table>
<thead>
<tr>
<th>Leaching Agents</th>
<th>NH4OH</th>
<th>NH4OH+</th>
<th>NH4OH+</th>
<th>NH4OH+</th>
<th>NH4OH+</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal Recovery</td>
<td>V&lt;77%</td>
<td>V&lt;76%</td>
<td>V&lt;78%</td>
<td>V&lt;96%</td>
<td>V&lt;61%</td>
</tr>
<tr>
<td>Recovery from</td>
<td>Mo&lt;98%</td>
<td>Mo&lt;98%</td>
<td>Mo&lt;98%</td>
<td>Mo&lt;85%</td>
<td>Mo&lt;83%</td>
</tr>
<tr>
<td>Aquous Acids</td>
<td>Ni&lt;27%</td>
<td>Ni&lt;28%</td>
<td>Ni&lt;30%</td>
<td>Ni&lt;88%</td>
<td>Ni&lt;83%</td>
</tr>
<tr>
<td>Solution</td>
<td>AI&lt;3.5%</td>
<td>AI&lt;2.6%</td>
<td>AI&lt;0.3%</td>
<td>AI&lt;3.5%</td>
<td>AI&lt;0.3%</td>
</tr>
</tbody>
</table>

Ultrasonic agitation is also used in extraction of Mo, V, and Ni from spent HPC by acid leaching. H2SO4 and citric acid were used. The ultrasonic vibration was more effective for metal extraction. More than 95% of all valuable metals were extracted in short time at relatively low temperature [49].

**b) Alkali Leaching**

Alkali leaching uses aqueous alkaline solution (NaOH or Na2CO3), which mixed with H2O2 as leaching agent to extract the metals from spent HPC as shown in Fig. 6. High purity of MoO3 with small amount of Ni, Co and V could be extracted selectively from unroasted spent catalysts. As an environmental friendly H2O2 solution, it can reduce the investment of process by reducing steps of separation.

![Fig. 5. Rejuvenation process for spent residue HPC [40].](image-url)
processes [42-44].

Microwave-assisted leaching were also used to leach vanadium (V) and molybdenum (Mo) from spent catalysts in sodium hydroxide medium [50]. The authors studied the influence of microwave power, leaching time, leaching temperature, and sodium hydroxide concentration on the leaching efficiency of spent catalyst. The efficiency of leaching V and Mo reached to more than 94. NaOH and ultrasound-assisted oxidative treatment with H₂O₂ showed the better performance for sulfur removal from spent catalyst [51]. Sulfur and other metals dissolved together to the solution using ultrasound-assisted oxidative treatment with H₂O₂, while the covered sulfur was removed from the spent catalyst without affecting the dissolution of valuable metals.

c) Bioleaching

Bioleaching is new techniques based on transforming the solid compounds to be extractable by microorganisms’ secret organic or inorganic acids during the metal dissolution. Typical microorganisms, which can recover metals, are bacteria such as Thiobacillus ferrooxi- dans and Thiothrix, as well as the fungi such as Aspergillus and Penicillium genera [47–52]. The efficiency of bioleaching to extract metals is 3-20% higher than the chemical leaching but it takes longer time of leaching comparing with other leaching methods. Fungus Aspergillus Niger was used for bioleaching of heavy metals from spent catalyst [53]. FCC catalyst was taken as a model for bioleaching tested in batch cultures with spent catalysts at various pulp densities (1–12%). The bioleaching was compared with mineral acids such as sulfuric, nitric acids, and organic acids such as citric, oxalic, and gluconic acids. The bioleaching have higher metal extraction than acid leaching. The Niger was able to mobilize Ni (9%), Fe (23%), Al (30%), V (36%) and Sb (64%) at 1% pulp density. Bioleaching process is regarded as cost effectiveness, simple in operation and higher recovery of heavy metals [54]. The authors adapted various microorganisms of bacteria and fungus. The Pb-ion showed high resistance to bioleaching while Mn ion was easily bioleached by adapted microorganisms.

d) Super Critical Fluid Leaching

Supercritical fluids are used to leach metals from microporous solids due to their unique properties of very high liquid-like density, gas-like movement, low viscosity, and higher diffusibility. In supercritical phase, high liquid-like density can result in a high capacity for solutes. It is shown that the efficiency of recovery Co can enhance about 14.2% with less amounts of supercritical solvents as leaching fluids [55].

3) Roasting

Roasting process of spent refinery catalysts with roasting agents can promote the solubility of metal contaminants such as Mo, V, and Co in water. These metals remain in the solid residue after water extraction. Alkaline compounds such as sodium and potassium salts are the most roasting agents. Sodium salts such as Na₂CO₃, NaCl and NaOH roasting agents are used for roasting the spent catalysts. The ground spent HPC is roasted in air at 600°C using fluid bed calciner to clean C and S deposits. The mixture of calcined compounds with Na₂CO₃ needs to be roasted again in air at 750°C to covert Mo and V oxides to Na₂MoO₄ and NaVO₃. The leached sodium carbonate roasted product is stirred and mixes with Mo and V, filtrating the insoluble Co, Ni, Al₂O₃ from the Na₂MoO₄ and NaVO₃ solutions. Adding NH₄Cl into the residue solution to precipitate NH₄VO₃. Then filtration, drying, and calcination are provided to the precipitate at 500°C to V₂O₅. Adding CaCl₂ or lime into precipitation tank at room temperature to recover Mo as MoO₂. During the roasting with sodium salts, ~ 90-95% of Mo and V can be recovered. The residue contained Co, Ni and Al₂O₃ can be stirred with caustic soda at 500 psi and 250°C. Filtering out the NaAlO₂, the residue insoluble NiO and CoO can be further recovered to Ni and Co [25–26]. The efficiencies of recovering Mo, V, Ni, Co and Al from spent processing catalysts by NaOH as roasting agent are up to 98.9%, 95.8%, 98.3%, 98.5% and 90.6% respectively. The process flow diagram is shown in Fig. 7 [7, 45]. Potassium salts such as KHSO₄ can be used for spent hydproprocessing catalysts. Mo, Ni, Co and Al react with KHSO₄ to produce soluble salt of metals in water under high temperature.

\[
\begin{align*}
\text{NiO + 2KHSO}_4 & \rightarrow \text{NiSO}_4 + K_2\text{SO}_4 + H_2O \\
\text{CoO + 2KHSO}_4 & \rightarrow \text{CoSO}_4 + K_2\text{SO}_4 + H_2O \\
\text{Al}_2\text{O}_3 + 6\text{KHSO}_4 & \rightarrow 2\text{Al}_2(\text{SO}_4)_3 + K_2\text{SO}_4 + H_2O \\
\text{MoO}_3 + 2\text{KHSO}_4 & \rightarrow \text{MoO}_2\text{SO}_4 + K_2\text{SO}_4 + H_2O
\end{align*}
\]

Then apply precipitation or solvent extraction methods to recover these solubilized metals. Using potassium salts as roasting agents can recover up to 90% of Mo, Co, Ni and Al. Fig. 8 shows the flow-recovering diagram using KHSO₄ as potassium salts [7, 46].

Marafi, M (2008) summarized metal recovery using different leaching and roasting methods as shown in Table V.
4) Chlorination

Metals from spent catalysts can recover by chlorination technique. This process transforms the metals into volatile and non-volatile chlorides in a selective manner. The residual oil in spent catalyst is extracted and removes by solvent. The metal sulfides, Al₂O₃ and coke in the spent catalyst undergo gaseous chloride between 500-600°C, and then V, Mo and Al become volatile chlorides.

Through granules of anhydrous NaCl to separate AlCl₃ from other chlorides, MoCl₅ can be separated by granules of crystallized KCl and VCl₄ is recycled by condensation at 60°C. Ni and CoCl₂ are not volatile and will remain as solid residue in the column. The recovered efficiency of Mo, V and Al are ~90%wt. The volatilization of Co and Ni are negligible. It was reported that V, Mo, Co and Ni from spent HPC could be recovered without Al by selective chlorination by roasted and unroasted spent catalyst. The unroasted spent catalyst is treated for chlorination at 500°C during ration time of 30 min with a gas mixture having Cl₂/N₂ or Cl₂/O₂ ratio equal to one. The recovery efficiency of Mo, V is 98% and 80% respectively and the limitation of chlorination of alumina is between 3%-9%. Under same condition of gas mixture with Cl₂/O₂ ratio equal to one, the recovery efficiency of Mo, V and Al from roasted sample that is free from carbon and sulfur are 97%, 82% and less than 3%. Final residue consists of alumina and which is environmentally friendly. The chlorination apparatus is shown in Fig. 7.

![Fig. 7. Recovering flow diagram of spent catalyst with roasting agent NaOH [46].](image)

![Fig. 8. Flow diagram of recovering spent catalyst with roasting agent KHSO₄ [46].](image)

Se In Cho et al. showed that carbon- chlorination was the most effective technique to remove metals from spent equilibrium catalyst. The activity was not restore because of the chlorination conditions. The most effective method to rejuvenate spent catalyst was washing with weak acid after converting metals to water-soluble form by calcination [56].

5) Electrochemical Dissolution

Electrochemical dissolution is used to recover metals from spent HP and FCC catalysts using cerium. The spent catalyst containing sulfides of Mo, V and Ni with carbonaceous material and sulfur is added to the solution, which contains Ce⁴⁺ ions in the anode side of electrochemical cell (Fig. 8). The Ce⁴⁺ ions transfer to the catalyst side and react with carbon and metal deposits, aqueous Ce³⁺ ions are generated and oxidized to Ce⁴⁺ to change oxidize coke to CO₂. It converts metals to soluble oxides [52]. The half-cell reaction for cerium is:

\[ \text{Ce}^{3+} \rightarrow \text{Ce}^{4+} + e^- \]

The net anodic reactions are:

\[ \text{C}_x\text{H}_y + (2x)\text{H}_2\text{O} \rightarrow \text{XCO}_3 + (4x+y)\text{e}^- + (4x+y)\text{H}^+ \]

Metal sulfides + water → electrons + hydrogen ions + aqueous metal species + sulfate ions

For anodic reactions of typical hydrotreating catalyst metals:

\[ \text{NiS} + 4\text{H}_2\text{O} \rightarrow \text{Ni}^{2+} + \text{SO}_4^{2-} + 8\text{e}^- + 8\text{H}^+ \]

\[ \text{MoS}_2 + 12\text{H}_2\text{O} \rightarrow \text{MoO}_4^{2-} + 18\text{e}^- + 2\text{SO}_4^{2-} + 24\text{H}^+ \]

Water may be separated to form oxygen at the anode:

\[ 2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + O_2 + 4\text{e}^- \]
The net anodic reactions are balanced by the net cathodic reactions, which are determined by the presence of species in the catholyte, cell potential and mass transport characteristic in the cell. The cathode reactions by using nitric acid as the catholyte

$$3\text{H}^+ + \text{NO}_3^- + 2e^- \rightarrow \text{HNO}_2 + \text{H}_2\text{O}$$

$$\text{H}^+ + \text{HNO}_2^- + e^- \rightarrow \text{NO} + 2\text{H}_2\text{O}$$

$$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$$

Fig. 8. Electrochemical Cell [43]

6) Reuse of Spent Refinery Catalysts for Other Applications

The increasing demand for high quality transportation fuel, processing heavy crudes, and high level of environmental standards have increased the quantity of spent refinery catalysts, which require a sustainable management. The spent refinery catalysts can be regenerated or reactivated. If the catalytic activity cannot be returned to original levels, it can be utilized as a source of other useful materials, and/or metals in the spent catalyst are recovered. Then the stabilized residues shall be disposed by an environmentally friendly method. The regenerated catalysts can also be used for less demanding refinery operations. The regenerated spent refining oil hydrotreating catalyst might be used for hydrotreating of kerosene, and the regenerated Kerosene hydrotreating catalyst can be applied for naphtha hydrotreating [57].

7) Construction Materials

Spent FCC catalysts have potential to be used for construction materials such as asphalt filler, cement production, brick production and ceramic frits. Up to 5% of spent FCC catalysts can meet the specifications of typical asphalt filler. Adding 5% of spent FCC catalyst into brick production can produce very satisfactory quality and environmentally friendly bricks. The cement production is one of the best methods to reuse spent FCC Catalysts as up to 6% of the cement raw material (Zeolite Y) due to their content of silica and alumina. Under high temperatures, silica and alumina can react with lime to produce Portland cement. These solids are not hazard. The Spent FCC catalysts have to be evaluated before using in cement production in order to determine how much can be added into the process due to the presence of alkali which promote undesirable agglomeration of the cement during curing stage. Spent FCC catalysts can also utilize for prepare frits which are materials of glazing ceramic tiles. Glazes made of certain amount of spent FCC catalysts have the same aesthetic and technical characteristics with the typical materials [58-59]. Spent hydrotreating catalysts are restricted to use for cement production due to its hazardous nature. However, it can be used to prepare other applications shown in Table VI.

<table>
<thead>
<tr>
<th>TABLE VI: APPLICATION OF SPENT HYDROTREATING (HTC) CATALYSTS IN OTHER PROCESS [58]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spent Catalyst Type</td>
</tr>
<tr>
<td>--------------------------------</td>
</tr>
<tr>
<td>Residue HP unit</td>
</tr>
<tr>
<td>Metal(V and Ni) contaminated spent residue HDS catalyst (decokeled)</td>
</tr>
<tr>
<td>Decoked spent HDS catalyst</td>
</tr>
<tr>
<td>Metal fouled spent catalyst</td>
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<tr>
<td>Metal fouled spent catalyst</td>
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<tr>
<td>Spent (decokeled) CoMo/Al_2O_3 and NiMo/Al_2O_3 catalyst from gas oil/naphtha HT unit</td>
</tr>
<tr>
<td>Spent (decokeled) CoMo/Al_2O_3 and NiMo/Al_2O_3 catalyst from HT unit</td>
</tr>
<tr>
<td>Spent (decokeled) CoMo/Al_2O_3 and NiMo/Al_2O_3 catalyst from HT unit</td>
</tr>
</tbody>
</table>

a) Converting Waste Plastic to Fuels

The traditional ways to dispose off the increasing amount of waste plastics such as polyethylene, polypropylene and polystyrene are landfilled and incinerated. These methods are very expensive and cause air pollution and soil contamination. Spent FCC catalysts can be utilized in catalytic degradation at high temperatures to covert waste plastics into basic petrochemicals, which can be used as chemical feedstock or fuels. This method is not only control product yield and product distribution from degradation, but also helps to reduce reaction temperature, which leads to economical process with valuable products. The spent FCC catalysts consist of 5-40% zeolite, which can significantly promote the economic potential of waste plastic recycling process [60-63]. In the process, heavy hydrocarbons are converted into light products containing C5- C11 liquid hydrocarbons under lower temperature. The efficiency of catalytic degradation is much higher than thermal degradation.

b) Final Disposal: Landfilling

If the above methods are not useful, disposal of spent catalysts in landfills is the last remaining option. Only non-hazardous spent catalyst can be disposed. Therefore, spent catalysts should be treated for stability to reduce harmful materials before landfilling. For example, some reactive metals in spent catalysts can be converted into non-leachable minerals in the apatite and barite group. These minerals are capable to resist to acidity and degradation by geological and chemical condition. Similarly, Sealsafe technique is used to add calcium containing cement powder and aluminosilicate powder into the waste material in water. This treatment can covert to an impermeable solid that has non-leachable property. Other methods such as cement based solidification and immobilization also utilize for treating arsenic and heavy metals in spent catalysts [64-72].

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V. CONCLUSION

Hydrotreating catalyst is alumina matrix impregnated with mixtures of Co, Ni, Mo and W. FCC catalysts consists of two components: crystallize zeolite and alumina matrix. Reforming catalyst is bi-functional catalyst, which contains platinum (Pt) or rhenium (Re) on a gamma alumina support base. Catalytic activity and selectivity are reduced with time. Catalyst deactivation can attribute to: poisoning, fouling/coking and thermal degradation/sintering. Poisoning refers to strong chemisorption of contaminants from the reacting substances or products of the reaction on the catalyst active sites. Heavy metals, sulfur, organic nitrogen, water, oxygenated organics, etc. are common poisoning materials. It can be preventing by removing impurities form the feedstock in the catalytic process. Fouling is coke formation by carbon deposit. It can be reduced by selection of reaction conditions or using gasifying agents. Thermal degradation or sintering is caused by the loss of catalytic surface area and the loss of support area due to crystallite growth of the catalytic phase and support collapse and due to pore collapse on crystallites of the active phase. The spent HPC contains high deposition of C, Al, V, Ni, P and Mo, which affect the structure of catalyst with irregular shapes. There is some loss of porosity of amorphous silica-alumina and this can destroy part of zeolite structure for spent FCC catalysts. Spent reforming catalyst is very similar to spent HPC and it contains impurities such as coke, sulfur, nitrogen metals and water. There are three ways to manage the spent refinery catalysts: regeneration and rejuvenation reuse for other applications and landfilling final disposal. Regeneration and rejuvenation are used to de-coke and recover valuable metals, by using oxygen to burn coke and other impurities on the catalyst surface. They include leaching, roasting, chlorination and electrochemical dissolution. Leaching is performed by acidic and basic medium, bioleaching and supercritical fluid. The acidic leaching used organic or inorganic acids to de-coke spent catalysts, extract and recover metals. Basic leaching is similar to acidic leaching to extract metals on the surface using basic leaching agents. Bioleaching is based on transform solid compounds to be extractable by microorganisms’ secret organic or inorganic acids during metal dissolution. Supercritical fluids leach metals from micro porous solids due to their special properties. Roasting spent refinery catalysts by sodium and potassium salts can promote the solubility of metal contaminants in water. Chlorination is transforming metals into volatile and non-volatile chlorides in selective manner. Spent refinery catalysts can utilize for construction materials such as asphalt filler, cement production, brick production and ceramic frits. Spent FCC catalysts can convert waste plastics into chemical feedstock or fuels to reduce air pollution and soil contamination. If these techniques are not then the last option is landfilling. Since only non-hazardous spent catalysts can be disposed, they need to be pretreated to remove these harmful materials.

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