

Refining Waste Spent Hydroprocessing Catalyst and Their Metal Recovery

Meena Marafi, Mohan S. Rana

Abstract—Catalysts play an important role in producing valuable fuel products in petroleum refining; but, due to feedstock's impurities catalyst gets deactivated with carbon and metal deposition. The disposal of spent catalyst falls under the category of hazardous industrial waste that requires strict agreement with environmental regulations. The spent hydroprocessing catalyst contains Mo, V and Ni at high concentrations that have been found to be economically significant for recovery. Metal recovery process includes deoiling, decoking, grinding, dissolving and treatment with complexing leaching agent such as ethylene diamine tetra acetic acid (EDTA). The process conditions have been optimized as a function of time, temperature and EDTA concentration in presence of ultrasonic agitation. The results indicated that optimum condition established through this approach could recover 97%, 94% and 95% of the extracted Mo, V and Ni, respectively, while 95% EDTA was recovered after acid treatment.

Keywords—Spent catalyst, deactivation, hydrotreating, spent catalyst.

I. INTRODUCTION

REFINING catalysts are primarily used to improve the quality of products by enhancing the operational efficiency during the refining process. Worldwide refining catalyst demand is expected to grow 3.6 %/year to 4.7 billion in 2020 [1]. A catalyst is a specific to a hydrotreating reaction where removal of hetero-atoms (S, N, O, etc.) and metals were carried out. Worldwide economic and ecological developments are forcing refiner to produce better or cleaner fuel quality products [1], [2]. Hence in order to further maximize conversion, severe process conditions can be employed with the expense of a lower catalyst life [3]. The refinery catalysts broadly classified based on their usage in the refinery as shown in Fig. 1. Among various refining process, the catalyst is dominating in hydroprocessing than fluid catalytic cracking (FCC) and reforming. Usually, in complex refineries at about 8–10 petroleum refining processes generate waste catalysts, which are mainly based on the feed quality. Hydroprocessing (HDS & HCR) requires large amount of catalyst, which means larger amount of spent catalyst will be generated [4]. Particularly, the Middle East producing the large amount of fossil fuels being explored as hub of heavy oil upgrading. In addition, the qualities of heavy crudes are more complex and difficult to process, which significantly deactivates catalyst and reduces its lifespan. Therefore, the evolution of the spent catalyst and their classification are

required more study due to which contains heavy metals, sulfur, nitrogen and hydrocarbons [5]. The main objectives were to reduce the amount of waste going to landfill both for environmental reasons and escalating costs. Kuwait National Petroleum Company (KNPC) is heavily using hydroprocessing (hydrotreating and hydrocracking) catalyst based on their processes, which is generating the large amount of spent catalyst (ca.7000 ton/year). Moreover, the quantity of spent catalysts will increase further once refineries operate with heavy crude oil (Lower Fars) having higher amount of metals (150 ppm) [6].

Refinery atmospheric residue desulfurization (ARDS) spent catalysts were investigated for their physicochemical characterization in order to understand composition as well as textural properties. Subsequently, chemical leaching tests were performed using EDTA as chelating agent and ultrasonic agitation during the metal extraction.

Disposal of waste spent catalyst under stringent environmental regulations is the major challenge for disposal of hazardous spent catalysts. Also, the cost and demand for metals have been growing significantly. In this context, the proposed spent catalyst recovery process can serve based on economic and environment issues. Hence metal recovery and recycling are the best solution for handling spent catalysts. The objective was to evaluate the metals removal efficiency of EDTA at different operating conditions and reusability of recovered EDTA.

II. EXPERIMENTAL

Spent catalysts were obtained from KNPC refinery ARDS units. Their chemical composition was evaluated by means of inductively coupled plasma (ICP) analysis, where 1 gram of spent catalyst was treated in concentrated hot HCl and HNO₃ acids in a 1:3 ratio. Subsequently, digested mixture was cooled and filtered in order to perform metal analysis: Ni, V and Mo contents were 5.3%, 13.6% and 5.9% (w/w), respectively.

The carbon content on spent catalyst was determined by using thermogravimetry analysis (TGA). The ICP results indicated that a considerable amount of foreign species were deposited on the catalyst. The spent catalysts were collected from KNPC's ARDS system of the three reactors [R1 (HDM), R2 (HDM/HDS), R3 (HDS)]. Spent catalyst's extrudates were deoiled, decoked, crushed, and ground to fine powder [7], [8]. Therefore, the first step, de-oiling and decoking (at 600 °C for 8 h), was carried out while in the second step, EDTA treatment and separation of individual metal compounds, is carried out as shown in Fig. 2. After leaching experiments, the solutions were filtered and analyzed by ICP to determine

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metal extraction yield. EDTA was used in excess that was separated and its recovery was more than 95 wt%.

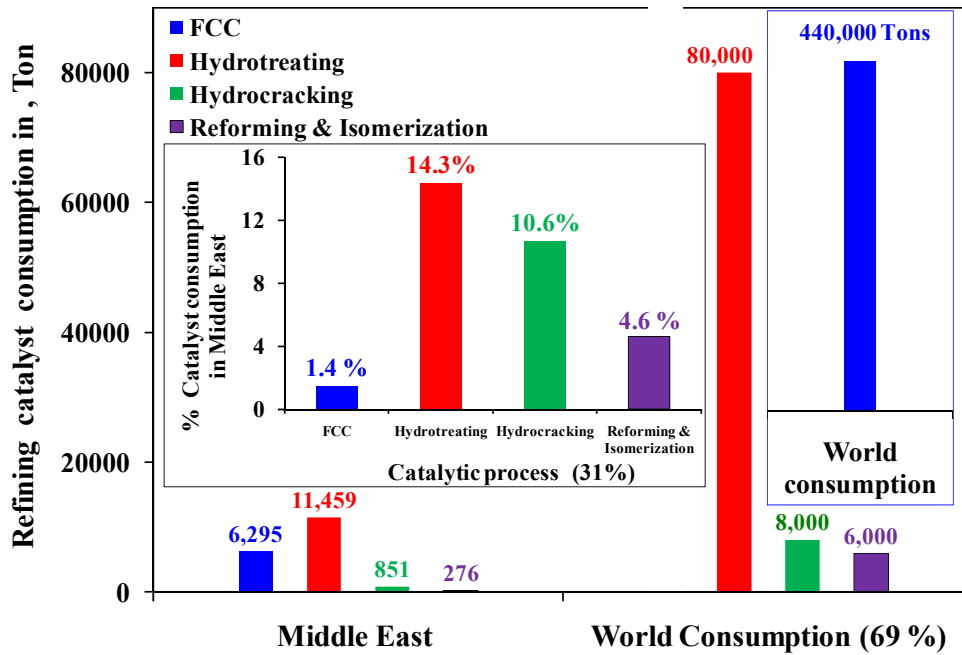


Fig. 1 Worldwide catalyst consumption in refining

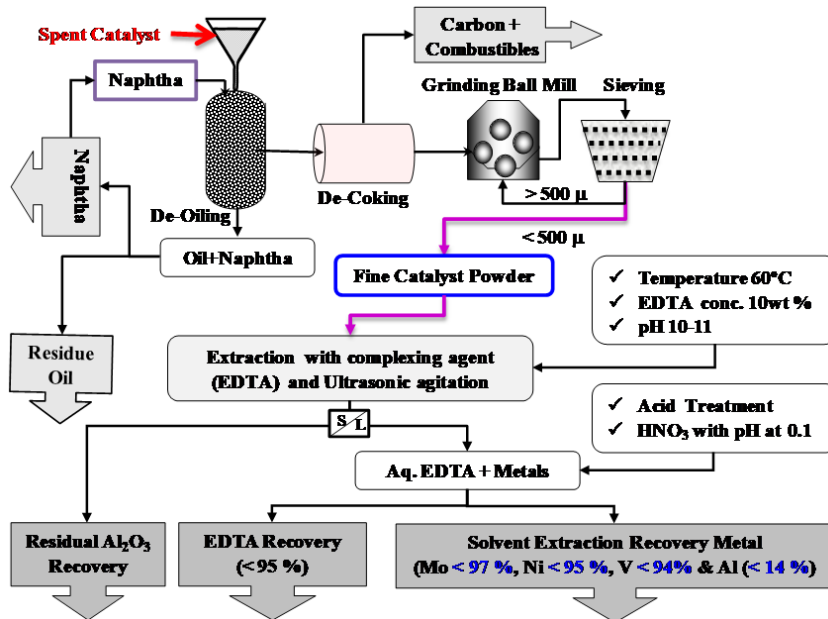


Fig. 2 Flow diagram of metal recovery process using EDTA as leaching agent

III. RESULTS AND DISCUSSION

A. Characterization of Spent Hydroprocessing Catalysts

The fresh and spent catalyst composition was determined from C, H, N, S analysis, which indicated that the deposition of foreign elements from the heavy feedstock. Based on the contamination, a preliminary description of the spent catalyst

will enable the catalyst user to process best option for recycling, regeneration and re-use. Spent catalyst characterization indicated that considerable amount of metals and carbon species has been deposited as shown in Fig. 3. Spent catalyst has about 60% decrease in surface area and pores volume. Factors that affect the catalyst performance and

spent catalyst composition are the quality of feedstock, catalyst textural properties and the run length [9]. Typically, the higher metal (Ni & V) content in the feed leads to faster deactivation of catalyst. The macro-pore catalysts retain more metals than micro-porous catalysts [10]. Total H/C ratios of the coke on these catalysts were found to be in the range of 0.3 to 0.4, indicating the strong presence of the hard coke consists of polyaromatic species.

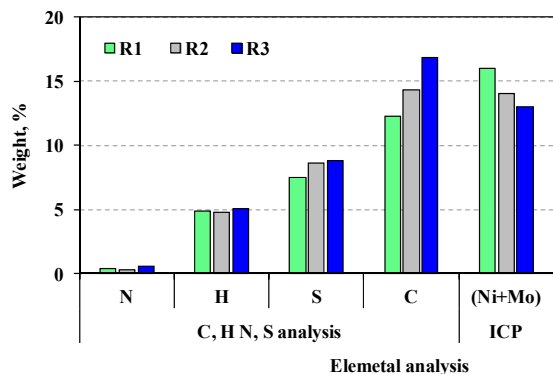


Fig. 3 Spent catalyst deposited species analysis

Low H/C ratio was also attributed to the formation of asphaltene containing coke which particularly decomposes in presence of oxygen at high temperature, as shown in Fig. 4. However, coke deactivation falls under the category of reversible poisoning with some limitations (% recovery of active catalytic sites), while metals deposition (V and Ni) leads to the irreversible loss of activity. Thus, metal depositions are usually the main cause for unloading of catalyst because its deposition is permanent and cannot be reversed. The metal is usually deposited on the catalyst surface. The deposition of metals on catalysts surface reduces the pore diameter or pore mouth and causes diffusion limitations. Due to this, the activity of catalyst decreases and it has to unload from the reactor.

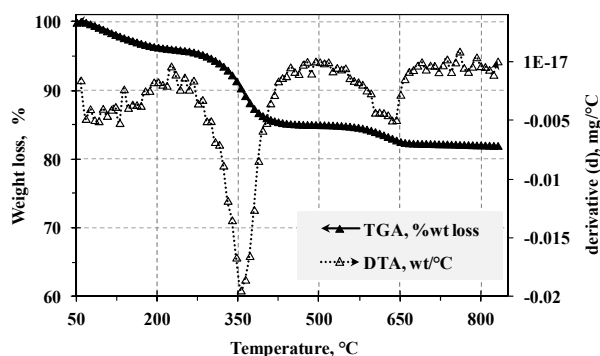


Fig. 4 TGA analysis for deposited carbon

B. Leaching Methods and Metal Recovery

Fig. 2 showed overall leaching flow scheme where two major steps were discussed. The leaching of metals from the fine powder catalyst is the second step where the process

involves selective extraction of metals (Ni, Mo, V) in presence of EDTA using conventional and ultrasound agitation. EDTA is the most widely used chelating agent because it has very strong affinity to interact with transition elements. It has hexadentate ligands that have high capacity to interact with metal ions and can bind in the form of complex. It is also a hexaprotic acid or base as shown in Fig. 5.

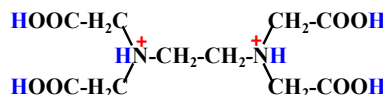


Fig. 5 Molecular structure of EDTA and protonated groups

In order to look in the chemistry, an increasing in H^+ ion concentration leads to protonated catalyst surface or a positive charge, which enhances sorption capacity of solid and forms metal-chelant complexes. It is evident from EDTA molecule that there are 4 acidic protons while the two amino groups would also be protonated at lower pH values, so these are the 5th and 6th acidic protons, which have very high pK values. Each proton in EDTA has different pK values, which significantly affect their affinity to form metal complexes. A comparison of the effectiveness of metal removal with process conditions is investigated such as leaching time (Fig. 6), temperature (Fig. 7), concentration (Fig. 8) and comparison between conventional and ultrasonic agitation (Fig. 9). During the processing, the pH is crucial factor e.g., if the pH is too low, then the overall K becomes lower due to less ionization (Y^{4-}) whereas at higher pHs, EDTA is expected to be fully ionized and form complexes with metal ions in the solution [11]. It was observed that Mo showed more extraction than Ni and V in all type of experimental variables. Fig. 6 showed metal extraction with time where the recovery of metals increased slowly up to 98%.

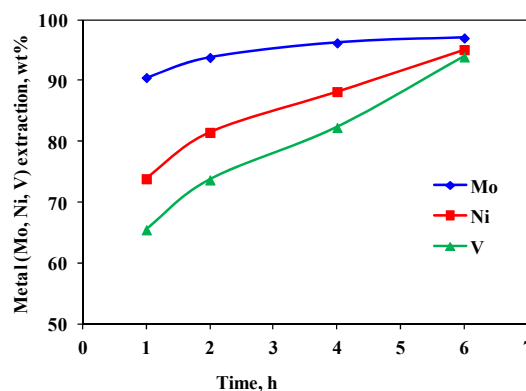


Fig. 6 Effect of leaching time on metal recovery

EDTA exhibited high activity for the leaching even at lowest temperature, 35 °C, which further increases with temperature as shown in Fig. 7. This is due to the fact that ionization usually increases with temperature which increases the H^+ concentration in solution. It appears that EDTA plays significant role in the solubilization of metals at high pH (>

10). At higher pHs, EDTA is fully deprotonated and likely to form metals complexes.

The influence of EDTA (liquid) concentration on Mo, Ni, and V leaching from the spent HDS catalyst was determined by varying the concentration of EDTA. Fig. 8 summarized metals extraction after 6 hour leaching where higher the EDTA concentration, the greater the release of metals.

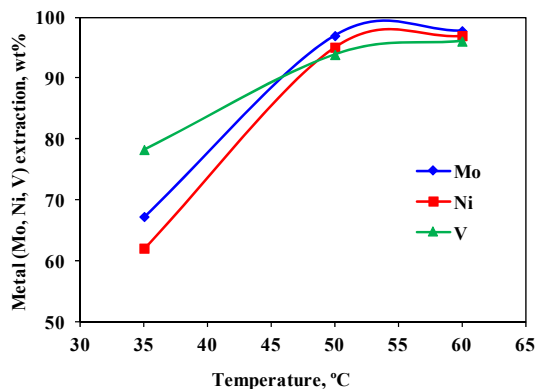


Fig. 7 Effect of leaching temperature on metal recovery

The saturation of EDTA concentration is fast and very limited difference has been observed between the three metals. It was observed that by increasing the amount of extractant solution and keeping the concentration of EDTA constant, an improvement in the extraction while 1:40 solid to liquid ratio was taken as the optimum ratio for use in all other experiments. It was assumed that further increase in extractant solution will not improve the metal recovery as large amount of EDTA was already used in 1:40 [12].

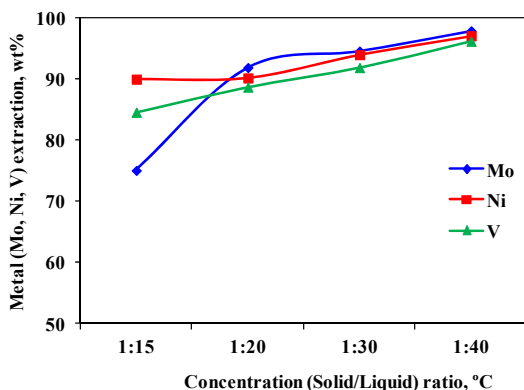


Fig. 8 Effect of solid to liquid ratio on the recovery of metals

Using EDTA as leaching agent, experiments were conducted in presence of ultrasound agitation and results were compared with the conventional method (Fig. 9). The ultrasonic vibration was more effective by enhancing the leaching rate mainly due to the ionization of leaching agent as well as separation of surface metal from the bulk catalyst support. Moreover, it does not require sophisticated equipment or intensive technical training for utilization. The operating

principles associated with the process of ultrasonication (20-100 KHz) intensity are related to the power supplied during the leaching. The ultrasonic density is calculated by using volume and energy supplied, which is based on per sample volume. The influence of ultrasonic agitation enhances the extraction of valuable metals such as Mo, V, and Ni from spent hydroprocessing catalysts specifically using EDTA as an acid leaching. EDTA with ultrasonic agitation leads enhanced (2-3%) leaching efficiency towards all metals

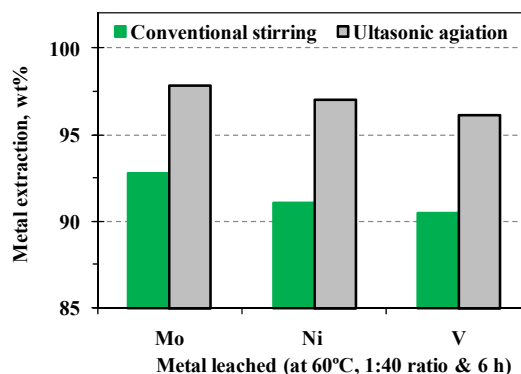


Fig. 9 Effect of agitation on metal recovery

The EDTA was recovered after the separation of metals in which dechelation process was performed by acidification. In order to separate EDTA as solid or re-usable material, the filtrate of solution was treated with HNO_3 at pH 1.8. The precipitated EDTA (H_4EDTA) can be purified and washed in aqueous solution. On the other hand, the metals (V, Mo and Ni) in solution can be separated by using a solvent extraction method. The individual metals (Mo, Ni, V and Al) were separated from the leached solution as a metal salts by using Cyanex-272 as a solvent [13]. This leaching method is specifically developed for surface deposited and active metals for their purified recovery. Alumina in spent catalyst is in bulk and its recovery process has been reported separately [6], [14].

Cyanex-272 reagent (20% Cyanex-272) in white spirit was used for solvent extraction by shaking equal volume of aqueous and organic phase in a thermostated ultrasonic bath at 40 °C. The separation was initially carried out with HNO_3 where pH ranges were very close, which was significantly improved by using H_2SO_4 . The equilibrium pH of the aqueous phase was varied in the range 0 to 7 using sulfuric acid and sodium hydroxide in order to adjust the required pH. The Mo was extracted (100%) at pH=0 with a small amount of V as contaminated element which can be eliminated by increasing pH up to 2.5. Hence, V can be effectively extracted up to 98.9% between pH 2.1 and 2.5. Separation of Al is complex because of its interference with V, where Al extraction started at pH 1 and increases up to 10% at pH 2.5. However, further increase in pH (2.5 to 3.3) will extract about 97% of Al. Ni is the last element to be separated, the extraction (ca. 6%) of which is overlapped slightly with Al (at pH 3.3). However, an increase in pH between 3.3 and 7 can separate about 99.8% of Ni.

IV. CONCLUSION

Large amount of catalyst and catalytic material will be generated in future due to the highly contaminated feedstock. The selected metal recovery process is a cost effective, high yield and environmentally friendly. Metal leaching is influenced by parameters such as type of chelating agents, leaching time, temperature, catalyst to liquid (S/L) ratio, and stirring during the leaching. Based on the said study following points can be concluded.

- CHNS analysis revealed that the spent catalyst contained (wt.%): C (14.4), H (4.9%), N (0.4) and S (8.3).
- TGA analysis indicated that two different (300-400 °C and 550-650 °C) types of carbon are deposited on the catalysts' surface.
- The results revealed that addition of EDTA enhanced leaching of metals remarkably, which was significantly improved with ultrasonic stirring.
- The EDTA and ultrasound assisted leaching method is a relatively low cost, less energy intensive and permits maximum recovery (> 95%) of metals.

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REFERENCES

- [1] Global Hydroprocessing Catalyst (HPC) Market (2015): An Analysis, <http://www.researchandmarkets.com/reports/1958130/>
- [2] World Refining Catalyst Market, The Catalyst Group Resources; The Intelligence Report, May 2014.
- [3] M. Marafi, A. Stanislaus, E. Furimsky, Handbook of Spent Hydroprocessing Catalysts: *Regeneration, Rejuvenation, Reclamation, Environment and Safety*, 2nd edition, Elsevier, 2017.
- [4] M.S. Rana, J. Ancheyta, S.K. Sahoo, P. Rayo, Carbon and metal deposition during the hydroprocessing of Maya crude oil, *Catal. Today* 220-222, 97-105, 2014.
- [5] M. Marafi, A. Stanislaus, Options and processes for spent catalyst handling and utilization. *J. Hazardous Materials*, 101, 123-132, 2003.
- [6] M. Marafi & M. S. Rana, Refinery waste: the spent hydroprocessing catalyst and its recycling options, *WIT Transactions on Ecology and The Environment* 202, 219-230, 2016.
- [7] M. Marafi, S. Al-Omani, H. Al-Sheeha, A. Stanislaus, Utilization of metal-fouled spent residue hydroprocessing catalyst in the preparation of an active HDM catalyst, *Ind. Eng. Chem. Res.* 46, 1968-1974, 2007.
- [8] M. Marafi, A. Stanislaus, Spent catalyst waste management: A review: Part II-Advances in metal recovery and safe disposal method, *Res., Cons. and Rec.*, 53, 1-26, 2008.
- [9] E. Furimsky, F. E. Massoth, Deactivation of hydroprocessing catalysts, *Catal. Today*, 52, 381-495, 1999.
- [10] M.S. Rana, V. Samano, J. Ancheyta, J.A.I. Diaz, A review of recent advances on process technologies for upgrading of heavy oils and residua. *Fuel*, 86, 1216-1231, 2007.
- [11] S. Goel, K.K. Pant, K.D.P. Nigam, Extraction of nickel from spent catalyst using fresh and recovered EDTA, *Journal of Hazardous Materials* 171, 253-261, 2009.
- [12] A. E. Martell, R.M. Smith, 2004. NIST Standard Reference Database 46 Version 8.0. NIST Critically Selected Stability Constants of Metal Complexes Database. US Department of Commerce, National Institute of Standards and Technology
- [13] M. Marafi, Method for recovering Mo, V, Ni, Co and Al from spent catalyst using ultrasonic assisted leaching with EDTA, *US Patent* 2012/0111150 A1.
- [14] M. Marafi, A. Stanislaus, Alumina from reprocessing of spent hydroprocessing catalyst. *Catal. Today*, 178, 117-123, 2011.

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