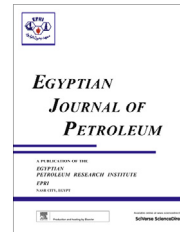




Egyptian Petroleum Research Institute
Egyptian Journal of Petroleum

www.elsevier.com/locate/egyjp
www.sciencedirect.com



FULL LENGTH ARTICLE

Hydrotreating of waste lube oil by rejuvenated spent hydrotreating catalyst



Sadeek A. Sadeek ^a, Hoda S. Ahmed ^{b,*}, Ebaa A. ElShamy ^b,
 Hussien A. El Sayed ^b, Asma A. Abd El Rahman ^b

^a Zagazig University, Department of Inorganic Chemistry, Egypt

^b Egyptian Petroleum Research Institute, Refining Department, Egypt

Received 8 May 2013; accepted 19 September 2013

Available online 29 April 2014

KEYWORDS

Hydrotreating;
 Rejuvenation;
 Reclamation;
 Spent catalyst;
 Waste lube oil

Abstract Large quantities of catalysts are used in the Egyptian refining industry for the purification and upgrading of various petroleum streams. These catalysts gradually lose activity through deactivation with time and the spent catalysts were usually discarded as solid waste. On the other hand, waste lube oil contains heavy metals coming from undergirded base oil and additives, these metals have carcinogenic effect and cause serious environmental problems. Studies are conducted on the reclamation of metals, rejuvenation and reuse of the spent hydrotreating catalyst (Mo–Ni/Al) which have been used in re-refining of waste lube oil at Alexandria Petroleum Company. Three leaching solvents were used: oxidized oxalic acid, benzoic acid and boric acid at different concentrations (4%, 8% and 16%), different oxidizing agents (H₂O₂ and Fe(NO₃)₃) and different modes of addition of oxidizing agents (batch and continuous). The results indicated that 4% oxalic acid + 5% Fe(NO₃)₃ at continuous addition of oxidizing agents was the most efficient leaching solvent to facilitate metal removal and rejuvenate catalyst. The fresh catalyst was applied for re-refining of waste lube oil under different reaction temperatures (320–410) °C in order to compare the hydrodesulphurization (HDS) activity with both the fresh, treated and spent catalysts. The results indicated that the rejuvenation techniques introduce a catalyst have HDS activity nearly approach to that the fresh of the same type.

© 2014 Production and hosting by Elsevier B.V. on behalf of Egyptian Petroleum Research Institute.

Open access under [CC BY-NC-ND license](https://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Hydrotreating catalysts consist of critical metals such as Mo, Co, and Ni, as active metals and are generally supported by alumina or silica alumina and are usually used in hydrotreating of petroleum. These catalysts deactivate with time, and partial or complete regeneration can be carried out depending on the severity of the processes due to carbon or sulfide deposition. In the long term, the regeneration of these catalysts will

* Corresponding author.

E-mail address: adohahmed30@yahoo.com (H.S. Ahmed).

Peer review under responsibility of Egyptian Petroleum Research Institute.



Production and hosting by Elsevier

become impossible due to irreversible deactivation, and spent catalysts would discard as solid wastes [1–3].

The volume of these solid wastes has increased significantly worldwide and in Egyptian petroleum refining industries due to a steady increase in upgrading of feedstock or distillates to meet the environmental regulations for low sulfur fuels.

Several alternative methods such as disposal in landfills, reclamation of metals, regeneration/rejuvenation, reuse, and utilization as raw materials to produce other useful products are available to the refiners to deal with the spent catalyst problem. The choice between these options depends on technical feasibility and economic consideration [4–7].

On the other hand, the composition of a typical waste lubricating oil is a stable dispersion of undergirded base oil and additives with high concentration of metals, varnish, gums and other asphaltic compounds coming from the overlay of bearing surfaces and degradation of the fresh lubricant components [8]. Chlorinated solvents may also be present in significant quantities as a result of the breakdown of additive packages and the addition of chlorine and bromine that act as lead scavengers in leaded gasoline. Polynuclear aromatic hydrocarbons (PAHs) are of particular concern due to their known carcinogenicity [9,10]. Therefore, recycling and re-refining of waste into virgin lubricating oil may be a suitable option for protecting the environment from hazardous waste. Another benefit associated with waste lubricating oil recycling could be the economic gain due to the high price of mineral oil [8,11].

In this study hydrotreating spent catalyst is rejuvenated which has been used in re-refining of waste lube oil for five years at Alexandria Petroleum Company and tested in re-refining of the waste lube oil from this company.

2. Experimental

2.1. Feed

Waste lubricating oil was treated by solvent extraction using (5/1 *N*-methyl-2-pyrrolidone (NMP), 1% KOH), stirring for 1 h at 70 °C and settling for 2 h at 50 °C.

2.2. Catalysts

- Spent catalyst, which has been used in re-refining of waste lube oil (Cat: C20-7-05 TRX after 5 years life time), at Alexandria Petroleum Company.
- Fresh catalyst (Cat: C20-7-05 TRX) supplied from Alexandria Petroleum Company and used as hydrotreated catalyst for waste lube oil. The chemical and physical characteristics of the fresh catalyst are illustrated in Table 1.

2.3. Pretreatment of the catalyst

2.3.1. Catalyst washing

The catalyst was covered and contaminated with a layer of petroleum derivative such as waste lube oil, so it must be washed with different organic solvents (ethanol, benzene, and carbon disulfide CS₂), in order to be cleaned. The carbon disulfide (CS₂) solvent allows the recovery of considerable

Table 1 Characteristics of fresh and spent catalysts.

Characteristics	Fresh	Spent
<i>Chemical compositions (wt%)</i>		
Mo	15.01	9.58
Ni	3.56	2.55
Al	34.74	33.91
P	–	10.55
Si	–	4.12
Others	0.55	0.91
<i>Physical characteristics</i>		
Surface area (m ² /g)	186.2	103.6
Pore volume (cc/g)	0.4196	0.266
Pore radius (Å)	37.13	34.54

amounts of sulfur accumulated in the catalyst. The solvent with sulfur is then distilled and reused for new portions of the catalyst, such a treatment of milled catalyst (100 ml of each solvent/10 g of the catalyst) is carried out for 12 h with agitation at room temperature in a closed flask, and then the product is filtered and dried in air at room temperature. Carrying out this treatment for less than 12 h gives less sulfur recovery. The washed catalyst is then heated at different temperatures in an electric oven to eliminate the carbon and sulfur residues in air as CO₂ and SO₂, respectively.

2.4. Leaching treatment

The temperature is increased from 100 to 350 °C at a rate of 50 °C/h, and then the product is maintained at 350 °C for 1 h, heated to 450 °C at 25 °C/h, and maintained at this temperature for 24 h. After cooling to room temperature, the formed yellow-green catalyst is ready for further treatment.

(A) Oxidized benzoic acid solution

- To 10 g of spent catalyst 500 ml of (4, 8 and 16)% benzoic acid that is oxidized by 5% H₂O₂ and diluted in 10% NaOH solution is added, in a 1 L flask.
- Heated for 60 min at 95–100 °C with stirring. At the end of the heating time, the content is cooled to room temperature then filtration is carried out.
- After filtration, the benzoic acid solution is reduced to one – third of its original volume which contains the leaching metals. The solid (unfiltered catalyst) is dried in atmosphere, heated at 110 °C, and calcined at 450 °C for 4 h, which represents the treated catalyst.

(B) Boric acid leaching solution

- To 10 g of spent catalyst 500 ml of (4, 8, 16)% boric acid solution that is oxidized by 5% H₂O₂, is added, in a 1 L flask.
- Heated for 60 min at 95–100 °C with stirring. At the end of the heating time, the content is cooled to room temperature then filtration is carried out, heated at 110 °C, and calcined at 450 °C for 4 h.

(C) Oxalic acid solution

Different concentrations of oxalic acid solution are used (4, 8 and 16)% prepared with 5% H₂O₂ and Fe(NO₃)₃ as oxidizing agent for the leaching experiments.

Download English Version:

<https://daneshyari.com/en/article/1756892>

Download Persian Version:

<https://daneshyari.com/article/1756892>

[Daneshyari.com](https://daneshyari.com)