The Effect of Ultrasound for Impurities Removal on Spent Catalyst from Naphtha Hydrotreater (NHT) Processing Unit

Sumarno[a], Ummu Dzawilhijjah, Thariq Ridho Firmansyah
and Prida Novarita Trisanti

Department of Chemical Engineering, Institut Teknologi Sepuluh Nopember, 60111 Surabaya, Indonesia

[a]Corresponding author: onramus@chem-eng.its.ac.id

Abstract. Solid catalysts are widely used to improve process efficiency in oil refinery industry, such as in Naphtha Hydrotreater (NHT) unit. In this unit, Ni/Mo catalysts are used. During the processing, the catalysts will be contaminated with impurities, such as (sulfur (S), iron (Fe), and arsenic (As), in the crude oil feed, then becomes deactivated over a period of time. Regeneration of the spent catalyst can be used as alternative method to reduce the generation of hazardous waste from spent catalyst. There are many methods to regenerate the spent catalyst such as leaching, microwave, and ultrasound. In this present study, the effect of ultrasound process in enhancing the removal of impurities on spent catalyst (Ni/Mo) was investigated. The mixture of spent catalyst (Ni/Mo) and water (1/20 (w/v)) was treated by ultrasound at 30°C, 20% amplitude, and various time (5-45 minutes). After ultrasound process, solid product was analyzed by Scanning Electron Microscopy (SEM), X-ray fluorescence (XRF), and Brunauer Emmet Teller (BET). The content of impurity in spent catalyst were decreased after ultrasound processing. At low temperature (30°C) and short time (25 min), the content of S was decreased from 17.3% to 1.8%, Fe from 13.1% to 2.4%, and As from 2.3% to 1.3%.

INTRODUCTION

In oil refinery industry, solid catalysts are widely used to improve process efficiency [1]. Catalyst has a chemical compound such as metal and metal oxide that make the hydrocarbon formation easier, so the product has high selectivity [2]. One of the applications is for hydrotreating process in Naphtha Hydrotreater (NHT) unit that uses Ni/Mo or Co/Mo catalyst. These catalysts are used to improve the purification process from sulfur, nitrogen, and metal by Hydrodesulfurization reaction (HDS), Hydrodenitrogenation (HDN) dan Hydrodemetallization (HDM) [3]. At certain time, catalyst will deactivate and need regeneration. The deactivation process is caused by structure change and interaction between the catalyst and impurities during processing. That condition is a big problem in industry because the regeneration catalyst need high cost [4]. There are six factors that caused the deactivation process such as: poisoning, fouling, thermal degradation, attrition/crushing, leaching, and the reaction vapor and solid or solid and solid [5]. But in some cases, most of deactivation catalyst is caused by fouling, poisoning, and thermal degradation [6]. Some components that can contaminate and cause deactivation catalysts by poisoning processes in the oil refinery industry are Nickel (Ni), Vanadium (V), Arsenic (As), Ferrous Iron (Fe), Sulfur (S) and Carbon (C) [7]. Catalyst deactivation by the poisoning is caused by chemisorptions because of the strong interaction between the feed flow and the catalyst active site. It makes an accumulation of contaminants from the feed flow and makes a competition to get the space in the catalyst surface. Physically, that contaminants reduce the surface catalyst area and make the structure change of catalyst surface [6].

Catalyst regeneration is the process to regenerate spent catalyst so it can be reused for many purposes. Furthermore, spent catalyst is dangerous waste [4]. This process also decreases the purchase cost for new catalyst. Some researcher already studying about regeneration catalyst. Stanislaus and Marafi (2011) did metal extraction such as Mo, V, Ni and Co in spent catalyst using ultrasound method with leaching. Leaching process can use sulphuric acid as anorganic acid and citric acid as organic acid [1]. Metal extraction using citric acid is better than using sulfuric acid and the recovery more than 95% at low temperature in short reaction time. Soares and Pinto (2012) did the molybdenum extraction from Ni/Mo or Co/Mo spent catalyst by sonication method and microwave [8]. Sonication method with leaching using 10 g/l sodium hydroxide produced 66% Mo liquid after 10 minutes processing for Ni/Mo and Co/Mo catalyst. By microwave method using 4 cycle for 30 seconds product 89% and 91% for Ni/Mo and Co/Mo catalyst. By the previous research, sonication method can increase the surface area of

catalyst. So that, aim of this experiment is to study the effect of operating condition in sonication method to purify the spent catalyst.

MATERIAL AND METHODS

Materials

The materials used in this experiment were spent catalyst of Nickel Molybdenum DN-3100, which was acquired from NHT unit of PT Pertamina RU IV Cilacap, and aquadest.

Methods

The experiment started with making a mixture of spent catalyst and water with ratio 1:20 weight of catalyst per volume of water. After that, the mixture treated by ultrasound at 30°C, 20% amplitude for various time (5-45 minutes). The solid product of the processed material was separated from the mixture and dried. Then it was analyzed by Scanning Electron Microscopy (SEM, X'pert Pro PANalytical), X-ray fluorescence (XRF, PANalytical), and Brunauer Emmet Teller (BET, Quanthacrome Instruments). The scheme of equipment used is shown in Fig. 1.
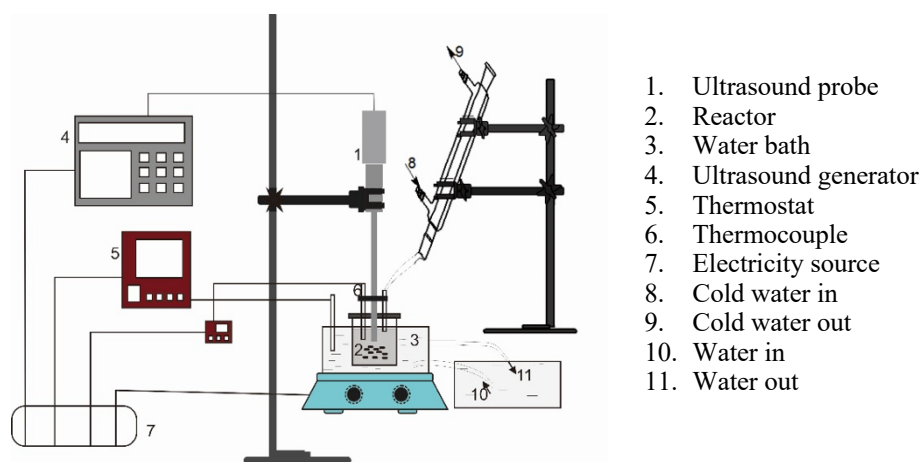

1. Ultrasound probe
2. Reactor
3. Water bath
4. Ultrasound generator
5. Thermostat
6. Thermocouple
7. Electricity source
8. Cold water in
9. Cold water out
10. Water in
11. Water out

**FIGURE 1.** Sonication apparatus

RESULTS AND DISCUSSION

Solid catalyst used in this experiment is Ni/Mo catalyst from PT. Pertamina RU IV Cilacap. Ni/Mo catalyst is used in *Naphtha Hydrotreater* (NHT) unit and produced by Criterion type DN 3100. This catalyst usually arranged by molybdenum (Mo) with nickel (Ni) as a promoter and alumina silicate as a catalyst support [9]. As a comparison, spent catalyst was analyzed the components using XRF (X-Ray Fluorescence) as shown in Table 1. By XRF results, beside Mo, Ni, Al, and Si component, spent catalyst also contains sulphur (S) and other metals like ferrous iron (Fe), vanadium (V), and arsenic (As). Those components are contaminant inside Ni/Mo catalyst [1]. The highest percent weight of contaminants in Ni/Mo spent catalyst are S, Ni, Fe.

Sulphur is the highest component on crude oil after carbon and hydrogen [10]. Sulphur that contains in crude oil is divided into four categories, are: *mercaptans, sulfides, disulfides* and *thiophenes*. Sulphur component in oil refinery as a contaminant causes deactivation or decreasing catalytic activity and also some environmental problems [11]. Usually Fe component or compound deposit come from the corrosion of upstream installation. Fe do not give an effect to catalyst poisoning, but it gives an effect in increasing pressure drop. It is caused by the formation of small particles that penetrate catalyst pores [12]. Meanwhile, small weight percentage of V and As is observed. These contaminants are also dangerous to catalytic activity in Hydrodesulfurization reaction (HDS) [13].

TABLE 1. XRF Result for spent catalyst

Component	(%-weight)
Ni	13.7
Mo	4.9
Al	23.6
Si	2.1
S	17.3
Fe	13.1
V	0.03
As	2.3

Sonication was used to clean the contaminant of spent catalyst like sulphur (S), ferrous iron (Fe), and arsenic (As) using water which is abundant and cheap solvent. Sonication time was conducted for 5-45 minutes in 30°C with 1:20 mixture ratio (w catalyst /v water). To compare the effect of sonication process for catalyst regeneration, analysis was also conducted for the weight percentage of some components like S, Fe, and As. Figure 2 is a plot that informs about the change of the amount of contaminant in certain reaction time.
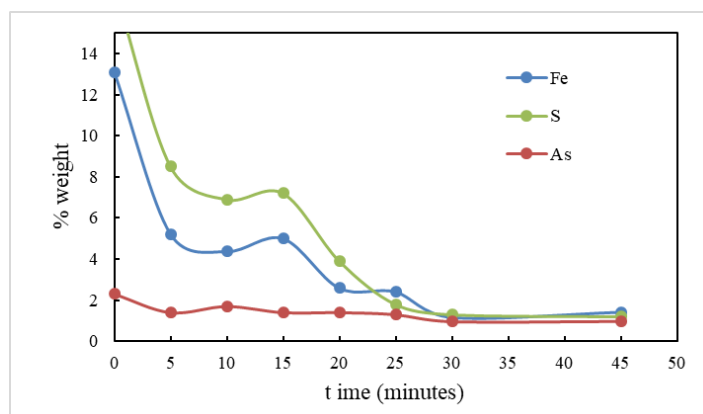
FIGURE 2. XRF Analysis for S, Fe, and As

The weight percentages of S, Fe, and As decrease with sonication time. Sonication causes a decreasing weight percentage about 93.1% (for Sulphur contaminant). Before sonication process sulphur weight percentage is 17.3% and it decreases into 1.2% after 45 minutes of sonication process. The amount ferrous iron also decrease and its weight becomes to about 91.1%. Before sonication process ferrous iron weight percent is 13.1% and decrease into 1.16% after 30 minutes of sonication process. Meanwhile arsenic (As) lost its weight percent about 58.3%. Before sonication process As weight percent is 2.3% and decrease into 0.96% after 30 minutes sonication process. Sonication can increase the solvent polarity, so the water can product OH* and H* radical ion that can easily solve some component like S, Fe and As [7].

To analyze the morphology in the surface of catalyst, SEM micrographs were taken and shown in Fig. 3. The photographs are spent catalyst before sonication process (a), and after sonication process for 25 minutes (b). Figure 3(a) showed that spent catalyst have a rougher surface before the sonication process. It is caused by the accumulation of contaminant in the surfaces or catalyst pores. After sonication process, the catalyst surface is softer as shown in Figure 3(b). The deposits material on the surface is released.
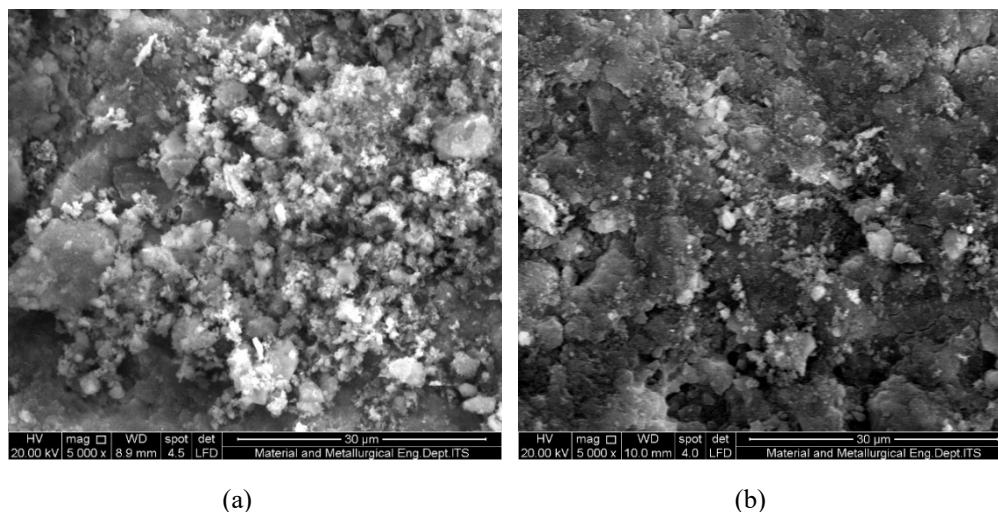
(a)   (b)

FIGURE 3. SEM Photograph for (a) spent catalyst (b) after sonication for 25 minutes.

Sonication process can act as a cleaning method to dissolving the contaminant on the surface of catalyst by production of OH and H radical. Highly intensive ultrasound wave caused the acoustic cavitation, and microbubble collapse produce myriads of micro jet. Solid liquid sonication is a heterogeneous system, and make it easier for production of microbubbles, than collapse in near solid surface. Inrush of liquid from one side of the collapsing bubble produces powerful jet of liquid targeted at surface. Therefore, there was a surface cleaning destruction of boundary layer surface activation improved mass and heat transfer [14]. Cavitation effect in sonication also increases the polarity of water so water as a solvent which can easily dissolved sulphur, ferrous iron and arsenic [15].

To analyze whether the results of this regeneration can be used in industrial process, we analyzed the product using BET to analyze the surface area, pore volume and average pore diameter. Table 2 shows characterization results of the catalyst after sonication process. The catalyst's surface area increases about 4.97%. But pore and average pore diameter decrease after sonication process because larger surface area make the pore diameter and pore volume decreased. Based on Lloyd [9] usually Ni/Mo catalyst have a surface area about 200-300 m^2/g and pore volume about 0.5-0.7 cm^3/g.

TABLE 2. BET analysis comparison for spent catalyst before and after sonication

Treatment	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Average Pore Diameter (nm)
Spent catalyst	166	0.60	14.5
After sonication (25 minutes)	175	0.56	12.8

CONCLUSIONS

Sonication method can help leaching process of spent catalyst to improved contaminant cleaning in the surface of the catalyst like S, Fe, Ni, As, and C. Longer sonication process can make the contaminant cleaning more effective. The optimum condition in sonication process achieved for 20 minutes sonication time and reduce the amount of contaminant like S, Fe, and As about 1.9%; 3.08%, and 0.4% weight. Under sonication process there was collapsing bubble produces powerful jet of liquid targeted at surface. There was a surface cleaning destruction of boundary layer surface activation improved mass and heat transfer. Cavitation effect in sonication also increases the water's polarity so water as a solvent can easily dissolved sulphur, ferrous iron, and arsenic.

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