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Experimental Study on Factors Affecting the Recovery of Nickel from Spent Catalyst

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Abstract

In this study, the recovery of nickel from spent NiMo/Al_2O_3 catalyst was investigated using 1 L stainless steel autoclave batch reactor. The effect of leaching process parameters such as temperature (40-80°C), time (1-4 h), pressure (1-3 bar), average particle size (69-550 µm) and agitation speed (400-600 min^{-1}) on nickel extraction. The nickel percent in spent catalyst was found about 2.18%. The results obtained show that recovery of about 94% of nickel from spent catalyst was accomplished under the following conditions: temperature 80°C, pressure 1 bar, average particle size 200 µm, agitation speed 600 min^{-1}, nitric acid concentration 40% and solid to liquid ratio1:50 after 4 h.

Keywords: Leaching; Spent catalyst; Nickel recovery

Introduction

Nickel is widely used as a catalyst in chemical and petrochemical industries. Due to their low cost competing replacements, these are the catalysts of choice in several industries. Such catalysts use silica and alumina as supports [1]. As these catalysts, is used, metals from the feedstock deposit on the internal surface of its pores and its external surface, eventually plugging the pores and decreasing the activity of the catalyst to such an extent it does not give the desired product quality [2]. If the regeneration of these catalysts is not economically feasible, they are discarded from petroleum processing and, at present, large dumps of spent catalysts are growing. Hence, the spent catalysts disposal poses an unavoidable environmental issue, which necessarily requires high capital investment, huge swaths of land and massive efforts [3]. In many countries, the hazardous nature of the spent catalysts is attracting the attention of environmental authorities and the refiners are suffering pressures from them for safe handling of spent catalysts. Several alternative methods such as reclamation of metals, disposal in landfills, utilisation as raw materials to produce other useful products and regeneration and reuse are available to the refiners to deal with the spent catalyst problem. The choice between these options depends on technical feasibility and economic considerations [4]. The recovery methods of nickel from spent catalysts can be classified as thermal treatment, chlorination, acid leaching, alkali leaching, bioleaching. The pyrometallurgy process was applied to the spent catalyst by Llanos et al. [5] who used alkali roasting, and Kim et al. [6] explored a low-temperature sulphuric acid baking and mild acid leaching for maximum dissolution of metal values from a spent Ni-MO/Al_2O_3 hydroprocessing catalyst. However, hydrometallurgical process can be regarded as the desired route for recovery of metals due to its economic operation, environmentally friendly and simplicity. Alkaline or acidic leaching was used by many researchers by using many reagents. Marcantonio [7] invented a process to extract valuable metals. In this study, the spent catalyst was roasted at (400-600°C) and then contacted with an aqueous solution of ammonium sulfate ($(NH_4)_2SO_4$), ammonium carbonate ($(NH_4)_2CO_3$) and hydrogen peroxide. The optimum leach conditions were 0.5 M $(NH_4)_2SO_4$, 1 M $(NH_4)_2CO_3$ and 80°C for three hours was obtained. Angelidis et al. applied a two-step of leaching alkali (sodium hydroxide) followed by acid (sulfuric acid) procedure and studied the selective recovery of metals, such as Mo, Co and Ni, from hydrodesulfurization (Mo-Ni/Al_2O_3–SiO_2 and Mo-Co/Al_2O_3) catalysts [8]. Al-Mansi and Abdel Monem used sulfuric acid as a solvent to recovery of nickel from the spent catalyst (NiO/Al_2O_3) resulting from the steam reforming process [9]. It was found that 99% of nickel was extracted at 50% sulfuric acid concentration, particle size less than 500 µm, solid to liquid ratio (1:12) by weight for more than 800 rpm and 5 h at 100°C. Sahu et al. invented a process for nickel and alumina recovery by using 3 vol.% of sulfuric acid with a small amounts of a persulphate salt additives (such as potassium, sodium and ammonium) [10]. It was concluded that as a leaching process is achieved with sulfuric acid alone, the recovery of nickel about 11.95% at 70°C and 4 ml/g after 6 h. High percent of nickel about 99.6% was extracted by using the additives and at 90°C, 1 g of persulphate salt, 4 ml/g liquid to solid ratio and after 1 h. Mulak et al. discussed a method of leaching by using oxalic acid solution with hydrogen peroxide addition [11]. The optimum conditions that give the high extraction of metals 65% Ni, 90% Mo, 33% Al and 94% V was obtained (3 M H_2O_2 and 0.5 M $H_2C_2O_4$ solution at 50°C after 4 h). A combined acid-leaching was proposed by Lai et al. to recover valuable metals from spent hydrodesulfurization (HDS) catalyst [12]. An acid solution consisting of concentrated HCl/H_2SO_4/HNO_3 with a volume ratio of 1:1:2 was used to leach the metals. The leaching yields of target metals (Ni, Mo and V) in the 1st stage of leaching reached 99, 90 and 99%, respectively under these conditions, solid to liquid ratio 40 g/l, 1 h leaching time, and 70°C temperature. Oza et al. investigated recovery of nickel from spent nickel catalysts using ultrasonication-assisted nitric acid leaching [13]. The effect on nickel recovery of temperature, solid to liquid (S:L) ratio, time of digestion, and nitric acid concentration were studied in detail and optimized for the ultrasonication route. High purity and faster recovery were accomplished for ultrasonication-assisted leaching than the chelation method (7 h) and conventional acid leaching (9 h). It was found that 95% recovery of nickel was produced

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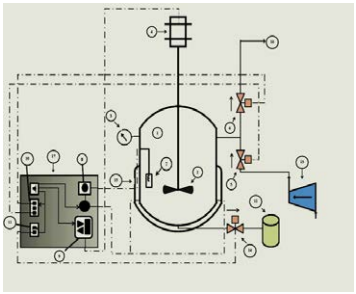
at 90°C, S:L ratio 1:10 (g:ml) and 40% nitric acid concentration in 50 min. Mousa et al. investigated the recovery of nickel from the fly ash of the fired power station residue using nitric acid [14]. The influences of the acid concentration (10%, 20% and 30%), temperature (30-60°C) and time were studied. The recovery rates increase with the increase in temperature and nitric acid concentration, and at the first half of an hour, most of the nickel was recovered. 80% of nickel was recovered at 30% nitric acid solution and 60°C. Mousa et al. used ammonium hydroxide to recover nickel from the fly ash of heavy oil [15]. The effects of rotational speed (200-1000 rpm) and temperature (50-80°C) were studied. It was found that the nickel recovery increased with increasing temperature till 70°C. The best rotational speed was obtained at 600 rpm where above 600 rpm the nickel recovery doesn't increase further. The controlling steps were investigated, and it was found that the transfer through the film surrounding the particle (interphase) is the controlling step. Sheik et al. studied the influence of leaching parameters such as temperature (60-90°C), acid concentration (1.5-5 M), and average particle size (75-601 μm) on nickel recovery using nitric acid. Romas et al. used nitric acid leaching of a spent NiO-Al_2O_3 catalyst [16,17]. The results obtained show that at the following conditions: temperature 65°C, average particle size 75 μm, reaction time 120 min, stirring speed 600 min^{-1}, nitric acid concentration 50% and solid/liquid ratio 1:3. About 85% extraction was achieved. In this study the effects of temperature, time, average particle size, pressure, and agitation speed on the recovery of nickel from spent catalyst by using nitric acid solution as a leaching agent were investigated. The optimum conditions that give the maximum percentage of nickel were obtained.

Experimental device

An autoclave stainless steel reactor, was used to process the experiments, its volume (1 liter). The inner diameter was 11.5, the thickness of the shell wall was 10 mm, and the height was 30 cm. This autoclave was provided by a 3-phase motor with N_{max} equal to 1300 rpm, which able to agitate mixer that consists of stainless steel shaft and three turbine propeller blades impeller, the diameter of the impeller was 3 cm. The agitation speed was regulated by the digital regulator (50 digits) in the board, each degree in the board equals to almost 22 rpm. Six heaters were tied uniformly around the shell of the reactor (100 kW for each) and isolated by asbestos cloth layer the temperature of the reactor was controlled by controller. Pt 100 stainless steel thermocouple was put on the inside wall of the shell and connected to the regulating system on the board. Two solenoid valves (1/4 inch) were used to charge air to the reactor and discharge vent gases from it, which put on the upper side of the reactor wall. Manual stainless steel valve was planted on the bottom of the reactor to discharge the mixture of the product after leaching process was finished. Gage valve (10 bars) was connected to the wall of the shell to read the inside reactor pressure. All of the control options were put on the control board outside of laboratory hood. Figure 1 shows the details of the apparatus [18].

Materials and Method

The spent NiMo/Al_2O_3 catalysts used in this study were supplied by Midland oil Company refinery of Al-Dora which used these catalysts as a hydrogenation catalyst. The weight percent of nickel in spent catalyst was 2.18%. Solid sample of roasted spent catalyst particles were analyzed for nickel content by mean of Atomic Absorption Spectrometry at the analytical laboratory of Ibn Sina Company. This value was used in the calculation of nickel recovery for each experiment as shown next section. The spent catalyst was roasted at 500°C about



1	An autoclave reactor	10	Power Switch of the inlet and outlet air valve
2	Three propeller turbine blades impeller	11	Power Switch of the leachate
3	Pressure Gage (10 bars)	12	leachate shell
4	Electrical motor	13	air compressor
5	Inlet Air Solenoid Valve (1/4 inch)	14	Outlet product manual valve (1/2 inch)
6	Outlet Air Solenoid Valve (1/4 inch)	15	Asbestos isolator layer
7	Pt 100 thermocouple	16	Vent Gas
8	Temperature controller system (pt100)	17	Autoclave board
9	The digital regulator of the mixer		

Figure 1: An autoclave reactor.

5 h to minimize the amount of oil and sulfur present on the catalyst; then the samples were ground and sieved to various particle sizes (69-550) μm. The nitric acid was diluted to 40% solution and the solid to liquid ratio was 1/50 (10 gm of spent catalyst in 0.5 liters of nitric acid solution) this ratio remains constant at all experiments. The autoclave reactor was switched on, and the temperature was adjusted to (40-80°C). The agitated regulator was set at the desired mixing speed (400-800 min^{-1}). The HNO_3 solution was added to 10 gm of spent catalyst and inserted into the reactor. The air was compressed to the reactor to reach the desired pressure (1-3 bar). After the time you want (1-4 h) was reached the solenoid valve of discharging vent gas was switched on until 2 bar pressure was reached and then open the manual product valve then the solution was filtered to separate the unreacted nickel and impurities. Samples of solution from all experiments were analyzed for nickel using Atomic Absorption Spectrometry.

Results and Discussion

The dissolution of nickel oxide from the spent catalyst follows the following reaction [16,17].

$$NiO+2HNO_3 \rightarrow Ni(NO_3)+H_2O \quad (1)$$

Effect of reaction temperature

The effect of temperature on nickel recovery is shown in Figure 2 under the conditions of atmospheric pressure, average particle size of 200 μm and agitation speed of 600 min^{-1}. The dissolution rate was low at lower temperature and increase with an increase in leaching temperature. At 40°C, 76.9% of nickel extraction was obtained in 4 hours while the percent increased to 86% by increasing the temperature to 80°C in the first hour. After, Ni extraction increase slowly to reach 94.3% in 4 hours. This increasing may be imputed to many reasons; firstly, is rising the temperature of leaching will increase the rate of reaction between the value mineral and the solvent (spent catalyst and nitric acid) according to Arrhenius equation Eq.(2) that relate the temperature and the reaction rate takes place at this temperature.

$$k = k_o e^{\frac{-E}{RT}} \quad (2)$$

Secondly, is increasing in diffusion coefficient with the temperature increasing. Another reason that an increasing in a leaching temperature causes an increase of kinetic energy of particles (molecules' speed) and

collide very frequently causing an increase of collision frequency of the molecules which leads to accelerating the reaction.

Effect of pressure

The effect of pressure on the recovery of nickel was shown in Figure 3. It was found that there is an adverse effect of the pressure on the leaching recovery. As the pressure increase the percentage of nickel will slightly decrease. At optimum conditions, the recovery of nickel is 94.3% at atmospheric pressure and decreases to 89.6%. while the pressure increases to 3 bar.

Effect of average particle size

In order to study the effect of average particle size on the nickel recovery a set of experiments were conducted, Figure 4 was illustrated at the conditions of other variables of 80°C temperature, 600 min^{-1} agitation speed and atmospheric pressure. The results show that the recovery percent of nickel increases with reduction of the average particle size. This behavior continues until the mean particle size reaches 250 µm because the reduction of average particle size increases the interfacial area between the liquid and solid; therefore the smaller is the distance that the solute must diffuse within the solid and the higher is the transfer rate of the reactant and products reaction. From 250 µm to 180 µm it was observed that no significant effect of average particle size on the nickel recovery and it remains almost constant. At very fine particles (lower than 180 µm) it was found that the nickel dissolution rate was decreased very slightly with the decreasing of average particle size, these phenomena may be according to impede the circulation of liquid with the presence of the fine particles and thereby lead to reduced mixing speed and thus the recovery of nickel will decrease [19]. The optimum average particle size of 200 µm was observed in this study.

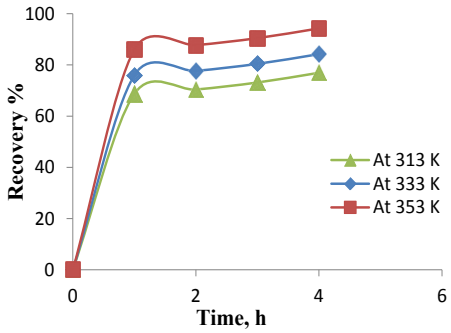


Figure 2: The effect of temperature on Ni recovery at conditions: 200 µm size, 600 min^{-1} and 1 bar.

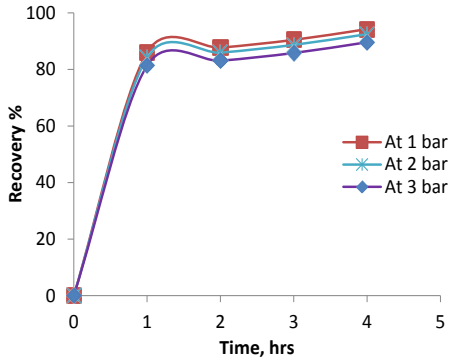


Figure 3: The effect of pressure on Ni recovery at conditions: 600 min^{-1}, 80°C and 200 µm.

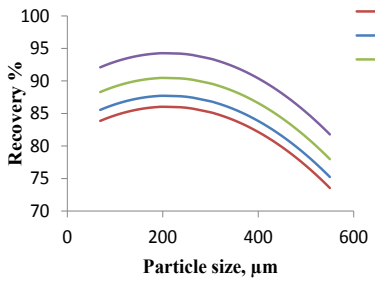


Figure 4: The effect of average particle size on Ni recovery at conditions: 600 min^{-1}, 80°C and 1 bar.

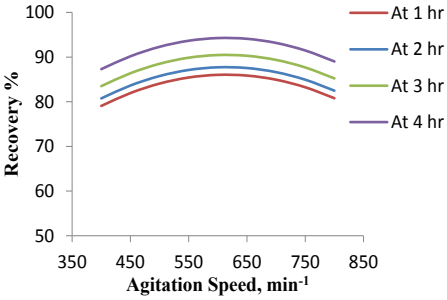


Figure 5: The effect of agitation speed on Ni recovery at conditions: 200 µm, 80°C and 1 bar.

Effect of agitation speed

Figure 5 shows the effect of agitation speed at the conditions of temperature 80°C, average particle size 200 µm and atmospheric pressure. It was concluded that the figure could be divided into two regions. The first one begins from the lowest agitation speed to the 600 min^{-1}. It was observed slightly increasing of nickel recovery with agitation speed from 400 min^{-1} to 600 min^{-1} which only 7% of recovery was achieved. The second region was detected after 600 min^{-1}, in this region the agitation speed did not significantly influence the leaching rate. This indicates that the external diffusion of HNO_3 between the surface of particles and the fluid is fast, and hence does not control the dissolution of nickel within the investigated range of agitation speed this agree with Ramos and Mousa et al. study [18].

Conclusions

From the results of this investigation the following conclusions can be drawn:

- The optimum leaching conditions were obtained as temperature 80°C, pressure 1 bar, average particle size 200 µm and agitation speed 600 min^{-1} after 4 h which give the percentage recovery about 94%.
- The rate of nickel recovery was increased with increasing the temperature up to 80°C and the pressure give the adverse effect on the nickel recovery which decreases with the pressure increasing.
- The nickel percentage recovery increases with the reduction

of average particle size until 250 μm. Then the reduction of average particle size doesn't affect the nickel recovery.

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