Molybdenum Extraction from Spent Catalyst Using Citric Acid: Characteristic and Kinetics Study

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Abstract. Interest on the extraction of valuable metals from secondary resources has been increasing recently due to the environmental consideration. It includes the spent catalyst from hydrodesulfurization process from the natural gas purification unit in fertilizer industry to reduce sulfur content. With composition of molybdenum as one of the active elements, the spent hydrodesulfurization (HDS) catalyst is indeed interesting to study, in order to be able to recover the molybdenum which is increasing within decades in need and unit price. In this study, recovery as well as extraction kinetics of molybdenum will be observed to calculate design parameters for scaling up process. The raw material used in this work is spent catalyst from PT. Pupuk Kujang Cikampek, Karawang, Indonesia. Leaching process was conducted with particle size -200 mesh, solid ratio of 1:5 and leaching time up to 120 minutes in the atmosphere condition by variated temperature (60, 80, 90°C) and pH (1.5, 2, 2.5) of citric acid. The solid samples before leached were analyzed using Energy Dispersive X-Ray (EDX), while the leaching filtrate samples were analyzed using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). The result of the experiment showed the maximum recovery of molybdenum at temperature of 90°C, during 120 minutes, and acid pH 1.5, 2, 2.5 were 71.20%, 34.66%, and 19.29% respectively. The independent variables used in this study showed a significant effect of molybdenum recovery, especially the acids pH. The kinetic model was evaluated by following the Shrinking Core model which considers diffusion is suitable to predict the leaching mechanism of molybdenum using citric acid.

Keywords : secondary resource, spent catalyst, molybdenum, leaching, recovery

1. Introduction
Molybdenum is one of the important metals in human life and industry. The use of molybdenum as an important refractory metal are alloying agent in cast iron, super alloy steels as well as catalysts, lubricants and pigments in chemical applications [1]. International Molybdenum Association (“IMOA”) recently reported that global molybdenum consumption in 2019 at 259,100 tonnes with steel industry represents the largest use of
molybdenum. For the required material that has the ability to appropriate operating conditions, Mo is extensively used in various industrial technologies [1]. Among all industrial applications, Mo catalyst is widely used in petroleum desulphurisation to minimize sulphur dioxide emissions from fuel combustion [2], [3]. Therefore catalysts not only enable for economical fuel purification, but also contribute to environmental safety through low sulphur emissions [3], [4].

Secondary resources need to be developed from industrial waste materials especially spent catalyst, due to the promising economic value and insufficiency of Mo primary mineral resources in the future, also to find more useful ways for Mo recovery [5]. The most vital spent catalysts containing valuable metals are Mo, Co, Ni, V, Al from secondary resources [5], [6]. However, aligned with its frequent use, catalysts have a tendency to quickly deactivate [4]. As a result, a large number of deactive HDS catalysts become spent catalysts because they contain toxic elements in the catalyst such as V, Ni, Mo, and Co, and can be easily leached out with water causing secondary pollution, therefore it needs to be processed in order to meet environmental regulations [7]. About hundreds of thousands of tonnes per year in the worldwide spent catalysts are generated [8], [9]. It is also a serious problem for many industries due to the disposal of heavy solids as well as environmental considerations, therefore important to recover valuable metals from spent catalysts and minimize industrial problems.

There are several options for environmental friendly valuable metal recovery methods. One of them are hydrometallurgical processing due to low energy requirements, low gas emissions, resulting waste, and complete recovery of metals. Leaching is one of hydrometallurgy process, where used leaching agent to extract element from spent catalyst. Parameters such as type of leaching agent, pH, particle size, solid-liquid ratio, temperature, time of leaching, and stirring speed that affect metal leaching to increase the metal recovery. Over the past few years, recovering valuable metals from spent catalysts has been carried out [3], [10], [11]. The various reagents that widely used in the leaching of molybdenum are inorganic groups such as H₂SO₄, HNO₃, HCl, NaOH, H₂O₂ [12]–[15], and chemical mixtures [16] that have received attention from industrial waste. With inorganic acid as leaching reagent about 15% - 90% of the metal recovery is obtained from the spent catalyst [11]. However, the use of inorganic acids is related to environmental problems that produce harmful byproducts from secondary resources [17]. In recent years, researchers have investigated replacing the use of organic acids as leaching agents such as citric acid, oxalic acid, and acetic acid [18]–[22] often known as organic acids.

In order to optimize the conditions of the leaching process for scaling up, it is important to study a suitable kinetics model to predict these conditions adequately. Yagi and Kunii has been described that the basic model leaching process is shrink core model for heterogeneous solid-liquid reaction [23]. The shrinking core model has been used in several leaching study, for example Anna Szymczycha [6] reported that leaching process is controlled by chemical reaction on the surface of particles for various experimental conditions. Furthermore, the results of the research by Hasan [24] showed that the leaching process kinetics were controlled by liquid film diffusion. However, different from the two previous researchers, the experiment from Wanta [25] and Hendrik [21] have investigated the shrinking core model was not suitable to describe the phenomenon of leaching process. Therefore, this model although accurate for several conditions it should be investigated for various leaching processes with different materials and conditions.

Thus in this study not only from an environmental point of view, but the performance and kinetics of molybdenum leaching from spent catalysts using citric acid will be evaluated in order to establish suitable parameter design for scaling up stage.

2. Materials and Methods

2.1 Material

Sample of spent catalyst waste from desulfurization process were collected from PT. Pupuk Kujang, Cikampek, Karawang, Indonesia. The Particle size of Samples under 200 mesh in powder form were sieved to obtain the desired particle size. Citric acid monohydrate (C₆H₈O₇·H₂O) (M = 210.14 g / mol, from Merck KgaA) is used to leach molybdenum from spent catalysts as an organic leaching agent, and demin water produced by the Laboratory of Energy Conversion and Pollution Prevention, Department of Engineering Chemistry, Gadjah Mada University, Yogyakarta. The spent catalyst powder was analyzed using EDX (Energy Dispersive X-Ray) to identify elemental content and XRD (x-ray diffraction) to identify material characterization.

Several studies have been conducted from other industrial sample materials on the presence of valuable metals with various minerals in spent catalysts. It was suggested from manganese recovery using citric acid research study, based on the composition analysis the manganese content is about 1.22% w/t, then the Si and Al
compositions are also found to be dominant in the spent hydrocracking catalysts from petroleum refineries. The hydrocracking spent catalyst profile shows zeolite-Y as the major mineral for the mineral characterization by XRD analysis [26]. In another study, spent oil refinery catalysts using biogenic organic acids metal composition measurements, element Ni was associated with silicate mineral. Lanthanum partially exists in the sulfide and Al exists in the spent FCC catalyst as both Al2O3 and zeolite-Y. The XRD patterns of the catalyst sample used in this study shows the main mineral components of the spent FCC catalysts were zeolite-Y and Al2O3[27]. Similarly, the spent catalysts from the reforming unit PT. Petrokimia Gresik, Ni and Al metal elements were the main focus of this study. The EDX analyzed results showed that the main metal elements of this sample were aluminum and nickel which were 16.67 and 6.50%wt [28].

2.2 Leaching Experiment

Leaching process was done in a three-neck flask with a condenser, thermometer and stirrer in a waterbath equipped. The experiments were conducted for 120 minutes, 20% (w/v) solid liquid ratio with various pH (1.5, 2, 2.5) citric acid solution. The leaching containing 250 ml citric acid solution was poured into the three-neck flask placed on waterbath and left to reach a temperature of 60, 80 and 90 °C, then 50 g sample powder was added in to the flask and mixed by a stirrer with a stirring speed of 400 rpm. The samples of 3 ml volume were taken at various time intervals at 5, 15, 20, 40, 60, and 120 minutes during the leaching experiment. Then, the suspended solids in the filtrate were separated using a centrifuge and filtered again using a 0.22 µm syringe filter to obtain maximum separation. The chemical samples were then analyzed using inductively coupled plasma (ICP-OES) to analyze the concentration of molybdenum in the samples.

3. Result and Discussion

3.1 Raw Material Characterization

The spent catalyst materials powder was characterized with EDX (energy dispersive x-ray) Shimadzu edx-8000 fluorescence spectrometer and the elemental composition was given in Table 1. It showed that mostly the powder contained 59.829 % w/t Mo along with 26.547% Al and other metals. For the mineral characterization, XRD X’Pert 3 Powder instrument was utilized.

| Element  | Mo  | Al  | Co  | Fe  | Si  | As  | Nb  | Cu  | Ca  | V  | Cr  | Zn  | Se  |
|----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|----|-----|-----|-----|
| Composition (wt. %) | 59.829 | 26.547 | 9.747 | 1.223 | 1.059 | 0.987 | 0.168 | 0.142 | 0.082 | 0.07 | 0.07 | 0.04 | 0.037 |
Figure 1. XRD pattern of spent catalyst (a) and NiMoS / γ-Al₂O₃ catalyst samples after calcination (b)

Figure 1(a) showed the XRD pattern for the spent catalyst and the commercial NiMoS / γ-Al₂O₃ catalyst samples after calcination from industrial hydrotreating reactor fig 1(b) where the sample catalyst was used in this study had the same pattern in the results of the characterization analysis of the research conducted by Marcelo [29]. On the other hand Aleksey Pimerzin [30] reported that the pattern diffractions showing both diffraction peaks supported by Al₂O₃ (PDF No. 48-367) were taken from the PDF-ICDD database of crystalline material. Therefore the elemental composition of Al is also found to be dominant in the EDX analysis in Table 1.

However, a peak at 2θ = 26 ° (PDF No. 21-868) CoMoO₄ was found in the XRD pattern of the spent catalyst sample and a characteristic graphite peak at 2θ = 30.7 ° (JCPDS-PDF: 00-001-0640) which is also named pregraphite like carbon was found to be similar to new peak at 2θ = 32 ° on the spent catalyst [30].

3.2 Effect of citric acid pH

To examine the effect of citric acid pH on molybdenum leaching efficiency, experiments were carried out with variations in citric acid pH of 1.5, 2 and 2.5 with a leaching temperature of 90 °C, a ratio of 20% S/L ratio, a stirring speed of 400 rpm and a leaching time of 120 minute. Figure 2(a) showed the results of the recovery of Mo increases steadily with the decrease of the citric acid pH from 2.5 to 1.5 during 120 minutes leaching process. The maximum recovery of molybdenum at citric acid pH 1.5, 2, 2.5 were 71.20%, 34.66%, and 19.29% respectively. The recovery of Mo increased significantly from 19.29% at pH of 2.5 to 71.20% with citric acid pH of 1.5. Due to the different degrees of acid dissociation used in this experiment, acid concentration was represented in pH value. pH value can describe the phenomenon of leaching in the existence of H⁺, when the pH of the acid used is lower it allows the presence of a greater number of H⁺ ions. Thus the ion exchange reaction between H⁺ and Mo⁺ will increase to form molybdenum sitrate. In addition, the metal leaching mechanism in organic acids was influenced by complex reactions (metal chelation) [26].

There are three carboxylic groups which result in three stages of partial dissociation with Ka <1 in the case of citric acid. [28,29,30].

\[ C_6H_8O_7(aq) \iff 3H^+(aq) + (C_6H_5O_7)^3-(aq) \]  
(1)

Meanwhile, the proton attacks (3H⁺) to metals in the spent catalyst is

\[ MoO₃ + 6H^+ \iff Mo^{3+} + 3H₂O \]  
(2)

And then further complexation/chelation occurs in

\[ 3(C_6H_5O_7)^3-(aq) + 3Mo^{3+} \iff Mo(C_6H_5O_7)_3 \]  
(3)
3.3 Effect of leaching temperature and time

The influence of temperature to obtain an effective molybdenum recovery from spent catalyst, the leaching test was performed at 60, 80, and 90 °C while maintaining other parameters such as 1.5 citric acid pH, 120 minutes reaction time, 20% S/L ratio and stirring speed 400 rpm. The results were presented in Figure 2(b). It has been observed that temperature slightly affects molybdenum recovery of Molybdenum where the recovery was increased steadily with increase in temperature during 120 minutes leaching process. The percentage of dissolved metal increased and reached 51.70%, 62.62%, and 71.20% Mo at the end of 120 minutes as long as the temperature increased at 60, 80 and 90 °C, respectively. This phenomenon was in line with the Arrhenius rate law, because it has a tendency which states that an increase in temperature will increase the reaction rate, an increase in temperature of 10 degrees can increase the reaction rate twice [34].

The effect of time was analyzed in the range from 5, 15, 20, 40, 60, and 120 minutes. The experiment condition were carried out using citric acid pH of 1.5, 20% S/L ratio, and 400 rpm stirring speed. The trend of molybdenum recovery in Figure 2(b) showed the effect of time on leaching efficiency. The leaching efficiency Mo increases steadily with the increase of time from 0 to 120 min, with a level of molybdenum 39.5% to 71.2%.
3.4 Kinetic study

The reaction kinetics in leaching processes consisting of solid and liquid phases are explained using heterogeneous reaction models [23]. Shrinking core model was introduced at the first time by Yagi and Kunii [23] who visualized a few steps that occurred during the reaction which related to the conversion equation for a spherical particles. The steps are as follow:

1. Diffusion process of reactant through the liquid film around the surface of the solid particle.
2. Diffusion of reactant through layer of ash on the surface of the unreacted core.
3. Reaction of reactant with solid at this reaction surface.

The molybdenum leaching process involves more than one phase i.e. solid-liquid phase which is a heterogeneous process, also considered a spherical particle. To control the leaching process, it is important to determine quantitative measurements of the leaching kinetics and mechanism. Several models linking the reacted fraction (x) and time (t) were analyzed on existing experimental data. Commonly for liquid-solid reaction systems the process is controlled by diffusion or chemical reactions on the surface of the particles. With chemical reaction control, the reaction rate will produce an equation which is defined as (Equation (4)):

\[ 1 - (1 - x)^{1/3} = k_r t \]  

(4)

If the process is diffusion through the ash layer controls, reaction rate is defined as an equation (Equation (5)):

\[ 1 - 3(1 - x)^{2/3} + 2(1 - x) = k_d t \]  

(5)

x is the conversion of reactants represented by the recovery of the manganese, \( k_r \) is the kinetic parameter for the surface reaction control, \( k_d \) is the kinetic parameter for diffusion through ash layer control and t is the reaction time in minutes.

Kinetic modeling is completed when the solid-liquid reaction model fits to the experimental data [35]. Activation energy can be calculated following Arrhenius correlation as follows (Equation (6)). \( k_c \) is the rate constant, A the collision frequency, \( E_a \) the activation energy, \( R \) the universal gas constant and T is the absolute temperature.

\[ k_c = A e^{-\frac{E_a}{RT}} \]  

(6)

For plotting purposes, the Arrhenius equation is rearranged into linear equation as Equation (7).

\[ \ln k_c = - \frac{E_a}{R} \left( \frac{1}{T} \right) + \ln A \]  

(7)

The kinetic study of leaching process was carried out in the citric acid pH of 1.5 during 120 minutes leaching process. To examine the mechanism of reaction between the particles of spent catalyst and the citric acid leaching solution, a trial was made to fit the kinetic data gained from the leaching experiments with Equation (4) and (5) of SCM. By plotting that equation versus time at different temperatures, Figures 3(a) and 3(b) showed the kinetic data defined in straight lines. Reaction control is evaluated from the linearity of the line by looking at the correlation coefficient \( R^2 \) value. The value of the kinetic model \( R^2 \) obtained from the graph can be seen in Table 2. The slope of the plot as shown in Figure 3 is determined as the reaction rate constant (k). By comparing the \( R^2 \) values of the two models, the diffusion model through the ash layer had a higher \( R^2 \) value which indicated a better relation with the experimental data.
Figure 3. Shrinking core model for kinetics of leaching Mo (a) Chemical reaction control (b) Diffusion control

Table 2. R² Value of Kinetic Models

| Temperature (°C) | R² Value          |
|------------------|-------------------|
|                  | Chemical Reaction | Diffusion     |
| 60               | 0.6149            | 0.6305        |
| 80               | 0.7840            | 0.8042        |
| 90               | 0.8090            | 0.8208        |

To verify whether the model prediction was suitable, the analysis on activation energy was carried out using Equation (6). By plotting ln kc versus 1/T from Equation (7), Figure 4 shows the value of activation energy, $E_a$ can be obtained from the slope of the line equation. From the calculation result, the activation energy value of molybdenum was 31.60 kJ/mol. The prediction where the reaction was controlled by the diffusion model because of the correlation coefficient value, $R^2$ diffusion was better than chemical reactions and diffusion.
models generally have an activation energy value (Ea) for heterogeneous reaction mechanisms was controlled film diffusion (Ea < 20 kJ/mol) and by reaction surface chemistry (Ea > 40 kJ/mol) [23,36].

![Kinetics analysis Arrhenius equation plot](image)

**Figure 4.** Kinetics analysis Arrhenius equation plot

4. Conclusion

From the results of this experiment, it can be concluded that citric acid as organic acid had a promising potential to use as a leaching agent with the good capability of molybdenum recovery. An optimum operating conditions for leaching of molybdenum using citric acid were pH of 1.5, temperature of 90°C, time of 2 hours with the obtained recovery of molybdenum at 71% and it is still possible to increase with time. Based on the value of correlation coefficient (R²), the best mathematical model describe molybdenum leaching mechanism from spent catalyst was diffusion through ash layer. The value of apparent activation energy was 31.60 kJ / mol.

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References

[1] Suzette M. Kimball, “Mineral Commodity Summaries 2015 Mineral Commodity Summaries 2015,” *U.S. Geol. Surv.*, no. October, p. 188, 2015.

[2] I. Asghari, S. M. Mousavi, F. Amiri, and S. Tavassoli, “Bioleaching of spent refinery catalysts: A review,” *J. Ind. Eng. Chem.*, vol. 19, no. 4, pp. 1069–1081, 2013, doi: 10.1016/j.jiec.2012.12.005.

[3] L. Zeng and C. Y. Cheng, “A literature review of the recovery of molybdenum and vanadium from spent hydrodesulphurisation catalysts. Part I: Metallurgical processes,” *Hydrometallurgy*, vol. 98, no. 1–2, pp. 1–9, 2009, doi: 10.1016/j.hydromet.2009.03.010.

[4] A. Akcil, F. Veglio, F. Ferella, M. D. Okudan, and A. Tuncuk, “A review of metal recovery from spent petroleum catalysts and ash,” *Waste Manag.*, vol. 45, pp. 420–433, 2015, doi: 10.1016/j.wasman.2015.07.007.

[5] M. Marafi and A. Stanislaus, “Utilization of Metal-Fouled Spent Residue Hydroprocessing Catalysts in the Preparation of an Active Hydrodemetallization Catalyst,” pp. 1968–1974, 2007.

[6] A. Szymczycha-Madejqa, “Kinetics of Mo, Ni, V and Al leaching from a spent hydrodesulphurization catalyst in a solution containing oxalic acid and hydrogen peroxide,” *J. Hazard. Mater.*, vol. 186, no. 2–3, pp. 2157–2161, 2011, doi: 10.1016/j.jhazmat.2010.11.120.

[7] M. Marafi, “Studies on rejuvenation of spent residue hydroprocessing catalysts by leaching of foulant metals: influence of inorganic salt additives on the leaching efficiency of organic acids,” vol. 18, pp. 141–151, 1993.
[8] A. Bharadwaj and Y. Ting, “Bioresource Technology Bioleaching of spent hydrotreating catalyst by acidophilic thermophile Acidithiobacillus brierleyi: Leaching mechanism and effect of decoking,” *Bioresour. Technol.*, vol. 130, pp. 673–680, 2013, doi: 10.1016/j.biortech.2012.12.047.

[9] M. Marafi and A. Stanislaus, “Spent catalyst waste management: A review. Part I-Developments in hydrotreating catalyst waste reduction and use,” *Resour. Conserv. Recycl.*, vol. 52, no. 6, pp. 859–873, 2008, doi: 10.1016/j.resconrec.2008.02.004.

[10] H. Tri, B. Murti, A. Wijaya, Y. Iskandar, H. Setiawan, and W. Astuti, “LANTHANUM AND NICKEL RECOVERY FROM SPENT CATALYST USING CITRIC ACID: QUANTITATIVE PERFORMANCE ASSESSMENT USING RESPONSE SURFACE METHOD,” pp. 91–100, 2018.

[11] W. Astuti, N. M. Prilitasari, Y. Iskandar, D. Bratakusuma, and H. T. B. M. Petrus, “Leaching behavior of lanthanum, nickel and iron from spent catalyst using inorganic acids,” *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 285, no. 1, 2018, doi: 10.1088/1757-899X/285/1/012007.

[12] H. I. Kim, K. H. Park, and D. Mishra, “Sulfuric acid baking and leaching of spent Co-Mo/Al2O3 catalyst,” *J. Hazard. Mater.*, vol. 166, no. 2–3, pp. 1540–1544, 2009, doi: 10.1016/j.jhazmat.2008.11.051.

[13] A. Khoshtevi, H. Zoyobashizadeh, M. Mozammel, and S. K. Sadreza, “Kinetics of pressure oxidative leaching of molybdenite concentrate by nitric acid,” *Hydrometallurgy*, vol. 111–112, no. 1, pp. 52–57, 2012, doi: 10.1016/j.hydromet.2011.10.002.

[14] R. Banda, T. H. Nguyen, S. H. Sohn, and M. S. Lee, “Recovery of valuable metals and regeneration of acid from the leaching solution of spent HDS catalysts by solvent extraction,” *Hydrometallurgy*, vol. 133, pp. 161–167, 2013, doi: 10.1016/j.hydromet.2013.01.006.

[15] V. Ruiz, E. Meux, M. Schneider, and V. Georgeaud, “Oxidative leaching of molybdenum and cobalt from an unroasted spent CoMo/Al2O3 3 catalyst using H2O2,” *19th Int. Congr. Chem. Process Eng. CHISA 2010 7th Eur. Congr. Chem. Eng. ECCE-7*, pp. 5307–5315, 2010.

[16] S. P. Barik, K. H. Park, P. K. Parhi, and J. T. Park, “Direct leaching of molybdenum and cobalt from spent hydridesulfurization catalyst with sulphuric acid,” *Hydrometallurgy*, vol. 111–112, no. 1, pp. 46–51, 2012, doi: 10.1016/j.hydromet.2011.10.001.

[17] Y. Ding, S. Zhang, B. Liu, H. Zheng, C. Chang, and C. Ekberg, “Resources , Conservation & Recycling Recovery of precious waste from electronic waste and spent catalysts ; A review,” *Resour. Conserv. Recycl.*, vol. 141, no. October 2018, pp. 284–298, 2019, doi: 10.1016/j.resconrec.2018.10.041.

[18] D. P. Sari et al., “Valuable Metals Extraction From Hydrocracking Spent Catalyst Using Citric Acid,” *Semin. Nas. Tek. Kim. “Kejuangan” Pengemb. Teknol. Kim. untuk Pengolah. Sumber Daya Alam Indonesia.,* no. April, pp. 1–5, 2018.

[19] H. Manurung et al., “RECOVERY OF RARE EARTH ELEMENTS AND YITTRIUM FROM NON-MAGNETIC Departemen Teknik Kimia (Sustainable Mineral Processing Research Group ), Fakultas,” 2020.

[20] H. T. B. M. Petrus et al., “Effect of temperature and acid concentration on lanthanum extraction from spent catalyst using organic acid,” *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 478, no. 1, 2019, doi: 10.1088/1757-899X/478/1/012017.

[21] H. Setiawan, H. T. B. M. Petrus, and I. Perdana, “A kinetics study of acetic acid on cobalt leaching of spent LIBs : Shrinking Core Model,” vol. 01033, pp. 0–4, 2018, doi: 10.1051/matecconf/201815401033.

[22] M. F. Menouny and H. S. Ahmed, “Treatment and reuse of spent hydrotreating catalyst,” *Energy Sources, Part A Recover. Util. Environ. Eff.*, vol. 30, no. 13, pp. 1213–1222, 2008, doi: 10.1080/15567030600829048.

[23] O. Levenspiel, Chemical reaction engineering, vol. 38, no. 11, 1999.

[24] H. Arslanoğlu and A. Yaraş, “Recovery of precious metals from spent Mo–Co–Ni/Al2O3 catalyst in organic acid medium: Process optimization and kinetic studies,” *Pet. Sci. Technol.*, vol. 37, no. 19, pp. 2081–2093, 2019, doi: 10.1080/10916466.2019.1618867.

[25] K. C. Wanta, I. Perdana, and H. T. B. M. Petrus, “Evaluation of shrinking core model in leaching process of Pomalaa nickel laterite using citric acid as leachant at atmospheric conditions,” *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 162, no. 1, 2016, doi: 10.1088/1757-899X/162/1/012018.

[26] H. T. B. M. Petrus et al., “Manganese Recovery from Hydrocracking Spent Catalyst Using Acidic and Its Kinetics,” vol. 4, no. 2, pp. 230–239, 2019, doi: 10.23960/ins.v4i2.226.

[27] M. P. Dewi, H. Tri, B. Murti, and N. Okibe, “Recovering Secondary REE Value from Spent Oil Refinery Catalysts Using Biogenic Organic Acids,” 2020, doi: 10.3390/catal10091090.

[28] H. Tri, B. Murti, H. Manurung, R. J. Aditya, R. Amanda, and W. Astuti, “Bioleaching of Valuable Metals from Spent Catalyst Using Metabolic Citric Acid by Aspergillus niger,” vol. 898, pp. 23–28, 2020, doi: 10.4028/www.scientific.net/AMM.898.23.

[29] M. R. Amora, M. E. Pacheco, D. C. S. Azevedo, C. L. Cavalcante, and F. M. T. Luna, “Deactivation Analysis of Industrial Spent Catalysts Applied to Lube Oil Hydrotreating in a Pilot Plant,” *Chem. Eng. Technol.*, vol. 42, no. 5, pp. 1018–1026, 2019, doi: 10.1002/ceat.201800252.

[30] A. Pimerzin, A. Roganov, A. Mozhaev, K. Maslakov, P. Nikulshin, and A. Pimerzin, “Active phase transformation in industrial CoMo/Al2O3 hydrotreating catalyst during its deactivation and rejuvenation with organic chemicals treatment,” *Fuel Process. Technol.*, vol. 173, no. December 2017, pp. 222–230, 2019, doi: 10.1016/j.fuproc.2018.01.008.

[31] R. G. McDonald and B. I. Whittington, “Atmospheric acid leaching of nickel laterites review. Part I. Sulphuric acid
technologies,” *Hydrometallurgy*, vol. 91, no. 1–4, pp. 35–55, 2008, doi: 10.1016/j.hydromet.2007.11.009.

[32] J. Wang et al., “Kinetics study on the leaching of rare earth and aluminum from FCC catalyst waste slag using hydrochloric acid,” *Hydrometallurgy*, vol. 171, pp. 312–319, 2017, doi: 10.1016/j.hydromet.2017.06.007.

[33] H. B. T. M. Petrus, K. C. Wanta, H. Setiawan, I. Perdana, and W. Astuti, “Effect of pulp density and particle size on indirect bioleaching of Pomalaa nickel laterite using metabolic citric acid,” *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 285, no. 1, 2018, doi: 10.1088/1757-899X/285/1/012004.

[34] H. S. Fogler, *Elements of Chemical Reaction Engineering*, 4th ed. 2006.

[35] H. Ebrahimzade, G. R. Khayati, and M. Schaffie, “Leaching kinetics of valuable metals from waste Li-ion batteries using neural network approach,” *J. Mater. Cycles Waste Manag.*, vol. 20, no. 4, pp. 2117–2129, 2018, doi: 10.1007/s10163-018-0766-x.

[36] C. . Wen, “Noncatalytic Heterogeneous Solid Fluid Reaction Models,” *Ind. Eng. Chem. Res.*, vol. 47, no. 6, pp. 459–471, 1968, doi: doi:10.1021/ie50705a007.