Subcritical Water as a Solvent for Extraction of Nickel and Aluminum Ions from Reforming Spent Catalysts

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Abstract. Spent catalysts are categorized as hazardous waste because they still contain heavy metal elements. It indicates that spent catalysts need to be treated before they discharge to the environment. In this study, spent catalysts treatment was done using subcritical water extraction method. The extraction process was conducted by varying temperature and extraction times. Temperature was varied at 100–250°C, whereas time extraction was varied at 15–45 minutes. Operating pressure and particle size were kept at 70 bars and ~60+70 mesh, respectively. The content of aluminum (III) (Al³⁺) ions and nickel (II) (Ni²⁺) ions were analyzed using UV–vis spectrophotometer. The experimental results showed that the highest content of both metal ions was achieved at 250°C and 45 minutes. The content of extracted Al³⁺ ions and extracted Ni²⁺ ions at those conditions was 623.39 and 35.03 ppm, respectively.

1. Introduction
Catalysts are the material used in various chemical processes and aim to increase the rate of reaction. Catalysts usually use in chemical industries, such as fertilizer and oil industries. However, the use of catalysts for a long time causes it to become saturated. These catalysts are usually called spent catalysts. Spent catalysts can be classified as hazardous waste because it still contains heavy metal elements, such as aluminum (Al), nickel (Ni), iron (Fe), cobalt (Co), zinc (Zn), and magnesium (Mg) [1]. Thus, in order to avoid contaminating the environment and harming humans, spent catalysts have to be processed first before it is removed to the environment.

One of the spent catalyst processing is using the hydrometallurgy method which heavy metal ions are extracted from the spent catalysts. Most studies related to this method have been conducted using an acid solution in certain operating conditions [2–4]. Based on previous studies, the percentage recovery of heavy metal ions was quite high (more than 90%) depending on operating conditions [5–6]. It indicates that this process has been well developed. However, to maximize the extraction process, it is necessary to use a high concentration of an acid solution. Although for better results, the use of those solutions can pollute the environment. In other words, another green solvent is needed as an alternative to extract those heavy metal ions, for example, subcritical water.
The replacement of solvents from acidic solutions into water has a large advantage because water is cheap, easy to found, easy to be handled and not harmful to the environment. Subcritical water is defined as water which is at 100–374°C and moderate pressure so that it keeps water in the liquid phase [7]. This type of water has specific physical properties, such as the viscosity and density of subcritical water is smaller than water at room pressure and temperature, but the ability of water to diffuse is higher [7–8]. These characteristics are used in various chemical processes, especially in the extraction process. In addition, water in subcritical conditions tends to be more acidic than its initial condition [8–9]. In the extraction process of metal ions, the acidic condition has to be created in the system so that the chemical reaction between solvents and solids can occur as shown in this following reaction:

\[
2y(H^+) + M_xO_y \rightarrow xM^{y+} + yH_2O
\]

where M is a metal element.

In this study, the main focus was to apply a subcritical water solvent for extracting spent catalyst samples from PT. Petrokimia Gresik. The experimental results from this study are expected to overcome the waste problem.

2. Materials and methods
The spent catalysts used in this study were from the reforming unit, PT. Petrokimia Gresik. These samples were analyzed for metal content in those samples using Energy Disperse X-ray (Shimadzu, EDX–8000). The results showed that the main metal elements of this sample were aluminum and nickel which were 16.67 and 6.50%wt. Thus, the two metal elements were the main focus of this study.

The extraction process of the spent catalyst was conducted using a series of subcritical extraction equipment as presented in Figure 1. Demineralized water was used as a solvent. The temperature was varied at 100, 150, 200 and 250°C while the extraction time was varied at 15, 30 and 45 minutes. Other operating conditions, such as sample mass, sample particle size and operating pressure were maintained at 5 grams, –60+70 mesh and 70 bars, respectively. After the extraction process time was reached, the operating conditions were returned to the atmospheric conditions. The experimental sample was taken and separated between the solid–liquid phase using a centrifuge. The liquid phase was analyzed for aluminum and nickel ions content using a UV–vis spectrophotometer using dimethylglyoxime and eriochrome cyanine R as complexing agent.

![Figure 1. The series of extraction process equipment](image-url)
3. Results and discussion

3.1. The effect of temperature in the subcritical water extraction process

Temperature is an important parameter in the extraction process because it will affect the diffusion rate and reaction rate. The experimental results of this study are presented in Figure 2 and 3.

Based on Figure 2 and 3, the maximum concentration of Al\(^{3+}\) and Ni\(^{2+}\) ions that can be obtained during the extraction process were 623.39 and 35.03 ppm, respectively. This result was achieved at the same operating conditions, namely at 250°C and 45 minutes. Figure 2 and 3 showed that the trends of aluminum and nickel ions concentration in the liquid phase increase when the operating temperature was raised. It means that the extraction process using subcritical water as the solvent can be activated by temperature. This phenomenon can happen because each molecule moves faster during the diffusion steps and the frequency collision between reactant molecules become bigger during the chemical reaction steps.
The role of temperature in this process is not only related to diffusion and reaction rate but also pH scale in the system [8–9]. pH indicates the amount of hydrogen ions (H\(^+\)) present in the system and these ions will react with metal compounds contained in the raw samples. This reaction causes the metal bond in solid phase break and form water-soluble metal ions (Al\(^{3+}\) and Ni\(^{2+}\) ions) [10]. To obtain the H\(^+\) ions, the breakdown of the hydrogen bonds present in water needs to occur. The amount of hydrogen bond makes H\(^+\) ions difficult to obtain. However, the strength of hydrogen bonds will decrease by increasing temperature [11–12]. In this study, the use of subcritical water conditions was carried out in order to produce acidic conditions in the system so that the chemical reaction steps could occur. Also, the change of lower pH values also affects the solubility of aluminum (III) ions and nickel (II) ions in water [13].

3.2. The effect of extraction time in subcritical water extraction process
Another parameter that affects the extraction process using subcritical water solvents is the extraction time. The experimental results are presented in Figure 4 and 5.

![Figure 4. The effect of extraction time in the extraction process of Al\(^{3+}\) ions](image)

![Figure 5. The effect of extraction time in the extraction process of Ni\(^{2+}\) ions](image)
Figure 4 and 5 show that the longer the extraction process was carried out, the higher the aluminum and nickel ions would be extracted. The long extraction time will increase the frequency of contact between water (in subcritical condition) and metal compounds (in solids) so that the extraction process will run more maximum and be able to extract more metal ions.

As previously explained, the effect of temperature will affect the quality of the extraction process using subcritical water. Based on Figure 4 and 5, when the operating temperature at 100 and 150°C, the extracted aluminum and nickel ions concentration had different tendencies where the increase in extracted nickel ion concentration was not significant while for aluminum ions, the extracted aluminum ions increases. This phenomenon is caused by the small amount of H⁺ ions formed at these two temperatures so that there is a “seizure” of H⁺ ions for the reaction of aluminum and nickel compounds. Because the aluminum content in the spent catalyst (raw materials) is more than the nickel content in the spent catalyst, the H⁺ ion will attack and react more with aluminum compounds.

Besides being related to the frequency of intermolecular contact reactant (chemical reaction step), the length of the extraction process will also affect the amount of solvent entering the particle. The longer processing time used to extract, the amount of solvent that can enter into solids will continue to increase [13]. This phenomenon will cause lower subcritical water viscosity so that solvents will be easy to enter the sample pore of the spent catalyst.

4. Conclusion

Temperature and time are important parameters in the extraction process include this extraction process using subcritical water. The experimental results showed that the higher the temperature and the longer the extraction process were carried out, the higher the aluminum and nickel ions would be extracted. During the extraction process, the maximum concentration of Al³⁺ and Ni²⁺ ions that can be obtained were 623.39 and 35.03 ppm, respectively. This result was achieved at the same operating conditions, namely at 250°C and 45 minutes.

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