

Recovery of Cobalt from leach solution of spent oil Hydrodesulphurization catalyst using a synergistic system consisting of VersaticTM 10 and Cyanex[®]272

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Abstract. Catalyst are often used in the petroleum refinery industry, especially cobalt-based catalyst such as CoMoX. Every year, Indonesia's oil industry produces around 1350 tons of spent hydrodesulphurization catalyst in which cobalt makes up for 7%wt. of them. Cobalt is a non-renewable and highly valuable resource. Taking into account the aforementioned reasons, this research was made to recover cobalt from spent hydrodesulphurization catalyst so that it can be reused by industries needing them. The methods used in the recovery of cobalt from the waste catalyst leach solution are liquid-liquid extraction using a synergistic system of VersaticTM 10 and Cyanex[®]272. Based on the experiments done using the aforementioned methods and materials, the optimum condition for the extraction process: concentration of VersaticTM 10 of 0.35 M, Cyanex[®]272 of 0.25 M, temperature of 23-25°C (room temperature), and pH of 6 with an extraction percentage of 98.80% and co-extraction of Ni at 93.51%.

1. Introduction

Petroleum consists not only of hydrocarbons, but also contains impurities such as sulfur, nitrogen, oxygen, and metals (mainly Ni and V). The presence of these contaminants results in damage to equipment, catalysts, poor product quality, and environmental pollution [9], therefore they should be removed. In petroleum processing, hydrodesulphurization process is the way to remove all of these contaminants. The oil and oil fraction hydrodesulphurization process are universally carried out by the catalytic reaction between hydrogen and the sulfur components present in the oil and its fractions to produce hydrogen sulfide (H₂S) which can be easily separated from the oil. In naphtha pretreatment, this is done by using a cobalt-molybdenum catalyst to avoid contact between sulfur and precious metal catalysts used in the oil reform process, which cannot tolerate the presence of sulfur.

The cobalt (CoMoX) catalyst used in the hydrodesulphurization process is usually solid. CoMoX ($\gamma - Al_2O_3 - CoO - MoO_3$) is the most commonly used catalyst for hydrofining. CoMoX takes on the appearance of a dull blue solid. In general, the active constituents present in the catalyst are cobalt oxide in the form of CoO 6.00%wt. and molybdenum oxide in the form of MoO₃ 20.2%wt. [3]. However, The Cobalt Development Institute also mentioned that its active constituents consist of cobalt oxide in the form of Co₃O₄ in the amount of 3-5%wt. and molybdenum oxide in the form of MoO₃ in the amount of 14%wt [8]. The cobalt catalyst is used in the industry continuously in a

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continuous process. As the catalyst continues to be used and regenerated, the catalyst activity will decrease until it is uneconomical to regenerate it, leaving the catalyst disposed of into waste. On average, the lifespan of a cobalt catalyst is 3 to 5 years.

Based on calculations made using Schuman & Shalit method [7] using the latest data from international energy statistics from US Energy Information Administration [10], given that the aggregate production of oil refineries in Indonesia reaches 889.3 thousand barrels/day, it will produce spent catalyst waste of 1,350 tons/year. Thus, the wasted cobalt metal is about 7% of that amount [3], which is 70 kg of cobalt/1 ton of catalyst waste. This amount is very significant considering that cobalt is a metal that has a high selling value. The price of cobalt in mid-2016 is \$27,000 per ton or about Rp 356,000,000 per ton, so we can assume that the oil industry can recover around 34 billion rupiahs per year.

Based on the aforementioned reasons, cobalt recovery from spent catalyst weight is necessary. One commonly used method is liquid-liquid extraction. Cobalt is generally extracted using a single extractant (SX) such as Cyanex[®]272. Cyanex[®]272 can extract cobalt with an efficiency of >98.6% but this process requires two stages and produces large excess of organic phase [4]. Thus, some institutions also used Versatic[™] 10 because this extractant has a low percentage of extraction on impurities such as magnesium and calcium metals. However, the use of this extractant is inefficient because it requires extraction and stripping of two stages to achieve the desired level of purity of cobalt extraction. It can be concluded that single extractants are generally not selective to cobalt when compared with other impurities found in leach liquor, such as copper, zinc, iron (II), cadmium, calcium, magnesium, and manganese. Therefore, a technique often used in the field of extractive hydrometallurgy to obtain higher separation efficiency and metal concentration is to use a synergistic mixture of multiple extractants (SSX). When Versatic[™] 10 is used as a component in a synergistic extractant mixture with Cyanex[®]272, the percentage of cobalt extraction is increased to 97.48% [6]. Mubarak and Hanif did an extraction experiment with a synergistic mixture between Versatic[™] 10 20%vol. and Cyanex[®]272 20%vol. at pH of 6.95 and temperature of 40°C.

2. Materials and Methods

2.1. Materials

In the extraction process, the extractants used are Versatic[™] 10 and Cyanex[®]272. Versatic[™] 10 is a synthetic tertiary carboxylic acid that has many branches and has a trivial name of neodecanoic acid. Versatic[™] 10 has 10 carbon atoms on the main chain and is liquid at room temperature. In this experiment, Versatic[™] 10 was imported from Haihang Industry Co., Ltd. Cyanex[®]272 (C₁₆H₃₄PO₂H) is an extractant that belongs to the acid extractant class, in which its main component is bis-(2,4,4-trimethylpentyl) phosphinic acid compound that has POOH as an active group [11]. In this experiment, Cyanex[®]272 was given by BASF Indonesia. The reason why this extractant mixture is chosen to recover the cobalt metal is:

- The synergistic mixture of Versatic[™] 10 and Cyanex[®]272 meet the fundamental criteria that include low solubility properties in aquatic phases, have good stability to survive several months of recycling on the extraction process without degradation, will not form a stable emulsion with the aquatic phase when stirred, has a high-loading capacity, not flammable, non-volatile, relatively inexpensive, soluble in organic solvents, and has good extraction kinetics.
- Versatic[™] 10 and Cyanex[®]272 synergistic mixture is a commonly used mixture for cobalt separation of leach solution in sulfuric acid or chloride media by liquid-liquid extraction method. In addition, this synergistic mixture can also extract cobalt metal ions up to high concentrations at optimum pH.

In general, Versatic[™] 10 and Cyanex[®]272 extractants are soluble in aromatic and aliphatic solvents, stable against heat and hydrolysis so the solvent used to dilute them is kerosene. Selection of kerosene as an organic solvent is due to:

- Kerosene density is quite low at 0.6 g/L thus reducing possible errors at two phase separation as the boundary between two phases is visible.
- When compared with other organic solvents having a dielectric constant above 2.2, kerosene is the best solvent ever tested with a 2-2.2 dielectric constant. Increasing the dielectric constant will increase the solvency of the solvent.
- Low kerosene viscosity makes the value of surface tension also low. With a low surface tension the extractant can pull the metal from the aqueous phase more easily.

2.2. Methods

The samples used in this experiment were from the leach solution of spent catalyst waste from Hydrogen Plant UP VI Balongan that contained 1.3263 mg/g of Co and 156.17 of Ni. In this study, extraction experiments were performed using the Versatic™ 10 and Cyanex®272 extractant synergic mixtures dissolved in kerosene. In the process of extraction of cobalt metal, the variations being tested are aquatic phase pH and extractant concentration. Both of these variables can affect the extraction efficiency.

In this paper, two studies were conducted with different types of test variables. The first tested variable is the extractant concentration variable, then after the optimal concentration of extractant is known, a second research is done with pH variation of the leaching solution. In the experiment of concentration variation, the extraction was done three times (single stage SX using Versatic™ 10, SSX using Versatic™ 10 and Cyanex®272 where the concentration of Versatic™ 10 is varied and Cyanex®272 is at 0.25 M, and SSX using Versatic™ 10 and Cyanex®272 where the concentration of Cyanex®272 is varied and Versatic™ 10 is at 0.25 M) with variation of extractant concentration of 0,25 M, 0,35 M, 0,4 M and 0,5 M. In the experiment of pH variation, pH variation was performed by NaOH into the solution. The addition of NaOH changes the pH of the acid to a less acidic state. The pH variations were 4, 4,5, 5, 5,5, and 6. The extraction process for each variation was performed using a magnetic stirrer, with a volume ratio O:A (organic:aquatic) of 1:1, with the volume of each solution being 20 ml. Stirring was done for 60 minutes per sample. The next process is the separation of organic and aqueous phase. The two phases naturally separated into two layers after the extraction process was completed. The separation of the two phases is done using a separation funnel. AAS (Atomic Absorption Spectroscopy) test is used to view the results of the liquid-liquid extraction process for the aqueous phase, so that the metal content of the aqueous phase can be known. The AAS test is done in Laboratorium Kimia Terpadu IPB Baranangsiang.

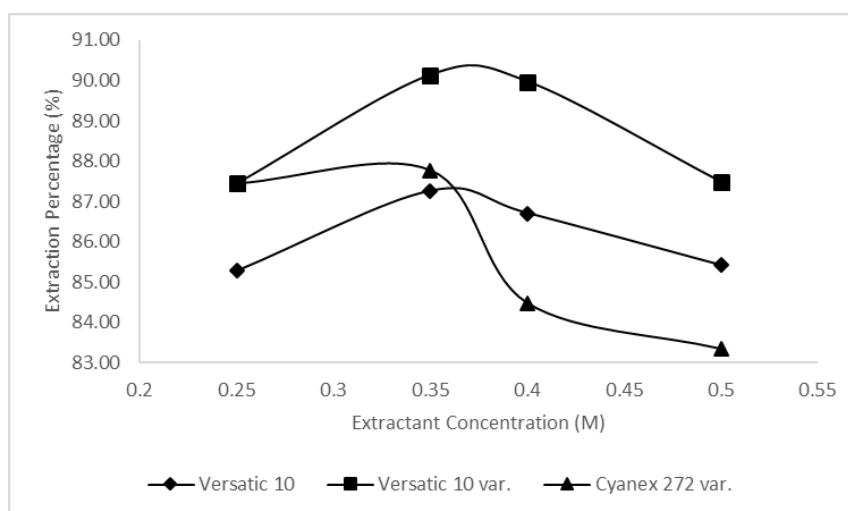
3. Results and Discussion

3.1. Extractant Concentration Variation Results

The extraction process was carried out using a synergistic mixture of Versatic™ 10 and Cyanex®272 dissolved in an organic solvent called kerosene. This synergistic mixture is mixed with the leach solution that has its pH converted to 0.5 beforehand – following the minimum operating conditions proposed by Cheng, et al. [2]. The process of changing the pH is done by adding NaOH solids gradually until the pH reaches 0.5. The mixture is then filtered using a filter paper to remove the Na₂SO₄ salt content which can interfere with the extraction process and the separation process later in the separatory funnel. The volume ratio between the organic phase and aquatic phase is 1:1. After that, the solution is stirred at 750 rpm (3 mot) for 30 minutes at room temperature. After stirring, the mixture is transferred to and kept at the separatory funnel for 15-30 minutes until there is a separation between the organic phase and the aqueous phase. Result of AAS analysis of aquatic phase after extraction and calculation of efficiency of cobalt extraction process shown in Table 1 and Figure 1.

Table 1. Results of Extractant Concentration Variation.

Extractant Concentration (M)	Co Concentration (mg/g)	Extraction Efficiency (%)
Versatic TM 10 (V.) 0.25 M	0.159	85.28
V. 0.35 M	0.155	87.26
V. 0.4 M	0.162	86.71
V. 0.5 M	0.158	85.42
Cyanex [®] 272 (C.) 0.25 M + V. 0.25 M	0.167	87.45
C. 0.25 M + V. 0.35 M	0.131	90.14
C. 0.25 M + V. 0.4 M	0.134	89.97
C. 0.25 M + V. 0.5 M	0.167	87.48
V. 0.25 M + C. 0.35 M	0.163	87.45
V. 0.25 M + C. 0.4 M	0.207	87.77
V. 0.25 M + C. 0.4 M	0.206	84.49

**Figure 1.** Results of Extractant Concentration Variation.

The AAS test is carried out on the aqueous phase - not the organic phase because kerosene is a flammable solution - after the extraction process so that the amount of cobalt that remains in the organic phase can be known and the amount will be compared with the amount of cobalt metal prior extraction. The smaller the number of cobalt metal on the AAS results indicates that more cobalt metal is successfully extracted, whereas on the contrary if there is a lot of cobalt metal in the AAS results, then the amount of cobalt metal extracted is small so that much remains in the extraction solution.

3.1.1. Single Stage SX Using VersaticTM 10

Le Chatelier principle states that changes in any factor in the system will affect the system equilibrium. If one part is added then the equilibrium will shift to the side which is not added so adding the amount of extractant theoretically will add the product that is produced. When ionized, the active group COOH in VersaticTM 10 will form a COO⁻ group and will bind to the cobalt ion to form the extracted metal compound. The more COOH active groups that is present in the mixture the higher the percentage of cobalt metal extraction. This is evidenced by the increase in the percentage of extraction when the concentration is increased from 0.25 M to 0.35 M.

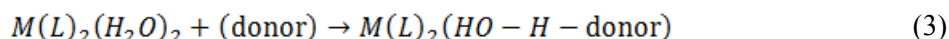
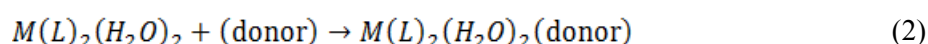
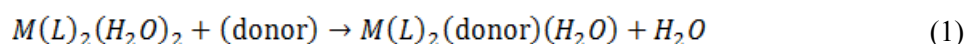
The amount of bonded metal will always be lower than the theoretical amount because the extractant will form a dimer bond where the neodecanoic acid compounds will bind together because of the hydrogen bond. The formation of dimers occurs because of the presence of hydrogen bonds at a

high enough concentration where the collision between the extractants is greater. The dimer effect affects the extraction process if the metal content in the leach liquor is low. Further increases in the concentration of the extractant will not increase the percentage of significant extraction - it can be seen that the percentage of extraction decreases as the extractant concentration is above 0.35 M. So, the addition of extraction becomes inefficient from an economic point of view.

3.1.2. Single Stage SSX Using Versatic™ 10 and Cyanex®272

The mechanism of the Co^{2+} extraction process is where two molecules of Versatic™ 10 bind one M^{2+} molecule. The increase in the percentage of cobalt extraction is quite large with the increased concentration of Versatic™ 10. However, the percentage of extraction that can be achieved by Versatic™ 10 can still be improved by using the SSX method. Therefore, Cyanex®272 is added to increase the percentage of cobalt extraction. Figure 1 shows that the addition of Cyanex®272 increases the percentage of cobalt extraction. The image also shows that the percentage of extraction higher when the concentration that is being varied is Versatic™ 10. This indicates that Cyanex®272 is a synergist in this synergistic mixture. This result is consistent with the hypothesis given by Wilson [11].

The existence of two different types of ligand complexes leads to an increase in the hydrophobic character of the metal complexes produced between the cobalt and the extractant thus permitting the formation of more stable compounds or the binding of higher quantities of metal ions. In general, the reaction occurring in this process is the condition where the more acidic extractant ligand (A) has not been able to meet the coordination capacity of the MA_z chelate so the synergist (S) will trigger the formation of MA_zS_x adduct which has a higher extraction ability than the MA_z parent chelate. The extraction mechanism that occurs is the coordination between the extractant ligand and the metal ion and if the coordination number of the metal ion is not fulfilled then the water molecule will enter into the inner sphere. Furthermore, the water molecule will be displaced by a ligand from a donor (synergist) that has a higher affinity to the metal ion (reaction 1). Another mechanism may also be the expansion of the coordination spheres of the metal ions, thus increasing the probability of the ligand of the synergist to bind to the complex (reaction 2). In addition, donor ligands may also bind to a metal-chelate complex by hydrogen bonding with water molecules present in the inner sphere (reaction 3).



in which the reactions above take place with the assumption that the metal ions are bound in the form of hexa co-ordination in simple aqua complex $\text{M}(\text{L})_2(\text{H}_2\text{O})_2$ and L is the bidentate ligand.

However, the addition of excessive amount of Cyanex®272 will decrease the percentage of cobalt extraction. This phenomenon can be explained by three possibilities. First, this phenomenon occurs due to the increased viscosity that occurs to the Cyanex®272 extractant when its concentration is increased. Ayanda, et al. declares that if Cyanex®272 is saturated up to 12-20 gram/dm³ Co^{2+} , then its viscosity will rise to >150 cst [1]. In this condition, the ability of the magnetic bar to mix the mixture becomes reduced so that the percentage of extraction also becomes reduced. Secondly, there may also be antagonistic extraction happening in which Versatic™ 10 and Cyanex®272 extractants are joined together with each other thus inhibiting MA_z formation. Thirdly, just like Versatic™ 10, Cyanex®272 can also form dimers if their concentration is higher than metal concentrations. This phenomenon can be seen in Figure 1 where the percentage of extraction decreases when the concentration of Cyanex®272 is more than 0.35 M to the extent that the extraction percentage is even lower than the extraction using single stage Versatic™ 10 SX.

3.2. Leach Solution pH Variation Results

pH of aquatic phase is a highly influential variable on the extraction process. This is because in the separation process using extraction method, the optimum pH value is needed to be known where the ionic compounds to be taken is bound to the extractant while the impurities do not because their optimum extraction pH are in a different range. The pH of the leaching solution was varied with a pH range of 4-6 wherein the percentage of extraction using a Versatic™ 10 0.35 M/Cyanex®272 0.25 M synergistic mixture at each point of variation is shown in table 2 and figure 2.

Table 2. Leach Solution pH Variation Results.

pH	Co Concentration (mg/g)	Extraction Efficiency (%)
0.5	0.131	90.14
4	0.0153	96.62
4.5	0.0133	97.06
5	0.0083	97.90
6	0.0055	98.80

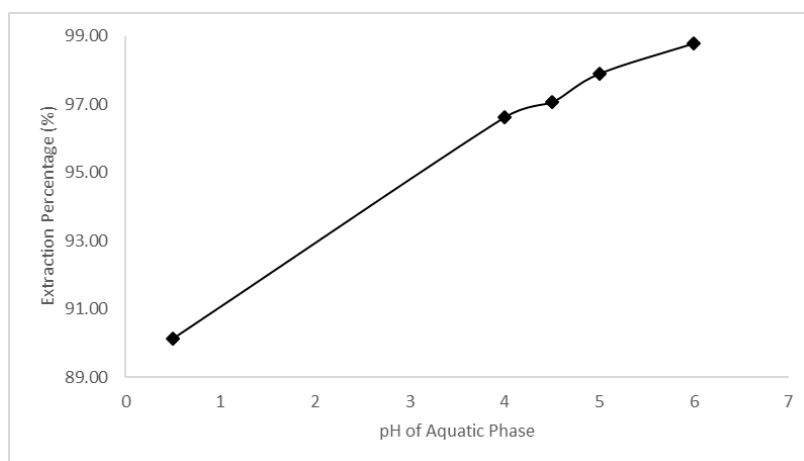


Figure 2. Leach Solution pH Variation Results.

In accordance with the figure above, it can be seen that the greater the pH of the waste the greater the percentage of cobalt extraction. The highest value of extraction efficiency (98.80%) was achieved at the pH of 6. Increase in pH causes an increase in the percentage of extraction. But, with higher value of pH, the extraction percentage will gradually decrease. pH system will affect the metal ions and extractants. At low pH, the ability of extraction decreases due to the effect of proton donation to the extractant. The proton donation causes imperfect dissociation of the extractant molecules so that the metal ion extraction process is not running perfectly. The cobalt extraction process increases with increasing amount of proton concentration up to a certain concentration.

The extraction process begins with the extractant dissociation process. After that, the activated group of the ionized extractant binds the metal ion so that the metal compound will bind to the extractant. The cobalt ion will move from the aqueous phase into the organic phase. The reaction is a reversible reaction, so that if the process reaches the equilibrium point, then the reaction will shift and the percentage of extraction will not increase anymore. After the metal ions are bonded with the extractant, the H^+ and SO_4^{2-} ions will be released, and will return to the aquatic phase. In theory, the release of the ion will affect the pH. However, the addition of these ions has no effect on the actual percentage of extraction. This is due to the presence of Co^{2+} ions in the mixture so that it can still bind to phosphate ions or carboxylates and also because the based extractant already underwent perfect ionization so that the pH change does not decrease the extraction efficiency.

At high pH, the extraction ability decreases due to the hydrolysis of the ion. The hydrolysis reaction will result in a soluble metal hydroxide compound. This causes the metal that is not in ionic form to be difficult to extract. The hydrolysis reaction is the reaction of the breakdown of the O-H bond on the hydrate ion $[M(H_2O)_6]^{n+}$ formed when the salt of the metal cation is hydrated in water. This reaction occurs because the tensile forces between the ion and the water molecule are so large that the O-H bond on one or more water molecules will break. The dissociation constant (K_b) for the hydrolysis reaction of Co^{2+} is 14.12×10^{-11} in which the greater the dissociation constant for the hydrolysis of the metal ions indicates the pH at which the metal ion is hydrolyzed lower. Ma, et al. proves that the cobalt metal will be hydrolyzed upon reaching a pH of 7.5 [5]. Therefore, a decrease in the percentage of extraction will occur when the system pH is >7.5 .

3.3. Optimum Condition of the Extraction Process

In this experiment, it was concluded that the optimum condition of the cobalt metal extraction process from spent catalyst waste was by using an initial leach solution pH of 6, VersaticTM 10 concentration of 0.35 M, and Cyanex[®]272 concentration of 0.25 M resulting in an extraction percentage of 98.80 %. Unfortunately, this was accompanied by co-extraction of Nickel at 93.51%, thus additional treatment is needed to separate cobalt from the organic phase.

4. Conclusion

Based on the results of research and analysis conducted, it can be concluded that the operating condition of liquid-liquid extraction process that yields optimum cobalt extraction by using the VersaticTM 10/Cyanex[®]272 extractant synergic mixture:

- Leach solution pH of 6.
- VersaticTM 10 concentration of 0.35 M.
- Cyanex[®]272 concentration of 0.25 M.

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