Ni Metal Extraction with Surfactant Variation on Double Surfactant Emulsion Liquid Membrane Technology

Yuliusman¹, A R Nafish¹, C S Salsabila¹, M P Ayu¹, and M Isa¹

¹Departement of Chemical Engineering, Faculty of Engineering, Universitas Indonesia

E-mail: usman@che.ui.ac.id, azmia.rizka@ui.ac.id, cut.shafira@ui.ac.id, maretha.putri@ui.ac.id, muhammad.isa73@ui.ac.id

Abstract. Nickel metal extraction from hydrotreating catalyst waste is an attempt to recover purer Ni metal using extraction process. Emulsion liquid membrane with double surfactant was chosen because this extraction method has the highest separation efficiency, shorter time of process, and simple process steps. The double surfactant that was varied in this study was a mixture of Span 80 with Tween 20 and Span 80 with Tween 80. The experimental results showed that the best nickel extraction was obtained using Cyanex 272 extract with a concentration of 0.06 M, 8% (w/v) surfactant double Span 80 with Tween 20, with an internal phase ratio and organic phase of 1: 1. The extraction process lasts for 15 minutes with a stirring speed of 250 rpm.

1. Introduction
The development of industrial processes is increasing massively at this time. A large number of catalysts are used in several fertilizer industries, the oil and gas industry, and other chemical sectors to make the reaction go faster. This catalyst will be deactivated from time to time and when the activity decreases below the acceptable level, the catalyst must be regenerated and can be reused. But when regeneration is no longer possible, the catalyst has decreased function to a very low level, so further regeneration may be economically inadequate. In such cases, used catalysts that cannot be regenerated tend to be disposed of as solid waste [1].

These used catalysts are categorized as hazardous and toxic wastes because they contain several hazardous metals such as nickel metal. A total of 14720-14800 mg / kg of nickel metal is contained in the catalyst which is spent from the hydrotreating process [2]. This makes the metal recycling and recovery process an alternative to avoid and reduce catalyst waste and prevent environmental pollution. Based on data from the Indonesian Ministry of Environment and Forestry (2014), there are 193 million tons of 200 million tons of hazardous and toxic waste that can be reused. This amount of waste can generate 20 billion rupiah from recycling used catalyst waste.

Generally, the process used for recovering nickel metal contained in the solid waste is leaching catalyst using an acid [3]. The leaching process using strong acids has become a commonly used method for recovering nickel metal from used catalysts, which is then followed by a metal recovery process with a purer concentration [4].

To get the desired metal, it is necessary to do further separation between the leaching agent and the metal solution. The method commonly used for metal separation processes with leaching agents is liquid-liquid extraction, electrowinning, liquid membrane, evaporation, crystallization and hydroxide...
deposition [5]. Based on previous research, it is known that the emulsion liquid membrane (ELM) has the highest separation efficiency when compared to the classic type of separation [6]. In the liquid membrane technology, extraction and stripping by receiver phase occurs simultaneously making it more time-efficient, selective and simple.

The components that make up the MCE are extractants, surfactants, organic solvents and internal phases. Emulsions generally can be formed using a single type of emulsifier / surfactant, but it was proven that the formation, stability, and functional groups of the emulsion can be enhanced by the use of two or more kinds of surfactant [7]. The parameters that can provide high stability in surfactants are Hydrophilic-Lypophilic Balance (HLB), where these parameters express a relationship to hydrophilic and lipophilic properties in a surfactant. The performance of the surfactant mixture is better than the single surfactants in emulsion formation because it has synergistic properties marked with the maximum water solubility values in kerosene [8]. Surfactants commonly used for stabilizing W / O emulsions are Span 80, Tween 80 and Tween 20. Surfactants used in emulsion formation usually have a value of Hydrophilic-Liphophilic Balance (HLB) in the range 2-18.

| Table 1. Experimental condition used for elm extraction |
|-------------------------------------------------------|
| Internal aqueous phase                               |
| Organic phase                                        |
| Solvent                                              |
| Carrier                                              |
| Surfactant aqueous phase                             |
| External aqueous phase                               |
| Treat ratio                                          |
| Stirring speed                                       |
| Time operation                                       |
| Temperature                                          |
| V<sub>int</sub> = 50 ml                               |
| V<sub>org</sub> = 50 ml                              |
| Kerosene                                             |
| 0,06 M                                               |
| 8%                                                   |
| 100 ml                                               |
| 1:1                                                  |
| 200 – 400 rpm                                        |
| 15 min                                               |
| 353 K                                                |

2. Experimental

2.1. Materials
The solution used for the double surfactant emulsion liquid membrane extraction in this experiment was leached liquor as a result of the leaching process of Ni metal on hydrotreating catalyst using citric acid and EDTA leaching agents.

The extractant used in the extraction process is Cyanex 272 which is dissolved using kerosene. Kerosin used in experiments was obtained from Merck (M). The surfactants used in this experiment were Span 80, Tween 80 and Tween 20 obtained from Merck (M).

2.2. Emulsion Stability Test
To perform ELM method, it is necessary to have an emulsion with optimal content. The type of surfactant used during the ELM process will affect the stability of the emulsion in the ELM system. Emulsion stability necessary for the extraction process can take place more optimal. Apart from that, another important factor is to obtain the stability of the emulsion through a combination of the use of several types of surfactants in the stages of making emulsions.
The W/O type surfactant used was Span-80 as a single surfactant and a mixture of Span-80 with O/W type surfactants namely Tween 20 and Tween 80 as multiple surfactants. 0.2 M H2SO4 acts as a stripping phase. Extractant with a good level of selectivity against Ni is Cyanex 272 diluted using kerosene until it reaches a concentration 0.06M. The Cyanex 272 solution that has been prepared will be mixed with 8% (w/v) Span-80 and 8% (w/v) mixed surfactants (Span-80 with Tween-20 and Span-80 with Tween-80) to form an organic phase or liquid membrane phase.

2.3. Extraction with emulsion liquid membrane

After getting the best combination of double surfactants then the extraction process can be done. The extraction process begins by making a feed solution with a pH of 6. Emulsions will be made by emulsifying aqueous solution (stripping phase) with the formulated organic phase. The same volume of 50 ml part of organic solution and the strip solution will be stirred continuously at a speed of 1000 rpm. Emulsions will be cooled to room temperature and ready for extraction studies. Emulsions must always be new and fresh every time you do the extraction.

The prepared emulsion is then dispersed into a vessel which is stirred with an external solution (hydrotreating catalyst waste). Stirring speed is controlled at 250 rpm. Then the mixture will be incorporated into the separatory funnel to separate the external phase (feed) with the ELM phase. The aquatic phase will be filtered to remove entrainment and the raffinate phase will be analyzed using AAS. The range of parameters used in this study for the extraction of Ni metal ELM from hydrotreating catalyst waste can be seen in Table 1.

3. Results and Discussions

3.1. Membrane stability

Emulsion in this research is a combination of internal phase (H2SO4) and organic phase (mixture of Cyanex 272, kerosen, and surfactant) [9]. In this research, the type of surfactant was varied to span 80; mixtures of span 80 with tween 20; and mixtures of span 80 with tween 80. The operating conditions used were optimum conditions obtained from previous studies, namely 8% surfactant concentration, Cyanex 272 0.06 M, ratio of internal phase:organic phase is 1:1, stirring duration is 1 hour, and stirring speed of 1000 rpm. After the emulsion process is complete, the emulsion must be immediately separated into a 100 ml measuring cup so that stability can be observed for 4 hours.

![Emulsion Volume Change with Time](image)

**Figure 1.** Emulsion Volume Change with Time (t= 4 hours)

At Fig. 1 decreasing the volume of the emulsion indicates an emulsion leak. After 4 hours, it can be seen single surfactant span 80 has a constant decrease while the double surfactant has a significant
decrease volume and separate between emulsion and internal phase. Emulsion droplets relates with decreasing of significant volume in internal phase.

At Fig. 2 comparison between single surfactant and double surfactant in a period of 45 minutes, a mixture of span 80 + tween 20 can maintain the stability of the emulsion phase better than the single surfactant span 80, this is indicated by a very small decrease in volume at the 15th minute which is equal to 1 ml. Whereas in the 30th minute the decrease in both of these mixtures only had a slight difference, which was equal to 0.2 ml to mix with tween 20 and 0.5 ml to mix with tween 80. In 45th minutes we can see with clearly the decreasing significant volume of span 80 + tween 80 which is indicates the emulsion leak. The decrease in volume continued in both mixtures until the internal phase began to form at the bottom layer of the mixture. This internal phase formation indicates that the surface tension between the internal and organic phases in the emulsion begins to decrease.

![Figure 2. Emulsion Volume Change with Time (t=45 mins)](image)

From the observations it was found that internal phase leakage in span 80 + tween 20 began to occur in the 70th minute, whereas in span 80 + tween 80 began to occur in the 54th minute. Qualitatively, it can be concluded that from the three types of surfactants, the span 80 mixture with tween 20 is the best type of surfactant suitable for the MCE application in this experiment.

3.2. HLB Analysis

HLB value is a quantity used to determine the shape of an emulsion. Hydrophilic - Liphophilic Balance (HLB) surfactant system is a molecular equilibrium characteristic between parts of hydrophilic properties (like water) to parts of lipophilic properties (like oil). The form of the emulsion can be in the form of W / O (water / oil) when it has a HLB value between 3 to 6 and dissolves in water, while the form O / W (oil / water) from 8 to 18 and dissolves in oil. The use of double surfactants observed was between mixtures of span 80 with tween 20 and span 80 with tween 80. Each HLB value of these three types of surfactants was 4.3; 16.6; and 15.

In order to find out the HLB value produced from double surfactants, it is necessary to do an HLB analysis by titrating a 0.2 M H2SO4 solution with an organic phase. The titration process is carried out with the condition slowly stirred (around 250 rpm) and stop when there is a change in color from the clear color to the cloudy white. The results of HLB analysis can be seen in Table 2.
Table 2. H₂SO₄ Titration Results

| No. | Emulsion Weight (gr) | H₂SO₄ ml |
|-----|----------------------|----------|
|     | Span 80 | Tween 20 | Tween 80 |
| 1   | 4       | -        | -        | 2        |
| 2   | 2       | 2        | -        | 3.9      |
| 3   | 2       | -        | 2        | 3.8      |

HLB value of the mixtures can be calculated using this formula:

$$HLB_{mix} = f_A \times HLB_A + (1-f_a) \times HLB_B$$  \hspace{1cm} (1)

Where HLBmix is the HLB value of mixtures, HLBA is a HLB value of W / O type surfactant (span 80) and HLBB is a HLB value of O / W type surfactant (Tween 20 & Tween 80). The results of processing data from the HLB analysis test can be seen in Table 3.

Table 3. HLB Analysis Test Result

| Surfactant Type | HSO₄ (0.2M) ml | fA | fB | HLBmix (0.2M) gr | HSO₄ (0.2M) Water/Oil (w/w) |
|-----------------|----------------|----|----|------------------|-----------------------------|
| Span 80         | 2              | 1  | -  | 4.30             | 2.01                        | 0.0402                     |
| Span 80 + Tween 20 | 3.9         | 0.52 | 0.48 | 10.31           | 3.92                        | 0.0783                     |
| Span 80 + Tween 80 | 3.8        | 0.53 | 0.47 | 9.34            | 3.82                        | 0.0763                     |

The calculation results show the highest solubility of water phase in oil is span 80 with tween 20 mixture with mixtures HLB value of 10.31 and has a water phase solubility value in oil of 0.0783. If the solubility value is sorted, it was obtained that the double surfactant span 80 + tween 20> double surfactant span 80 + tween 80> single surfactant span 80. The combination of span 80 and tween 20 surfactant as a double surfactant is quantitatively proven to have good ability to stabilize the emulsion compared to the others. This ability is due to span 80 and tween 20 mixed surfactants having the most synergistic properties.

3.3. Extraction

After obtaining the best combination of double surfactants then the extraction process can be done. This process begins by making a leached liquor to pH 6 first. The effect of pH on extraction efficiency is caused by competition between H⁺ and Ni²⁺ in fighting for anions. Therefore, it is expected that with increasing pH the extraction ability increases because the number of H⁺ is less so that the competition of H⁺ and Ni²⁺ in the fight against extractant anions is reduced and Ni²⁺ can more easily react with anions than extractants [8]. However, if the pH is higher than 6 it can cause the interface between the external and internal phases to be saturated by complex ions from extraction ionization and water transport will occur which causes decreased extraction to even break the existing emulsion [9].

The extraction process was carried out by mixing the feed phase with ELM for 15 minutes at a speed of 250 rpm. Then this mixture is incorporated into the separatory funnel to separate the external
phase (feed) with the ELM phase. The feed phase which is initially light green turns into a cloudy green after the extraction process is done.

From the results of the AAS, it was found that the external phase containing nickel with 661.5 ppm and after the MCE extraction, the nickel contain is 606.6 ppm in internal phase. From these results it was found that the percentage of extraction was 91.7%. This percentage value is quite high when compared to previous studies which only used a single surfactant, which was 81.51% [10]. From this it is proven that double surfactant is a better alternative to overcome emulsion leakage in the extraction process of the emulsion liquid membrane.

4. Conclusions

Span 80 and Tween 20 double surfactants proved superior in maintaining the stability of the emulsion volume. The optimum condition of the MCE manufacturing process is with a concentration of 8% double surfactant of span 80 with tween 20, 0.06 M Cyanex 272 extractant concentration, internal phase: organic phase ratio of 1: 1, stirring for 1 hour at 1000 rpm. As for the extraction process, the optimum percentage of extraction was 91.7% with pH of feed phase 6, extraction time for 15 minutes, stirring speed of 250 rpm, and membrane phase ratio: feed phase of 1: 2

Acknowledgments

This research was funded by Hibah Publikasi Internasional Terindeks Tugas Akhir (Hibah PITTA B) Universitas Indonesia 2019 with contact number NKB-0802/UN2.R3.1/HKP.05.00/2019. The author declares no conflicts of financial interest.

References

[1] Cano, J., Zamarripa, G. Z., Pedroza F. R. C., Aguilar, M. J. S., Macias, A. H., Vielma, A. C, “Kinetics and statistical Analysis of Nickel Leaching from Spent Catalyst in Nitric Acid Solution” International Journal of Mineral Processing, Vol. 148, pp. 41-47, 2016.
[2] Mardyanika, Yus A.P, “Pemanfaatan Spent Catalyst RCC 15 Limbah Pertamina sebagai Bahan Tambah pada Campuran Beton”, Teknologi dan Kejuruan, Vol. 35, No. 2, pp.191-200, 2012.
[3] Yuliusman. “Recovery of Cobalt and Nickel from Spent Lithium Ion Batteries with Citric Acid Using Leaching Process “. E3S Web of Conferences 67. 03008, 2018.
[4] Yuliusman. “Acid Leaching and Kinetics study of Cobalt Recovery from Spent Lithium-ion Batteries with Nitric Acid”. E3S Web of Conferences 67. 03025, 2018.
[5] Barik, S. P., Park, L. H., Nam, C. W. “Process Development for Recovery of Vanadium and Nickel from an Industrial Solid Waste by a Leaching-Solvent Extraction Technique”. Journal of Environment Management, vol.10, No. 15, pp. 1457 – 1472, 2014.
[6] Kislik, V. S.” Liquids Membranes Principle & Applications in Chemical Separation & Wastewater Treatment. Amsterdam: Elsevier, 2010.
[7] Dickinson, Eric. “Mixed Biopolymers at Interfaces: Competitive Adsorption and Multilayer Structures”. Journal of Food Hydrocolloids, vol 25, pp. 1966 – 1983, 2011.
[8] Mulyazmi. “Penggunaan Surfaktan Campuran terhadap Pembentukan Kestabilan Emulsi W/O”. Jurnal Teknos, vol. 6, No.2. 2006
[9] Yuliusman. “Leaching and Kinetics Process of Cobalt from Used Lithium ion Batteries with Organic Citric Acid”. E3S of Conferences 67. 0-3036, 2018.
[10] Huda, Mihtabul. “Perolehan Kembali Logam Ni dari Limbah Katalis Hydrotreating dengan Teknologi Membran Cair Emulsi Menggunakan Ekstraktan Xyanex 272“: Skripsi. Depok: Universitas Indonesia. 2017.