Platinum Recovery from Spent CCR Platforming Catalyst with Oxalic Acid and Aqua Regia Leaching

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Abstract. In aligning to the rapid industrial development, the needs of catalyst nowadays are increasing. Oil and gas industry is one of the example especially in Continuous Catalytic Cracking Platforming Unit, in which the process produces Pt/Al2O3 catalyst waste approximately 2000-3000 kg/year and contains of 3200 ppm platinum metals. It becomes the reason why organic acid leaching and aqua regia leaching is needed to recover the platinum metals to save cost because its price is very expensive and spent catalyst waste is also considered as hazardous and toxic materials. In this experiment, there are two different methods used to obtain the recovery of platinum metals from spent Pt/Al2O3 catalyst. The methods used are leaching with oxalic acid and leaching with aqua regia. The experiment showed that leaching with aqua regia results in higher leaching efficiency percentage with the number of 19.917%. The result is obtained with operation temperature of 300°C and solid-liquid ratio of 20 g/L.

1. Introduction

Platinum is a silvery metal and considered as rare earth metal that has really high price. In a very fine condition, platinum has been many used as a catalyst. Oil and gas industry in Indonesia mostly used platinum as their catalyst in catalytic reforming process of straight-chain naphtha to rich-aromatic octave level gasoline. The catalytic reforming process is performed in Continuous Catalytic Platforming Unit in Pertamina Balongan Petroleum Refinery. The Pertamina Balongan’s Platforming Unit produces up to 3000 kg/year spent platinum catalysts. Spent platinum catalyst is also considered as hazardous and toxic materials therefore a platinum recovery method is needed. Moreover, platinum is very pricey with the price of IDR 450139,00 per grams [1], which drives the urgency of doing platinum recovery from spent Pt/Al2O3 catalyst.

The platinum metal recovery can be done with leaching method. The factors that can affect leaching process are type of leaching agent, leaching agent concentration, stirring speed, solid-liquid ratio, contact time, temperature, and particle size. Mostly, mineral acid is used as the leaching agent because of its ability to produce high leaching percentage and it is quite cheap. From previous research, the leaching efficiency percentage obtained from leaching with mineral acid (aqua regia) is 90% [2]. Another alternative which can be used as the leaching agent is organic acid, such as oxalic acid, because of its easiness to dissolve in water and can be degraded naturally. The leaching efficiency percentage...
for this leaching agent is 82% with leaching temperature condition of 60oC with 10 hours of stirring and the leaching agent concentration used is 0.3M [3].

2. Experimental

2.1. Sample Preparation

Determine the metal content of spent catalyst using XRF PANalytical before going to the furnace. Spent catalyst weighed to 100 gram and put in the quartz trays. Pre-heated the furnace until the temperature become 450oC. Put the quartz tray into the furnace and set the ramping time 10oC per minutes until the temperature reach 900oC and wait until 3 hours. After that, set down the temperature to reach 200 oC and take the quartz trays, put it in the dessicator. After that, determine the metal content of spent catalyst using XRF PANalytical. It was going to observe Pt and impurity likes Si and S content had decreased by furnace or not.

When the XRF analysis has finished, the samples grounded until the size became 100 mesh. It will increasing the surface area so it can enhance the effectively of leaching process.

2.2. Leaching with Oxalic Acid

Oxalic acid is a colorless acid and is an organic carboxylic acid that melts at 189oC with sublimation. In this leaching process, oxalic acid is used as the leaching agent. The independent variable for this procedure is the oxalic acid concentration. Meanwhile, the fixed variables are operation temperature, contact time, stirring speed, and solid/liquid ratio. The first step before doing the leaching process is to make the oxalic acid solution for four concentration variations (0.3M, 0.5M, 0.7M, and 1.0M). Dihydrate Oxalic Acid is used as the leaching agent because its easiness to dissolve in water. The solid/liquid ratio used for this process is 10 g/L and the leaching process was done with a magnetic stirrer at 60oC for around 10 hours. Determination of Pt content in leached liquor by using ICP-OES Agilent Technologies 5110.

2.3. Leaching with Aqua Regia

Aqua regia is a solution composed of two strong mineral acid which are chloride acid (HCl 37%) and nitric acid (HNO3 65%). The composition ratio of the chloride acid and nitric acid is 3:1 (volume ratio).

All variables used for this process refer to optimum condition for UOP 896-930 method. The solid/liquid ratio of 20 g/L is used in this method. For the leaching process, it used stirring speed of 300 rpm at approximately 300oC. This method needed to be done in fume hood and use safety equipment because it produced plenty of hazardous chlorine gas. Determination of Pt content in leached liquor by using ICP-OES Agilent Technologies 5110.

3. Results and Discussions

This section discusses about the experimental results. The research focus on leaching process with oxalic acid and aqua regia as the leaching agent. The experiment aims to determine which leaching agent gives better result in leaching efficiency percentage and more effective to recover platinum metals from the spent catalyst. Leaching efficiency can be calculated using this formula:

\[
\text{Leaching efficiency} = \frac{\text{Pt concentration in leached liquor}}{\text{Pt concentration after furnace}} \times 100\%
\]

3.1. Sample Characterization and Preparation

According to the theory, the smaller particle size will increasing the surface area. The particle size range of 80-120 mesh is known as the most optimum particle size [3]. In this experiment the spent catalyst is firstly burned at 900oC for approximately 3 hours. This aims to eliminate the silica and sulphur content in the spent Pt/Al2O3 catalyst. Silica and sulphur has an disadvantage as for the support
of platinum and could prevent the catalyst deactivation because of the reaction between $\gamma$-Al$_2$O$_3$ and SO$_2$ [4]. The presence of silica and sulphur in the spent catalyst will complicate the leaching process of platinum.

![Figure 1.](a) Spent Pt/Al$_2$O$_3$ catalyst after furnace (b) Spent catalyst 100 mesh

The spent Pt/Al$_2$O$_3$ is characterized through XRF (X-ray Fluorescence) analysis before and after furnace treatment to determine the metal content from the spent catalyst. The result from XRF analysis of spent catalyst Pt/Al$_2$O$_3$ is described in Table 1.

| Table 1. XRF Analysis Result For Spent Catalyst Pt/Al$_2$O$_3$ | Concentration (%) |
|---|---|
| **Element** | **Before Furnace** | **After Furnace** |
| Pt | 0,3 | 0,32 |
| S | 0,02 | 0,01 |
| Si | 0,16 | 0,04 |
| Al | 51,45 | 50,3 |
| O | 46,39 | 45,1 |
| Fe | 0,29 | 0,29 |
| W | 0,04 | 0 |
| Ni | 0,06 | 0,02 |
| Na | 0,02 | 0,02 |
| Cr | 0,02 | 0,02 |
| Cl | 0,97 | 0,09 |
| Ca | 0,02 | 0,01 |
| Ba | 0,01 | 0 |
| P | 0,12 | 0,1 |
| Sn | 0,1 | 0,09 |

From the XRF analysis, it can be seen that there are fifteen elements in the spent Pt/Al$_2$O$_3$ catalyst. The five most dominant elements are aluminium, oxygen, sulphur, platinum, and ferrum. The number of aluminium is dominating because the aluminium acts as the support catalyst meanwhile the platinum acts as the active site of catalyst.

### 3.2. Leaching with Oxalic Acid

Leaching is a process to extract a substance from its solid after being contacted with any kind of solution [5]. The leaching agent used for the leaching process can be an organic acid or a mineral acid.
Since the use of mineral acid is more hazardous to the environment than organic acid, this experiment tried to use organic and see the effect of organic acid usage [6].

In this experiment, the oxalic acid concentrations are varied into 0.3M, 0.5M, 0.7M, and 1.0M. The leaching process is done with a magnetic stirrer at 60°C for 10 hours. After the 10 hour leaching process was done, the solution was filtered, and the filtrate was analyzed with AAS (Atomic Absorption Spectroscopy). The Atomic Absorption Spectroscopy was a quantitative test and the result described below in Table 2 & Fig. 2.

Table 2. AAS Analysis Result for Leaching with Oxalic Acid Concentration Variations

| Oxalic Acid Concentration | Sample | Result |
|---------------------------|--------|--------|
|                           | mL     | mg/L   | ppm   |
| 0.3M A                    | 10     | 8.89   | 88.90 |
| 0.3M B                    | 10     | 8.82   | 88.17 |
| 0.5M A                    | 10     | 8.73   | 87.26 |
| 0.5M B                    | 10     | 9.10   | 91.03 |
| 0.7M A                    | 10     | 9.11   | 91.10 |
| 0.7M B                    | 10     | 9.29   | 92.88 |
| 1M A                      | 10     | 17.70  | 176.92|
| 1M B                      | 10     | 18.06  | 18.63 |

Figure 2. Correlation between oxalic acid concentration and leaching efficiency percentage graph

From Table 1, it can be seen that the leaching efficiency for 0.3 M ; 0.5 M ; 0.7 M and 1 M are 2.76% ; 2.78% ; 2.87% and 5.58%. From this result, the best concentration for Pt leaching is using 1 M oxalic acid with the current condition.

From Fig. 3, it can be seen that the leaching percentage did not increase significantly but starting from 0.8M until 1M of oxalic acid, the percentage increased very sharply. The highest oxalic acid concentration that can be used for leaching is 1M. Using the oxalic acid concentration more than 1M in leaching process, the solution has reached its saturation point that marked by the appearance of crystal.

Platinum metal which is initially present in the solids of the spent catalyst will be bound by a leaching agent (oxalic acid) because of the anions from organic acids [7]. If the concentration of organic acids is increased, the ability and the amount of acidic anions formed will also increase. The increase in the number of acidic anions causes an increase in platinum metal concentration in the filtrate. Leaching
agent likes oxalic acids is classified in the class of weak acids and weak electrolytes, and platinum is very inert metal and difficult to react. This is the reason why leaching efficiency is only get 5.58%. Even though the operating conditions used are optimum conditions according to reference, platinum metal is in fact unable to be leached. The fact that platinum metal itself is unable to react with organic acids (oxalic acid) will greatly affect the results of the percentage of platinum recovery obtained from the results of leaching. Therefore, further research could be compared the leaching efficiency between using oxalic acid and aqua regia as leaching agent.

3.3. Leaching with Aqua Regia

Aqua regia is a very acidic solution formed from concentrated hydrochloric acid (37% HCl) and concentrated nitric acid (65% HNO₃). The two are mixed with the volume ratio of HCl: HNO₃ 3: 1. The research phase in this method uses concentrated acids so it is very dangerous and must be done in a fume hood. The variables used in this method are optimum conditions according to the UOP method 896-930. The optimum conditions used, namely the ratio of solid/liquid 20g/L at an operating temperature of 300°C. The operating time used depends on the speed of the evaporating and boiling solution.

The percentage of leaching efficiency in this process is 19.72% with a platinum concentration in leached liquor is 631 ppm. Some of the factors that give an impact of results from leaching efficiency with aqua regia described below: [8]

1. The process carried out with a lot of stages and the heating process with an open magnetic stirrer causes the possibility of mass loss through the evaporation process.
2. The temperature control in hotplate do not describe the real temperature of the solution
3. The influence of a magnetic bar that has been dirty and contaminated due to overuse and cannot be cleaned completely

Figure 3. Leaching process with aqua regia in fume hood

4. Conclusions

From the leaching experiment with oxalic acid, the highest leaching efficiency percentage is 5.58%. The leaching was fixed with 1M of oxalic acid stirred at 60°C for 10 hours. And for the leaching experiment with aqua regia, the leaching efficiency is 19.72%. The leaching was fixed using UOP 896-930 method. From those two experiments, the leaching process with mineral acid (aqua regia) is still more effective than with organic acid (oxalic acid) despite its harmfulness to the environment. Although
the organic acid is more environmentally friendly, it is a weak acid and do not have the same power to do an oxidation process like aqua regia.

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