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Manganese Recovery from Hydrocracking Spent Catalyst Using Citric Acid and Its Kinetics

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Abstract—Aiming for recovery and kinetics of manganese from hydrocracking spent catalyst using citric acid, this study has been conducted. In order to justify the performance of citric acid, a comparative study has been conducted using both inorganic and organic acids in the same pH condition of about 1,5 - 2. pH was used as the controlled variable due to the different dissociation degree of the acids. In comparison to that of inorganic acid, the manganese recovery is four times higher when citric acid was applied. Acetic acid performed 33% lower in manganese recovery compared to the citric acid. Moreover, kinetics study was conducted with three varying temperature of 30°C, 60°C, and 90°C. From the resulted data, it can be concluded that the kinetics of mengan leaching from spent catalyst using citric acid is in accordance to the shrinking core model. The controlling step is product diffusion with activation energy (Ea) of about 23.27 kJ/mol calculated using Arrhenius expression. With higher selectivity and leaching reagent which is harmless to the environment, the application of citric acid in manganese leaching from spent catalyst will indeed support the enactment of sustainable development aspect in recycle processing.

Keywords—citric acid, spent catalyst, kinetics, manganese.

I. INTRODUCTION

Manganese (Mn) is valuable metal that is essential for steelmaking, with the industry accounts for 85% to 90% of the total manganese consumption globally, it is also a key component in alumunium alloy production. In non-metallurgical aplication, it is used to produce dry-cell batteries, plant fertilizer components, animal feed and colorants for brick. In the next 10 year production demand and price of manganese will increase along with the development of world's steel production, although the use of manganese per tonne of steel has been on a declining trend in recent years [1].

Manganese is used to produce dry cell batteries such as lithium-ion batteries (LIBs). Since Sony 1991 dominated electronic market, LIBs have been widely used for portable electronics such as cell phones, laptops, digital cameras, etc. For the production LiBs, total manganese consumption up to 18 % [2] and the electrolytic manganese metal demand is about 0.7 million ton/year [3], this amount is enough to increase world's total manganese consumption.

Manganese is non-renewable natural resource that is produced from exploration activities, and the activity will be stopped if the primary source of manganese has been exhausted. During the past decade, much research work was conducted to recover valuable metals from secondary resources. Thus, there is a need to maintain the production of manganese by recycling from other materials or urban mining. One of the material urban mining is spent batteries. Recycling spent batteries can obtained manganese of 87,9 % and 96,4% with inorganic acid [2][4].

The other abundance secondary resource is spent catalyst. During the past decade, many research work was conducted to recover valuable metals from spent catalyst [5-7], recovery metals from spent catalyst can obtained metals of 15% - 90% with inorganic acid [7]. Hydrocracking spent catalyst is solid waste from petroleum industry that is classified as hazardous materials due to its high metal concentration which can classify them as "artificial ores", they can serve as the secondary raw materials to replace the primary resources to fulfill the global demand for manganese [8].

One of the recovery methods of manganese is by leaching. Leaching is a hydrometallurgical method which has been widely used to extract metals from low grade ores. Leaching factors that can increase the metal recovery are temperature, particle size, acid type, pH, liquid-solid ratio, addition of other compounds, stirring speed, pre-treatment and leaching time. In the kinetic aspect, manganese leaching process is a heterogenouse reaction which involves more than one phases i.e. the solid-liquid phase [4, 11]. In the heterogenous reaction, shrinking core model is an appropriate model to evaluate the reaction mechanism.

Recovery of valuable metals from secondary resources have been studied thoroughly using inorganic acid [9]. However, the usage of inorganic acid in valuable metals leaching from secondary resources posseses some drawback related to the environemntal issue [10]. Not to mention the additional process to treat the liquid waste containing the inganic acid that will add the invesment as well as production cost [10].

Thus in this study, not only in a sense of environemental point of view but the performance and kinetics of manganese leaching from spent catalyst using citric acid will be evaluated in order to determine the parameter design worth for scaling up stage.

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II. Materials and Method

A. Material

Sample of hydrocracking spent catalyst were obtained from PT. Pertamina, Tbk, Balongan, Indonesia. The sample was in the powder form and shieved to meet the particle size of under 200 mesh. The manganese content is about 1.22 % w/t based on compositional analysis by X-ray fluorescence (XRF, PANalytical Epsilon 3rd) as shown in Table 1. For the mineral characterization, X-ray diffraction (PANalytical X'Pert3 Powder: Cu Kα radiation, at 2θ range 5° to 80°, with accelerating voltage of 40 kV and the applied current of 40 mA) was utilized. The spectras of the hydrocracking spent catalyst shows the zeolite-Y as the major mineral that is presented in Figure 1. This zeolite-Y is the material support of the catalyst which is in the form of aluminosilicate. Thus the composition of Si and Al were found dominant as shown in Table 1.

B. Reagents

The reagents used to leach manganese from hydrocracking spent catalyst were citric acid monohydrate ($C_6H_8O_7*H_2O$)(M = 210,14 g/mol, from Merck KgaA), acetic acid glacial from Merck & Co, Inc, hydrocloric acid (HCl) analytical grade from Merck & Co, Inc, sulfuric acid (H_2SO_4) from Merck & Co, Inc. and demin water that was produced by Laboraturium Of Energy Conversion and Pollution Prevention, Department of Chemical Engineering, Universitas Gadjah Mada, Yogyakarta.

C. Leaching Procedure

All of the experiments were conducted in a three-necked flask with 150 mL of acid solution that was set in a desired constant temperature (30 °C, 60°C and 90°C). Once the set temperature achieved, 30 grams of sample, the hydrocracking spent catalyst, with particle size of under 200 μm was then added. Stirring was applied in a fixed rotation speed of 300 rpm. The manganese leaching was carried out for 4 hour. Determination of manganese concentration was done by analyzing the liquid sample by using X-ray fluorescence PANalytical Epsilon 3rd (XRF). For kinetics study of manganese leaching from hydrocracking spent catalyst using citric acid, the sample was taken in time interval of 5, 15, 30, 60, 120, and 240 minutes of about 1 mL.

Manganese recovery was then calculated in accordance of equation 1

% Recovery = (manganese extracted in the acid/manganese in the initial solid sample)

III. Results And Discussion

A. Recovery of manganese from hydrocracking spent catalyst using citric acid in comparison with other acids

Acid type and pH are among the parameters of leaching that are important in increasing the metal recovery. The effect of acid type was investigated by comparing citric acid with inorganic acids (hydrochloric acid and sulfuric acid) and other organic acid (acetic acid) on the same operating condition.

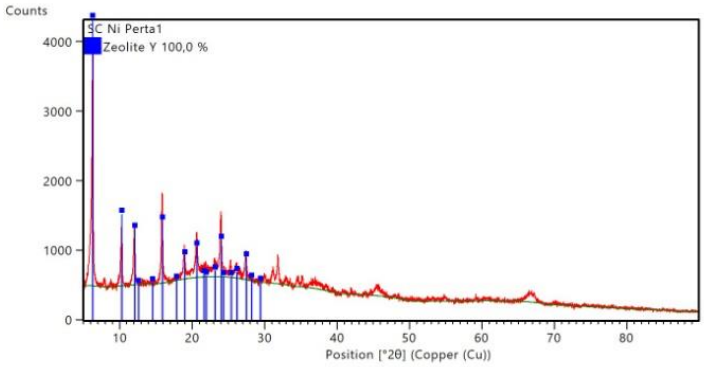

Fig. 1. Cement Mill Apparatus

Table 1. Component analysis of hydrocracking spent catalyst using X-ray fluorescence (XRF)

Metals	% wt
Al	33,514
Si	43,331
La	9,178
Ni	6,155
Fe	2,789
Ti	1,387
Mn	**1,220**
Others	2,426

The comparison with inorganic acid was done at pH of 1.5 and temperature of 90℃ for 4 hours and the comparison with other organic acid was done at pH of 2, temperature of 90℃ for 4 hours that was found to be the highest manganese recovery obtained. The recovery of manganese using various acids can be seen in the Figure 2.

Recovery manganese from secondary resource of inorganic acid mostly can obtained manganese ± 90% because it is using high consentration of about 8-12 M, therefore the solvent become acidic [2, 9-10, 12]. The result in Figure 2 shows that the recovery of manganese with citric acid gave ± four times higher recovery than inorganic acid (hydrochloric acid and sulfuric acid) at the same pH 1.5. In comparison with the other organic acid, it gave ± one and a half time higher recovery than acetic acid at the same pH 2. The concentration of the acid is represented in the value of pH due to different degree of dissociation of the acids used in this experiment. Leaching phenomena is distinguished by the the existence of H^+ represented by the pH value. The results showed that citric acid as a manganese extracting agent from spent catalyst has superior properties in the recovery of manganese metal compared to inorganic acids (sulfuric acid and hydrochloric acid) and acetic acid.

This phenomenon is due to the mechanism of metal leaching in the organic acid that is not only dominated by H^+ but by the anionic reactions (metals chelation) (equation 3). The metal chelation will shifted the equilibrium of proton attack to the right (equation 2). Consequently, the organic acids possess more remarkable leaching efficiency compared with inorganic acids [9-10, 12, 14].

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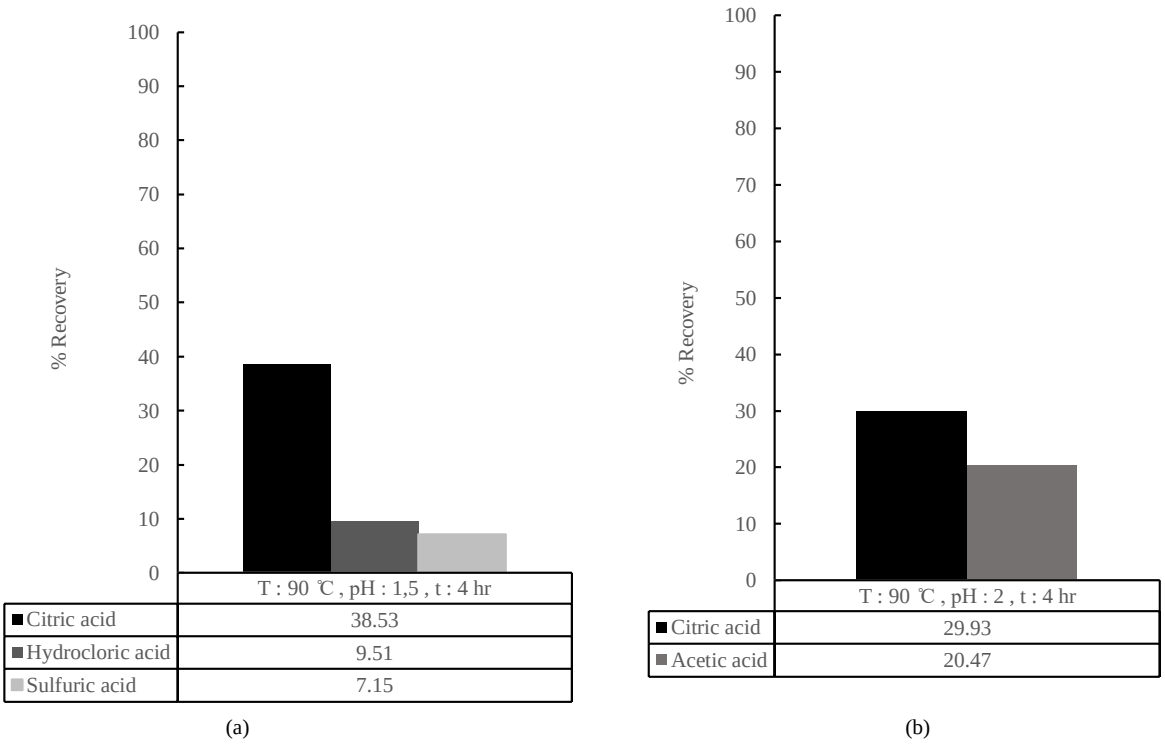

Fig. 2. Recovery of manganese using various acid a) in comparison with the inorganic acids (hydrocloric and sulfuric acid) b) in comparison with organic acid (acetic acid)

Citric acid has three carboxylic groups thus in the dissociation process has three stages, the disassociation process in the carboxylic acid is classified as partial disassociation because carboxylic acid is a weak acid with a value of Ka < 1 [10]:

Ionization using 1 mole of citric acid :

$$C_6H_80_7 \leftrightarrow C_6H_7O_7^- + H^+$$
$$C_6H_80_7^- \leftrightarrow C_6H_6O_7^{2-} + 2H^+ \quad (1)$$
$$C_6H_80_7^{2-} \leftrightarrow C_6H_5O_7^{3-} + 3H^+$$

Proton attack: $2H^+$ to Mn or other metal

$$MnO + 2H^+ \leftrightarrow Mn^{2+} + H_2O \quad (2)$$

Chelation :

$$C_6H_50_7^{\ 3-} + Mn^{2+} \leftrightarrow Mn_3(C_6H_5O_7)_2 \quad (3)$$

The leaching of manganese using citric acid requires two moles of citric acid to get three moles of manganese metal, it is proven that citric acid is able to get best recovery of manganese compared to other organic acids [14, 18].

B. Effect of leaching temperature and time

The study on the effect of leaching temperature was carried out in the temperature ranging from 30 to 90℃ and pH of 2. Based on the results in Figure 3, the recovery of manganese increased with increasing temperature. The change of temperature from 30 to 90℃ increased manganese recovery from 19.64% to 40.75% after 4 hours of leaching. A similar trend also occurred in the research conducted by Xiangping Chen et all [15].

Leaching time affects the process of contact of liquid (acid) and solids, thus longer leaching time will increase the recovery of manganese. The trend of manganese recovery in Figure 3 shows that the recovery will increase over time. The low recovery of manganese from hydrocracking spent catalyst in low temperature shows low reactivity.

C. Kinetics Analysis

Determining the kinetics parameters as well as the controlling rate step in the manganese leaching of hydrocracking spent catalyst, heterogenous reaction models were chosen to verify the experimental data. The manganese leaching leaching process was analyzed using the shrinking core model with particles of hydrocracking spent catalyst was considered as spherical particles. There are three types of mechanism in shrinking core model that is able to control the process of leaching: diffusion through film layer, diffusion through ash layer (non reactive materials, in this case is the silica aluminate which is the support of the catalyst) and chemical reaction. Diffusion through film layer is deemed impossible to control the process because during the leaching of manganese, the process employed sufficient stirring that the film layer formation in the solid surface happens to the negligible. The sufficient stirring condition was taken from other similar studies with the same experiment methodology [6-7, 9-10]. Thus the probable mechanisms controlling the process are diffusion through ash layer and chemical reaction. For the diffusion through ash layer the rate of equation follows the equation 4 [16-17]:

$$1 - 3(1-\alpha)^{2/3} + 2(1-\alpha) = k_d t \quad (4)$$

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While the chemical reaction controls the rate of equation, it is formulated in accordance to the equation 5:

$$1-(1-\alpha)^{1/3}=k_c t \quad (5)$$

where α is the conversion of reactants represented by the recovery of the manganese, kc is the rate constant of chemical reactions (min-1), kd is the apparent diffusion constant (min-1), t is the leaching time (min). According to previous research, most metal leaching process is controlled by diffusion through ash layer [11, 16]. This is due to the existence of some materials that is not dissolved during the leaching process and form ash layers, in this study is the existence of aluminosilicatyour statenebte structure as shown in Figure 1.

In order to be able to obtaine the kinetics equation, the data as shown in Figure 3 were manipulated and fitted to the equation 1 and 2 as shown in Figure 4. The verification of the kinetics model was evaluated using correlation coefficient (R^2) values. The slope of the plots as shown in Figure 4 was determined as the apparent rate constant (k). AS it can be seen in Figure 4, the R^2 value of diffusion through ash layer is better than that of chemical reaction with the average value of 0.965. The values of activation energy were determined from the Arrhenius conseption as formulated in equation 6.

$$\boldsymbol{k = Ae^{-Ea/RT}} \quad (6)$$

Where k is the reaction rate constant A is the frequency factor, Ea is the apparent activation energy, and R is the universal gas constant (8.314 $J \cdot k^{-1} \cdot mol^{-1}$), respectively.

Liniarization of the Arrhenius equation was done to calculate the value of activation energy by plotting the ln(k) versus (1/T) determined from the equation 3 that forms a straight line with a slope of (-Ea/R) as shown in Figure 5. The value of activation energy for this particular reaction is 23.27 kJ / mol apparently.

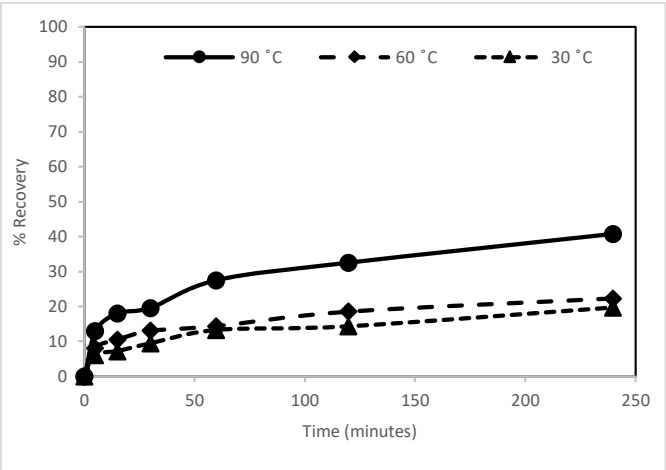
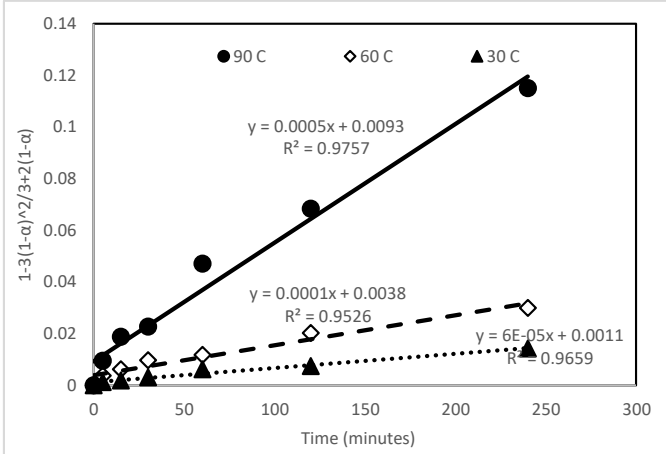


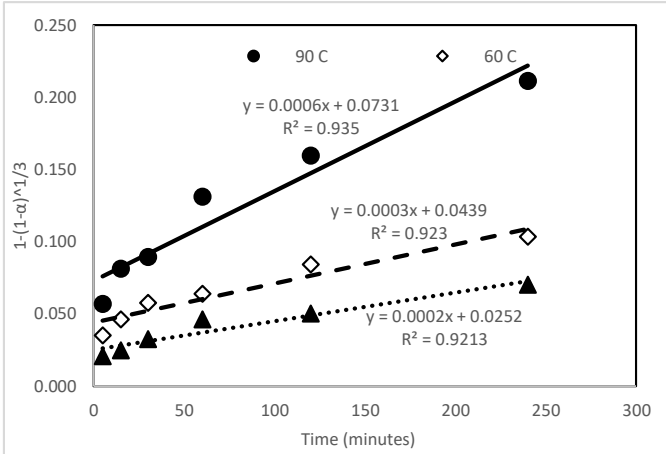
Fig. 3. Effect of leaching temperature and time at pH 2 in the manganese leaching from spent catalyst using citric acid.

Table 2. The Activation Energy (Ea) from other studies

Activation energy (Ea)	Materials	Kinetic model	References
25 kJ/mol	Spent lithium-ion batteries	Shrinking core model: diffusion ash layers	[2]
18.83 kJ/mol	low-grade manganese carbonate ores	Shrinking core model: diffusion ash layers	[15]



(a)



(b)

Fig. 4. The correlation of kinetics variable (a) diffusion ash layer (b) chemical reaction and leaching time

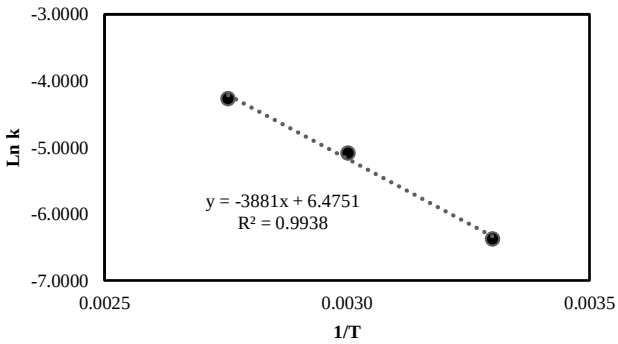


Fig. 5. Arhenius plot of ln(k) and (1/T) to determine the activation energy

IV. Conclusion

From the results of this experiment, it can be concluded that citric acid can be used as a leaching agent to replace inorganic acids and other organic acids (acetic acid) with the good capability of manganese recovery. An optimum operating conditions for leaching of manganese using citric acid are pH of 1.5, temperature of 90℃, time of 4 hours with the obtained recovery of manganese at 64% and it is still possible to increase with time.

Based on the value of correlation coefficient (R^2), th mathematical model that is best to describe manganese leaching phenomenon from hydrocracking spent catalyst is diffusion through ash layer. The value of apparent activation energy is 23.27 kJ / mol

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