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Lamtoro charcoal (*I. leucocephala*) as bioreductor in nickel laterite reduction: performance and kinetics study

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Abstract. The performance and kinetic of nickel laterite reduction were studied. In this work, the reduction of nickel laterite ores by anthracite coal, representing the high-grade carbon content matter, and lamtoro charcoal, representing the bioreductor, were conducted in air and CO₂ atmosphere, within the temperature ranged from 800°C and 1000°C. XRD analysis was applied to observe the performance of anthracite and lamtoro as a reductor. Two models were applied, sphere particle geometry model and Ginstling-Brounhstein diffusion model, to study the kinetic parameters. The results indicated that the type of reductant and the reduction atmosphere used greatly influence the kinetic parameters. The obtained values of activation energy vary in the range of 13.42-18.12 kcal/mol.

1. Introduction

Nickel is one of the most important materials in the world. 66% of nickel consumption used for stainless steel making, while the others 18% used in other alloys making, and the rest used for other purposes. There are two main nickel sources, sulfide ore and laterite ore. At least, 60% of nickel demand is supplied by sulfide ore besides 80% of nickel deposit lies on laterite ore [4]. Laterite is a highly weathered material rich in secondary oxides of iron, aluminium, or both. In addition, laterite often contains minor amounts of nickel, cobalt, and chromium [5]. One of the reasons that laterite ore is not used as the main nickel source is because of its low nickel content but recently China as the biggest stainless steel producer had found a way of utilizing laterite ore. They used it to produce nickel pig iron (NPI), as a substitute for pig iron in the stainless steel making process, using blast furnace or rotary kiln – electric furnace (RKEF). One of the important processes in NPI making is the reduction process. In the conventional NPI production, coal was used as a reductor. There have been several studies of nickel laterite reduction. But to the best of our knowledge, very few works have been presented on studying the kinetic of nickel laterite reduction. The kinetic study of nickel laterite reduction using gaseous reductant shows that the reduction mechanism was diffusion controlled [7] but the kinetic study of nickel laterite reduction using solid reductant has not been studied yet. Therefore, this present work investigated the kinetic of nickel laterite reduction using lamtoro charcoal as bioreductor. The performance and the kinetic parameters were studied.



2. Materials and method

Anthracite and lamtoro charcoal were used as reducing agent. Laterite and anthracite coal were provided by Indonesian Institute of Sciences and lamtoro charcoal was obtained from the traditional charcoal maker. All of the materials above were crushed using a mortar and then screened to get the desired size (-100+120 mesh). Laterite was characterized by XRD (Shimadzu 7000), XRF (Thermo Scientific Niton XL3t). The proximate analysis of reductants was done by PAU UGM as shown in table 1 and 2.

Table 1. Main Components of Laterite from Pomalaa, Southeast Sulawesi.

Components	SiO ₂	Fe ₂ O ₃ /Fe ^{*)}	NiO/Ni ^{*)}	MgO	Al ₂ O ₃	Na ₂ O	Cr ₂ O ₃
(wt.%)	26,94	43,83/30,60	3,19/1,73	12,67	5,13	2,73	1,63

^{*)} Analyzed using XRF Metal

Table 2. Proximate Analysis of Reductors (%wt).

Reductor Type	Moisture	Volatile matter	Ash	Fixed Carbon
Anthracite coal	2,3	7,4	2,5	87,9
Lamtoro charcoal	7,0	17,8	4,4	70,8

1.1. Pelletization

Laterite, starch, and anthracite charcoal were mixed together with laterite/reductant/binding agent ratio of 4:1:0.3. Then 5 mL of distilled water was added to the mixed sample and shaped into a ball pellet by hand. The pellet was dried at 110°C for 5 h. By using the same procedure, other pellets were made with lamtoro charcoal and carbon raiser as a reductor.

1.2. Reduction of the pellets

The pellets were roasted using two different atmospheric conditions, air and CO₂. Muffle furnace was used for air atmospheric roasting and tube furnace was used for CO₂ atmospheric roasting with CO₂ flow rate of 3 L/min. The pellets were roasted at temperature of 800, 900, and 1000°C with roasting time varied from 15 to 240 minutes. After the roasting process, the pellets were cooled and placed in a desiccator. Thereafter, the pellets were crushed using a mortar and were characterized using XRD (Shimadzu 7000).

1.3. Fraction of reduction reaction

To evaluate the kinetics parameters, the term fraction of reaction (f) was used. Eq (1) represents the formula for fraction of reaction. The equation was modified from the term used in iron ore reduction process [1]. The maximum weight loss of a pellet in Eq (1) was obtained from the maximum weight loss of laterite and reductant. The maximum weight loss of laterite was obtained from the total of removable oxygen from laterite. The total of removable oxygen from laterite is the oxygen binds to the iron and nickel.

$$f(t) = 100 \frac{\Delta W_t}{\Delta W_{\max}} \quad (1)$$

where:

f = fraction of reaction.

ΔW_t = weight loss of pellet (g).

$\Delta W_{\max}$ = maximum weight loss of pellet (g).

1.4. Kinetic models

The experimental data (f) were applied to the following mathematical models:

Sphere Particle Geometry Model

$$1 - (1 - f)^{1/3} = kt \quad (2)$$

where:

t = time (s).

k = kinetic constant (1/s).

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right)$$

where:

k_0 = pre-exponential factor (1/s).

E_a = activation energy (kcal/mol).

T = reduction temperature (K).

R = universal gas constant (kcal/mol/K).

Ginstling-Brounhstein Diffusion Model

$$1 - \frac{2}{3}f - (1 - f)^{2/3} = kt \quad (3)$$

3. Results and discussions

3.1. Materials Characterization

The chemical compositions of nickel laterite used in this research were showed in table 1. The laterite was dominated by Fe and Si element and based on the analysis of the XRD pattern using Match 2 software figure.1, the main mineral composition of the laterite was goethite (FeOOH), lizardite ($\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$), clinochlorite ($(\text{Mg}, \text{Fe}^{2+})_5\text{Al}(\text{AlSi}_3\text{O}_{10})(\text{OH})_8$), and quartz (SiO_2). The proximate analysis of the reductants was done by PAU UGM and the results were showed in table 2. The results showed that all of the reductants used had different characteristics. Anthracite coal had the highest fixed carbon content and the lowest ash content, lamtoro charcoal had the highest moisture and volatile matter content while carbon riser had the lowest fixed carbon and volatile matter content.

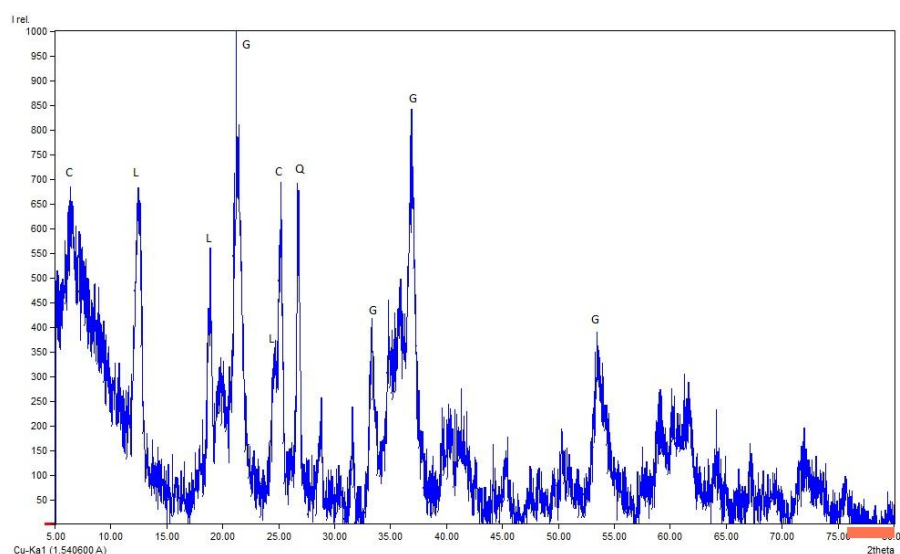


Figure 1. XRD pattern of initial laterite ore analyzed with Match! 2 Software.

3.2. Fraction of reaction

Experimental data which were the sample mass from time to time converted into a fraction of reduction reaction (f). The maximum weight loss from a pellet made with one type of reductant is different from a pellet made with the other type of reductant because the ash content of a reductant is different from the other reductant. The maximum weight loss of the pellet is 80.4% for the sample made with anthracite coal, 81.9% for the sample made with lamtoro charcoal, and 73.5% for the sample made with carbon raiser. Figure 2 shows the graphical representation of the fraction of reduction vs time.

From the experimental data, the fraction of reaction value was already reached a constant value before reached its maximum value at certain time. The maximum value of the fraction of reaction was 48%. It could happen because the reduction reaction has stopped. The reason of it could be two things. The first reason is the ratio between laterite and reductant was not high enough which makes the reductant has already used up before could reduce the minerals completely. The second reason is the existence of reaction between iron oxide and quartz which form fayalite (FeSiO_4) [2]. Fayalite has relatively low melting point (1100°C) [6] and already melt during the reduction process which makes the porosity of the pellet decreased. The decreasing of porosity of pellet could prevent reducing gas diffusion. On the other hand, fayalite could also act as a nucleating agent on iron metal forming process. During the reduction process, the iron metal layer formed on the surface of fayalite and prevent the contact of reducing gas. The fraction of reaction reached a constant value faster at a higher temperature. It could happen because the reaction rate is faster at a higher temperature. The reaction has stopped even when CO gas is used as a reductant instead of using solid reductant like in this study [7]. It concluded that the second reason was better at explaining why the reaction has stopped. The reduction reaction was fast at the early stage of the reduction process because, at the early stage, the devolatilization of the reductant occurs alongside the dehydroxylation of the minerals in the laterite which makes the weight loss of the sample is very high.

There was a slope change on the fraction of reaction vs time data on 0-5 minutes and 5-60 minutes reduction duration. This could happen because there were changes of reduction mechanism between these two periods. In the early stage of reduction, the process will follow the reaction controlled mechanism and after that, the process will follow diffusion controlled mechanism [7]. The changes of slope in the previous study happened at 20 minutes reduction duration [7], but in this study, the changes happened at 5 minutes duration time. It could happen because the reaction happened in this two study is different. The changes of slope happened in the very early stage of the reduction. These early changes made the evaluation of kinetic parameters could only be done starting at 5 minutes reduction time.

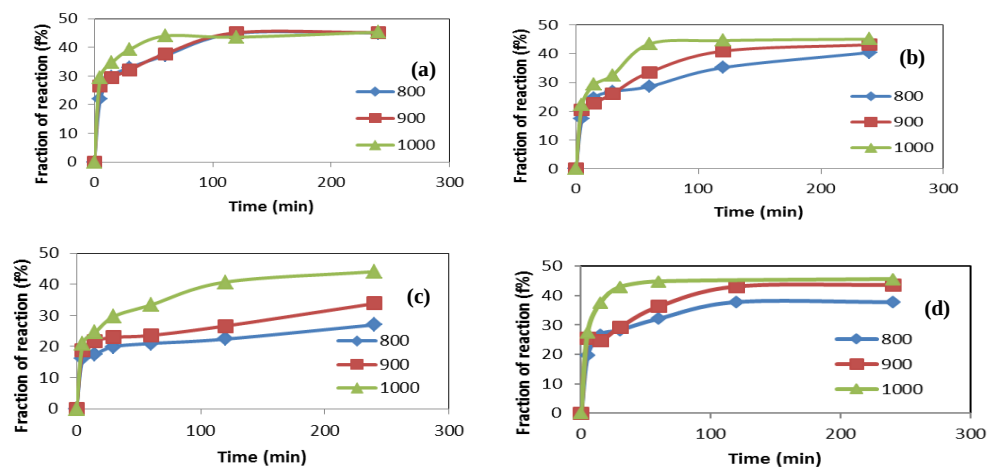


Figure 2. Fraction of reaction as a function of time of the laterite with anthracite (a), and lamtoro charcoal (b) in air atmospheric condition and with anthracite (c) and lamtoro charcoal (d) in CO_2 atmospheric condition.

The maximum value of the fraction of reduction was almost the same (around 47%) for both reductions happened in the air and CO₂ atmosphere, but based on the XRD analysis of the reduced sample, the mineral phase of both samples was different. The comparison of XRD pattern of the reduced samples was shown in figure. 3. The reduction in CO₂ atmosphere proceeds completely, compared with the reduction in air atmosphere based on the loss of hematite and magnetite peaks. It could happen because there is oxygen in the air atmosphere reduction which could oxidized the reduced mineral in the sample.

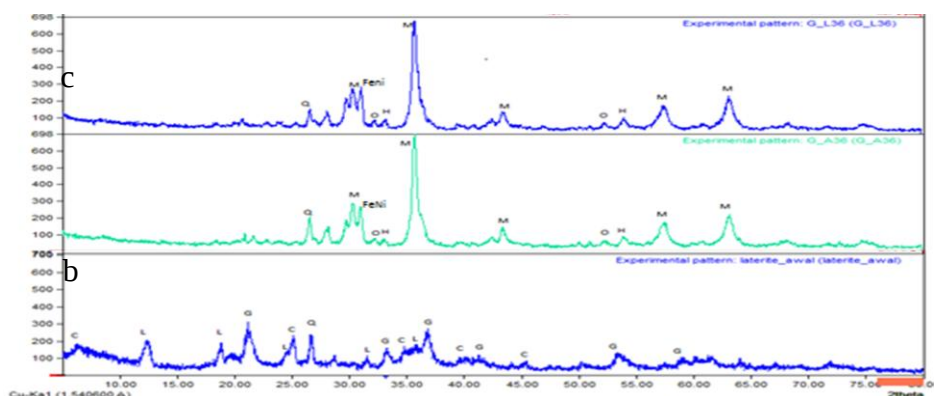


Figure 3. XRD pattern coal-laterite roasted in air atmospheric condition using lamthoro charcoal (c) anthracite (b) for 240 minutes at 1000°C and original nickel laterite (a) [Q: quartz; O: olivine; H: hematite; M: magnetite].

As it can be seen in Figure 3 that the reduction of nickel laterite using lamthoro charcoal is similar to that of coal represented by anthracite. The formation of ferronickel has been reached in similar operating condition at 1000°C for 240 minutes.

3.3. Kinetic Analysis

For the kinetic analysis of the experimental results, the kinetic model equations (2) – (3) have been applied to the experimental data for the temperatures of 800, 900, and 1000°C. The graphical representation of the fitting of experimental data to the kinetic model was shown in figure 4 and figure 5. Based on the simulation, both models could represent the reduction process well enough because the error in the data fitting process was small enough for both models applied. However, based on the literature study, the diffusion model was considered as the model that could represent the process. It also fitted with the reason why the reaction stopped at a certain time. The kinetics parameters obtained from the evaluation of the data using diffusion model was listed in table 3. The variation of activation energy means that the reaction mechanism happened is different for each reductant and atmosphere condition. The reaction mechanism differences happened because the reactions which took place consist of various step such as carbon oxidation, reducing gas diffusion, and reduction reaction hence the reaction was very complex.

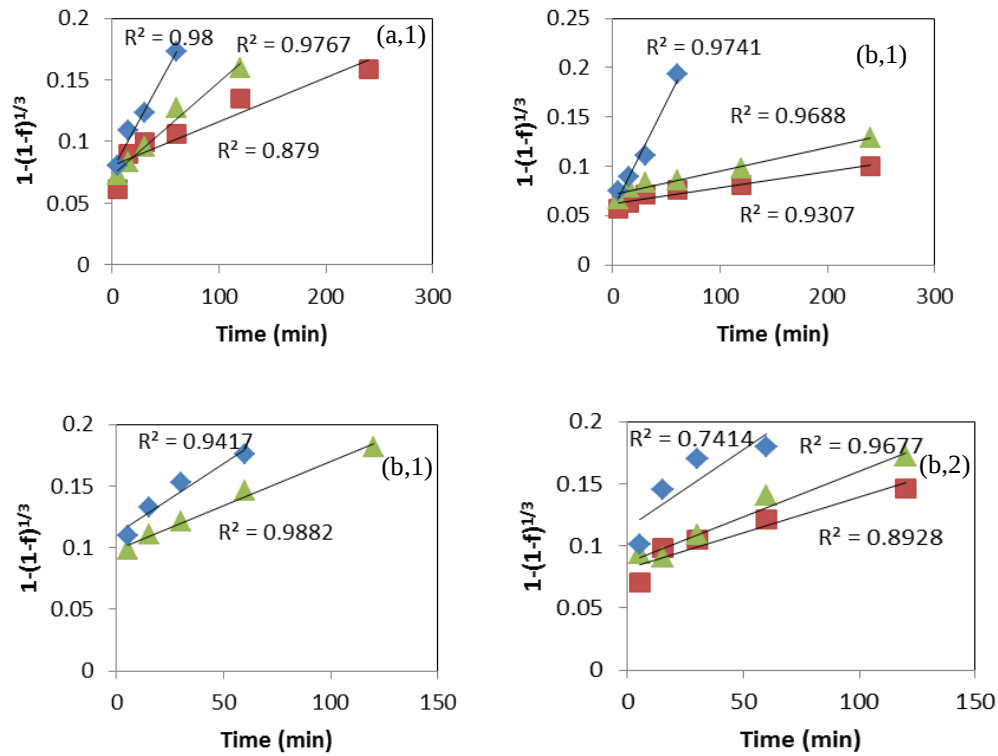


Figure 4. Applications of the sphere particle geometry model to the experimental data of sample reduced with anthracite coal (a) and lamtoro charcoal (b) in air atmosphere (1) and CO₂ atmosphere (2) at temperature of reduction of 800 (■), 900 (▲), and 1000°C (◆).

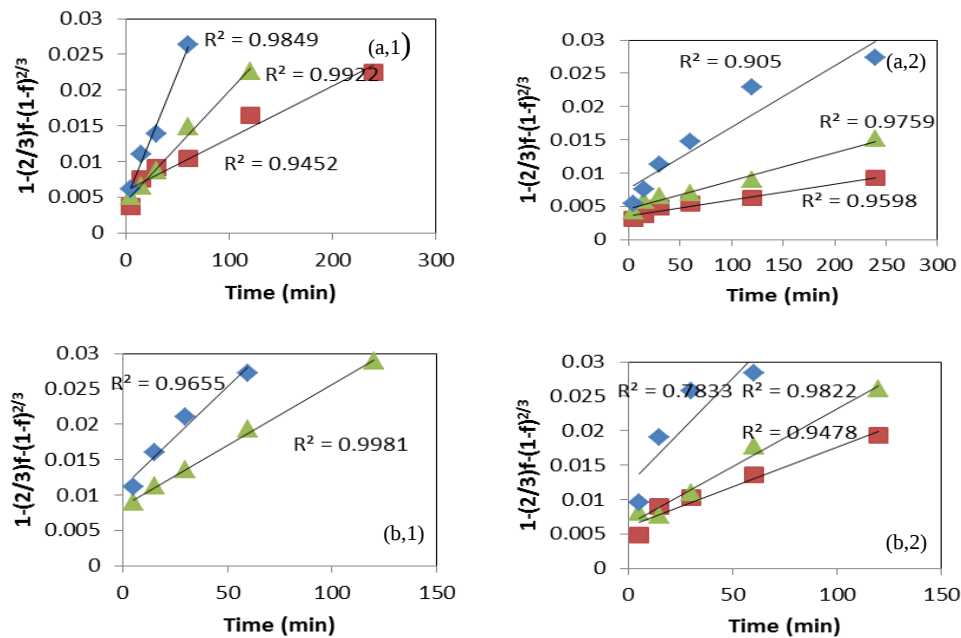


Figure 5. Applications of the Ginstling-Brounshstein diffusion model to the experimental data of sample reduced with anthracite coal (a) and lamtoro charcoal (b) in air atmosphere (1) and CO₂ atmosphere (2) at temperature of reduction of 800 (■), 900 (▲), and 1000°C (◆).

Table 3. The value of Activation Energy (E_a) dan k_0 from Simulation of Ginstling – Brounhstein Diffusion.

Reductant Type	Atmosphere			
	Air		CO2	
	k_0 (1/min)	E_a (kcal/mol)	k_0 (1/ min)	E_a (kcal/mol)
Anthracite coal	0.3182	17.4445	0.1083	18.1217
Lamtoro charcoal	0.0930	14.6658	0.0182	13.4162

4. Conclusions

From the results the following conclusions were drawn the maximum value of the fraction of reaction is about 47% and lamthoro biochar could perform as good as the coal as a reductor. Both models applied were good at representing the experimental data, but Ginstling-Brounhstein diffusion model was considered better at representing the process because it has a relatively smaller error and was supported by literature study. From applying Ginstling-Brounhstein diffusion model, the obtained value of activation energy was varied around 13.42 kcal/mol to 18.12 kcal/mol depends on the type of reductant and the reduction atmosphere used.

Acknowledgments

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