Kinetic study of nickel laterite reduction roasting by palm kernel shell charcoal

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Abstract. Demand to process nickel-bearing laterite ore increase as continuous depletion of high-grade nickel-bearing sulfide ore takes place. Due to its common nickel association with iron, processing nickel laterite ore into nickel pig iron (NPI) has been developed by some industries. However, to achieve satisfying nickel recoveries, the process needs massive high-grade metallurgical coke consumption. Concerning on the sustainability of coke supply and positive carbon emission, reduction of nickel laterite ore using biomass-based reductor was being studied. In this study, saprolitic nickel laterite ore was being reduced by palm kernel shell charcoal at several temperatures (800–1000 °C). Variation of biomass-laterite composition was also conducted to study the reduction mechanism. X-ray diffraction and gravimetry analysis were applied to justify the phenomenon and predict kinetic model of the reduction. Results of this study provide information that palm kernel shell charcoal has similar reducing result compared with the conventional method. Reduction, however, was carried out by carbon monoxide rather than solid carbon. Regarding kinetics, Ginstling-Brounstein kinetic model provides satisfying results to predict the reduction phenomenon.

1. Introduction
Nickel is a key mineral used to manufacture various metal-based product. Nickel however, mostly used in manufacture of stainless steel [1]. Nickel ore comes in two types of deposit, namely laterite and sulfide ores. Because of difficulty to extract nickel from laterite, about 58% of nickel demand is supplied by sulfide ores [2,3]. However, 78% of nickel deposit comes within laterite ores [2].

Indonesia has abundant deposits of laterite ores with 15% possession in the world[2]. Before 2013, this deposit successfully place Indonesia as first producer of nickel alongside Philipines [4]. However, it is exported as raw ore. In 2013, Ministry of Energy and Natural Resources issued a regulation to process any mineral-bearing ores before exporting [5]. This issue forces various country to invest smelter in Indonesia, in which several had already been planned to built.
Technology used to process nickel laterite involve massive metallurgical coke which definitely not environmentally friendly neither sustainable. The process uses carbon within the coke to reduce the oxide form of nickel and iron within laterites. Replacement of the coke using bioreductors is being developed by some researchers. In 2015, yield of reducing laterite using bioreductor has been studied [6]. Kinetics, however, has not been studied.

Indonesia owns established palm oil industries in which subsequently provide biomass. Based on this fact, kinetics of reducing nickel laterite by palm kernel shell charcoal is being studied. The objective of this study is to predict the phenomenon involved in the reduction of nickel laterite using palm kernel shell charcoal as well as provide kinetic model for the reduction.

2. Materials and Methods

2.1. Laterite Ore
Saprolitic laterite ore was obtained from Pomalaa, South East Sulawesi, Indonesia. XRF analysis shows that the sample has high Fe and Si content (Table 1). The sample also has high nickel and magnesium content, indicating that the ore belongs to saprolitic type.

| Si  | Fe  | Ni  | Mg  | Co  | Mn  | Cr  | Al  |
|-----|-----|-----|-----|-----|-----|-----|-----|
| [wt%]| [wt%]| [wt%]| [wt%]| [wt%]| [wt%]| [wt%]| [wt%]|
| 13.8| 32.4| 3.9 | 6.69| 0.18| 0.6 | 1.21| 1.49|

2.2. Reductors
Both reductors was obtained from LIPI Lampung, Indonesia. Proximate analyses of the reductors are given in Table 2.

| Reductor                     | Ash Content [wt%] | Moisture Content [wt%] | Volatile Matter [wt%] | Fixed Carbon [wt%] |
|-----------------------------|-------------------|------------------------|-----------------------|--------------------|
| Anthracite                  | 2.5               | 2.3                    | 7.4                   | 87.9               |
| Palm Kernel Shell Charcoal  | 4.6               | 7.7                    | 20.4                  | 67.3               |

2.3. Sample Preparations
Both laterite and reductors were crushed and screened using standard ASTM sieve screen to obtain particle size of -100+120 mesh. Laterite and reductant were mixed together with reductant:laterite ratio of 1:4 while the PKSC was also mixed with ratio of 1:3. Mixture of 5 g was taken, added by 3 mL of distilled water, and then shaped into ball pellet. Pellet was dried at 90 °C for 2 h, and then continued at 110 °C for 3 h.

2.4. Reductions
Muffle furnace with heating rate of 20 °C/min was used to process the pelletized samples. Muffle was heated into the desired temperature and then 10 pellets within 5 ceramic crucibles were charged into the muffle. Each of ceramic crucibles represents reducing time of 5, 15, 30, 60, and 120 min. Once the reduction process reached the designated time, the representing crucible was taken out of the furnace and the samples within were cooled to room temperature inside enclosed compartment to prevent re-oxidation of samples.
2.5. Measurements
Pelletized samples were weighted before and after reduction at room temperature. Percentage of reaction is calculated as mass loss in the designated time divided by maximum mass loss. As for XRD, certain pellets with highest mass loss percentage were chosen to represent certain data points. The chosen pellets were then grounded to be analyzed by XRD.

3. Results and Discussion

3.1. Comparison of Reduction by Anthracite and Palm Kernel Shell Charcoal
Figure 1 and Figure 2 show the XRD patterns of saprolite reduced by anthracite coal and palm kernel shell charcoal at different reduction temperatures. It is shown in these figures that peaks formed were similar, which means that reduction by palm kernel shell charcoal offers similar yield compared to coke. Furthermore, magnetite intensity of laterite reduced by coconut shell charcoal was higher in both temperatures, which means that coconut shell charcoal may have better capability to reduce laterite than anthracite.

![XRD patterns](image)

**Figure 1.** XRD pattern of saprolite reduced by anthracite coal at 1000 °C (a), 900 °C (b), and 800 °C for 2 h
3.2. Reduction Mechanism

According to the previous study on coal-based reduction of nickel laterite, there are several reaction which occur in the pellet while it was heated [7]. The reaction is shown below, metal oxide is denoted as Me.O.

\[
\begin{align*}
C + O_2 & \rightarrow CO_2 \\
CO_2 & \rightleftharpoons CO + 0.5 O_2 \\
CO + Me.O & \rightarrow CO_2 + Me.O_1 \\
C + Me.O & \rightarrow CO + Me.O_1
\end{align*}
\]

To study the dominance of reaction within pellet reduced by bioreductor, reduction is conducted at two different composition. With increasing the contact between carbon and metal oxides, the direct contact reaction of (4) should plays larger role and increase the rate of reaction. However, as shown by Figure 3 and 4, the reaction rate does not change significantly. This finding denotes that majority of reduction by bioreductor follows reaction (3), which is diffusion-based reaction. Because of this finding, Ginstling-Brounstein diffusion based models is used to predict the kinetics of nickel laterite reduced by palm kernel shell charcoal [8].

**Figure 2.** XRD pattern of saprolite reduced by palm kernel shell charcoal at 1000 °C (a), 900 °C (b), and 800 °C for 2 h
3.3. Reduction Kinetics
Kinetics of reduction was evaluated by Ginstling-Brounshtein model [8]. In this kinetics model, slopes of $\Omega$ versus time were calculated to determine the kinetics. Data which function only to show that reduction has not been completed are not included in the model. The model shows that higher temperature will produce faster kinetics. Table 2. shows that higher temperature will produce higher diffusion kinetics.

$$\Omega = 1 - \frac{2}{3} r - (1-r)^{2/3} \quad (5)$$

$$\Omega = k_d t \quad (6)$$

Where, $\Omega$ is a result of ginstling correlation, while $r$ represents reduction percentage and $k_d$ denotes diffusion reaction rate constant in terms of time ($t$).
Table 3. Diffusion Rate Constant ($k_d$) from Ginstling-Brounstein Regression

| Reduction Temperature [°C] | Time [min] | $\Omega$  | $k_d \times 10^4$ [min$^{-1}$] |
|----------------------------|------------|----------|-------------------------------|
| 800                        | 5          | 0.0153   | 8.8734                        |
|                            | 15         | 0.0255   |                               |
|                            | 30         | 0.0314   |                               |
|                            | 60         | 0.0431   |                               |
|                            | 5          | 0.0204   |                               |
| 900                        | 15         | 0.0304   | 11.8125                       |
|                            | 30         | 0.0380   |                               |
|                            | 60         | 0.0596   |                               |
|                            | 5          | 0.0341   |                               |
| 1000                       | 15         | 0.0421   | 12.4342                       |
|                            | 30         | 0.0626   |                               |
|                            | 60         | Not included |                               |

4. Conclusions
Reduction carried out in this experiment denotes that reduction of saprolitic laterite ore by bioreductor is a diffusion-based reaction. Reduction proceeds faster with higher reducing temperature. However in this research, yield of nickel may be better comprehended if the reduced sample is further being analyzed. SEM-EDX is an option to comprehend the phase separation of nickel-bearing iron from the laterite body. Magnetic separation is also a good option to shows the quantitative nickel yield of reduction.

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