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Microwave-assisted roasting time on Ilmenite Bangka Belitung extraction using hydrometallurgical method

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Abstract: Titanium Dioxide (TiO_2) was extracted from Bangka Ilmenite through a hydrometallurgical process employing the microwave-assisted method using a 20% HCl solution. The highest crystallinity percentage in XRD result, reaching 75%, was achieved after a roasting duration of 25 minutes, with a corresponding crystallite size of 35.57 nm at the TiO2-Anatase phase's peak intensity of 25.24°. Analysis of the extracted ilmenite revealed alterations in its compound composition, notably an increase in TiO_2 content. The most substantial increase in TiO_2 content, rising to 69.7% from 33.76%, was observed after 25 minutes of roasting. UV–Vis spectroscopy revealed an energy band gap of 2.329 eV.

Keyword: TiO_2, Ilmenite Bangka, hydrometallurgy, roasting

1. Introduction

The utilization of mineral resources in Indonesia has been a subject of substantial concern and scrutiny in recent years. Indonesia, renowned for its abundant and diverse mineral reserves, has the potential to become a global mining powerhouse. However, the effective exploitation and management of these resources have yet to reach their optimal potential. This underutilization is a matter of paramount importance, both in economic and environmental terms, as it affects the nation's development, sustainability, and competitive edge in the global market (Sihombing et al., 2022).

Mining and mineral processing typically do not achieve 100% recovery, resulting in the presence of both byproduct minerals and, in some cases, even primary minerals that remain and are discarded with the tailings (piles or accumulations of waste from the tin mining and washing processes). If the cassiterite mineral mining system does not improve its mineral recovery, it is possible that the former mining areas will become grounds for communities to engage in mining activities once more. This could open up opportunities for illegal mining activities by the public and disrupt reclamation programs that have been implemented at the former mining sites (Herman, 2015).

Based on previous research findings, one of the minerals under investigation is ilmenite ($FeO.TiO_2$ or $FeTiO_3$), which contains 30-65% TiO_2 (Samal et al., 2010). Ilmenite, due to its significant accumulation, serves as a valuable source of titanium, primarily used in the alloy industry. Its resistance to heat and corrosion, coupled with its low specific gravity, renders titanium a crucial material in the aerospace industry. Ilmenite ($FeTiO_3$) is also extensively utilized for extracting Titanium Dioxide (TiO_2), an inorganic semiconductor widely employed in various human needs, including raw material for paint, the paper industry, and plastics (Nayl et al., 2009). TiO_2 also holds substantial potential for applications in gas sensors, environmental purification, and photovoltaic cells (Zhang et al., 2009). Moreover, ilmenite can be directly employed as a component in exhaust gas adsorption for four-stroke engine vehicles. Additionally, it finds application as a raw material in the production of ceramic tile bodies. These diverse applications underscore the multifaceted utility of ilmenite, making it a valuable resource with profound implications for various industrial and environmental sectors. (Herman, 2021).

In recent years, the extraction of valuable minerals from naturally occurring ores has become an increasingly significant area of research, driven by the demand for raw materials in various industrial applications. Ilmenite, a titanium-iron oxide mineral, stands out as a valuable source of titanium, which finds extensive utilization in aerospace, medical, and other high-tech industries. As a result, the efficient and environmentally friendly extraction of titanium from ilmenite ores is of paramount importance (Sampath et al, 2023).

Traditional methods for ilmenite extraction often involve energy-intensive and environmentally detrimental processes, such as high-temperature reduction in a blast furnace. In this context, the application of hydrometallurgical techniques has gained traction due to their potential to reduce the environmental impact of mineral processing. One notable advancement in this realm is the use of microwave-assisted roasting, which has the potential to significantly enhance the extraction of valuable elements from mineral ores (Nguyen et al, 2018).

Microwave-assisted roasting is a technique that leverages the specific heating properties of microwaves to enhance the decomposition of minerals in ores, leading to improved metal extraction yields. The efficiency and selectivity of microwave heating have shown promise in various mineral processing applications. This technique has been previously applied to various ores, including ilmenite, to improve extraction efficiency. However, the influence of roasting time, a critical parameter in the process, has not been thoroughly investigated in the context of ilmenite hydrometallurgical extraction (Javad et al, 2012). This study aims to address this knowledge gap by examining the effect of microwave-assisted roasting time on ilmenite extraction using a hydrometallurgical method. Hydrometallurgical method based on (Kang et al, 2020), through processing: microwave roasting with Na_2CO_3, leaching process with using HCl and microwave calcination. Systematic investigation, this research endeavors to establish a comprehensive understanding of how varying roasting times influence the extraction efficiency, and product purity. Na_2CO_3

2. Experimental

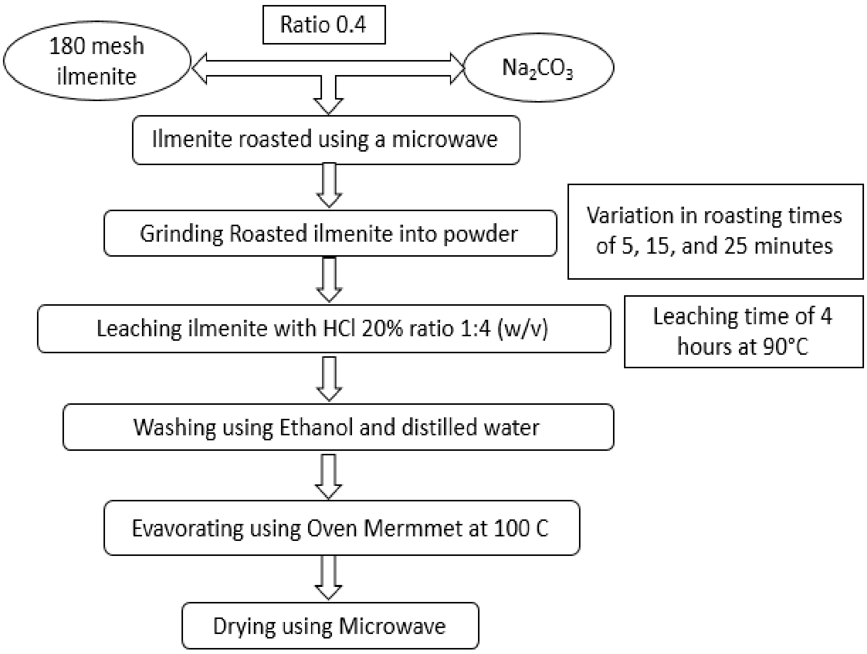

Figure 1. Experimental flow chart

Ilmenite sand (PT. Timah, Bangka, Indonesia) is prepared by grinding it to separate the bonds with accompanying minerals, reduce the material size, and enhance reactivity during the leaching process. Subsequently, the ground sand is sieved using a mesh with a size of 180. The roasting process is carried out using Microwave Assisted (SHARP-R-728(W)-IN/R-728(K)-IN/R-728(S)-IN) with varying roasting times of 5, 15, and 25 minutes. The microwave heating program is set at 100P (percentage). After the roasting process, the sample is finely ground and filtered, and then the leaching process is conducted using HCl. HCl leaching is adjusted to a 20% concentration with a roasted ilmenite to HCl ratio of 1:4 (w/v). The leaching process is run for 4 hours at a temperature of 90°C. After the leaching process is completed, the sample is washed three times, dried, and calcined using a Microwave. In order to ascertain the elemental composition and oxides present in the leached sample, X-ray Fluorescence (XRF) characterization is employed. Concurrently, X-ray Diffraction (XRD) characterization is utilized to determine the crystalline structure of the minerals within the sample.Other paragraphs are indented too. The band-gap energy was determined using UV-Visible diffuse reflectance spectroscopy (DRS).

3. Result and Discussion

The ilmenite extraction process involves the stages of roasting, leaching, and calcination. Each ilmenite sample has varying compositions. The ilmenite used in this study originates from Bangka Belitung, Indonesia. The crystal structure of ilmenite is depicted in Figure 1. The highest peaks of ilmenite from Bangka are observed at 27.56°, 51.8°, 54.07°, and 77.4°. These peaks correspond to the American Mineralogist Crystal Structure Database (AMCSD) for Rutile-TiO_2 with the database code AMCSD 0001735, Ilmenite with AMCSD 0000925, and Hematite with AMCSD 0000143. The primary components of Bangka Belitung ilmenite are TiO_2 and Fe_2O_3, along with several other elements, including SnO_2, ZrO_2, ZnO, P_2O_5, CaO, V_2O_5, MnO, WO_3, Re_2O_7, PbO, Bi_2O_3, Eu_2O_3, and Yb_2O_3. Morphology of ilmenite from Bangka, as depicted in Figure 2, reveals a non-uniform rock formation or irregular shapes with an average particle size of 216.05 μm.

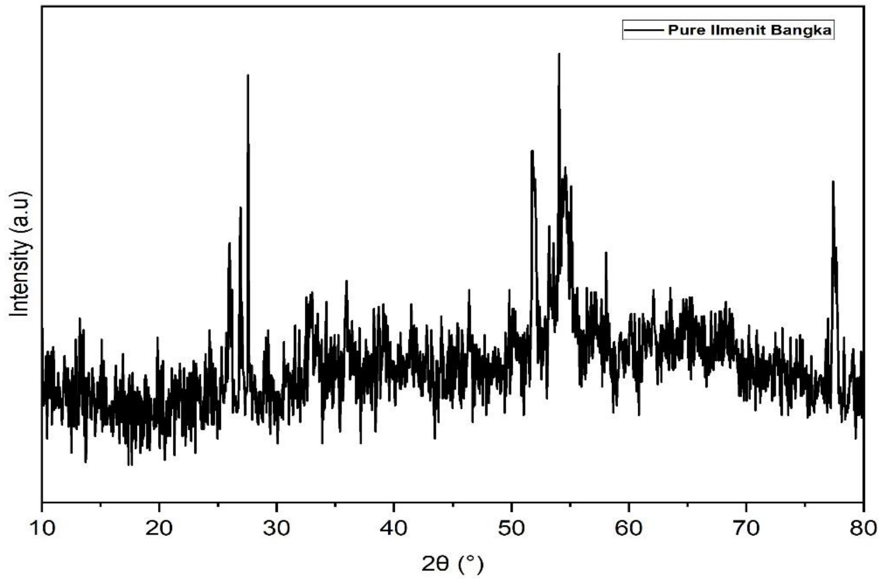

Figure 2. XRD patterns of Pure Ilmenite Bangka Belitung, Indonesia

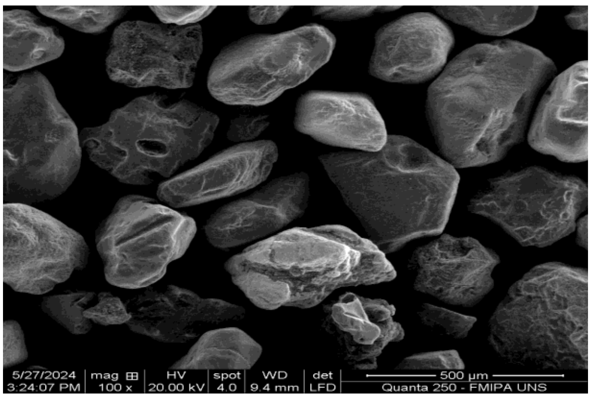

Figure 3. SEM images of Ilmenite Bangka Belitung

Figure 4 shows the diffractograms of ilmenite that has undergone roasting for 5, 10, and 25 minutes, followed by leaching and calcination processes. The highest peak for a roasting time of 5 minutes is observed at 81.6° and 75.96°, corresponding to some of the peaks in TiO2 Anatase as per the AMCSD code database 0019093. The highest peaks for a roasting time of 15 minutes occur at 25.33°, 35.52°, and 36.87°, and the highest peaks for a roasting time of 25 minutes are at 25.24°, 35.52°, and 54.06°. These peaks for the 15 and 25-minute roasting times align with the TiO_2 Anatase peaks in the AMCSD code database 0019093. Apart from the peaks mentioned above, the presence of additional peaks such as those for Fe_2O_3 indicates the existence of impurities in each sample. Among the three roasting times, the highest peaks are observed at 15 and 25 minutes. The smallest level of impurities, as indicated by the observed peaks, is found at the 25-minute roasting time. Furthermore, the crystallinity shown in Table 1 is calculated using the Debye–Scherrer formula, allowing us to determine the average particle size for each sample.

$$D = k\lambda/\beta cos\theta \quad (1)$$

where λ is the wavelength of X-rays (λ = 1.541874 Å), D is used for the crystallite size of samples, β represent full width at half-maximum (FWHM) of the representative peak and 2θ is the Bragg difraction angle (Nabi, et al, 2019). From Table 1, the crystallinity level of each sample is obtained. As the roasting time increases, the percentage of crystallinity also increases.

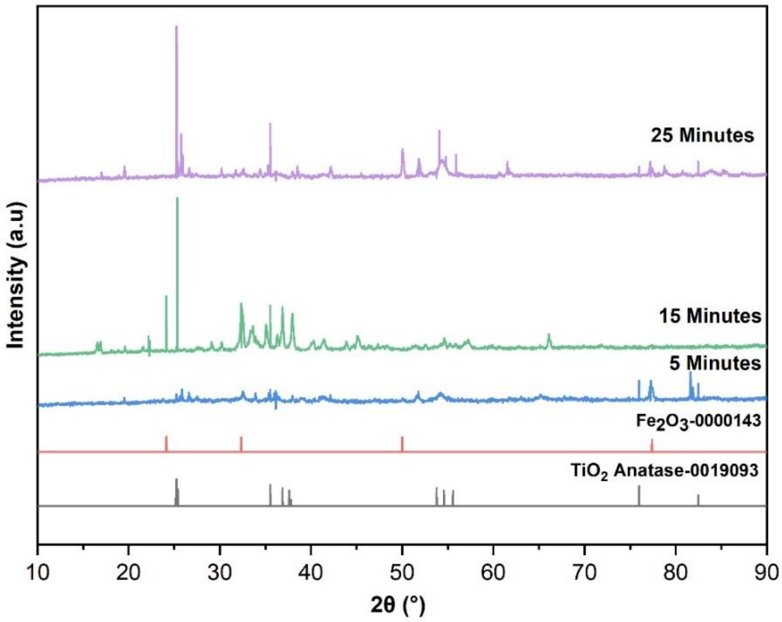

Figure 4. XRD patterns of ilmenite extraction using microwave with roasting times of 5, 15, and 25 minutes.

Table 2. Crystallinity of XRD result

Roasting Time (Minutes)	D (nm)	Crystallinity (%)
5	101.6	50
15	70.24	74
25	35.57	75

Subsequently, XRF utilizes X-ray interactions as its fundamental principle to analyze the elemental composition of materials. This technique demands a substantial number of representative samples, presuming the material's homogeneity. It is particularly adept at measuring elements prevalent in powders or minerals. Bangka ilmenite, appearing as a black powder, was analyzed using XRF, revealing its mineral composition to be predominantly Fe_2O_3 at 53.70% and TiO_2 at 33.76% (Wahyuningsih, 2013). Additionally, trace minerals including SnO_2 (3%) and SiO_2 (2.42%) were detected, along with various associated minerals such as MgO, Al_2O_3, MnO, NiO, Cr_2O_3, V_2O_5, SO_3, ZrO_2, P_2O_5, CaO, and ZnO. The XRF results with roasting time treatment for ilmenite are shown in Table 3. The TiO_2 content increased with longer roasting times, whereas the Fe_2O_3 content decreased with longer roasting times. Other compounds were still detected despite the roasting treatment of ilmenite, indicating that the synthesis time was not yet optimal. The presence of other compounds might also occur due to the leaching process of ilmenite.

Table 3. XRF result of variations in microwave roasting Time

Samples	5 minutes	15 minutes	25 minutes
	Oxides % (w/w)		
TiO_2	56.6	61.8	69.7
Fe_2O_3	39.53	24.0	21.3
MnO	2.18	2.14	2.37
Cr_2O_3	0.73	1.16	1.19
ZrO_2	1.2	1.5	1.0
SnO_2	3.1	2.3	1.0
V2O5	0.44	0.21	0.23
ZnO	0.13	0,06	0.06

Ultraviolet-visible (UV-Vis) spectrometry was utilized to ascertain the band-gap energy, using reflectance data (R) obtained from the UV-Vis spectrometer. The band-gap energy of the semiconductor particles was derived by plotting the function $(F(R)\ hv)^{1/2}$ against the photon energy in electron volts (eV) (Mulyono, et al, 2017).

$$F(R) = (1 - R)^2 / 2R \quad (2)$$

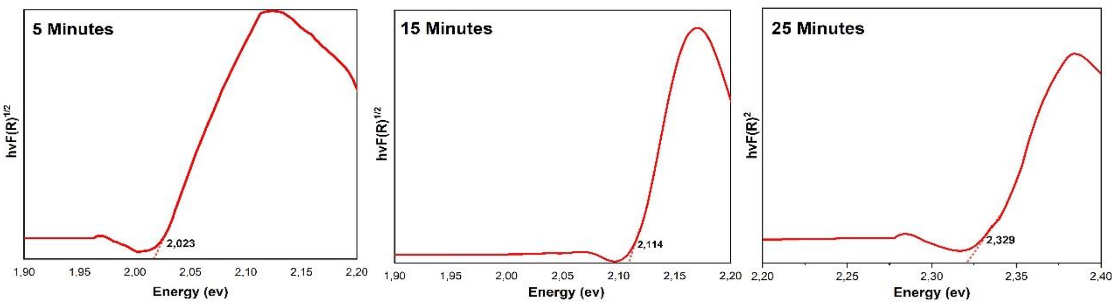

Figure 5. Band gap energy (eV) of ilmenite after extraction at 5, 15 and 25 minutes

The Modified Kubelka-Munk Theory is utilized in this study due to its high accuracy in results with TiO2 (Mulyono et al., 2017; Kartikowati et al., 2023). Analysis of Figure 5, which examines three different ilmenite extraction methods, shows that the Eg values, ranked from smallest to largest, are 2.023 eV, 2.114 eV, and 2.329 eV, corresponding to synthesis durations of 5, 15, and 25 minutes, respectively. The smaller band gap can be attributed to the presence of Fe and other impurities in the synthesized TiO_2, which create new energy levels near the valence or conduction band edge. This reduced band gap energy allows the synthesized TiO_2 to absorb low photon energy from visible light within the wavelength range of 500 to 600 nm, more precisely, this can be observed in Table 4. Furthermore, Figure 5 illustrates that an increase in roasting time is associated with a rise in Eg, indicating that longer roasting durations result in higher Eg values.

Table 4. Band gap energy (eV) of ilmenite samples

Roasting Time (Minutes)	Band gap energy (eV)	Wavelength, λ (nm)
5	2,023	612.53
15	2,114	586.28
25	2,329	532.15

4. Conclusion

The extraction of ilmenite from Bangka was conducted using hydrometallurgy, involving microwave irradiation for roasting and calcination, and HCl for leaching. Optimal results were achieved after 25 minutes of roasting, with a crystallinity of 75% and a crystallite size of 35.57 nm at 25.24°, indicating the TiO_2-Anatase phase. The TiO_2 content increased from 33.76% to 69.7%. The widest energy band gap, 2.329 eV, was observed after 25 minutes. Despite increased TiO_2 production, optimization is needed as significant amounts of Fe_2O_3 remain undecomposed.

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