Synthesis of zeolite catalyst for palm oil cracking process by means of microwave induced local kaolin leaching

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Abstract. Kaolin mined in Belitung Indonesia mostly consists of SiO2 and Al2O3 and is better off calcined at a temperature of about 700 °C for at least 2 hours to be reactive. This research is conducted to observe the effect of implementing microwave irradiation in the leaching process as the most crucial step in the hydrothermal synthesis of a zeolite catalyst, using a leached metakaolin (LMK) as the source of SiO2. The irradiation of microwave certainly outperforms the conventional leaching process of Metakaolin, as expected in the hypothesis. The modification of the microwave oven with the addition of a hole on the top chamber and alteration of the waveguide is conducted to improve the focusing of electromagnetic radiation onto the extraction column. Installation of the faraday cage gives rise to better polarization, not to mention a safer procedure. The conventional leaching of 25 grams of Metakaolin undertaken in the previous year takes 45 minutes to complete, while microwave-assisted leaching takes only 30 minutes or 30% more efficiently. The acid solution used in leaching undergoes electromagnetic influence that increases the dipole and polar reactivity and raises the acidity of the raffinate or catalyst by more than 15%, which is necessary for the cracking process catalyst. The starting materials consist of silica, alumina, Na2O, distilled water with a quantity of silica in the seed smaller than silica in the LMK and the minute amount of impurities, mainly common dirt of soil. The power consumed by the magnetron to irradiate the microwave was set at 450, 600, and 800 W, respectively. The appearance and size characterization of the produced zeolite catalyst was conducted using SEM (Scanning Electron Microscope). Meanwhile, the acidity characterization as the highlighted focus is carried out by applying Hammett’s indicator titration of ammonium solution. A rise of acidity up to 25% or 0,71 (mmol NH3/gr) from 0.63 (mmol NH3/gr) in conventional method.

1. Introduction
In particular, producing alternative energy, liquid fuel is increasingly in demand due to the concern of fossil oil disadvantages. Indonesia and Malaysia are the primary producer of palm oil, the search for biofuel has been in development ever since. A cracking process needs to be implemented to convert palm oil to liquid fuel such as biodiesel, biogasoline, and biokerosene.

Kaolin mined in Belitung Indonesia mainly consists of SiO2 and a reactive Al2O3 and is better of calcined at a temperature of about 700°C for at least 2 hours to be reactive. This mixture is an amorphous phase of Metakaolin (MK), used as a primary component for several types of zeolite catalyst synthesis. The irradiation of microwave indeed outperforms the conventional leaching process of Metakaolin, as expected in the hypothesis. The modification of the microwave oven with the addition of a hole on the top chamber and alteration of the waveguide is conducted to improve the focusing of electromagnetic radiation onto the extraction column. Installation of the faraday cage gives rise to a better polarization,
not to mention a safer procedure. The conventional leaching of 250 grams of Metakaolin undertaken in the previous year takes 45 minutes to complete, while microwave-assisted leaching takes only 30 minutes or 30% more efficiently. The acid solution used in leaching undergoes electromagnetic influence that increases the dipole and polar reactivity and raises the acidity of the raffinate, which is necessary for the cracking process catalyst.

2. Related Work

Several researchers have carried out similar experiments in achieving catalysts for the hydrocracking process, better known as zeolite Y. Different kaolin contents with various pretreatments have been performed to obtain ready to extract grain. Mechanical processing such as grinding, milling, and screening are the common methods to produce fine powder or granules.

2.1. Common preparation of Metakaolin

Some papers show that LMK can be used as nutrients in synthesizing Zeolites and preparing a surface area of 400 m²/g and a pore size of 0.7 nm. The LMK could have been obtained through the leaching process of Metakaolin using H₂SO₄ 5.2N at 90°C for 2 hours. Ajayi et al. revealed that leaching metakaolin using H₂SO₄ > 50% wt in the starting material would result in a Si/Al > 5 wt/wt [1]. They also have successfully separated silica and alumina in Metakaolin using 3M HCl at 115°C for 2.5 hours, resulting in an LMK with a silica/alumina ratio between 20-40 mol/mol, suitable for nutrients in synthesis Zeolite ZSM5. Leaching metakaolin using H₂SO₄ has also been performed by Adeoye J.B et al., which produces LMK with a molar ratio between 3-8 mol/mol [2].

![Figure 1. Flow diagram of the research.](image)

Firstly, the kaolin originally from Belitung Indonesia is calcined at a temperature of 700°C for 2 hours to produce an amorphous Metakaolin (MK) phase with a reactive SiO₂ and a reactive Al₂O₃, as nutrients in synthesis NaY-Zeolite. These two compounds have to be separated partly. Separation of reactive SiO₂ from Metakaolin is performed by implementing microwave-assisted leaching with HCl solution at 90 to 100°C for 2/3 hours to obtain a silica-rich raffinate/solid leftover better known as
leached Metakaolin (LMK), that approximately contains a molar ratio of SiO$_2$/Al$_2$O$_3$ between 7-10 mol/mol corresponding to the synthesis of Zeolite Y [3]. In addition, the ratio of LMK solids/acidic solution in the starting material determined of 5 %-w/w.

Feed material which consists of an LMK sample, NaOH, distilled water, and a tiny amount of a lynde type Y seeds, is added. These reactants are mixed on a particular pH to become a homogeneous suspension and remain homogeneous at room temperature for 10-11 hours during the aging stage. After aging, the reactant mixture is hydrothermally crystallized at the temperature of 93°C for 15-18 hours [4].

2.2. Improvement in Implementation
Subagjo and Rahayu have improved the catalyst’s surface, which is essential for the contact of reaction propagation by controlling the solvent's leaching temperature and pH [5]. Microwave as an electromagnetic wave results from magnetic field induction with high energy in the form of frequency. It does not need a medium to travel. As shown in the picture below, these magnetic and electric properties produce a dipole moment effect that influences the alcohol molecules and slightly less on triglyceride to vibrate or rotate.

![Microwave magnetic and electrical effects mechanism.][6]

This effect creates hydrogen ions that make the acidic property of solid raffinate or catalyst stay longer.

3. Material and Methods
The starting materials consist of Silica, Alumina, Na$_2$O, distilled water, and a tiny amount of impurities, mainly common soil dirt. The product with a molar ratio of silica from the LMK/silica of the seed of Lynde type Y was 4:1 mol/mol, considered the best. Zeolites are built by Al, Si, and O atoms. Hence the kaolin material is likely to be synthesized to produce Zeolite Y. But, the kaolin or kaolinite crystal structure has an inactive Si-O and Al-O bond. It is necessary to convert kaolin into active kaolin with active Si-O and Al-O bonds, such as Metakaolin. Metakaolin from kaolin Belitung Indonesia has been produced through calcination at a temperature of 700°C for 2 hours [3].

3.1. Material Pretreatment
The Si-O and Al-O bonds or silica and alumina can be separated by leaching using a solution of acids. It will produce silica-rich solids called leached Metakaolin (LMK) and alumina-rich liquids. When Metakaolin is leached and LMK has resulted, the Al sheet will dissolve, which will provide a different environment for Si atoms, thus forming micropore silica. Certainly proven that the result of the molar ratio of SiO$_2$/Al$_2$O$_3$ in LMK is affected by the leaching process [3].

3.2. Characterization LMK and Zeolite.
Characterization of LMK was performed using a gravimetric method to determine SiO$_2$ and Al$_2$O$_3$ content in LMK. Meanwhile, the characterization of Zeolites for size and structure comparison, a sample of zeolite Y catalyst is analyzed using SEM. And finally, the most highlighted characteristic of the zeolite catalyst that ensures that the catalytic cracking process would likely occur is the acidity. Hammett’s indicator titration was carried out using weak, mild, and strong ammonia.
3.3. Synthesis

The most crucial step in the hydrothermal synthesis of zeolite catalyst is the leaching process utilizing leached Metakaolin (LMK) as a source of SiO\textsubscript{2}. The 1 M acetic acid solution in the flask needs to be heated to evaporate and consecutively condensed to return to be liquid falling to the Metakaolin in the leaching chamber. The extraction occurs continuously when the extract comes down back to the flask and is usually heated by a hot plate or oil/water bath. This research is carried out to study the effect of implementing microwave irradiation in the heating and leaching process.

Better zeolite Y catalyst in terms of acidity as a crucial character is expected to appear in this research. The effect of implementing microwave irradiation in the leaching process hypothetically occurs to levitate the magnetic field influence and an increased reactivity achieved later on. The modification of the microwave oven with the addition of a hole on the top chamber and alteration of the waveguide is conducted to improve the focusing of electromagnetic induction onto the extraction column. The induction is expected to increase the acidity mainly and hopefully the physical surface area as well. Installing a simple Faraday cage circling the hole protect the operator simultaneously pops up the ion conductivity effect to the crystal.

![Figure 3. a) Microwave Irradiation Leaching Set and b) Diagram of Pressure Vessel.](image)

4. Result and Discussion

After conducting several chemical processes of experiments, adequate data and information were obtained with few repetitions due to unsatisfactory characterization results. Several modifications are undertaken to enhance the electromagnetic influence to boost the activity of hydrogen and hydroxyl ions in the solvent.

The zeolite catalyst resulted from the enhanced microwave synthesis was put on trial using a 2-liter high-pressure vessel as a refractionation column equipped with an electrical heater and water-cooled condensers. The yields for biodiesel and biogasoline products were 11\% and 9\%, respectively, which are considered sufficient for the start but need to be improved to be economically feasible.

4.1. Data and Measurements

Wet chemistry of titration was performed to determine the molar ratio of silica/alumina in LMK, and the range of 6-10 mol/mol ratios was obtained. The power consumed by the magnetron to irradiate the microwave was set at 300 W and 450 W, respectively. Characterization of Zeolite catalyst produced was conducted utilizing SEM. The best zeolite catalyst is obtained using a starting material composition of 2.6Na\textsubscript{2}O:Al\textsubscript{2}O\textsubscript{3}:10.41SiO\textsubscript{2}:694H\textsubscript{2}O, using enhanced microwave leaching at 300 W in 30 minutes duration. The microwave irradiation indeed outperforms Metakaolin’s conventional electric heater-based leaching process by as much as 30\% as expected previously in the hypothesis.
Table 1. Result of synthesis of zeolite catalyst using variation LMK type.

| Zeolite | SiO$_2$/Al$_2$O$_3$ (mol/mol) | Seed (%-w) | Crystallinity (%-w) | UCS (Å) | SiO$_2$/Al$_2$O$_3$ (mol/mol) |
|---------|-------------------------------|------------|---------------------|---------|-------------------------------|
| NaY-1   | 6                             | 10         | 47.3                | 24.88   | 2.39                          |
| NaY-2   | 8                             | 10         | 52.1                | 24.76   | 3.01                          |
| NaY-3   | 10                            | 10         | 61.7                | 24.70   | 3.52                          |
| NaY-4   | 23                            | 10         | 71.1                | 25.01   | 1.89                          |

Table 2. Effect of microwave irradiation in 30 min leaching process towards product acidity.

| Zeolite | SiO$_2$/Al$_2$O$_3$ (mol/mol) | Irradiation power | Crystallinity (%-w) | Seed used (%-w) | Total Acidity (mmol NH$_3$/gr) |
|---------|-------------------------------|------------------|---------------------|-----------------|-----------------------------|
| NaY-3   | 10                            | 0 W              | 61.7                | 10              | 0.62                        |
| NaY-3   | 10                            | 450 W            | 60.6                | 10              | 0.65                        |
| NaY-3   | 10                            | 600 W            | 62.1                | 10              | 0.71                        |
| NaY-3   | 10                            | 800 W            | 62.3                | 10              | 0.71                        |
| NaY-3   | 10                            | 800 W            | 62.2                | 10              | 0.70                        |

4.2. Data Processing

Through widely used computation software for calculation and modeling, the data processing comes up with a simple graph to show the correct finishing point of research. The graph, a curve with a downward bending shape, gives a convincing conclusion to draw, as shown in figure 4.

![Figure 4](image_url)

Figure 4. Effect of Power implemented on microwave irradiation during leaching process.

The curve showed in figure 4 gives an interpretation of optimal usage of irradiation power at 600W. The last point of 0.7 mmol/gram acidity and 800 Watt irradiation power shows that the decreasing phenomenon of acidity occurred beyond 600 Watt. Meanwhile, the crystal's size, uniformity, and structures both resulted from conventional method and microwave effect implementation can be compared visually in figures 5 and 6. The microwave tremendously influences shaping the crystal in such a manner that makes it uniform and relatively smaller. Either the existence of hydrogen ion split from the acid solvent or direct upward effect of an electromagnetic whirlwind through the top hole modification of microwave oven. The Faraday cage circled the hole amplifies the induction.
Figure 5. The SEM micrograph of zeolite catalyst Zeolyte NaY3 produced a) without a microwave and b) with microwave induction 450 W.

Figure 6. The SEM micrograph of zeolite catalyst Zeolyte NaY3 produced a) without a microwave and b) with microwave induction 600 W.

5. Conclusion
A promising new modified procedure in synthesizing zeolite NaY catalyst for palm oil cracking process has been discovered by simply implementing adjusted irradiation of 2.5 GHz microwave during the leaching process of Metakaolin originally from Belitung kaolin. The data resulted from planned and thoroughly monitored experiments are considered fit to be concluded

Better crystal of catalyst with structure, size, and uniformity is perceived, the crystallinity of 62.3 (%wt) is obtained showing 10% increase when using 600W irradiation as the best power adjustment. However, the more significant achievement is the rise of acidity up to 25% or 0.71 (mmol NH$_3$/gr) from 0.65 (mmol NH$_3$/gr) in the conventional leaching method. The microwave irradiation increases the hydrogen ion trapped in the catalyst that is very beneficial for acidity requirement.

Using different raw materials, especially from other mine sites, would be an advantage for economic analysis. Another benefit of implementing microwave irradiation during leaching of Metakaolin is efficiency in time consumption by 30% from 60 minutes to less than 45 minutes respectively.
6. Reference

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