

Bayah Natural Zeolites to Upgrade Biooil

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Bayah Natural Zeolites to Upgrade the Quality of Bio Crude Oil from Empty Fruit Bunch Pyrolysis

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Highlights:

- Pyrolysis temperature influence characterization of products
- Bio crude oil can be upgraded by using zeolite as catalyst
- High crystallinity was observed in the base modified natural zeolites
- Improvement of textural properties was obtained after base treatment

Abstract. Currently, the fuel oil for transportation and industry is produced mostly from fossil fuels. Because fossil fuels are a limited resource, biomass could be an alternative resource. Empty fruit bunch (EFB) is biomass waste from fresh fruit bunch processing in palm oil mills. EFB can be converted to bio-crude oil through pyrolysis at temperatures from 400 to 600 °C. The quality of bio-crude oil must be upgraded due to its high oxygen content. Esterification of bio-crude oil potentially improves the quality of bio-crude oil by using zeolite as catalyst. The purpose of this research was to investigate the properties of Bayah natural zeolites for upgrading the quality of bio-crude oil from EFB pyrolysis. Bayah natural zeolite was activated using various NaOH concentrations. Characterization of the natural zeolites was performed by using X-ray diffraction (XRD), scanning electron microscope-energy dispersive X-ray (SEM-EDX), and nitrogen physisorption. The optimum ratio of Si/Al of the modified Bayah natural zeolites was 3.91. The surface area of the parent was initially 19 m²/g and increased significantly to 150 m²/g after treatment with 0.4 M NaOH solution. The application of the activated zeolites for bio-crude oil esterification successfully decreased the total acid number.

Keywords: *bio crude oil; catalytic esterification; EFB; natural zeolites; total acid numbers.*

1 Introduction

During the last 50 years, petroleum has been the main energy source for households, transportation, and industry. Petroleum is a fossil fuel that is a limited resource so that alternative energy resources are needed for a better future. The alternative resources must have a large supply and less impact on the environment. An example is biomass. Indonesia has biomass resources such as empty fruit bunch (EFB), rice husks, and other resources from agriculture and plantation activity. Biomass can be converted to fuel through technologies such as pyrolysis, gasification, and combustion.

Pyrolysis is the process of thermal decomposition of biomass reacting without or with little oxygen at temperatures from 300 to 650 °C [1]. The main products of pyrolysis are char, bio-oil, and gas. Bio-crude oil resulting from pyrolysis is composed of a mixture of organic vapors such as acids, alcohols, aldehydes, ethers, ketones, phenols, and hydrocarbons [2,3]. Slow pyrolysis occurs at temperatures around 400 to 500 °C with a relatively long residence time by utilizing high volatile matter from the material. In slow pyrolysis with temperatures around 450 °C more bio-oil can be produced compared to char and gas [4]. Gas contained in volatile matter produces uncondensed gas and condensed gas. Bio-oil comes from condensation of gas by a condenser.

The results of pyrolysis in the form of bio-crude oil have not yet reached the required biodiesel standard because crude bio-oil has high viscosity and moisture, a low heating value, a high corrosion rate, and low stability [5]. The bio-oil produced does not meet the standards of motor vehicle fuel [6]. This requires the separation of the bio-oil and the mixture that is not needed in order to approach the standard of physical properties for fuel. Chemical components of bio-oil can be separated by solvent extraction, column chromatography and distillation methods such as steam reforming, hydrodeoxygenation, and catalytic cracking. These methods not only require a large amount of energy but also a complex method of operation.

The catalytic esterification method reduces the acid content, water content, and increases the stability of the bio-oil by adding alcohol. The catalytic esterification method can improve the quality of bio-oil by reducing the water content and the acid number [6]. In addition, the heating value will double and the kinematic viscosity will decrease. [7]. Bio-oil esterification utilizes a solid acid catalyst that can neutralize organic acids and generates better stability. The esterification process removes water from the oil using the Dean-Stark trap during the process, thus producing water [6]. The reaction process can take place at room temperature with a short time, producing a high-quality product in the process of separating the reaction results of bio-crude oil [8].

Catalytic esterification using various kinds of zeolite is carried out to obtain high-quality bio-oil products. The catalytic esterification process in bio-oil with zeolite at a temperature of around 473 K is strongly influenced by the Si/Al ratio and the micro pore size of the zeolite to convert the phenolic alcohol according to [9]. Another study investigated the process of upgrading bio-oil from pyrolysis of oil palm empty fruit bunches to produce fuel using H-ZSM-5. The gasoline yield could reach up to 91.67% [10]. Then, three types of zeolite were used to improve the quality of the bio-oil, i.e. H-Y, H-ZSM-5, and H-Beta. The results showed that each zeolite has the characteristics of the product that is produced; the HY type zeolite produced more liquid fuel and less gas, but coke was formed. HZM-5 is more suitable for producing light olefins and H-Beta leads to intermediate products [11].

Synthetic zeolites are more expensive compared with natural zeolites. Indonesia is well known for its natural zeolite deposits, for example in Tasikmalaya, Klaten, Sukabumi, and Bayah. The total deposit of Bayah natural zeolites is about 68.5-82 million tons [12]. Several investigations of natural zeolites as catalysts have been conducted for various applications, i.e. glycerol carbonate synthesis [13] and ketalization [14]. Bayah natural zeolites can be optimized, including their potential as catalysts, in the process of upgrading bio-oil. For application in upgrading bio-oil, the Bayah zeolite must be activated first to improve its catalytic properties, such as Si/Al ratio, surface area, and pore size.

The aim of the present investigation was to study the effect of base treatment on the properties of Bayah natural zeolites and their application for upgrading bio-crude oil. The parent and activated natural zeolite samples were examined for the esterification process of bio-crude oil from the pyrolysis of oil palm empty fruit bunches.

2 Materials and Methods

2.1 Materials

In this research, bio-crude oil was produced from pyrolysis of oil palm empty fruit bunches at a temperature of 500 °C with holding time around 5 minutes. Bayah natural zeolites were activated using NaOH at various concentrations. Butanol (Merck 1019901000, ≥99.5%) was used as solvent in the catalytic esterification process. Furthermore, NH₄NO₃ was used during the ion-exchange procedure to obtain the NH₄⁺ zeolites.

2.2 Methods

2.2.1 Zeolites Catalyst Preparation

The natural zeolites were obtained from the zeolite mining area in Bayah, Banten Province. The Bayah zeolites were modified by using NaOH solution in a reflux apparatus. 10 grams of Bayah zeolites were added into the NaOH solution. In order to study the effect of NaOH concentration, the solution was varied at 0.2 M, 0.4 M, 0.6 M, 0.8 M, and 1 M. The mixture of zeolites and NaOH solution was heated for 2 hours at 70 °C. After that, the remaining solution was separated using a centrifuge. The modified zeolites were kept at room temperature for 24 h followed by drying for 6 h at 110 °C.

The ion exchange procedure was performed by using NH_4NO_3 solution. First, the zeolite was dissolved in 2 M NH_4NO_3 solution and heated at 85 °C for 2 hours under reflux. Then, the zeolite was separated with a solution using a centrifuge. The zeolite was dried at room temperature for 24 hours followed by drying in an oven for 6 hours at 110 °C.

The last step was calcination. The zeolite was calcined to evaporate the crystalline water content as well as the organic content in the zeolite. The calcination process was carried out for 6 hours at 550 °C to open the zeolite pores and to convert the NH_4^+ -zeolites to H^+ -zeolites.

2.2.2 Characterization

The activated natural zeolite was analyzed using XRD to determine the crystallinity of the samples. The type of XRD used was a Shimadzu X-ray diffractometer. The degree of relative crystallinity was calculated using the method described in our previous work [15]. The morphology and elemental compositions were studied by using SEM-EDX. Nitrogen physisorption was performed to determine the textural properties of the zeolites. The Brunauer-Emmett-Teller (BET) model was applied to determine the surface area of the natural zeolites.

2.2.3 Upgrading the Bio-oil

The activated zeolites were introduced into a bio-oil and butanol solution in a neck flask fitted to a Dean-Stark apparatus. Bio-oil was obtained via pyrolysis of empty fruit bunch in our pilot-scale plant reactor. The ratio of bio-oil and butanol was 1:3. Then the mixture was stirred vigorously for 6 hours at a temperature of 100-120 °C. The upgraded bio-oil products were analyzed for their acid number and viscosity. The acid numbers were determined by acid-base titration method

using KOH solution while the viscosity was analyzed using a Rotary Viscometer NDJ-55 (ASTM D-4402).

3 Results and Discussions

3.1 Activated Bayah Zeolite

The type of Bayah natural zeolite was determined by XRD. The crystallinity of the natural zeolites before and after activation was investigated by XRD intensity comparison. Figure 1 showed that the diffractogram pattern of the parent natural zeolite XRD was close to that of standard mordenite diffraction types [16]. Diffraction patterns of impurity phases such as quartz and clinoptilolite were also observed.

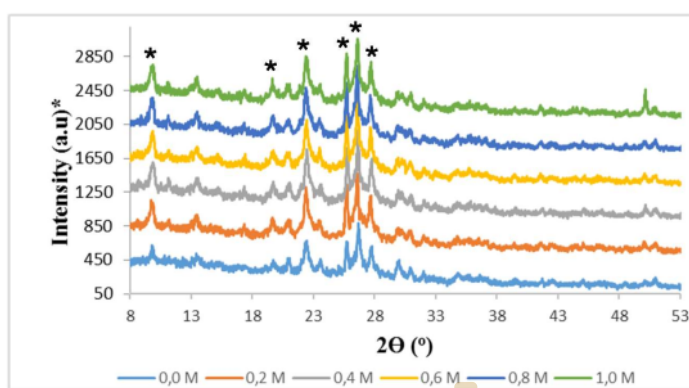


Figure 1 XRD patterns of Bayah zeolites activated at different concentrations of NaOH (0.0 M, 0.2 M, 0.4 M, 0.6 M, 0.8 M and 1.0 M).

There was a significant difference in the peak intensity of the XRD patterns for the conditions before and after activation (marked with a star symbol in Figure 1). Particles can block the active side of zeolites, especially before activation. It can be seen that the crystallization level was low before activation (Figure 2). The crystallinity was increased after treatment with 0.2 M to 1.0 M NaOH. The intensity peak of XRD was higher with increasing NaOH concentration. The highest percentage of crystallinity was obtained after the treatment of the zeolite with 0.4 M NaOH. The amorphous phase impurities were most likely partially dissolved in the NaOH solution, which led to an increase of the zeolites' crystallinity. However, a high concentration of NaOH solution (0.8 M and 1.0 M) led to a decrease in peak intensity, indicated by a decrease in the value of the percent crystallinity (Figure 2). This is most likely because of the high

concentration of NaOH damaging the crystal structure. The OH-attack on silanol groups as well as the hydrolysis of Si-O-Al bonds and Si-O-Si are called desilication [17].

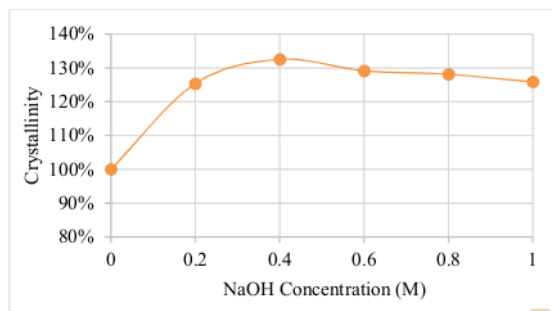


Figure 2 Average crystallinity for Bayah zeolite activated at different concentrations of NaOH (0 M, 0.1 M, 0.2 M, 0.4 M, 0.6 M, 0.8 M and 1.0 M).

The results of the SEM analysis showed that the zeolites without NaOH activation had heterogeneous, irregular shapes and mostly there were impurities on the crystal surface (Figure 3(a)-(b)). Then the crystal structure began to appear uniform and the size became smaller but there were still impurities on the surface and also the pores became wider (Figure 3(c)-(d)). Activated zeolite with 0.4 M NaOH concentration had more pores scattered on the surface than that with lower NaOH concentrations. In addition, the crystal structure was also more uniform (Figure 3(e)-(f)). At concentrations of NaOH higher than 0.4 M, it appears that the surface tended to be cleaner, but the pores began to become invisible compared to the 0.4 M NaOH concentration (Figure 4(a)-(b)). This indicates that crystallization was taking place faster because the zeolite crystal size changes become smaller in line with the addition of NaOH concentration [15]. High NaOH concentrations damage the crystal structures, characterized by the discovery of rectangular crystal shapes (Figure 4(c)-(f)). The loss of crystallinity decreases the adsorption capacity or the active sites of the zeolite.

Energy dispersive X-ray was performed to analyze the composition of the zeolites, especially SiO₂ and Al₂O₃, to find the Si/Al ratio. Activation of zeolites using NaOH causes a decrease in the Si/Al ratio due to the dissolution of silicate compounds, causing changes in the zeolite structure. The Si and Al ratios of the zeolites illustrate the function of the cation exchange capacity. A decrease in the Si/Al ratio indicates desilication or release of active sites of Si-OH and Si-O-Si due to OH-group attacks. The smallest ratio reduction was obtained at concentrations of 0.4 M and 0.6 M NaOH, with values of 3.91 and 3.83 (Table

1). A smaller Si/Al ratio means that the Al fraction in the zeolite is higher, so it can be used as an acid catalyst because of the Al Bronsted acid site [19]. The smallest Si/Al ratio was observed in the zeolite sample after treatment with 0.6 M NaOH.

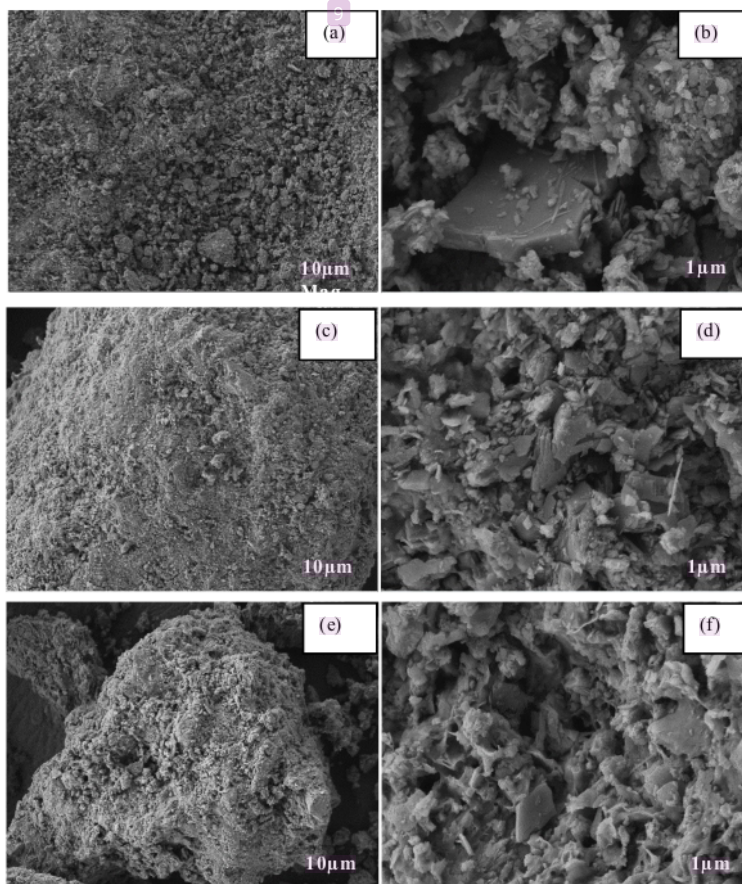


Figure 3 SEM Bayah zeolite activated with magnification 1.000x (left) and 10.000x (right) at NaOH concentrations (a,b) 0 M; (c,d) 0,2 M; (e,f) 0,4 M.

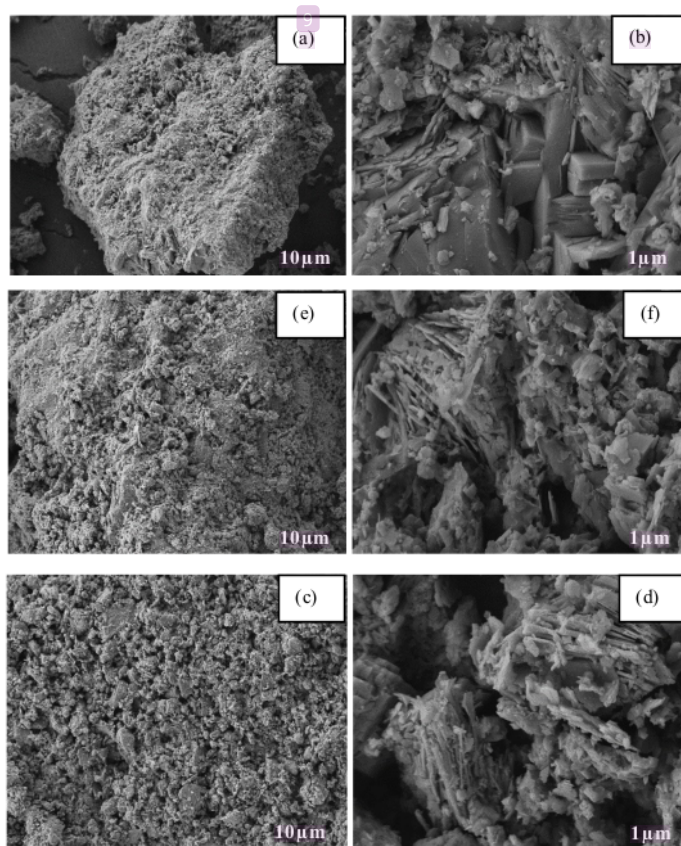


Figure 4 SEM Bayah zeolite activated with magnification 1.000x (left) and 10.000x (right) at NaOH concentrations (a,b) 0.6 M; (c,d) 0.8 M; (e,f) 1.0 M.

Table 1 Si/Al ratio for Bayah natural zeolite activated in different NaOH concentrations.

NaOH Concentration	Si/Al
Parent	4.75
0.2 M	4.68
0.4 M	3.91
0.6 M	3.83
0.8 M	4.51
1.0 M	4.19

The zeolite surface area was determined by using the Brunauer-Emmett-Teller (BET) model, as shown in Table 2. This method was used to determine the surface area of the zeolite using N₂ gas adsorption. The NaOH treatment successfully increased the surface area of the zeolites because defective silanol and amorphous silica were extracted from zeolites. During treatment with NaOH, the hydroxide anion (OH⁻) attacks the defective silanol and stabilizes the silicate anion. In this study, the optimum surface area occurred in the zeolites activated at an NaOH concentration of 0.4 M with a surface area of 150 m²/g and a mesoporous surface area of 28 m²/g. The higher NaOH concentration at concentrations of 0.6 M to 1.0 M reduced the surface area to 19 m²/g with a mesoporous surface area of 14 m²/g. This is most likely because the micropores collapsed into mesopores, which results in a decrease of surface area [17]. High NaOH concentrations can cause high negatively charged AlO⁴ tetrahedra content, which will inhibit the hydrolysis of Si-O-Si at low alkaline concentrations [20].

Table 2 Bayah natural zeolite activated surface area for various NaOH concentrations.

Sample	S _{BET} (m ² /g)	S _{mikro} (m ² /g)	S _{meso} (m ² /g)
Parent	19	6	23
0,2 M	129	108	21
0,4 M	150	122	28
0,6 M	117	97	20
0,8 M	18	6	12
1,0 M	19	5	14

The nitrogen adsorption isotherm of the parent natural Bayah zeolites showed low nitrogen content adsorbed in the low relative pressure (P/P₀) region, which indicates that the micropores were low (Figure 5). Hysteresis was observed in the higher region of P/P₀. This most likely occurred because the mesopores were high in the parent. The increased N₂ adsorption at low relative pressure was due to the gas molecules adsorption interacting with energized regions on the zeolite surface (Figure 5). The smaller the pore size, the higher the potential for adsorption, which causes an increase in adsorption energy and adsorption can occur at relatively low pressures. In this adsorption, the nitrogen gas forms a monolayer. This type of isotherms is a type I isotherm, which is a type of adsorption that occurs in micropore solids [21].

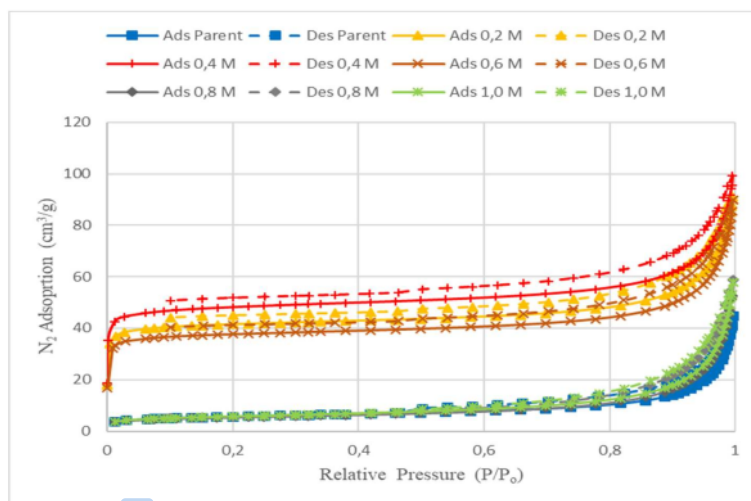


Figure 5 Isotherm adsorption – desorption of natural bayah zeolite before and after activation at different NaOH concentrations.

In natural Bayah zeolites that have been activated using NaOH and NH_4NO_3 , the isotherm is a combination between type I and IV (Figure 5). This type is a characteristic of gas adsorption on solid mesopore materials with a clearly visible hysteresis loop at relative pressure close to one. In zeolites with the same surface pressure, zeolite after desorption still has more nitrogen gas left than after adsorption. This happens because of capillary condensation caused by the presence of mesopores.

3.2 Upgrading Bio-crude Oil

The total acid number is an important indicator of the quality of bio-crude oil pyrolysis. Acid in bio-oil can be corrosive so this property should be eliminated. With a reduced acid content in bio-oil, the handling of the bio-oil becomes easier.

The total acid number of the bio-crude oil (CBO) of empty fruit bunch pyrolysis was 215.69 (Figure 6). After the esterification process, the total acid number of the bio-oil achieved the lowest value of 63.42 at an NaOH concentration of 0.4 M. A further increase in NaOH concentration (0.6 M, 0.8 M, and 1 M) increased the acid number. The total amount of acid in the esterification is caused by the zeolite surface area and the Si/Al ratio.

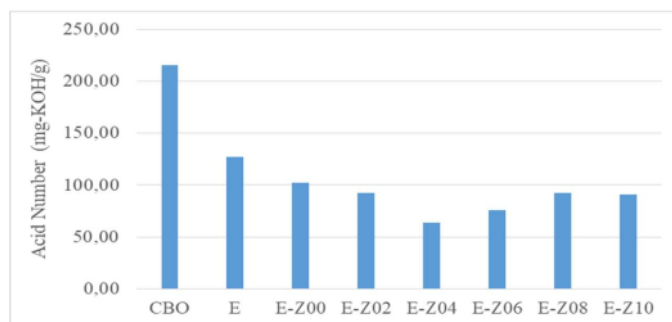


Figure 6 Total acid number of bio-oil for before and after Bayah zeolite activation at different NaOH concentrations.

The total acid number after esterification decreased with a larger surface area of the natural zeolite and a smaller Si/Al ratio led to a lower acid number in the bio-crude oil. It is most likely that the organic acids and carboxylates contained in the bio-crude oil were converted into esters [6-7,22-24]. The lowest total acid number occurred in the natural zeolite activated with 0.4 M NaOH with an Si/Al ratio of 3.91 and a zeolite surface area of 150 m²/g. Low Si/Al ratio NaOH has high Al content compared to silica. A high Al content in natural zeolites is acidic because Al is a Bronsted acid site. These acidic properties have a large influence on the bio-oil upgrading reaction [25,26]. Moreover, the surface area also plays an important role in the esterification process. The effect of surface area is also important in the isomerization reaction [27]. A higher surface area of the zeolite, organic acid, or carboxylate in bio-oil pyrolysis promote contact with butanol in the acidic part of natural zeolite. The esterification reaction rate will be higher and more esters will be formed.

Viscosity testing was used to determine the effect of the esterification process on the bio-oil production by EFB pyrolysis as well as the effect of the addition of activated catalyst types on the level of viscosity of fuel oil as gasoline (1.17 cSt). The viscosity of bio-crude oil has a high value of 243.89 cSt. The value discrepancy with the gasoline standard is large (Figure 7). Then, the bio-oil was upgraded without catalyst (sample E) with a kinematic viscosity value of 51.84 cSt. The addition of butanol solvent to bio-oil can cause the value of viscosity to decrease to 7.54 cSt at an NaOH concentration of 0.6 M [7,28]. The addition of zeolite to the esterification process decreases the viscosity because the heavy components in the bio-oil are reduced in the process of esterification [29].

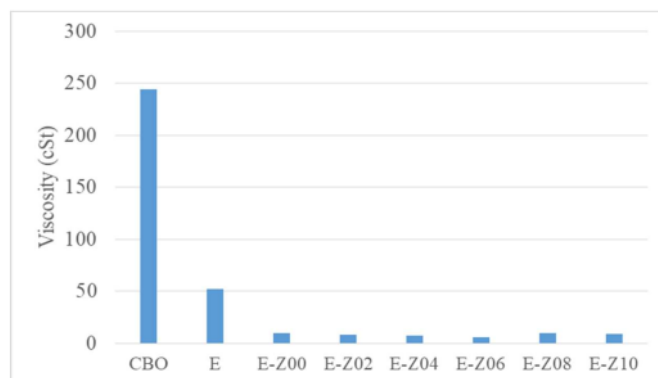


Figure 7 Viscosity of bio-oil before and after esterification.

4 Conclusions

The natural zeolite used in the esterification process of crude bio-oil was a mordenite-dominant type. Activation of natural zeolite Bayah with alkaline NaOH was carried out successfully. The optimum concentration of NaOH 0.4 M was characterized by an increase in crystallinity up to 32.51%, a ratio of Si/Al up to 3.98, and the largest surface area value was 150 m²/gram with a pore distribution in the mesoporous region. The upgrading of bio-oil with optimum conditions of 63.42 mg-KOH/gram acid number and 7.54 cSt kinematic viscosity was obtained with 0.4 M NaOH activated zeolites. Upgrading the bio-crude oil quality from empty fruit bunch pyrolysis by Bayah zeolite did not attain the gasoline standard, but the Bayah zeolite can be used for pre-treatment of bio-crude oil to decrease the total acid number and viscosity.

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