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Synthesis of Hematite-Zeolite Nanocomposites and Its Application as Catalyst in Aquathermolysis Reaction in Intermediate Crude Oil

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Abstracts

Non-conventional crude oil has 70% of total heavy crude oil reserves and potentially as an energy source. The enhancement of non-conventional crude oil production can be done by utilizing the Enhanced Oil Recovery (EOR) technique with steamflood. The nanocomposite of Activated Hematite-Zeolite has the best properties as a catalyst to provide aquathermolysis on crude oil than other catalysts in this study. These materials were successfully synthesized by using the microwave-assisted co-precipitation method. The XRD pattern represents mixing both hematite and zeolite in mordenite structure at 2θ equal 6.57^{o}; 9.77^{o}; 19.65^{o}; 22.36^{o}; 25.72^{o}; 26.36^{o} and at 30.1^{o}; 35.6^{o}; 40.9^{o}, respectively. A reduction in a viscosity of crude oil occured after the aquathermolysis test was run by nanocomposites about 30.03% and simultaneously enhance the ratio of C-H saturated. Hence, it had improved crude oil quality with larger molecules in crude oil divided into small molecules due to breaking C-C bonds.

Keywords: Nanocomposites, EOR, viscosity, aquathermolysis, hematite, zeolite

Introduction

Based on International Energy Agency data, energy consumption will increase by 25% in 2040 [1]. From all energy sources, about 81% of energy was used from crude oil [2]. This is because the energy density of crude oil is $45x10^9$ J/m^3 and higher than the other energy sources, such as sunlight, geothermal, and wind [3]. However, the conventional type of crude oil has reduced availability in nature, therefore one of the efforts to solve this that utilizes the non-conventional type of crude oil was to have 70% of total crude oil reserves [4]. Enhanced Oil Recovery (EOR) is one of the technologies that can be useful to work up non-conventional crude oil production [5].

In EOR, the reduction of crude oil's viscosity can be done through three methods, called chemical injection, gas injection, and steamflood [6,7]. One of the steamflood mechanisms is aquathermolysis, which is the most widely used method in the whole wide world, especially in the USA. This method would be conducted by injecting the steam into the reservoir to decrease the viscosity of crude oil with a bond dissociation reaction between the carbon atoms [8]. Unfortunately, after heat loss, the conventional crude oil can repolymerization into heavy crude oil again, as same as previous. Another problem of aquathermolysis is come from its process. It will take a long time so that can interfere the production way in a large scale. Clark states those liabilities can be handled by the addition of a catalyst in the aquathermolysis process. Thus, the time of the reaction can be shortened and the repolymerization event can be prevented caused by the impurity of crude oil like sulphur cannot be rebound with the crude oil chains [9].

Muraza, et al in 2015 shows nickel oleic has dropped viscosity of heavy crude oil in Niujuan

Field China about 64% [10]. Aromatic sulfonic molybdenum was researched by Yuanqing Wing, et al in 2010 successfully to reduce heavy crude oil by around 99.2% [11]. Xu, et al in 2012, applied aromatic sulfonic copper and aromatic sulfonic ferro to get the percentage of reduced heavy crude oil above 88% [12]. These materials are challenging in the synthesis and post-treatment process. Due to that fact, nanoparticles have researched by Ali Esfandyari B et al in 2014, shows the viscosity of heavy crude oil can be decreased by 32%, 24%, and 8% using the nanofluids of Al_2O_3, TiO_2 and SiO_2, respectively [13]. Another study conducted by S. Fatimah, et al in 2015 represents reduction of crude oil approximately 62% by hematite nanoparticles [14]. Based on these facts, hematite nanoparticles are the promising catalyst in the aquathermolysis process because they have a simple synthetic process and the low cost. However, hematite is very toxic for the environment, so it should be composited with other materials like zeolite.

Zeolite has Bronsted acid sites which can be utilized as catalyst in EOR. Those sites will be a proton source (H^+) in aquathermolysis reaction. H^+ ion is used to break a C-S bonding [10]. The C-H formation affected the improvement of crude oil quality. Therefore, the improvement of hydrogen in zeolite was needed and a cation exchange method can be used to do this. In natural zeolite, the cations frequently can be found are Na^+, Ca^{2+}, dan K^+ which are replacable by NH_4^+ as hydrogen source [15]. In addition, zeolite has a large surface area to allow the fast reaction of aquathermolyisis [10]. All the advantages of zeolite mentioned before, can make it as a good, promising catalyst combined with hematite in nanocomposites form.

There are many ways to synthesize nanocomposites as well as hydrothermal, co-precipitation, and sol-gel methods. One of all those methods, co-precipitation is the top method due to its benefits, such as simple, rapid process, and the high yield percentage. Hematite formation starts at 400 °C and the perfect formation occurs at 600 °C for 60 minutes. Accordingly, the microwave was used in these synthetic processes plays important roles, such as for reducing the duration of synthetic process and decreasing the external energy needs. Moreover, the uniform particle size would be obtained by utilizing the microwave [16]. Nanocomposite of zeolite-hematite was tasted in intermediate crude oil to get an insight of the influence in viscosity properties and quality of crude oil.

Material and Methods

Synthesis Activated Zeolite Nanoparticle

Top-down processing was applied for synthesis of this material. Zeolite from Bayah, Banten province was grinded by a ball mill for 8 hours with ball mass three times higher than zeolite mass (1:3). The small zeolite was annealed in the furnace at 400 °C for 60 minutes. Furthermore, the sample was dissolved by NH_4Cl (technical grade) with comparison 1:1 and 100 mL of distilled water in the condenser and heated for 6 hours at 90 °C. Zeolite has substituted cation by NH_4^+ was dried again in the furnace at 400 °C for 60 minutes. The activated zeolites were characterized by X-Ray Diffraction (BTX III Benchtop XRD Analyzer), Fourier Transform Infrared (Nicolet™ iSTM 5 FTIR Spectrometer).

Synthesis Nanocomposites of Hematite-Zeolite

About 0.56 g of the activated zeolite was dissolved into 32 mL distilled water and added 1.9 g $FeCl_3.6H_2O$ (Merck™). Solution was stirred with 600 rpm at ambient temperature. NaOH (technical grade) solution with concentration 8842 ppm was dropped slowly to form the brownish red color solution. However, the sample was heated by microwave for 5 minutes at medium intensity until precipitation took place. Precipitation of composites were washed and furnaced at 400 °C for 60 minutes. The nanocomposites of hematite-zeolite were characterized by X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR), and Scanning Electron Microscopy (SEM).

Aquathermolysis Test

The crude oil sample used in this study was obtained from Lirik Field, Riau province, with API gravity 33.3, specific gravity of 0.8585 (at 60˚F), pour point of 42.5˚C, wax content of 13.4%, and sulphur content of 0.079%. Further, Nanocomposites as catalysts were dissolved in distilled water (0.3 % in mass) and dissolved into intermediate crude oil as in prior research by Ferry Isakandar, et al., [17]. The mix solution was heated in the oven for 6 hours at 200 °C. The crude oil was tested by viscometer brookfield with 100 rpm and size is S62 at 42 °C. Moreover, the crude oil results from the aquathermolysis process was characterized by FTIR.

Results and Discussion

Activated Zeolite Nanoparticle

In Figure 1, the peak at 1400 cm^{-1} of wavenumber, indicates that zeolite was already activated due to the cation exchange by NH_4^+ [18]. This is because zeolite has a Si-O-Na functional group at 667 cm^{-1} while the Na^+ ion is a target for NH_4^+ in cation exchange and the Si-O-Al functional group at 1010 cm^{-1} acts as Bronsted acid sites [19]. Therefore, activated zeolite has intensity spectra of Si-O-Na decrease from raw zeolite due to ion NH_4^+ having replaced ion Na^+ in the cation exchange process. Furthermore, water contained in raw zeolite was declined during the activation process as seen by the reduction of O-H intensity at 3400 cm^{-1} [18].

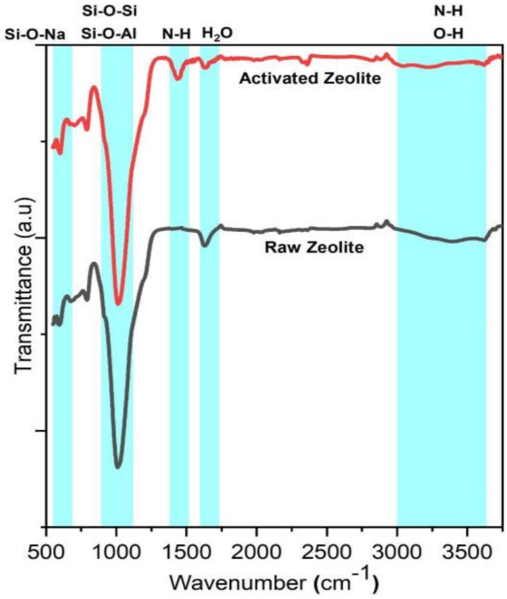


Figure 1. FTIR pattern of synthesis activated zeolite nanoparticles.

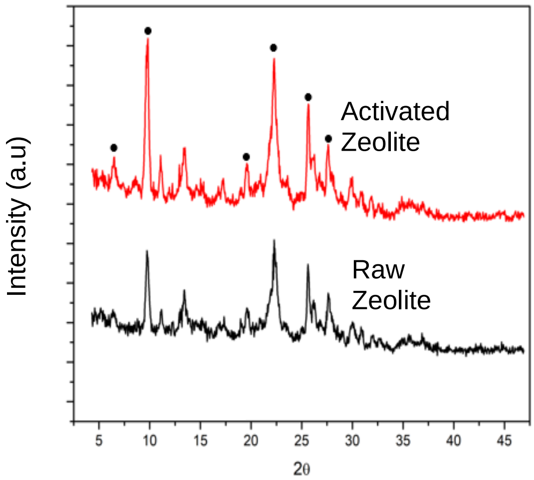


Figure 2. XRD pattern of synthesis activated zeolite nanoparticles.

XRD results as shown in Figure 2, shows the peaks appear at 2θ equal 6.57°; 9.77°; 19.65°; 22.36°; 25.72° and 26.36° by zeolite after the milling process and activated zeolite. All peaks are associated with mordenite zeolite structure and are found in the natural zeolite. The peaks between zeolite after the milling process and activated zeolite represent a steady trend due to the cation exchange reaction not changing in their structures.

Nanocomposites of Hematite-Zeolite

Figure 3 shows the XRD pattern of synthesized hematite-zeolite. It seems there are three new peaks appear at 2θ equal 30.1°; 35.6°; and 40.9° which correspond to the hematite structure [20]. XRD results also observed that the addition of hematite has no effect on the mordenite crystal structure. So, we can conclude that the microwave-assisted co-precipitation method is the exact method for nanocomposite synthesis. However, there are many undefined peaks in the XRD patterns, indicate that the crystallite phase on the hematite have not yet perfectly formed. Hence, it is still in an amorphous phase. Instead, zeolite will be impacted to highly adsorb reactant during co-precipitation process by their micropore structure.

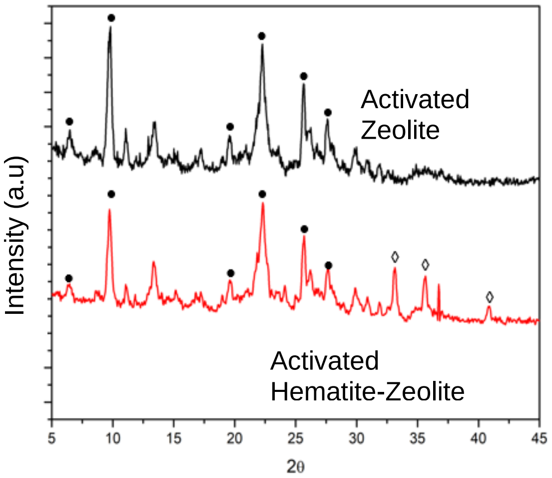


Figure 3. XRD pattern in nanocomposite of hematite-zeolite synthesis.

The FTIR spectra, as visualized in the Figure 4, shows N-H groups at wavenumber 1400 cm^{-1} are drastically declined because of a co-precipitation process that used NaOH as reactant. If analyzed by SEM as in Figure 5, zeolite has uniform pore sizes thus the ball mill process is not effective to make nanoparticles materials. The long process of synthesis will lead to the coagulation reaction among particles of zeolite. The pore size occurs in these materials as well as increases their surface area and is affected by improvement in catalytic reaction.

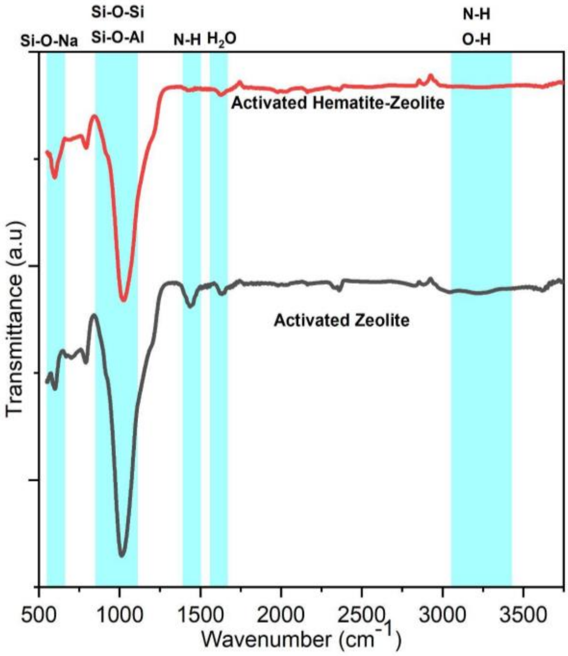


Figure 4. FTIR pattern in nanocomposite of hematite-zeolite synthesis.

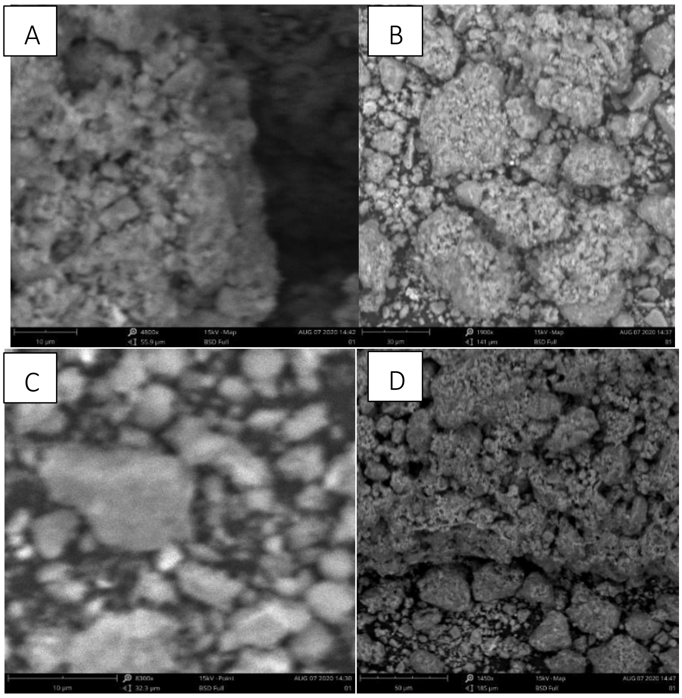


Figure 5. Zeolite surface analyzed by SEM, A and B with a magnification of 8300x, C with a magnification of 1900x, and D with a magnification of 1450x.

Aquathermolysis of Crude Oil

Table 1 shows that the greatest decrease in viscosity is catalyst activated hematite-zeolite by 30.3 % and followed by activated zeolite with 22.33 %. This represents that nanocomposites effectively merge the best properties from both zeolite and hematite. Zeolite has micropore structure and large surface area to contact with crude oil hence aquathermolysis process occurs on Bronsted acid state to donor ion H⁺. The existence of hydrogen had been prevented from repolymerization reaction as in equation 1 and 2. Besides, the hematite had been affected in the catalytic process due to their conductive characteristics thus heat would spread evenly on crude oil. The heat is used as energy to break atomic bonds.

$$RCH_2CH_2\circ + H^+ \rightarrow RCH_2CH_3 \quad (1)$$

$$RCH_2CH_2\circ + RCH_2CH_2\circ \rightarrow RCH_2CH_2CH_2CH_2R \quad (2)$$

Table 1. Effect of aquathermolysis process in viscosity of crude oil

Variation	Viscosity	Percentage Drop
Crude Oil	1,9686 P	0%
Aquathermolysis without catalyst	1,7223 P	12,51%
Aquathermolysis + Activated Zeolite	1,5291 P	22,33%
Aquathermolysis + Activated Hematite-Zeolite	1,3774 P	30,03%

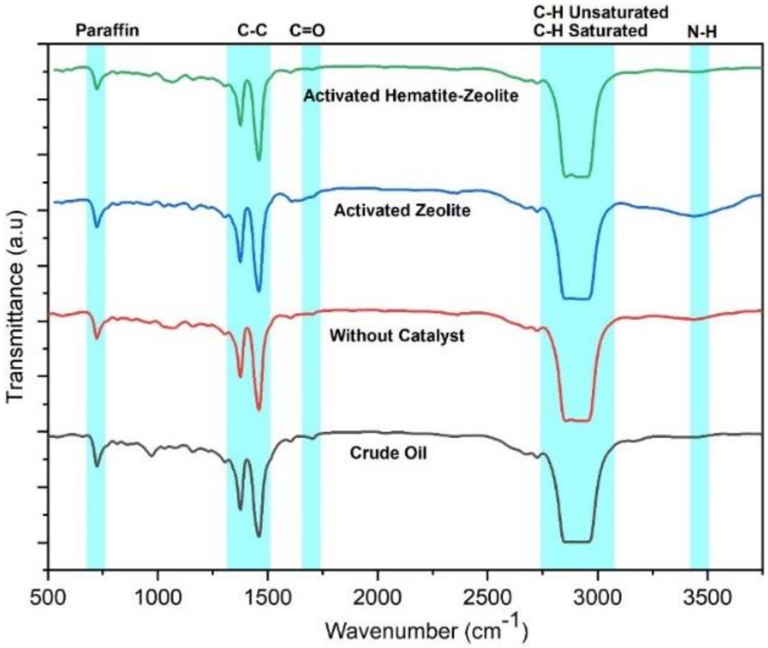


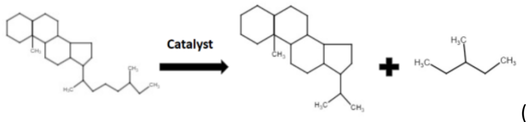
Figure 6. Aquathermolysis results with variation conditions.

The FTIR results in Figure 6, presents the functional groups of C-H saturated at 2800-2950 cm^{-1} and C-C stretch at 1350-1480 cm^{-1}. Furthermore, the N-H, C-H unsaturated, and C=O functional groups are also presence at wavenumber of 3350-3500 cm^{-1}, 3000-3050 cm^{-1} and 1680-1715 cm^{-1} respectively. It also can be seen the paraffin functional group at 730-750 cm^{-1}. All those functional groups have high absorption intensity. Hence, it can be predicted that not only paraffin contained in this hydrocarbon but also have a few of olefins [21]. From all of these characteristics, the crude oil is non-conventional type and to prove the aquathermolysis process is a success, the ratio comparison of functional groups in crude oil should be done.

Table 2 illustrates an increase of crude oil quality is found in aquathermolysis with activated hematite-zeolite as a catalyst. The improvement of C-H ratio proved that an aquathermolysis reaction occurs to cut C-C bonds in big molecules to C-H bonds as small or derivative molecules (equation 3) [22]. Briefly, the nanocomposites were managed in combination between hematite and zeolite thus the ratio C-H saturated is bigger than raw paraffin or crude oil.

Table 2. Ratio comparison of C-H saturated in aquathermolysis process

Variation	C-H (Saturated)/Paraffin
Crude Oil	3,1592
Aquathermolysis without catalyst	3,8913
Aquathermolysis + Activated Zeolite	2,8227
Aquathermolysis + Activated Hematite-Zeolite	4,7760



(3)

Conclusion

Nanocomposites of activated hematite-zeolite succeed to synthesis with 2θ spectrum at 6.57°; 9.77°; 19.65 °; 22.36°; 25.72° and 26.36° as zeolite with mordenite structure and at 30. °; 35.6° and 40.9° as hematite. In this research, these materials had dropped in the viscosity of crude oil by around 30% and were better than other catalysts or without catalyst. Therefore, activated hematite-zeolite could improve the crude oil quality with split paraffin into their derivative molecules.

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