The Properties of Microcellulose as Enhanced Oil Recovery Agent

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Abstract. The important factors in petroleum production are the nature of the reservoir rock surface and the interaction between oil and water in the reservoir. Both of these factors can affect microscopic efficiency in increasing oil recovery. In this study, microcellulose (MCC) was tested as a potential agent to increase oil recovery. MCC is used to decrease interfacial tension between oil and water. MCC is a cellulose with particle size ranging from 30 nm to 20μm. This study aims to determine the effect of MCC on interfacial tension between oil and water. MCC is obtained through the process of cellulose hydrolysis isolated from corncob. The results of hydrolysis reaction were characterized using FTIR, Scanning Electron Microscope (SEM). The particle size was determined using Particle Size Analyzer, and interfacial tension measurements using du Nouy tensiometer. The results of the study obtained MCC as a result of hydrolysis reaction with an average diameter particle size of 2.9 μm and 14 μm. The experimental results show that the addition of MCC with particle size 14 μm can reduce interfacial tension between oil and water from 11.3 mN/m to 6.85 mN/m, and the addition of MCC with particle size 2.9 μm can increase interfacial tension between oil and water from 11.3 mN/m to 21.74 mN/m. According to these data MCC has the potential to be used as an economic and environmentally friendly oil recovery agent.

1. Introduction
Petroleum production is currently only able to produce about 33% of petroleum from the total oil in the reservoir [1]. Thus, to maximize the production of oil, enhanced oil recovery (EOR) have to be implemented in the reservoir to maximize the oil production. EOR is a method used to increase oil recovery by adding certain materials from outside the reservoir. One method that is widely developed as an EOR agent is chemical injection [2]. Chemical injection is one of the EOR techniques by injecting chemicals in the form of alkaline, surfactants or polymer materials into the reservoir [3]. As an EOR agent, the chemicals injected into the reservoir have several functions such as increasing the oil mobility ratio, reducing the interfacial tension of oil and water, and also changing the surface properties of reservoir. Nowadays many nano/microfluid technologies are being developed as EOR agents [4]. Nano/microfluid are solid particles dispersed in liquid (suspension) with nano or micro particle size. Nano/microfluid properties that are able to be dispersed in water have been widely used for various applications, one of them as an emulsifier which can play a role in reducing the interfacial tension between two substances that do not mix with each other like oil and water [5]. Nano/microfluid have several advantages including having a high surface area, good thermal resistance, and good chemical reactivity [2]. The use of nano/microfluid as an EOR agent has been widely reported in previous years. Previous research was conducted by Jang in 2018 [6] using SiO₂ nanoparticles to change the wettability of reservoir rocks, this study shows that SiO₂ nanoparticles can
change the wettability of carbonate rocks by 63.7% to be more hydrophilic. The research was conducted by de Lara in 2015 [7] uses cyclodextrins as EOR agents that can change the surface properties of reservoir rocks to become more hydrophilic in rock conditions with low salinity. However, as an EOR agent the chemicals used must be cheaper, easier to obtain, environmentally friendly, and have multifunction in their use. One of the chemicals that is abundant in nature, environmentally friendly, and easily obtainable is cellulose. Cellulose is a type of polysaccharide that can be found in the trunk of a tree, fruit, grass, and other sources. Cellulose has good thermal properties. In general, cellulose can be degraded at temperatures around 200 °C [8].

In this study cellulose from corn cob was used as the main source to increase oil recovery. The use of corn cob as the basic material for the manufacture of EOR agents is motivated by the use of corn cob which is still very little. While each year the amount of waste is increasing. The increase in the amount of corn cob is due to corn production in Indonesia which always increases every year [9]. Based on statistical data from the Organization for Economics Cooperation and Development (OECD) in 2017 corn production in Indonesia amounted to 20.075 million tons and an increase in 2018 to 20.43 million tons. With this utilization, the agro-industrial waste has a high use value, besides the utilization of waste also makes the chemicals used become cheaper, easier to obtain, and very environmentally friendly. In this study, cellulose was obtained through isolated from corn cob and modification of the size of the cellulose to microcellulose. Microcellulose has a high thermal resistance of around 200 °C [5], and has properties such as suspensions that can be dispersed in water for a period of time with a zeta potential value of -15 mV making it possible to interact with oil and water [10], and reduces interfacial tension between oil and water. Of these properties, it is shown that microcellulose has the potential as an EOR agent.

Microcellulose obtained from cellulose hydrolysis using sulfuric acid with various concentrations and hydrolysis time. The microcellulose formed was then characterized using FTIR to determine its functional group, Scanning Electron Microscopy (SEM) to determine morphology, and Particle Size Analyzer (PSA) to determine particle size distribution. The effect of microcellulose on the interaction of oil and water is studied through interfacial tension measurements.

2. Experimental

2.1. Material
Corncob was collected from plantations located at Cicalengka, Bandung, West Java, Indonesia. Sodium hydroxide, hydrogen peroxide 35% (v/v), sulphuric acid 96 – 97% (v/v), sodium chloride 1% (w/v), calcium chloride 1% (w/v), and ethanol were supplied by Sigma Aldrich. The crude oil type heavy oil.

2.2. Methods

2.2.1. Isolation of cellulose
The chemical pre-treatments and bleaching using hydrogen peroxide were adapted from Singh et al (2017) [11]. Corncob were dried below sunlight, then they were mashed using grinding machine to become powder. The resulting powder filtered using an 80 mesh sieve. Then corncob powder is added with 2% (w/v) sodium hydroxide with a ratio of 1:10 (w /v) and refluxed at 80 °C for three hours. The mixture then filtered using a Buchner vacuum filter and rinsed using demineralized water and ethanol until the color of the solution becomes clear and neutral pH. Furthermore, the delignification process used 25% hydrogen peroxide (v/v). Corncob fibers from the reflux process were added 25% hydrogen peroxide (v/v) with a ratio of 1:20 (b / v) for six hours at 60 °C under constant mechanical stirring. The fiber then filtered using a Buchner vacuum filter and rinsed using demineralized water until the pH is neutral and the filtrate is clear. After that, the fiber was dried using a freeze dryer for 24 hours.
2.2.2. Acid hydrolysis
Cellulose hydrolysis reaction following the procedure described by Purwanti and Wulandari (2015) [12]. The isolated cellulose was reacted with sulfuric acid with various concentrations and hydrolysis time at a ratio of 1:25 (w/v) at 45 °C. The reaction was stopped by adding demineralized water ten times of initial volume. Then centrifugation at 9500 rpm for 15 minutes. The precipitate then dialyzed with the cellophane membrane for several days using deionized water and replacing the water until the neutral pH. The precipitate then sonicated for 30 minutes and dried using a freeze dryer.

2.3. Characterizations and measurements

2.3.1. Fourier transform infrared spectroscopy
Isolated cellulose and microcellulose were dried using freeze dryer, ground and pelletized using KBr. The samples were measured using FTIR (Shimadzu Prestige 21) in the range from 4000 to 500 cm⁻¹.

2.3.2. Scanning Electron Microscopy
The morphology of the microcellulose produced by freeze drying was analysed using scanning electron microscopy (JSM-6510A). Isolated and microcellulose which have been dried, were mounted on a stub of metal and coated with carbon, then observed by microscope.

2.3.3. Particle Size Analyzer
Determination of the distribution of microcellulose particle size using Particle Size Analyzer (Bechman Coulter, ITB Pharmaceutic Laboratory). Measurements were made by dissolving microcellulose into aqua dm at 25 °C, then place sample into measurement chamber and they were observed. Measurements were made in the range of 0.15 - 10000 nm.

2.3.4. The stability test
The stability of microcellulose in water is determined by observing the time needed by microcellulose to settle. Microcellulose dissolved in demineralized water, sodium chloride 1% (w/v), and calcium chloride 1% (w/v) with a ratio of 1:10 (w/v). The mixture then allowed to stand at 25 °C and measure their time to be sediment.

2.3.5. Interfacial tension measurements
The interfacial tension (IFT) between crude oil and aqueous phase was measured using du nouy ring tensiometer. Crude oil and microcellulose solution 0.1% (w/w) were mixed with a ratio of 1:1 (v/v) and heated at a temperature of 70 °C and then measured the IFT using du nouy ring tensiometer.

3. Results and discussion

3.1. Isolation of cellulose
The chemical pre-treatment using NaOH 2% (w/v) was done to remove hemicellulose in the corncob. NaOH will break the bond of cellulose and hemicellulose, so that hemicellulose will be released from the main chain and dissolve into NaOH solution. The addition of NaOH can also cause lignin degradation. Then, the addition of 25% hydrogen peroxide (v/v) or the bleaching process can remove lignin and obtained white cellulose powder. This process is called delignification. The process should carried out more than once to ensure the cellulose is free from lignin. After the delignification process, filtering and washing of cellulose powder with demineralized water is carried out to obtain high purity cellulose. Removal of lignin in corncob causes a change a color from brown to white (Fig. 1). Where the removal of hemicellulose from the main chain of cellulose causes a change in the physical form of the fiber into powder. Isolation results obtained cellulose with a yield of 6.015%.

Isolated cellulose was characterized by FTIR to show that the lignin and hemicellulose have been removed during the isolation. The FTIR spectrum of corncob, commercial cellulose, and isolated cellulose are shown in Fig. 2. Based on FTIR spectrum, corncob spectrum and isolated cellulose there
are several different peaks. At wave numbers around 1200 cm⁻¹ indicate the presence of C-O groups from lignin. In the isolated cellulose spectrum, absorbance at 1200 cm⁻¹ wave numbers appears to be reduced. This indicates a decrease in lignin levels due to the isolation process. The cellulose spectrum isolated from the cellulose was then compared to the commercial cellulose IR spectrum. The spectrum of isolated cellulose and commercial cellulose used as standards has similarities to typical peaks. At wave number 3405 cm⁻¹ which shows the presence of O-H groups on cellulose, the peak at wave number 2912 cm⁻¹ indicates the presence of C-H, the peak at wave number 1159 cm⁻¹ indicates the presence of C-C bond, and the peak at wave number is around 1100 cm⁻¹ up to 1000 cm⁻¹ which shows the presence of C-O-C ether groups (glycosidic bonds and cellulose pyranose ring bonds) [13]. The peak difference is found in the isolated cellulose spectrum which shows the peak at 1734 cm⁻¹ which is a carbonyl group (-C = O). The presence of the carbonyl group identifies the presence of lignin in the cellulose from isolation. It means lignin still remain in our cellulose.

Figure 1. Images of the corncob fiber before isolation (a), and cellulose isolation result (b)

Figure 2. FTIR spectra of isolated cellulose, commercial cellulose, and corncob powder

3.2. Microcellulose extraction and stability
The hydrolysis of cellulose is carried out at various concentrations and hydrolysis time. The hydrolysis at a concentration of sulfuric acid 25-30% (v/v) temperature of 45 °C and time of 30 minutes showed that cellulose had not reached micro particle size. This is characterized by cellulose that still settles after stopped of the reaction. At concentrations of sulfuric acid 57% (v/v) and 60% (v/v) the temperature was 45 °C and time of 30 minutes there was no precipitate after stopped of the reaction.
At a concentration of sulfuric acid 62% (v/v) and 65% (v/v) at a temperature of 45 °C and a time of 30 minutes there is a black precipitate, this indicates that cellulose has been degraded. For this reason, optimization of hydrolysis time was carried out at a concentration of sulfuric acid 57% (v/v) and 60% (v/v) to obtain microcellulose (MCC). The time optimization results are shown on Table 1. Based on Table 1 the conditions for obtaining MCC from isolated cellulose were at a temperature of 45 °C with sulfuric acid 57% (v/v) for 8 minutes (MCC A), and sulfuric acid 60% (v/v) for 5 minutes (MCC B). MCC in its dispersed form is shown in Fig 3.

| t (minutes) | [H$_2$SO$_4$] 57% (v/v) | [H$_2$SO$_4$] 60% (v/v) |
|------------|----------------------|----------------------|
| 4          | White precipitate     | White precipitate     |
| 5          | White precipitate     | Dispersed in the water|
| 8          | Dispersed in the water| There is no precipitate|
| 10         | There is no precipitate| There is no precipitate|
| 15         | There is no precipitate| There is no precipitate|
| 30         | There is no precipitate| There is no precipitate|

Figure 3. MCC A and MCC B

MCC was characterized by FTIR to showed function group of MCC. IR spectrum of MCC was then compared by isolated cellulose spectrum. Based on Fig. 4 MCC has similar pattern with isolated cellulose. This indicates that cellulose hydrolysis does not change the cellulose structure but only changes the particle size of cellulose. The hydrolysis also does not degrade cellulose until becomes monomer. The difference of the spectrum only in the peak intensity. The MCC spectrum has higher absorbance at the peak with a wave number of 3406 cm$^{-1}$ indicated O-H group. This is due to the hydrolysis that degrades cellulose into a shorter chain so that more O-H groups in MCC will be produced by hydrolysis reactions.

MCC has a colloidal properties which can be dispersed in water for a long time. In this study testing the stability of MCC to water, 1% NaCl (w/v), and CaCl$_2$ 1% (w/v) to determine the effect of salinity on MCC stability. Based on the results, MCC B were more stable than MCC A. Smaller particle sizes make MCC more easily dispersed in water for a longer time than particles that have a larger size. The addition of salt to MCC makes it unstable in water. The order of MCC stability in the solution is water $>$ NaCl 1% (w/v) $>$ CaCl$_2$ 1% (w/v). This is caused by the presence of ions will make the interaction of water with MCC less so that it will be easier to settle. Besides that the addition of salt also causes agglomeration of MCC which causes MCC to become larger so that it is difficult to be dispersed in water [2].
3.3. Particle size and morphological analysis

The particle size analysis shows that MCC A has an average diameter of 14.09 µm while MCC B has an average diameter of 2.96 µm. The results of the particle size analysis shown in Fig. 5. MCC from hydrolysis with 60% (v/v) sulfuric acid has a smaller average diameter than MCC from hydrolysis with 57% (v/v) sulfuric acid. The high acid concentration makes the amorphous cellulose chain more easily broken and to be more easily hydrolyzed to a smaller size.

The morphology of isolated cellulose and MCC A was characterized by Scanning Electron Microscopy (SEM). The results can be seen in Fig. 6. Based on the results, the morphology of cellulose has a wide fiber shape. This shows that cellulose has a large structure. SEM images show the presence of crystalline and amorphous regions in the cellulose structure. While the morphology of MCC A has a smaller fiber form than cellulose.
3.4. Interfacial tension water-oil

Interfacial tension (IFT) is an important factor to increase oil recovery. The decrease of IFT between oil and water can increase oil mobility so it can increase oil recovery. In this study, the measurement of the IFT between oil and water added with MCC was carried out. This is to determine the effect of MCC on the interaction of oil and water. The results of the study are shown in Fig. 7. The results showed that IFT between oil and water decreased from 11.3 mN/m to 6.85 mN/m due to the addition of MCC A. IFT has decreased because MCC A has many hydroxyl groups that can easily bind to water. In addition, the long MCC chain structure makes MCC have hydrophobic properties so that it can interact with oil. Both of these interactions make the intermolecular oil and water cohesion force decrease so that the oil and water IFT can be reduced. For the addition of MCC B, the IFT increased from 11.3 mN/m to 21.74 mN/m. This increase is caused by the small particle size which causes the hydrophobicity of MCC decrease because the cellulose chain becomes shorter so that the interaction of MCC with oil also decreases. In addition, the small particle size makes the MCC surface area larger so that it will be easier to interact with water. This causes the cohesion force on the water to increase so that there is an increase in the IFT of oil and water.

![Figure 7. IFT oil and water with the addition of MCC 0,1% (w/w)](image)

4. Conclusion

The cellulose hydrolysis obtained microcellulose with an average particle size of 2.9 µm and 14 µm. Microcellulose with a particle size of 14 µm can reduce the interfacial tension of oil and water by
60.62%, while microcellulose with a particle size of 2.9 µm increases the interfacial tension of oil and water by 51.97%.

5. References

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