Study on optimum parameters of high content paraffin wax microemulsion

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Abstract. As a by-product of crude oil processing, paraffin wax has high economic potential to be converted into microemulsion for various applications. Herein, paraffin wax microemulsion was prepared by emulsion inversion point (EIP) method in the presence of non-ionic surfactants. The focus of the study is to determine optimum preparation parameters for obtaining stable microemulsion. The initial results showed that paraffin wax microemulsion can be prepared when hydrophilic-lipophilic balance (HLB) value was 10 with a wax composition of 40 wt%. This HLB value is used as a reference for obtaining stable microemulsion by varying emulsification temperature and time. Emulsion stability was determined by observing phase change for 60 days, which then was quantized using particle size analyzer. The morphology of the microemulsion droplets was observed using optical microscope. The droplets showed a bright spot under polarized light owing to its solid phase in room temperature. Stable microemulsion with particle size average diameter of about 290.6 nm could be formed at emulsification temperature of 80 °C and emulsification time of 40 minutes.

1. Introduction

As by-product of crude oil processing, paraffin wax is a saturated hydrocarbon with carbon numbers range C18-C90, soluble in crude oil, but it will begin to precipitate when the oil cools to the wax appearance temperature (WAT) [1]. Generally it is used as raw materials for making candles, but it has a low economic value. To increase its economic value, the paraffin wax is converted into another product such as emulsions. Emulsions are dispersions made up of two immiscible liquid phases, called the dispersed phase that dispersed in the continuous phase, which is mixed using mechanical shear and surfactant. It is found in many industries, such as food, pharmaceutical, petroleum, agrochemical, paint, coating, and so on [2, 3]. Paraffin wax emulsions are generally used for waterproof coatings as hydrophobic properties to various surfaces, such as ceramic materials, paper, cardboard, wooden furniture, etc.

Emulsions are not formed spontaneously and they also tend to be unstable after the formation. To stabilize paraffin wax emulsion, anionic, cationic or non-ionic surfactants are frequently used [4].

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Nature of surfactant helps in deciding stability of microemulsion. A dipole and hydrogen bond interactions stabilizes non-ionic surfactant and electrical double layer stabilizes ionic surfactant (anionic and cationic). Surfactants are responsible for reducing the attractive forces that exists naturally in the form of surface tension. The choice of surfactant is based on the hydrophilic-lipophilic balance (HLB) value, help to develop desired emulsion. Surfactant with low HLB values are useful for forming water in oil (W/O) emulsions and high HLB values are used to form oil in water (O/W) emulsions [3]. HLB values between 10.25 and 10.75 were produce a stable wax emulsion solution because of its conductivity almost unchanged [5].

Previous study concluded that stable paraffin wax emulsions can be obtained by mixing all components in stages or adding aqueous surfactant to the oil, whereas the EIP method can produce emulsion with small droplet sizes and kinetically stable. EIP method as one of low-energy method was effectively used to prepare microemulsion. Low-energy emulsification method can utilize the chemical energy stored in the material and produce nano-emulsions almost spontaneously [2].

In the present study, we prepared paraffin wax microemulsions using the EIP method, and investigated the effect of surfactant concentrations, temperature of reaction, and stirring time on its stability and particles distribution. The properties of microemulsion were studied by optical microscope, particle size analyzer, and viscosity measurements.

2. Experimental

2.1. Materials
Paraffin wax was provided by PT. Kirana Mitra Abadi, Indonesia, with melting point is 57 ºC and oil content about 20 wt%. The paraffin wax was analyzed by using Gas Chromatography (GC) to obtain the distribution of hydrocarbon molecular weight. The main components of this paraffin wax are normal alkanes with a range of carbon numbers 22-30 which are classified as long-chain hydrocarbons (Figure 1). Non-ionic surfactants were sorbitan monooleate (Span 80) and polyethylene (20) sorbitan monooleate (Tween 80) were used without further purification. The water was deionized water.

2.2. Methods

2.2.1. Preparation of emulsion. Microemulsion was prepared initially from a mixture of paraffin wax and surfactant by adding water dropwise and stirring under various stirring time and heating temperature at 60-85 ºC. The rate of water addition was kept constant at approximately 1.5 mL/min.
The amount of paraffin wax in all emulsions was 40 wt%, while the addition of surfactant was varied from 5 to 9 wt%.

2.2.2. Microemulsion Characterizations. Little emulsion sample was placed in the sample bottle and weighed then dried for 1 hour at 100 °C to observed its solid content. The dried sample was weighed again and the solid content shown by Eq. 1:

$$\text{Solid content} = \frac{\text{sample mass after drying}}{\text{sample mass before drying}} \times 100\%$$

(1)

Emulsion stability was determined by observing phase change for 60 days, which then the fraction of emulsion phase was calculated according to Li (2010) calculation. The morphology of paraffin wax microemulsion was observed using optical microscope and to see the particle distribution. The particle size of microemulsion was determined using particle size analyzer (PSA) of Nanoplus Particulate Systems version 5.1 / 3.00.

3. Results and Discussions
A Stable emulsion can be formed using the right combination of surfactants which has an HLB value close to that required by the oil phase. HLB value describes the affinity of surfactant to the water and oil phase, and their effect on emulsion stability depending on volumetric proportion of the phase [6]. Base on previous report, HLB value that suitable for making stable microemulsion wax is between 9.5 and 10.3, for which there was no creaming [2]. In this study, microemulsions were initially prepared with high paraffin wax content (i.e. 40 wt%) and the amount of surfactant mixture of Tween 80 and Span 80 were ranging from 5 to 9 wt% to obtain appropriate concentration surfactant in the making of microemulsion.

Paraffin wax microemulsion in this study has a total solid content about 50 wt%. The advantage of high solid content paraffin wax is to reduce the cost of transporting wax emulsion from production site to the place of use, concentrated formulation is prepared with the content of the dispersed phase (wax) being about 50-60 wt% of the emulsion [7].
Figure 2 shows the stability of microemulsion as a function of surfactant concentration. Mixing Tween 80 and Span 80 as emulsifier at 5-10 wt% has lowest surface tension which plays an important role in mixing oil phase and water to form an emulsion. The highest microemulsion stability was obtained at a surfactant concentration of about 7 wt% and changed to be a solid emulsion phase at the concentration of more than 8 wt%. During the EIP process, the emulsion system changes from a W/O emulsion to an O/W emulsion and bicontinuous or lamellar structure can be formed during this process [2].

3.1 Effect of temperature
Paraffin wax used as the base material of microemulsion is solid at room temperature. During the emulsification process, paraffin wax has to be melted with increased of temperature for easier mixing with surfactant and water. Figure 3 shows microemulsion stability time as a function of temperature in different stirring time. Optimum parameter for achieving the highest microemulsion stability such as temperature and stirring time were obtained at 80 °C and 40 minutes. Making microemulsion at a temperature of 60 °C with both stirring times 30 and 40 minutes, microemulsion process can’t be occurred perfectly, because the emulsification temperature is close to the paraffin wax melting point. At a temperature of 85 °C microemulsion becomes thicker and turns into a solid phase after several times. This result is different from previous studies which stated that the stability of emulsions can be increased by increasing the temperature ranging from 55 to 85 °C [2]. It is possibly due to differences in paraffin wax composition used. The increase of temperature makes non-ionic surfactants more hydrophobic (with appearance of cloud point) [8].

3.2 Particle distribution
Particle size distribution of paraffin wax microemulsion which prepared at temperature 80 °C with different stirring time shows that the effective emulsification time to produce a stable microemulsion is 40 minutes. When the emulsification time increased, particle size distribution is decrease. At the emulsification time of 30 minutes, particle size is distributed at about 10 µm (Figure 4) and when the emulsification time raised 40 minutes, particle size is distributed at about 5 µm (Figure 5). This may occur because longer emulsification time at certain temperature can provides enough energy to break up the particle size. That is break up of droplets caused by adsorption of surfactants and droplet collisions which may or may not cause coalescence to occur [5]. A stable microemulsion can be formed if the droplet breaking up process is more dominant than droplet re-coalescence [9].

![Figure 4. Particle size distribution of microemulsion at stirring time 30 minutes](image-url)
Figure 5. Particle size distribution of microemulsion at stirring time 40 minutes

Figure 6. Microscopic image of paraffin wax microemulsion at 80 °C and emulsification time 30 minutes (a) and 40 minutes (b)

According to the particle size distribution data of PSA, paraffin wax microemulsions with good stability have an average diameter about 290.6 nm. Particle size distribution data becomes supporting data to the emulsion stability test where emulsification time at 40 minutes produces the highest microemulsion stability. This can occur because flocculation is prevented and allows the system to remain dispersed without separation. Examination of paraffin wax microemulsion under microscope are consistent with particle size distribution data, microemulsion at higher emulsification time has a smaller diameter appearance (Figure 6). Previous research has explained that coalescence can be prevented by small droplets, since these droplets cannot be deformed and therefore surface fluctuations can be prevented. Small droplet size causes a large decrease in the gravitational force and Brownian motion may be sufficient to overcome gravity [10].

4 Conclusion
The stability of microemulsion prepared using Tween 80 and Span 80 increases with increasing temperature and emulsification time to the optimum parameters, namely optimum stability at a
temperature of 80 ºC and emulsification time for 40 minutes, wherein the average particle size distribution 290.6 nm. Further studies to reduce particle size distribution to nano-emulsion will be carried out using nano bubble method.

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