Development of epoxide compound from *kapok* oil for enhanced oil recovery

M K Anam, Supranto, B Murachman and S Purwono*

Chemical Engineering Department, Universitas Gadjah Mada
Jalan Grafika No. 2, Kampus UGM, D.I. Yogyakarta, Indonesia.

*E-mail: spurwono@chemeng.ugm.ac.id

Abstract. Epoxide compound is made by reacting *Kapok* Oil with acetic acid and hydrogen peroxide with *in situ* method. The epoxidation reaction was varied at temperatures of 60 °C, 70 °C and 80 °C, while the time of reaction time was varied at 15 minutes, 30 minutes, 60 minutes and 90 minutes. The reaction rate coefficient for the epoxide was obtained as $\boldsymbol{k} = \boldsymbol{124,82}\,\mathbf{exp}\left(\frac{\boldsymbol{-24,14}}{\boldsymbol{R\,T}}\right)$. The addition of the epoxide compound 0.5% w/w in the formulation of SLS was able to reduce the IFT value up to 9.95 x 10^{-2} $m\underline{N}$/ m. The addition of co-surfactant (1-octanol) was varied between 0.1 and 0.4 % of the total mass of the main formulation (SLS + epoxide + water formation). The smallest interfacial tension value is obtained on the addition of co-surfactants as much as 0.2% w/w, with the IFT value is 2.43 x 10^{-3} $m\underline{N}$/m. The effectiveness of the chemicals was tested through micro displacement using artificial porous medium. The experimental results show that some chemicals developed in the laboratory can be used as EOR chemicals. The oil displacement experiments show that as much as 20 % to 80 % of remaining oil can be recovered by flooding it with the chemicals. The results also show that the oil recovery depends on type of chemicals and chemical concentration.

1. Introduction

The increasing demand for petroleum-based fuels and petrochemicals, along with the diminishing supply of new sources for oil, has escalated interest in improving the extraction of oil from existing reservoirs. Among the most promising processes is enhanced oil recovery (EOR). Currently, various researches in EOR technology are underway with intensity. One of the related researches that are given much attention is finding of chemicals for optimizing the enhancement of oil recovery. Even though many experiments have been done in this area, the applications in the field rarely succeeded. Expensive chemicals is certainly not the main reason for the failure, but more related to the process as application in the field is not properly guided by processes in the laboratory. There are many problems that need to be solved in the area of EOR basic research to allow results of research to be applied in the field.

From the earliest days, it was recognized that capillary forces caused large quantities of oil to be left behind in well-swept zones of water flooded oil reservoirs. Capillary forces are the consequence of the interfacial tension (IFT) between the oil and water phase that resists externally applied viscous forces and causes the injected and banked-up connate waters to locally bypass oil. Similarly, early efforts of enhanced oil recovery strove to displace this oil by decreasing the oil-water IFT. Though many techniques have been proposed and field tested, the predominant EOR technique for achieving low IFT is surfactant flooding.

Surfactants can be manufactured from various raw materials that are ultimately derived from petroleum or agricultural feedstock. Currently, most EOR surfactants are based on petrochemical feedstock. In the future a vicious cycle would be created, as the demand for more petroleum-based surfactants would increase proportionally to the demand for more oil for fuel and petrochemicals. To address this challenge, research is currently under way to develop surfactants, suitable for EOR, that are partially or completely derived from renewable agricultural crops. These offer the advantage of providing green, biodegradable, nontoxic, environmentally friendly alternatives that are not dependent on the availability of petrochemicals. There are several possible sources of chemicals for EOR such as lignin extracted from palm oil industrial waste or modification of the chemicals in order to reduce the IFT. One example is Sodium Ligno Sulfonate (SLS) which is useful in decreasing IFT for EOR industry. SLS can be made from Lignin of empty fruit bunches (EFB). However, the value of IFT of this surfactant is not low enough to be used in the reservoir. Surfactants which can be used as Surfactant Flooding should have a value of IFT$\leq 10^{-3} m$N/ m, while SLS only have IFT value around 1 - 4 mN/m [1].

1.1. Literature review
One of the ways to improve the performance of SLS is modify with some chemicals or adding with some co-surfactants. Improving the ability of SLS in reducing the interfacial tension can be done by adding epoxide compound and 1-octanol. Kapok oil has unsaturated fatty acids (double bond) up to 57%, thereby it has potential as epoxide compound. The bonding of SLS and epoxide compound is formed as a result of the opening of the oxirane ring [2]. The addition of 1-octanol can fill the empty space between the surfactant and reducing repelling effect surfactant [1]. Therefore the combination of epoxide compound and 1-octanol in the formulation of the SLS are expected to improve the quality of surfactants for EOR.

1.1.1. Epoxidation.
Epoxidation is defined as a reaction that aims to transform the double bond into epoxies. Epoxidation is an exothermic reaction, therefore it should be avoided the use of a high concentration of peroxide acid. The composition of fatty acid will influence kinetics of epoxidation reaction [2].

1.1.2.   Co-Surfactant.
Co-surfactant is chemical added to a process to enhance the effectiveness of a surfactant for reducing the surface tension of the liquid mixture. In the oil industry, co-surfactants are often used to increase the oil-solubilising capacity of micro emulsion surfactant systems. So that the layer formation stage between micelles and micro-emulsion can occur continuously. The addition of co-surfactant can produce low IFT because co-surfactant is able to enter into monolayer, thereby changes the curvature or stiffness of surfactant [3].

1.1.3.   Kinetics of Epoxidation.
Epoxidation is formation reaction oxirane ring of the double bond. There are two main reactions in the epoxidation reaction. First, is the formation of peroacetic acid. Second, is the epoxidation reaction itself.

Step 1   : AA + H$_2$O$_2$ $\leftrightarrow$ PAA   (1)

Step 2   : DB + PAA $\rightarrow$ EO + AA   (2)

Where:

        AA= acetic acid   EO = epoxide oil
        PAA = peroacetic acid   DB = double bond

Acetic acid mass balance can be written as:

$$\frac{d[AA]}{dt} = -k_1[AA][H_2O_2] + k_2[PAA] + k_3[DB][PAA]$$

(3)

2. Research Methodology

2.1. Raw Material

Sodium Lignosulfonate (SLS) was obtained from Weifang Longstar Chemical Inc. Shandong, China. *Kapok* oil was obtained from PT. Subali Makmur, Semarang. Co-surfactant: 1-octanol 99% was obtained from Sigma-Aldrich Co. LLC. Saponification materials were NaOH 5 M and Ethanol 96%. Materials for epoxidation are hydrogen peroxide 50% and acetic acid glacial. The catalyst is sulfuric acid 98%. Water injection to the formulation is taken from the Rantau Field PT. Pertamina (Persero).

2.2. Research Procedure

2.2.1. Saponification process. Saponification process is carried out at temperatures 85ºC (Campbell, et. al., 2009). The first step, NaOH solution was dissolved in ethanol, and then further reacted with Kapok oil which has been heated before. Its products are soap and glycerol. Separation of the two products is done with the addition of saturated NaCl solution [4].

2.2.2. Epoxidation Stage. Epoxidation process is using in-situ methods, where the reactants are reacted simultaneously. The catalyst used is sulphuric acid (H_2SO_4). Raw material are used is soap, hydrogen peroxide and acetic acid. The ratio of hydrogen peroxide and acetic acid is 1 : 1.4. The Weight of soap is 5 grams. The addition of the catalyst is as much as 2% of the total reactants [5].

2.2.3. Formulation Stage. Raw materials for developing surfactant formula are SLS, epoxies, co-surfactant, and injection water as a solvent. Formulation process was carried out using a hot plate at the temperature of 70 °C with the rotational speed on the scale 2.

2.3. Analysis

2.3.1. Concentration of double bonds. The measurement of iodine value is carried out by Wijs method. The concentration of double bond can be approached with iodine value [6].

$$[DB] = \frac{(B-S).N.12.69}{w}$$

(4)

Where:

    [DB]   = double bond concentration (mol/ml)

    N   = normality of $Na_2S_2O_3$

    B   = blank titration (ml)

    S= volume titration of sample (ml)

    w   = weight of sample

The conversion of fatty acids is calculated by equation from [7]:

$$\bar{x} = \frac{[DB]_0 - [DB]_t}{[DB]_0}$$

(5)

Where:

    x   = conversion

    $[DB]_0$ = initial concentration and $[DB]_t$ = concentration at time t

2.3.2. Epoxide concentration. The concentration of the epoxide formed is calculated from oxirane oxygen experiment, through the method of [8].

$$[OO]_e = \frac{1.6 . V . N}{w}$$

(6)

Where:

$[OO]_e$	= oxirane oxygen experiment;	N	= normality of HBR
V	= HBr solution for titration;	w	= mass of sample (gram)

2.4. Experimental set-up for flooding

The effectiveness of the chemicals was tested through micro displacement using artificial porous medium. The flow rates of oil, water and surfactant were controlled using pressurized gas. The porous media used in the oil displacement process was prepared from stainless steel cylinder and contain fine crushed core from Rantau formation, Aceh. It is proposed to be an artificial reservoir with dimension about 3.75 cm ID x 10.8 cm L. The porosity of the porous media was 0.4461, the density was 3.24 g/cm^3, and the permeability was 107 mD; and it was water wet. The cores were crushed to 30 / 60 mesh size which resulted in a mean particle size of 2.41 x 10^{-4} m in diameter. Porosity of a rock depends on the pore or grain size distribution, in which the small grains can fill the space between larger grains. Porosity is a strong function of grain size distribution (sorting).

The procedure is as follows: initially the reservoir model was filled with brine (1 to 3 % salt concentration) until it was 100 % saturated. Then, to represent oil migration, oil was injected into the medium until minimum water saturation (S_{wc}) of about 30 % is reached. After this, the medium was flooded by the same brine until minimum oil saturation, S_{or}, which was about 10 %. The oil remaining in the reservoir after this water flood was then subjected to various injections of different chemicals for further oil recovery.

3. Result and discussion
3.1. Effect of Temperature and Reaction Time on Epoxidation

Effect of temperature and reaction time were observed by comparing the results of the initial conversion double bond and conversion double bond at the end of the process. Comparison of temperature and reaction time on the conversion values can be found in Figure 1.

The increase in conversion indicates that the epoxidation reaction goes toward the product. Increasing reaction time will increase the conversion rates of the double bond into an epoxide compound. However increase in reaction time would also lead to the degradation of the oxirane ring [9]. At temperature 70 °C, the increase occurred at the beginning of the process of conversion. The conversion reaches a maximum value at the time of the reaction run for 30 minutes, and after that, the conversion decreases slowly. This is caused by the formation of by products from the reaction of epoxidation. According to [9], at temperatures above 65 °C, it will decrease the epoxide compounds due to opening of the oxirane ring. At temperatures of 80 °C, it is shown the decrease of conversion with increasing reaction time. This situation is due to a side reaction during the process of epoxidation.

3.2. Kinetics of Epoxidation

Based on Equation 5, the relationship $\ln\left\{[H_2O_2]_0 - [EO]\right\} = \ln X$ and reaction time for any temperature can be plotted. Figure 2 shows the experiment at temperature 60, 70 and 80 °C.
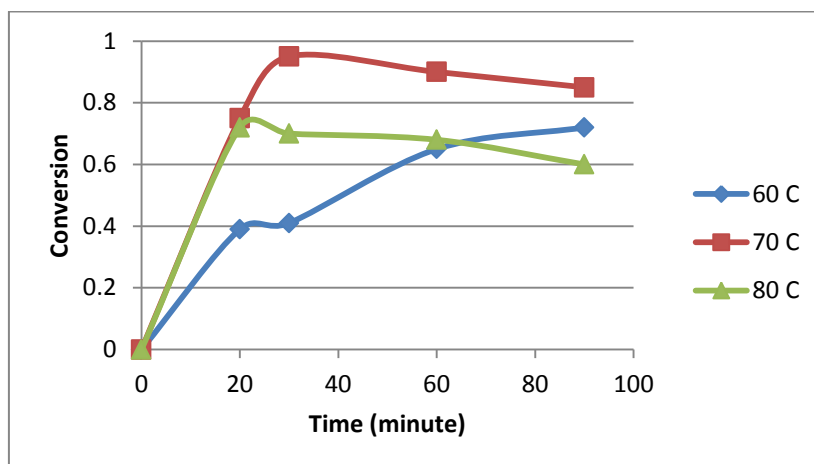
Figure 1.   Conversion at various operating conditions
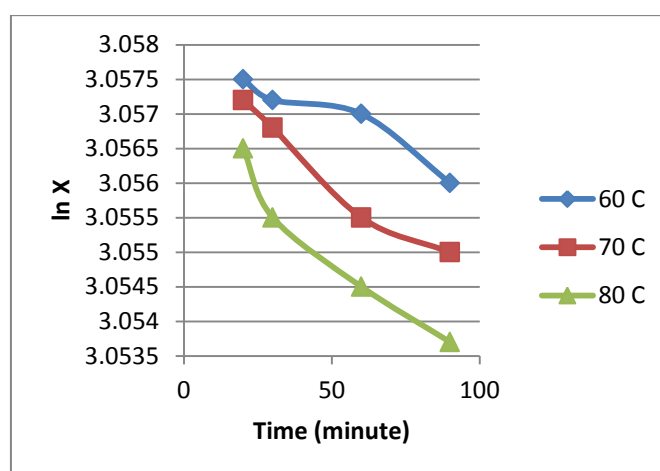

Figure 2.   Correlation of time and ln X

Based on Figure 2, it shows that the formation of the epoxide compound [EO] increases with time. The formation rate of epoxide compound is different in each reaction temperature, where the reaction temperature is higher (70 °C and 80 °C) gives a faster rate of formation than lower reaction temperature (60 °C).

The experiment at various temperatures was linearized to determine the reaction rate constant and comparison between the data and the model equations. The suitability was measured by the value of R Square (R^2). Linear equations that can be used to obtain the value of the constant of reaction rate (k). The values of reaction rate constants are shown in Table 1.

Table 1. Reaction rate constant (k)

T (°C)	Linear equation	R^2	Value of $k.10^{-6}$ (L mol^{-1}menit^{-1})
60	$y = -2.1553.10^{-5}t + 3.0579$	0.9888	1.24344
70	$y = -3.3140.10^{-5}t + 3.0576$	0.9968	1.91192
80	$y = -3.5181.10^{-5}t + 3.0568$	0.9724	2.02967

The value of the reaction rate constant at each temperature of the experiment can be used to determine the activation energy (*Ea*) and the frequency factor (*Ar*). Equation 7 can be used to determine the value of Ea and Ar.

$$\ln k = \ln A - \frac{Ea}{RT}$$

(7)

Table 2. Value of $\frac{1}{T}$ $\left(\frac{1}{Kelvin}\right)$ and $\ln k$

$\frac{1}{T}$	$\ln k$
0.003001651	-13.59762697
0.002914177	-13.16740098
0.002831658	-13.10763582

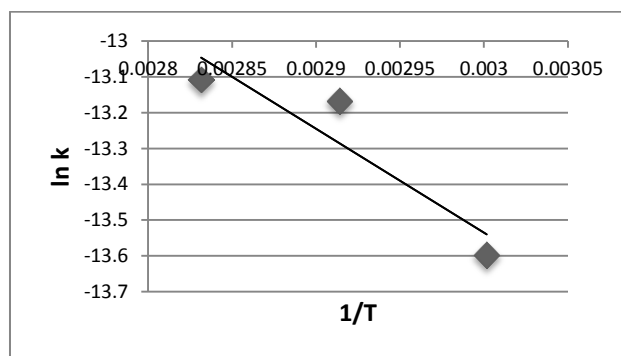Plot ln k versus 1/T will give the value of reaction rate constants.

Figure 3.   Temperature and reaction rate constant

The activation energy in the epoxidation was of 24.14 kJ / mol and the frequency factor of 124.82. Based on the Arrhenius equation, then the equation of the reaction rate constants can be formulated as Equation 8.

$$k = 124.82 \exp\left(-\frac{24.14 kJ/mol}{RT}\right)$$

(8)

3.3. Effect of Addition of Epoxide and Co-surfactant in Decreasing IFT Value
The addition of the epoxide compound and co-surfactant on the SLS are expected to reduce the value of IFT from SLS formulation. The results of measurement IFT value are presented in Table 3.

Table 3. IFT Value of Formulation

Type of Formula	Composition				IFT Value ($m\underline{N}$/m)
	SLS (g)	Epoxide (g)	Co-surfactant: 1-Octanol (g)	Formation water (g)	
Formula A	0.15	-	-	29.7	2.34
Formula B	0.15	0.15	-	29.7	9.95×10^{-2}
Formula C	0.15	0.15	0.03	29.7	6.08×10^{-3}
Formula D	0.15	0.15	0.06	29.7	2.43×10^{-3}
Formula E	0.15	0.15	0.09	29.7	2.53×10^{-3}
Formula F	0.15	0.15	0.12	29.7	2.53×10^{-3}

Table 3 shows the IFT value of Formulation of SLS. The difference of Formula A and Formula B is in the addition of the epoxide. Formula C is modification of the Formula B with the addition of co-surfactant 0.1%. In order to learn about effect of co-surfactant to IFT value, then the addition of co-surfactant on the Formula D was increased to 0.2%.The addition of co-surfactant in Formula E and F as much as 0.3% and 0.4% did not reduce in value of IFT. This is because of excess of the need of co-surfactant in formulations. This accords well with research done by [10] which states that the addition of co-surfactant generally ranges from 0.1 to 0.2% of the formulation.

3.4.   Oil recovery
In the EOR process, after injection of water (water flooding), some oil is still left in the reservoir due to high viscosity or high interfacial tension (IFT) between oil and the reservoir rocks. Therefore, after injection of chemicals which has higher mobility ratio, more oil can be recovered.

Figure 4 shows the process of water flooding followed by surfactant flooding. From the figure, it can be seen that after injection of water (2 % brine) some oil is still left in the reservoir. After injection of surfactant, more oil can be recovered. The oil displacement experiments show that as much as 20 % to 80 % of remaining oil can be recovered by flooding it with the chemicals.
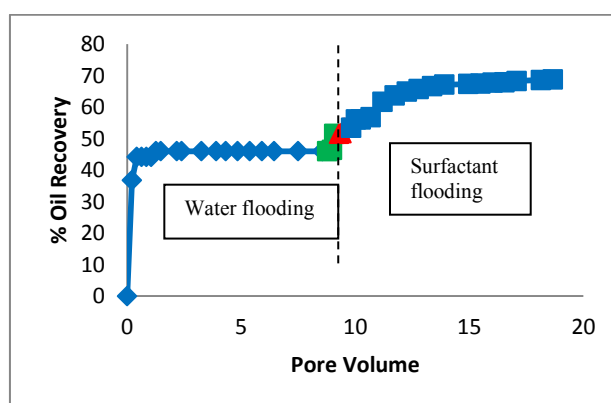

Figure 4. Example of water and surfactant flooding

Another studies of micro-emulsion demonstrate that if the mixture among oil, brine, surfactant and co-surfactant are in the form of micro-emulsion, the interfacial tensions (IFT) between oil/micro-emulsion and brine/micro-emulsion are very low (close to zero). Therefore, the oil which can be recovered after water flooding is high. The formation of a single-phase micro-emulsion with water-to-oil ratio close to unity requires a very high concentration of surfactant. In many cases, the addition of a fourth component, mainly alcohol, can facilitate the formation of a micro-emulsion at a lower surfactant concentration. Therefore, in this experiment, the results also show that for the same kind of surfactant, the amount of micro-emulsion will be different when the co-surfactant added is different.

Further study shows that the oil recovery increases when the chemical concentration is raised. The increasing oil recovery is caused by the increasing amount of micro-emulsion due to the lowering IFT.

4.   Conclusions
It can be concluded that rising temperature up to 70 °C with reaction time of 30 minutes can increase the conversion of *Kapok* oil to epoxide compound. Temperatures above 70 °C would lead to reduce in the conversion value, which caused by side reaction.

Epoxide compounds and co-surfactants added to the formulation can reduce IFT value. The optimum results can be obtained on additional co-surfactant 0.2%. The optimum results addition of co-

surfactant can be obtained on 0.2%.The addition above 0.2% did not give a reduction in the IFT value. The results show that these chemicals have potential uses as EOR chemicals.

Acknowledgment

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