PYROLYSIS OF LIGNIN FROM WASTE OF PALM OIL INDUSTRIES FOR THE DEVELOPMENT OF SURFACTANTS FOR ENHANCE OIL RECOVERY (EOR)

(Pirolisis Lignin dari Limbah Industri Kelapa Sawit untuk Pengembangan Surfaktan dalam Proses Enhance Oil Recovery (EOR))

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Abstract

Pyrolysis of lignin from waste of palm oil industries produces alcohol and its derivatives which can be sulfonated to become surfactant. The experimental procedures for the pyrolysis process were as follows: 1) dried palm oil husks at a certain weight were put into the pyrolysis reactor and heated up to a certain temperature; 2) the product leaving the reactor was cooled down to room temperature; and 3) the liquid product was collected in a flask while the gas product was put into a big bottle. The best temperature obtained for producing liquid product was 400 °C for lignin from palm oil fruit fibers and 350 °C for lignin from palm oil fruit stems. The surfactant developed was in the range between 34 and 38% from the pyrolysis product. In this experiment, the reaction rate was assumed to be in first order. The result showed that the surfactant obtained from the experiment could form emulsion with crude oil. This suggests that the surfactant developed can be used for EOR process.

Abstrak

Pirolisis dari lignin yang berasal dari limbah industri kelapa sawit dapat menghasilkan alkohol dan derivatif lainnya yang dapat digunakan sebagai surfaktan. Prosedur penelitian proses pirolisis ini adalah sebagai berikut: 1) serabut atau tandan sisa pengolahan kelapa sawit yang sudah dikeringkan dimasukkan kedalam reaktor dengan berat tertentu dan dipanaskan sampai suhu yang diinginkan. 2) produk pirolisis yang keluar dari reaktor kemudian didinginkan sampai mencapai suhu kamar, 3) hasil cair ditampung didalam gelas ukur dan hasil gasnya ditampung di suatu botol tertentu. Suhu paling baik yang dicapai adalah 400 °C untuk lignin yang berasal dari serabut dan 350 °C untuk lignin yang berasal dari tandan kelapa sawit. Surfaktan yang dihasilkan sekitar 34 sampai 38% dari produk pirolisis. Pada penelitian ini kecepatan reaksi dianggap order satu. Hasil penelitian menunjukkan bahwa surfaktan yang dihasilkan dapat membentuk emulsi dengan minyak mentah. Hal ini menunjukkan bahwa surfaktan yang dihasilkan dapat digunakan sebagai bahan untuk proses EOR.

I. INTRODUCTION

At the end of water flooding, the oil that remains in the reservoir is believed to be in the form of oil ganglia trapped in the pore -structure of the rock. These oil ganglia are entrapped due to the capillary forces. However, if a surfactant solution is injected to lower the interfacial tension (IFT) of the oil ganglia from its value of 20-30 dynes/cm to 10-3 dynes/cm, the oil ganglia can be mobilized and can move through narrow necks of the pores (Fayer, 1981). A typical surfactant is composed of a non polar (lypophile) portion and a polar (hydrophile) portion. Surfactants are classified into four groups depending on their polar, those are (Lake, 1989): anionic, cationic, nonionic and amphoteric. Within any one class, there is a huge variety of possible surfactants, but the most common primary surfactants used in the enhanced oil recovery (EOR) is petroleum sulfonate (Lake, 1989). However, this type of surfactant is very expensive. Besides, that if the price of oil increases, the price of this type of surfactant also increases. Therefore, an inexpensive surfactant for EOR should be pursued. In order to determine chemicals used in this experiment, some aspect have been set as follows: it is easily found in Indonesia, it can be produced inexpensively, it is industrial waste, it has high recoverability and it is not petroleum base.

In this research, lignin has been examined as surfactant. Lignin compounds (lignate and lignosulfonate) are side product of palm oil industries which are not useful. Since the capacity of Indonesian palm oil industries is huge, there are a lot of lignin will be disposed of in the field. Therefore, lignin is a potential EOR chemicals.

Palm oil trees (Elais quinensis Jacq) are eatable oil producer plants which grow very well in tropical region. Indonesia is the second largest palm oil industry in the world. In 1997, the total area of Palm Oil Plantation in Indonesia were more than 2 millions hectares which

produced around 29 millions tons of fresh palm oil fruits. This industry produces a lot of solid waste (palm oil fibers) from the processing since the randements are in the range of 16 to 24% of the weight. This waste is usually used as solid fuel. However, the calorific value is low. One possible way to handle this waste is pyrolysing the palm oil fibers to becomes valuable product. The solid waste of palm oil industries which consists of 30% lignin can be used as raw material of surfactant (Fengel & Wegener, 1995).

Lignin derivation which has been sulfonated can be used for improving oil recovery to replace the expensive available surfactant. However, this type of lignin sulfonate only reduce the interfacial tension slightly due to the long chain of lignin. Lignin which is polymer from phenyl can be pyrolysed to produce aromatic compound having low molecular weight. This aromatic compound is a good raw material for surfactant.

The goal of this pyrolysis is to get components which can be used as surfactant or co-surfactant for EOR processes from palm oil fruit fibers and stems. The research can be classified into two categories: (1) development of chemicals from pulp and palm oil industries, and (2) oil displacement process.

II. EXPERIMENT

A. Equipment

Figure 1 shows the diagram of the pyrolysis process. The reactor was made of stainless steel having 15 cm diameter and 25 cm length and surrounded by a heating system which was connected to a temperature controller. A Chromel-alumel temperature having 1.6 mm diameter was employed for monitoring the reactor temperature.

B. Procedure

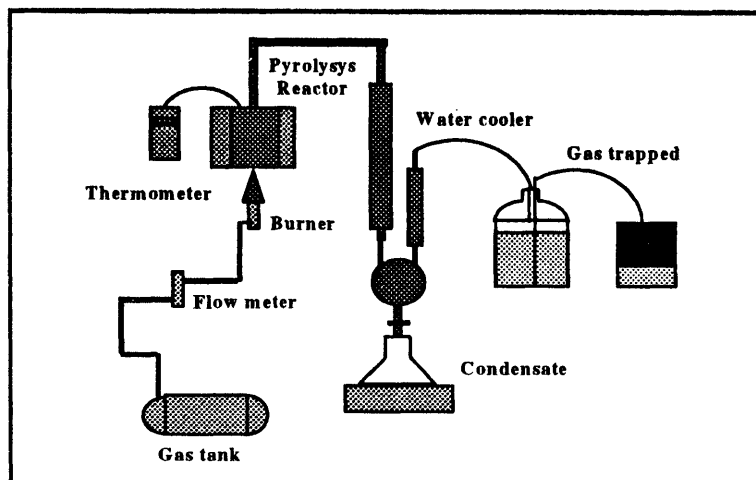The procedure of operations are as follows: lignin at a certain weight (40 g) was put in the

Figure 1. Equipment for Pyrolysis Experiment

reactor and heated up to 250 °C and maintained constantly. The initial time was estimated when the desired temperature was reached and the liquid product was taken and weighed as m_{co}. Then at certain intervals (10 min) liquid product was weighed to calculate m_c until a certain time. Then the reaction was held constant and stopped when there was no more liquid produced and was weighed as m_{oo}.

Besides that, the amount of gases produced were also measured. The heater was then turned off and the reactor was dismantled and the solid remained in the reactor was also weighed. The same procedure was repeated for interval temperatures of 50 °C. Pyrolisys processes were done for lignin from palm oil fruit fibers and palm oil fruit stem.

III. RESULTS AND DISCUSSION

A. Experimental results

In the pyrolysis experiments, the condensate formed was in the range of 25 to 45 percent of the original weight of palm oil fibers while the gas formed was in the range of 10 to 20 percent. This study demonstrated that more than 36 components, mainly alcohol like

methanol, ethanol and propanol, were produced during the pyrolysis process as shown in Figure 2. These product can be used as co-surfactants in the oil displacement processes (Silverstein, 1981). The other components can be sulfonated to be lignosulfonate with short chain which is easily dissolved in the water (Meyer, 1992). The experiment also showed that the condensate and gas formed were affected by the temperature in the reactor and the heating rate. The result showed that the amount of chemicals produced in the form of alcohols increased as the pyrolysis temperature increased. Further studies showed that the reaction rate of the decomposition process depended on temperature. Therefore, the pyrolysis products increased when the pyrolysis temperature increased.

Further experiment showed that a lot of methane was produced from the pyrolysis of palm oil fibers and fruit stems. The study showed that the amount of methane depended on the pyrolysis process temperature. The methane can also be used as tertiary oil recovery flood material since hydrocarbon gases are dissolved in the oil and reduce the oil viscosity. The process is known as miscible process. The experiments in the laboratory
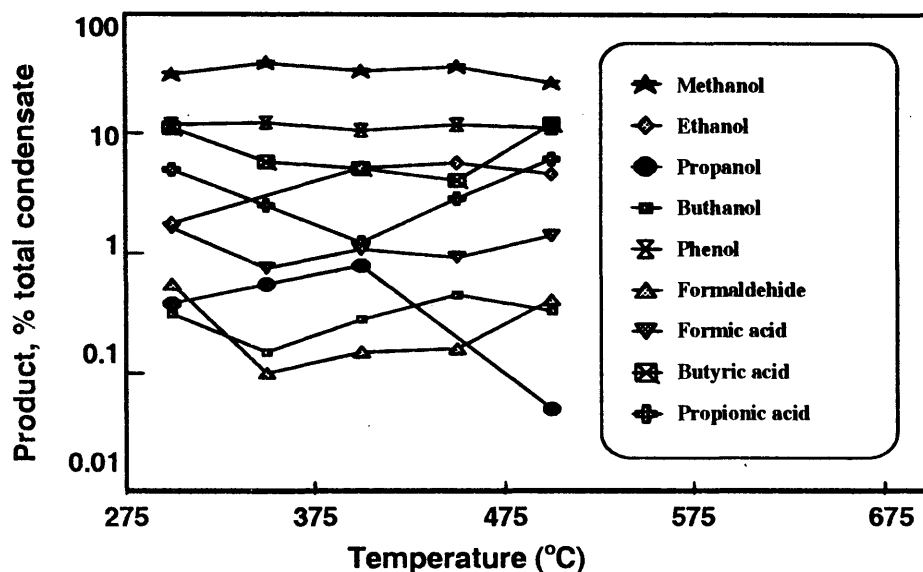
Figure 2. Example of the Pyrolysis Product

showed that the gas mixture, mainly methane, will reduce the oil viscosity up to 12 percent. When the oil viscosity in the reservoir decreases, it will become movable.

The total products of pyrolysis experiment are shown in Figure 3 and Table 1. The figures and tables show the effect of temperature on the liquid, gas and solid products.

From the figure, it can be seen that when the pyrolysis temperature is increased, the liquid and gas product increases while the solid product decreases. Liquid starts to drop at temperature around 190 °C while gas is produced at temperature around 120 °C. At relatively low temperature, the rate of liquid and gas formation is very sensitive to the changes of temperature.

The liquid produced from pyrolysis process consisted of light distillate and viscous tar. Tar was produced at relatively high temperature since at that temperature large liquid molecules were produced (Fengel & Wegener, 1995). The amount of tar increased when the pyrolysis temperature raised and the solid remain in the reactor drier.

One feature of pyrolysis reactions which is not fully understood is the role of the reactor surface. Surface reactions occurring during pyrolysis still need considerable clarification. These reactions probably include the initiation and termination of free radicals, coking, and the formation of metal oxides, metal carbides, and metal sulfides. Some investigators assume that the thermal decomposition of hydrocarbon is completely homogeneous gas phase reaction. Factors such as the material of construction, surface-volume ratio of the reactor, and chemical treatment of reactor surface often affect the rate of reaction and the product distribution. An investigation by Tsai and Albright et al. clearly indicated some of the important surface reactions occurring in reactors constructed of different metals during the pyrolysis of light paraffin (Tsai & Albert, 1976).

High molecule carbons are produced by a sequence that starts with gas phase reactions. The acetylenic compounds and diolefins condense forming aromatics. The aromatics react producing tar molecules, then tar droplets impinge on the metal surfaces or are formed there.
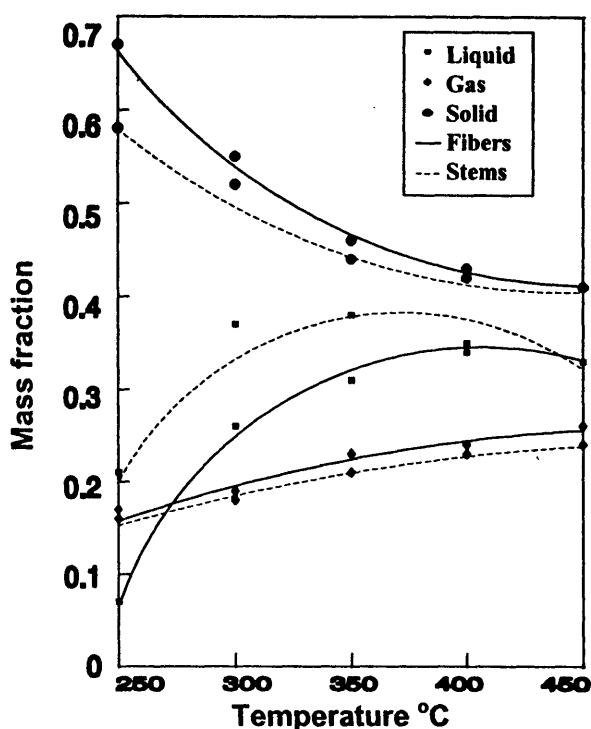
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Figure 3. The Effect of Temperature on Liquid, Gas and Solid Products

The droplets either wet or partially wet the solid surfaces, and finally the tar on the surface dehydrogenates, producing coke. In those cases in which the droplets only partially wet the surface, the coke formed has the appearance under the scanning electron microscope of a series of partially agglomerated spheres. This coke is designated here as globular. This type of coke contains no metal particles unless it becomes mixed with surface catalyzed coke.

For the two types of lignin, the liquid products were obtained maximum at temperature between 350 and 400 °C. At temperature above 400 °C the liquid product will decrease because at high temperature the lignin polymer molecules will be easier to crack forming incondensable smaller molecules (gas).

To form surfactant, the liquid product was added with NaOH and then was sulfonated using oleum while heated. The results were analyzed using Infra Red Spectrofotometer and Ultra Violet Spectrofotometer. The sulfonate compound was shown by wave number around 1095 – 1175 cm-1 (Silverstein, 1981). Table 2 shows the concentration of surfactant.

B. Kinetics of Pyrolysis Reaction

Generally, the pyrolysis of polymer such as lignin will produce gases, liquids and solids left in the reactor. To simplify the depolimerization reaction, we assumed that the reaction was first order and was written as follows (Tsai & Albright, 1976):

$$P \frac{k_1}{k_2} --> n_c\ C \qquad (1)$$

$$P -----> n_G\ G + n_S\ S \qquad (2)$$
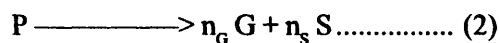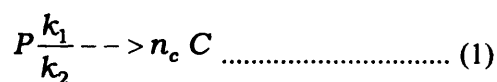
Table 1. Liquid, Gas and Solid Fractions in the Pyrolysis Process

Temp °C	Lignin from palm oil fruit fibers			Lignin from palm oil fruit stems		
	Mass fraction			Mass fraction		
	Liquid	Gas	Solid	Liquid	Gas	Solid
250	0.07	0.16	0.67	0.21	0.17	0.58
300	0.26	0.19	0.55	0.37	0.18	0.52
350	0.31	0.23	0.46	0.38	0.21	0.44
400	0.35	0.24	0.42	0.34	0.23	0.43
450	0.33	0.26	0.41	0.33	0.24	0.41

Table 2. Concentration of Surfactant from Pyrolysis Process.

Temperature, °C	From fruit fibers, %	From fruit stem, %
250	0.50049	4.800393
300	2.70425	11.28791
350	9.61961	13.34642
400	11.5701	17.26148

where P is lignin solid, C is liquid product, G is gas product, S is solid product, k is the reaction rate constant and n is the reaction coefficient.

The equation of the first order reaction rate for the pyrolysis process can be written as follows:

$$(-r_p) = -\frac{dC_P}{dt} = (k_1 + k_2)C_p \qquad (3)$$

with assumption that the weight of gases produced are smaller than the liquid products, so the initial condition for the above equation is: t = 0 (calculated when the desired temperature was achieved)

$$m_{P0} = m_{P\,initial} - m_{C0}$$

$$C_{P0} = \frac{\dfrac{m_{P0}}{MW_P}}{V}$$

Equation (3) becomes:

$$\int_{C_{P0}}^{C_P} \frac{dC_P}{C_P} = \int_0^t -(k_1 + k_2)dt$$

$$C_P = C_{P0}\,e^{-(k_1 + k_2)t} \qquad (4)$$

The equation for liquid formation can be written as:

$$\frac{dC_C}{dt} = n_C k_1 C_p \qquad (5)$$

$$\int_{C_{C0}}^{C_C} dC_c = n_C k_1 C_{P0}\int_0^t e^{-(k_1 + k_2)t}\,dt$$

$$C_C - C_{C0} = \frac{n_C k_1 C_{P0}}{(k_1 + k_2)}\left[1 - e^{-(k_1 + k_2)t}\right]$$

$$\frac{C_C - C_{C0}}{n_C C_{P0}} = \frac{k_1}{(k_1 + k_2)}\left[1 - e^{-(k_1 + k_2)t}\right] \qquad (6)$$

The amount of liquid produced can be written as liquid weight divided by the weight of initial lignin

$$\frac{C_C}{n_C C_{P0}} = \frac{\frac{m_c}{MW_C}}{n_c \frac{m_{P0}}{MW_{P0}}} = \frac{m_c}{m_{Pinitial} - m_{C0}} \frac{MW_{P0}}{n_c MW_c} \quad (7)$$

where t is reaction time at certain temperature C_{P0} is the solid concentration at t = 0 (gmole/l) C_p is the solid concentration at time t (gmole/l) C_{c0} is the liquid concentration at t = 0 (gmole/l) C_C is the liquid concentration at time t (gmole/l) $m_{Pinitial}$ is the weight of initial solid in the reactor (g) m_{P0} is the weight of solid at t = 0 (g) m_{C0} is the weight of liquid at t = 0 (g) m_C is the weight of liquid at time t (g) MW_{P0} is the molecular weight at t = 0 (gmole/g) and MW_C is the molecular weight of liquid (gmole/g).

Using the assumption that the weight of gases are very small:

$$\frac{MW_{P0}}{n_c MW_c} = 1 \quad \quad \quad \quad \quad (8)$$

So equation (7) becomes:

$$\frac{C_C}{n_c C_{P0}} = \frac{m_c}{m_{Pinitial} - m_{C0}} \quad \quad \quad (9)$$

Substitution of Equation (9) to Equation (6), resulting in:

$$\frac{m_c - m_{c0}}{m_{Pintial} - m_{c0}} = \frac{k_1}{(k_1 + k_2)}\left[1 - e^{-k_1 + k_2)t}\right] \quad (10)$$

with:

$$\frac{m_C}{m_{Pinitial}} = x_C$$

$$\frac{k_1(1 - x_{C0})}{(k_1 + k_2)} = K$$

Equation (10) becomes:

$$\frac{x_c - x_{C0}}{1 - x_{C0}} = \frac{k_1}{(k_1 + k_2)}\left[1 - e^{-(k_1 + k_2)t}\right]$$

$$x_c - x_{C0} = \frac{k_1(1 - x_{C0})}{(k_1 + k_2)}\left[1 - e^{-(k_1 + k_2)t}\right]$$

Equation for liquid weight as function of time can be written as follows:

$$x_c = \frac{k_1(1 - x_{C0})}{(k_1 + k_2)}\left[1 - e^{-(k_1 + k_2)t}\right] + x_{C0} \quad (11)$$

To calculate k_1 and k_2 a Least Square method was used in Equation (11) from the weight of liquid produced.

$$x_c = K\left[1 - e^{-(k_1 + k_2)t}\right] + x_{c0} \quad \quad \quad (12)$$

At t = ∞, $x_c = x_{c\infty}$ so that Equation (12) becomes:

$$K = x_{c\infty} - x_{c0}$$

$$x_c - x_{c0} = (x_{c\infty} - x_{c0})\left[1 - e^{-(k_1 + k_2)t}\right] \quad (13)$$

To calculate k_1 and k_2 a Least Square method was used for the following equation:

$$x_{c\infty} - x_c = (x_{c\infty} - x_{c0})e^{-(k_1 + k_2)t} \quad \quad (14)$$

to get a linear line, Equation (14) was manipulated to be:

$$\ln(x_{c\infty} - x_c) = \ln K - (k_1 + k_2)t \quad \quad (15)$$

By plotting a relationship between $\ln(x_{c\infty} - x_c)$ and time (t), the reaction rate constants (k_1 and

k_2) can be calculated. The slope will be $-(k_1+k_2)$ and the intercept is ln K which is equal to $k_1(1-x_{co})/(k_1+k_2)$. The values of k_1 and k_2 are shown in Tables III and IV.

From the Arhenius Equation, the reaction rate constant (k) as function of temperature (T) can be written as

$$k = k_0 e^{-E/RT} \quad\quad\quad\quad (16)$$

To get a linear line, the equation above was changed to be:

$$ln(k) = ln(k_0) - \frac{E}{RT} \quad\quad\quad (17)$$

Using a Least Square method, the value of k_0 and activation energy (E) for k_1 and k_2 can be calculated.

From the tables above, the value of reaction rate constant of the pyrolysis process are as follows:

Pyrolysis reaction for lignin from palm oil fruit fibers

$$k_1 = 4,330 \times 10^{-3} e^{-52,12/T} \quad (min^{-1})$$
$$k_2 = 6,294 \times 10^{-2} e^{-313,7/T} \quad (min^{-1})$$

Pyrolysis reaction for lignin from palm oil fruit stems

$$k_1 = 6,200 \times 10^{-6} e^{-4559,1/T} \quad (min^{-1})$$
$$k_2 = 2,493 \times 10^{-2} e^{-483,56/T} \quad (min^{-1})$$

The reaction rate constant for liquid formation (k_1) decreases when the temperature is increased, because at higher temperature more gas is formed. For the gas and solid formation reaction rate constant (k_2) should be higher when the temperature is raised. However, for this reaction, k_2 decreases when the temperature increases. This happens since at high temperature the viscous liquid (pyrolytic tar) which sticks to the cooler wall is not calculated as a liquid or solid product.

C. Test of Sweeping Ability

In order to determine whether or not the chemicals developed in the laboratory have potential as EOR chemicals, two kinds of tests have been carried out, i.e., micro-emulsion and oil displacement test.

Micro-emulsion. Hydrocarbons are usually insoluble in water but can be solubilized in the core of surfactant micelles. The droplet sizes of the oil swollen micelles are in the range from

Table 3. The Relationship Between ln($x_{c\infty}$ - x_c) and Time for Pyrolysis of Palm Oil Fruit Fibers

t, minute	ln($x_{c\infty}$ - x_c)				
	250 °C	300 °C	350 °C	400 °C	450 °C
0	-2.78187	-1.67006	-1.52924	-2.10518	-2.98218
10	-3.17299	-2.55480	-2.15714	-3.74078	-3.63365
20	-3.21336	-3.92479	-3.37580	-4.284.75	-3.90073
30	-3.58826	-4.67500	-4.10104	-4.67760	-4.22866
40	-3.71624	-4.87879	-4.57800	-5.24612	-4.70509
50	-4.19777	-5.12531	-4.89967	-5.40630	-5.21987
60	-5.11431	-5.40536	-5.44907	-5.57975	-5.50201
k_1 min^{-1}	0.00239	0.00751	0.001262	0.00389	0.00263
k_2 min^{-1}	0.03171	0.005429	0.005328	0.004871	0.003857

Table 4. The Relationship Between $\ln(x_{c\infty} - x_c)$ and Time for Pyrolysis of Palm Oil Fruit Sistem

t, minute	$\ln(x_{c\infty} - x_c)$				
	250 °C	300 °C	350 °C	400 °C	450 °C
0	-1.73852	-1.26981	-1.47725	-1.98677	-2.75691
10	-2.36844	-1.82163	-2.12808	-3.35651	-4.08977
20	-2.90002	-2.43705	-3.42354	-4.30864	-4.962.46
30	-3.61536	-3.61419	-4.210030	-4.82526	-5.32195
40	-5.12648	-4.52486	-4.82307	-5.14183	-5.61419
50	-6.16226	-4.49705	-5.22051	-5.44346	-5.83591
60	-6.54139	-6.05383	-5.58478	-5.74868	-6.05195
k_1 min^{-1}	0.002047	0.003263	0.01525	0.00506	0.00222
k_2 min^{-1}	0.06603	0.05237	0.05585	0.05314	0.04788

100 to 1000 Angstrom (Rossen, 1978). This aqueous solution is often optically transparent or translucent and is called micro-emulsion. Several studies show that if oil and water are in the form of micro-emulsion, the interfacial tension of oil and water is approaching zero. The procedure of micro-emulsion test is as follows: at the beginning, the chemical to be tested is dissolved in the brine with concentration between 500 and 20000 ppm. The solution is then combined with the same amount of crude oil, kerosene or diesel oil so that the total volume becomes 100 mL. Then the mixture is heated to 70 °C, stirred for 15 minutes and left overnight. The amount of micro-emulsion and the position (lower phase, middle phase, or upper phase) is measured. The results of micro-emulsion tests show that the surfactant produced can form micro-emulsion. 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, which is also produced in this process, facilitates the formation of micro- emulsion at a lower surfactant concentration (Rosen, 1978). Therefore, the results show that for the same kind of surfactant, the amount of micro-emul-

sion is changed when using different co-surfactant.

Oil displacement process. The effectiveness of the chemicals was tested through micro- displacement using artificial porous medium. The schematic diagram of the oil displacement apparatus is shown in Figure 4. The flow rates of oil, water and surfactant or polymer were regulated using Nitto-Seiko micro-flow meters. In this experiment a water bath was equipped to heat the porous medium up to reservoir temperature. A compressor or pressurized gas was used to push down the feed. The effectiveness of the chemicals were proved through micro-displacement using artificial sand packs as porous medium. The medium used in the oil displacement process was prepared from two glass plates containing fine quartz sands. The dimension of artificial reservoir was about 20 cm x 20 cm x 0.3 cm. The porosity of the medium was 20% and the volume was 15 mL.

Several chemicals produced from this pyrolysis process have been tested for their ability to sweep the oil after water flooding. The results showed that as much as 20% to 60% of remaining oil could be recovered by flooding it with these EOR chemicals.
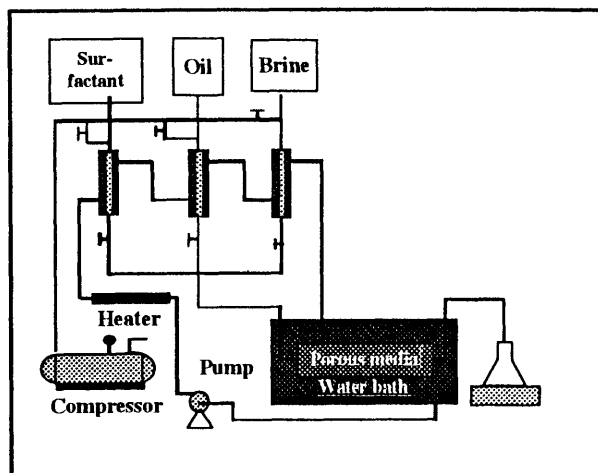
Figure 4. Oil Displacement Apparatus

The experiment shows that this non-petroleum base surfactants give a relatively good results. This is due to the structure of surfactant. A good surfactant must have two parts in its molecule: oil soluble portion (lipophilic) and water soluble portion (hydrophilic), and sometimes called amphiphilic because of its dual nature (Lake, 1989). Usually, aliphatic and aromatic hydrocarbons are considered as oil soluble portion, whereas the sulphonate or sulphate polar head are considered to be the water soluble portion.

IV. CONCLUSIONS

Pyrolysis of lignin from palm oil fruit fibers and stems (waste of palm oil industries) produces liquid, gas and solid which can be used as surfactant and co-surfactant for EOR process. The pyrolysis reaction is assumed to be a first order reaction. The best temperature obtained for producing liquid product is 400 °C for lignin from palm oil fruit fibers and 350 °C for lignin from palm oil fruit stems. The surfactant yield is in the range between 34 and 38% of the pyrolysis product.

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