

# On the use of sodium lignosulphonate for enhanced oil recovery

M M Azis<sup>1</sup>, H Rachmadi<sup>1</sup>, J Wintoko<sup>1</sup>, A T Yuliansyah<sup>1</sup>, W Hasokowati<sup>1</sup>, S Purwono<sup>1</sup>, Rochmadi<sup>1</sup> and B Murachman<sup>1</sup>

<sup>1</sup>Chemical Engineering Department, Faculty of Engineering, Gadjah Mada University, Jln. Grafika 2, Yogyakarta, Indonesia

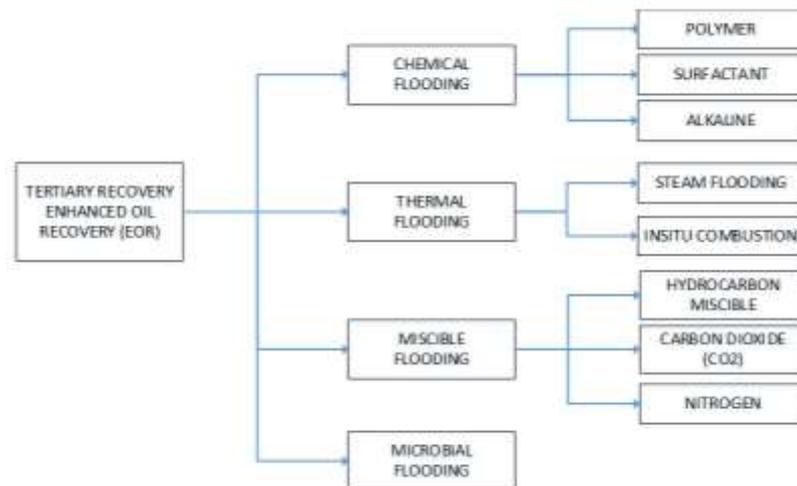
Emai : muhammad.azis@ugm.ac.id

**Abstract.** There has been large interest to utilize oil reservoirs in Indonesia by using Enhanced Oil Recovery (EOR) processes. Injection of surfactant as a part of chemical injection technique in EOR is known to aid the mobility and reduction in surface tension. One potential surfactant for EOR application is Sodium Lignosulphonate (SLS) which can be made from various sources particularly empty fruit bunch of oil palm and black liquor from kraft pulp production. Here, we will discuss a number of methods for SLS production which includes lignin isolation techniques and sulphonation reaction. The use of SLS alone as EOR surfactant, however, is often not feasible as the Interfacial Tension (IFT) value of SLS is typically above the order of  $10^{-3}$  dyne/cm which is mandated for EOR application. Hence, brief discussion on SLS formulation screening is provided which illustrates an extensive labwork experience during the SLS development in our lab.

## 1. Introduction

With a growing concern to improve national oil production, enhanced oil recovery (EOR) technology appears to be a promising technology in upstream operation and thus will play an important role in the near future. In addition to primary and secondary techniques, tertiary recovery of EOR is expected to be crucial with the aid of chemicals, thermal, miscible flooding and microbial flooding (Figure 1). Thermal flooding may include hot water and steam stimulation and in situ combustion. For chemical injection, polymers, surfactants and alkaline are common chemicals to aid improvement in oil production. Miscible flooding such as injection mixture of hydrocarbon solvents, carbon dioxide, nitrogen as well as biological (microbial) EOR are two promising techniques that is rapidly growing especially in research scale [1]. Despite of large interest in tertiary EOR, it is generally acknowledged that the knowhow and field experience of tertiary EOR is still limited in Indonesia.



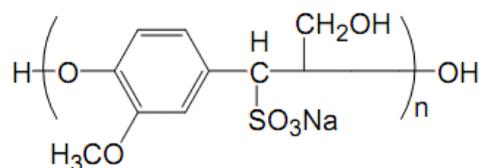


**Figure 1.** Tertiary recovery techniques for Enhanced Oil Recovery (EOR)

Screening of polymer or surfactant for EOR has been widely studied in literature [1]. Surfactant is a surface tension-lowering active compound which has bipolar structure. The head part favors water (hydrophilic), while the tail part behaves like an oil and thus water-insoluble (hydrophobic). As a result, surfactants tend to be at the interface between different phases degree of polarity such as water and oil. Surfactant serves to reduce surface tension, interfacial tension, improve the stability of the dispersed particles and control the types of emulsion formation [2].

Based on the charge on the ion, surfactant can be divided into four, namely anionic surfactants, cationic surfactants, zwitterionic surfactants and nonionic surfactants. [3]. For chemical injection, petroleum based sulfonate is a common surfactant for EOR. In order to decouple the price of surfactant and oil, there is a need to find an alternative which is economical, produced from abundant resources and reliable for the EOR application. One potential surfactant based on lignin is Sodium Lignosulfonates (SLS).

SLS has been known as plasticizer, flocculation agent and dispersant. As a surfactant, SLS has been able to lower the interfacial tension of two liquid phases and thus may be beneficial to increase the oil recovery from oil wells [4]. SLS is an anionic surfactants because it contains a negative charge on the hydrophilic part. The presence of sulfonate ( $\text{SO}_3^-$ ) and its salts ( $\text{NaSO}_3^-$ ) as well as the head of a hydrocarbon group as a tail causes SLS to be water soluble. The structure of SLS is depicted in Figure 2.



**Figure 2.** The structure of SLS

This paper aims to provide a mini review of SLS production from lignin, sulphonation reaction of lignin and SLS formulation to be used as EOR surfactant.

## 2. Sodium Lignosulphonate

### 2.1. Lignin isolation from kraft pulp black liquor

Lignin is derived from the Latin word "lignum" meaning wood. Lignin is a main constituent component of the vascular plants. The content of lignin varies by the type of wood. Softwood has a lignin content of about 24-33%, while hardwood has lignin content of 19-28% [5]. A number of softwood that can be found in Indonesia are hibiscus wood, wood bark, pine, wood rosin, pine and spruce bonsai. Indonesia also has a number of hardwood such as meranti wood, mahogany, teak, amber and wood suren.

Lignin can also be obtained from paper mill i.e. from the pulping process. Pulping is the process of dissolving the lignin with certain chemical compounds and separates them from the cellulose compounds. For large scale paper mill, there are two methods namely sulfite pulping and kraft pulping. Sulfite pulping uses sulfite compounds, thus one may obtain sulfonate compounds that dissolve in water. Kraft pulping method uses caustic and sodium sulfide compounds to degrade lignin into smaller molecules that dissolve in the black liquor.

Currently, black liquor is known as side product in paper mill and it has been used as a fuel in the boiler pulping. There is an interest to utilize a small portion of black liquor for an added value chemicals rather than just as a fuel. For this purpose, production of SLS from black liquor may provide an attractive route for black liquor utilization especially for EOR application.

Isolation of lignin is the initial stage in SLS surfactant production from black liquor. This process aims to extract lignin by precipitation method by reducing the pH. Typically, precipitation of lignin is conducted by adding certain amount of inorganic acid compound such as sulfuric acid and hydrochloric acid. Addition of acid aims to trigger acid precipitation to occur as a gel. According to Lim [6], the optimal pH for lignin precipitation occurs at pH = 2. The precipitated gel produced in isolation lignin, however, complicates the filtration process. To tackle this problem, chloroform is typically added as an organic compound that is insoluble in water. With the presence of chloroform, hydrogen bond will form between acid molecule in lignin and chloroform and thus replaces the water molecules that originally bound to the lignin acid. Replacement of water by halogenated organic compounds will increase the specific gravity and increasing the lignin polymer hydrophobicity. With the increase of specific gravity, lignin deposition will occur together with the organic compounds. Due to the increase of hydrophobicity, the deposited lignin can be easily separated from water (Lim, 1994). The drawback of lignin isolation method using an inorganic acid is not environmentally friendly as large amount of used acid needs to be disposed. Therefore, an alternative method using CO<sub>2</sub> has been reported in literature by Luong *et al.* [7]. Addition of CO<sub>2</sub> plays role to decrease the pH and addition of Alum (KAl(SO<sub>4</sub>)<sub>2</sub>.12H<sub>2</sub>O) resulted on large precipitation of lignin at pH of 4. With this process, lignin isolation is faster, efficient and more environmentally friendly.

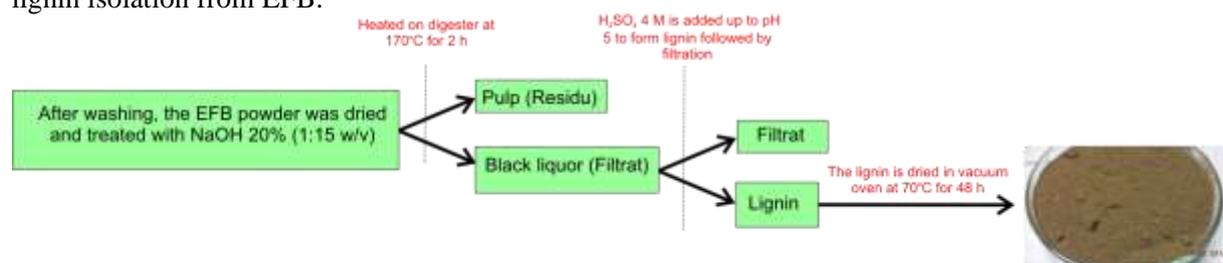
### 2.2. Lignin isolation from empty fruit bunch (EFB) of oil palm

There has been large interest to utilize empty fruit bunch of palm oil as raw material for SLS production. Palm oil business is one of the largest business sector in Indonesia where together with Malaysia, Indonesia is the largest producer of palm oil in the world. Utilization of solid waste from palm oil processing for SLS production may be beneficial particularly from economic point of view. The composition of palm oil solid waste as well as their content is presented in Table 1.

**Table 1.** The composition of different part of a palm oil tree

| No | Solid Waste             | Composition (wt.%) |                |        |     |     |        |
|----|-------------------------|--------------------|----------------|--------|-----|-----|--------|
|    |                         | Cellulose          | Hemi Cellulose | Lignin | Wax | Ash | Others |
| 1. | Fiber                   | 19,0               | 15,2           | 30,5   | 9,1 | 7,0 | 19,2   |
| 2. | Shell                   | 14,7               | 16,4           | 53,6   | 2,3 | 2,3 | 10,7   |
| 3. | Empty fruit bunch (EFB) | 35,8               | 21,9           | 17,9   | 4,0 | 3,0 | 17,4   |
| 4. | Palm frond              | 31                 | 17,1           | 22,9   | 2   | 2,8 | 24,2   |
| 5. | Trunk                   | 39,9               | 21,2           | 22,6   | 3,1 | 1,9 | 11,3   |

Synthesize of SLS from empty fruit bunch (EFB) of oil palm has been the focus of SLS research at UGM. Isolation of lignin from EFB is the first step in SLS synthesize. Figure 3 shows the process of lignin isolation from EFB.



**Figure 3.** Lignin isolation technique from Empty Fruit Bunch (EFB) of Oil Palm

Initially, EFB powder was reacted with NaOH to degrade the lignin in an autoclave (digester). Subsequently, the black liquor was then filtered with addition of H<sub>2</sub>SO<sub>4</sub> to obtain solid lignin. The solid lignin was then dried in an oven to obtain lignin powder.

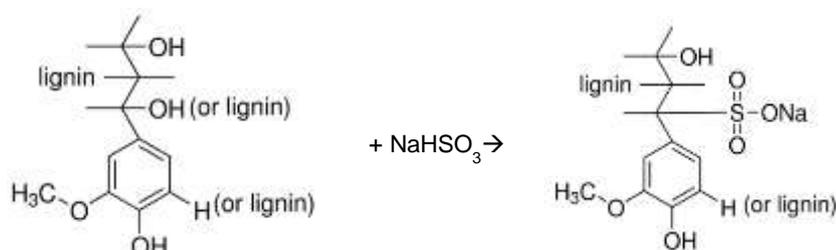
### 2.3. Lignin sulphonation

SLS can be synthesized from lignin by sulfonation reaction. Sulfonation reaction aims to insert sulfonate groups and thus changes the physical properties of lignin to be more polar as lignosulfonate salt [8]. There are several methods to carry out lignin sulphonation as has been reported by Inwood [4] in Table 2.

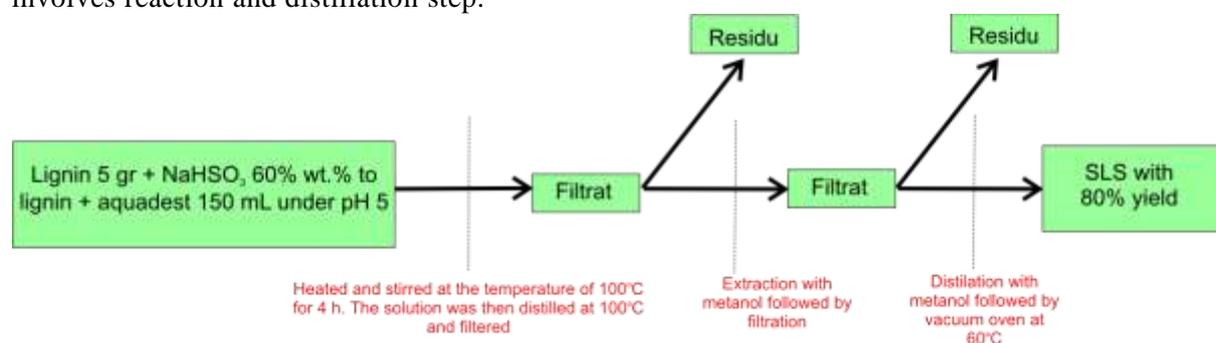
**Table 2.** Various methods for lignin sulphonation

| Starting Material | Reagent  | References |
|-------------------|--|------------|
| Phenolated lignin | sulfuric<br>1. 1 M NaOH + 37% formalin → 1M HCl<br>2. 40% NaHSO <sub>3</sub>             | [9]        |
| Phenolated lignin | sulfuric<br>0,5 M NaOH + CH <sub>2</sub> (OH)SO <sub>3</sub> Na                          | [9]        |
| Phenolated lignin | sulfuric<br>1. HCHO + 3M NaOH<br>2. C <sub>2</sub> Cl <sub>4</sub> + ClSO <sub>3</sub> H | [10]       |
| Alkali lignin     | -<br>1. HCHO<br>2. Na <sub>2</sub> SO <sub>3</sub>                                       | [11]       |
| Lignin            | -<br>SO <sub>3</sub> <sup>2-</sup> + CH <sub>2</sub> O                                   | [12]       |

In general, it can be inferred from the tabulated data that concentrated sulfuric acid, sodium bisulfate, sodium sulfate, chlorosulfuric acid and sulfur trioxide are capable of sulfonating lignin with a high efficiency. However, each reagents may have advantages and weaknesses such as corrosion problem. Lignin sulphonation in our lab was conducted with the aid of NaHSO<sub>3</sub> according to the following reaction:

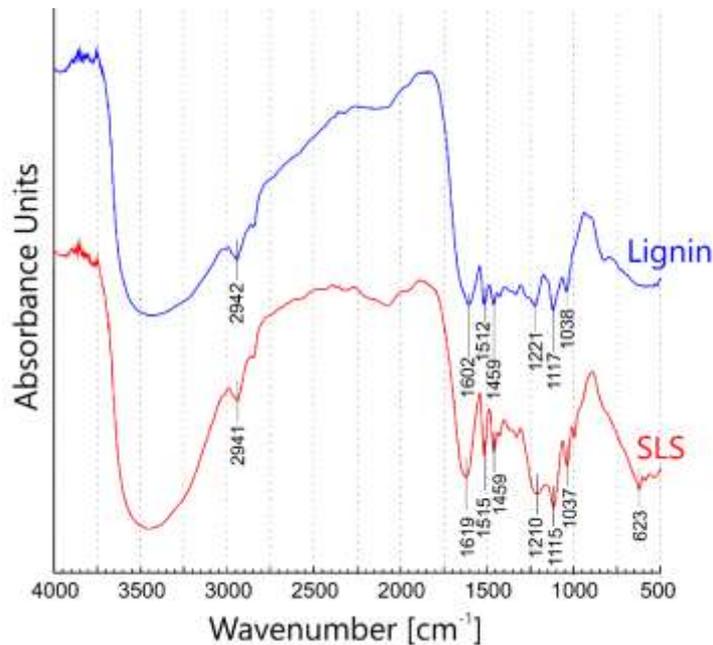


A brief schematic method to carry out lignin sulphonation is presented in Figure 4. The process involves reaction and distillation step.



**Figure 4.** Schematic diagram for lignin sulphonation with NaHSO<sub>3</sub>

FTIR analyses were conducted to evaluate the insertion of SO<sub>3</sub> group into lignin. Figure 5 shows the FTIR spectrophotograms of lignin and SLS using Shimadzu IR Prestige-21. In general, the spectra of lignin and SLS are relatively similar. However, the spectrophotogram of SLS shows more intensities to the presence of S-O vibration at 623 cm<sup>-1</sup>, vibration of SO<sub>3</sub> group at 1115 cm<sup>-1</sup> and vibration of symmetrical stretch of S-O at 1037 cm<sup>-1</sup>. Hence, it can be concluded that insertion of SO<sub>3</sub> group into lignin structure took place during sulphonation of lignin with NaHSO<sub>3</sub>.



**Figure 5.** FTIR spectrophotograms of lignin and SLS

### 3. Formulation of SLS for EOR application

There are requirements that has to be met by any surfactant for EOR application. These requirements are shown in Table 3. The most crucial part for SLS development for EOR surfactant was to find the appropriate formula in order to meet the requirements as mandated by SKK Migas. It is generally accepted that the EOR surfactant is developed based on field specific based on the field characteristic such as reservoir condition, brine etc. The up-scaling process from lab scale to field test is often far from trivial due to the field condition (practical issues) and the large amount of surfactant that is needed for the injection.

**Table 3.** The requirements of EOR Surfactant by SKK Migas

|                      |  |
|----------------------|--|
| IFT                  | $10^{-3}$ - $10^{-4}$ dyne/cm                              |
| Phase behavior       | Type III (Middle phase) or Type II (bottom phase)          |
| Compatibility        | Clear > 7 days   |
| Thermal stability    | IFT in the range of $10^{-3}$ dyne/cm for at least 90 days |
| Filtration ratio     | < 1.2  |
| Adsorption           | Average < 0.4 mg/g   |
| pH                   | 6-8  |
| Incremental recovery | $\geq 10\%$  |
| Price                | ca. 5 USD/kg   |

One of the challenge was to obtain IFT value within the range of  $10^{-3}$ - $10^{-4}$  dyne/cm. In our lab, measurement of IFT was typically conducted on TX-500 Spinning Drop Tensiometer. The result of IFT measurement of the SLS that we produced from black liquor gave  $9.15 \cdot 10^{-1}$  dyne/cm. As a result, formulation of SLS is needed by mixing it with long chain alcohol and PFAD (palm fatty acid distillate). We have been able to obtain a surfactant formula with the alcohol contain of less than 10% (wt.%) and gave the IFT value around  $10^{-3}$  dyne/cm. However, other aspect which is also crucial was to find a good thermal stability for 90 days test. Our test showed that the IFT value fluctuated and it

might go beyond the  $10^{-3}$  dyne/cm value during the 90 days test. As a result, finding the right formulae of EOR surfactant is probably the most intensive work in EOR development as large screening process is needed with the aid of ternary diagram. This issue is still under investigation and better formulation as well as better stability is continuously studied in our lab.

#### 4. Conclusions

With the growing concern to increase petroleum production, the use of tertiary EOR will play an important role in the future. Therefore, it is important to develop local surfactant which fulfils all the requirement for EOR surfactant. SLS appears as one of promising surfactant for EOR and may be produced from abundant sources such as black liquor and empty fruit bunch of palm oil. Here, we have presented the method for SLS production from those sources. Eventually, our experience shows that SLS may have a promising future with appropriate formulation and economically competitive with other surfactants.

#### Acknowledgements

We would like to acknowledge Pertamina UTC for the financial support as well as good collaboration throughout the SLS project at UGM. In addition, we also would like to thank Pusat Studi Energi (PSE) UGM for good arrangement and administration of the project.

#### References

- [1] Froning H R, Fussell D D and Heffern E W 2015 *Enhanced Oil Recovery in Encyclopedia of Chemical Technology* vol 17, ed Kirk Othmer ( Canada : John Wiley & Sons Inc)
- [2] Rieger M M 1985 Surfactant in Cosmetic in *Surfactant Science Series* (New York: Marcell Dekker Inc)
- [3] Rosen M J dan Kunjappu J T 2012 *Surfactants and Interfacial Phenomena* (Canada: John Wiley & Sons Inc)
- [4] Inwood J P 2014 *Sulfonation of Kraft Lignin to Water Soluble Value Added Products* (United States : ProQuest LLC)
- [5] Pollak A 2015 Lignin in *Encyclopedia of Chemical Technology* vol 17, ( Canada : John Wiley & Sons Inc)
- [6] Lim L 1994 *Isolasi Lignin dari Lindi Hitam Pabrik Kertas Leces* (Indonesia : Gadjah Mada University)
- [7] Luong N D, Binh N T T, Duong L D, Kim D O, Kim D S, Lee S H, Kim B J, Lee Y S and Nam J D 2012 An eco-friendly and efficient route of lignin extraction from black liquor and a lignin-based copolyester synthesis *Polym. Bull.* **68** 879-90
- [8] Teke J 2015 *Pengaruh Penambahan Epoksidasi Asam Risinoleat Minyak Jarak (Castor Oil) dan Kosurfaktan terhadap Kinerja Sodium lignosulfonate (SLS) dalam Menurunkan Interfacial Tension (IFT) pada Proses Enhanced Oil Recovery (EOR)* (Indonesia : Gadjah Mada University)
- [9] Matsushita Y and Yasuda S 2005 Preparation and evaluation of lignosulfonates as a dispersant for gypsum paste from acid hydrolysis lignin *Bioresour Technol.* **96** 465-470
- [10] Yasuda S and Asano K 2000 Preparation of strongly acidic cation exchange resins from gymnosperms acid hydrolysis lignin *J. Wood Sci.* **46** 477 - 479
- [11] Ouyang X, Ke L, Qiu X, Guo Y and Pang Y 2009 Sulfonation of alkali lignin and its potential use in dispersant for cement *J. Dispersion Sci. Technol.* **30** 1-6
- [12] Meister J J 2002 Modification of lignin *J. Macromol. Sci. - Polymer Reviews C* **42** 235-289