J. Eng. Technol. Sci., Vol. 53, No. 2, 2021, 210210

Development of Ultralow Interfacial Tension Lignosulfonate from Kraft Black Liquor for Enhanced Oil Recovery

Muhammad Mufti Azis[1,2*], Fergie Febrina[1], Ignesti Anindia[1], Galuh Almas Darmawati[1], Desi Amalia Fenyka[1], Suryo Purwono[1] & Rochmadi[1]

[1]Department of Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada, Jalan Grafika 2, Yogyakarta, 55281, Indonesia
[2]Centre for Energy Studies, Gadjah Mada University, Sekip K-1A Kampus UGM, Yogyakarta 55281, Indonesia
*E-mail: muhammad.azis@ugm.ac.id

Highlights:

- Synthesis of low-cost lignosulfonate as EOR surfactant from black liquor.
- Isolation of lignin from black liquor using a novel CO_2 bubbling method.
- The best mixture of surfactant gave ultralow IFT that is suitable for EOR application.

Abstract. Indonesia aims to implement large-scale enhanced oil recovery (EOR) to increase the national oil production. Chemical EOR is a promising technology to boost the production of old reservoirs with the aid of surfactants and polymers. Thus, the production of low-cost EOR surfactants from local resources with acceptable performance is highly attractive. The objective of the present work was to demonstrate the development of low-cost lignosulfonate surfactant production from kraft black liquor (BL). First, lignin was isolated from black liquor using a novel CO_2 bubbling technique, followed by addition of coagulants. Next, sodium lignosulfonate (SLS) was synthesized from the resulting lignin, followed by formulation of SLS with octanol and palm fatty acid distillate (PFAD) soap to obtain an ultralow interfacial tension (IFT) surfactant. The initial IFT value of the SLS solution was already high at 0.7 mN/m. After formulation, the composition SLS:PFAD soap:octanol = 70:22:8 (wt%) improved the IFT value to 3.1 10^{-3} mN/m. An ultralow IFT in the range of 10^{-3} mN/m as achieved here fulfills the required IFT value for EOR surfactant.

Keywords: *black liquor; EOR surfactant; formulation; IFT; lignin; sodium lingo-sulfonate.*

1 Introduction

The national energy policy of Indonesia (*Kebijakan Energi Nasional*) mandates the utilization of energy resources as national capital development. This is expected to create a multiplier effect towards increasing the welfare of society. The 4th most populated country in the world, Indonesia strongly relies on crude

Received 18 April 2019, Revised June 11, 2020, Accepted for publication November 19th, 2020.
ISSN: 2337-5779,
DOI: 10.5614/j.eng.technol.sci.2021.53.2.10

oil, as reflected in the present energy mix. Unfortunately, national crude oil production has declined continuously from 1.6 million of BOPD (barrels of oil per day) in 1995 to 786 thousand of BOPD in 2015 [1]. However, this oil production decrease has been accompanied by an increase in fuel consumption (known as *Bahan Bakar Minyak*, or *BBM*). To illustrate, Indonesia consumed 1.229 million BOPD of transportation fuel in 2015, which was fulfilled by the import of 548 thousand BOPD of transportation fuel [1]. Increasing the crude oil production has been set as a national agenda. The government of Indonesia committed itself to facilitating the implementation of enhanced oil recovery (EOR) in order to improve the production of existing reservoirs in Indonesia. To initiate EOR implementation, the government appointed 32 oil fields as pilot projects, as described in [1].

Chemical EOR is one of the most promising techniques to improve oil production by injection of surfactants or polymers into reservoirs [2]. The implementation of EOR in Indonesia will require large amounts of surfactants and hence it is important to produce surfactants with good EOR performance in economically sound manner by using local resources. Hence, the use of biomass-based surfactants is expected to play a role in lowering the operation costs of EOR compared to the use of existing petroleum-based surfactants. It is known that lignin is the second most abundant resource on earth. Hence, it is inexpensive and its utilization for EOR surfactants may be attractive [3]. Pioneering work on the utilization of lignosulfonates for EOR was done by DeBones and Whittington from Texaco in 1992, who reported the utilization of lignin to form a lignosulfonate-amine surfactant that could be applied in improved oil recovery (IOR) at realistic temperature and salinity conditions [4].

Production of lignosulfonate from kraft black liquor (BL) is an attractive option, as BL from pulp mills is often considered waste. Production of sodium ligno sulfonate (SLS) from various raw materials, such as oil palm empty fruit bunch (OPEFB) and BL from kraft pulp mills, have been reported in the literature [5-7]. In addition to BL, Setiati, *et al.* [8] synthesized SLS from bagasse, which resulted in an SLS solution that had good aqueous stability and was perfectly soluble and clear. Lignin utilization from OPEFB is an attractive pathway, as OPEFB is an abundant resource and thus inexpensive. Our experience, however, has shown that SLS synthesis from OPEFB is often limited by the small amount of lignin that can be extracted from OPEFB. This step often turned out to be a bottleneck in SLS synthesis in the lab. Thus, extracting lignin from BL is an attractive alternative to using OPEFB.

Extraction of lignin is an important step in the synthesis of SLS. Isolation of lignin from BL solution is typically conducted with addition of a strong acid to lower the pH, allowing precipitation of the lignin. Purwono and Murachman [6] conducted isolation of lignin from BL by addition of hydrochlorid acid and chloroform to facilitate filtration and sedimentation of the lignin. The lignin yield was highly affected by the amount of chloroform added to the BL solution. Luong, *et al.* [9] have reported a novel technique for lignin extraction from BL solution by using a combination of CO_2 and alum as coagulant. This technique eliminates the use of a strong, toxic acid and is considered a more environmentally-friendly method. With proper washing, the resulting lignin showed high purity, comparable to that of commercial lignin.

For chemical EOR application, it is important for the surfactant to reach ultralow interfacial tension (IFT) within the range of 10^{-3} mN/m. Hence, it is common to add or mix in a cosurfactant to obtain such performance. However, the final surfactant mixture should be stable and economically attractive, especially for large-scale implementation. Ganie, *et al.* [10] have proposed a mix of EOR surfactant that consists of lignin, amine and sodium dodecylbenzene sulfonate. They found that the mixture gave IFT lower than 1 mN/m. Formulation of SLS with sodium oleate and ethylene glycol buthyl ether (EGBE) has been reported to give IFT 2.1 10^{-3} mN/m [11]. Instead of mixing with a cosurfactant, modification of lignin to obtain lignin polyether sulfonate (LPES) with alkoxylation, allylation and sulfonation has been reported by Chen, *et al.* [12] to give ultra-low IFT. In addition, they also reported that modification of alkali lignin to lignin sulphobetaine zwitterionic surfactants (LSBA) also exhibited a promising result for oil recovery [13]. Kakoty and Gogoi [14] have reported that the mixture of natural surfactant of SLS, sodium dodecyl sulfate (SDS) and a small amount of Na_2CO_3 can obtain ultralow IFT, in the range of 10^{-1}-10^{-2} mN/m.

The first objective of the present study was to investigate the extraction of lignin from BL solution using CO_2 and two types of coagulants, namely aluminum sulphate ($Al_2(SO_4)_3.14H_2O$) [15] and poly aluminum chloride (PAC) [16]. It was expected that the optimal setting for both coagulants could be determined in order to obtain a large amount of lignin from BL solution. The second objective of this study was to synthesize SLS and formulate SLS with octanol and palm fatty acid distillate (PFAD) soap to obtain ultralow IFT within the range of 10^{-3} mN/m as required for EOR application [17-18]. The influence of SLS, PFAD and octanol composition was investigated systematically to obtain ultralow IFT values.

2 Materials and Experimental Methods

2.1 Materials

Kraft black liquor as main raw material was obtained from PT Riau Andalan Pulp and Paper (RAPP), Riau. For isolation of lignin, poly aluminum chloride as well as aluminum sulphate ($Al_2(SO_4)_3.14H_2O$), coagulants were obtained from Coal, Gas and Petroleum Technology Lab UGM. A number of chemicals, such as methanol, $NaHSO_3$ 39% (Merck), n-octanol 99% (Merck), NaOH and palm fatty acid, were obtained from the same lab. Crude oil with specific gravity of 52.8°API and saline water from the same field were also obtained from this lab for IFT measurement.

2.2 Experimental Methods

2.2.1 Isolation of Lignin from Kraft BL

The use of CO_2 to isolate lignin followed the method of Luong, *et al.* [9]. Bubbling of the CO_2 was conducted in a batch acrylic reactor equipped with a sparger. Approximately 500 ml of kraft BL solution was added to the reactor. CO_2 bubbling was carried out for 2 h, which caused the pH to decrease from ca. 12 to 8. The flow of CO_2 was maintained to ensure stable and uniform distribution of CO_2 in the liquid as well as to minimize foam formation.

In order to decrease the pH as well as to facilitate lignin precipitation, addition of coagulant to the BL solution was carried out, using 2 types of coagulants: poly aluminum chloride (PAC) and aluminum sulphate ($Al_2(SO_4)_3.14H_2O$). The volume of BL solution used for lignin precipitation experiments was maintained at 150 ml. The variation of coagulant amounts that were added to the BL solution is presented in Tables 1 and 2.

Table 1 Variation of the amount of aluminum sulphate added to the BL solution.

Sample	Mass of aluminum sulphate (g)	Coagulant Concentration (g/ml)
A	1506	0.1506
	2505	0.2505
	3508	0.3508
B	2509	0.2509
	3008	0.3008
	3504	0.3504
C	2001	0.2001
	4004	0.4004
	4504	0.4504

After addition of the coagulant, the pH of the BL solution typically dropped, allowing the lignin to precipitate. Here, the amount of coagulant was varied and the pH was measured regularly to evaluate the lignin yield. The BL solution was then allowed to settle overnight.

The solution was then filtered to separate the lignin from the liquid solution. Subsequently, the lignin was washed with aquadest to remove impurities from the coagulant. The lignin powder was then dried in an oven (Memmert UN30) at 70 to 80°C. The color of the extracted lignin turned to be dark brown, which is the original color of the lignin. The mass of lignin was then weighed in a digital analytical balance.

Table 2 Variation of the amount of PAC added to the BL solution.

Sample	Mass of PAC (g)	Concentration of PAC (V = 200mL)	Volume of PAC coagulant added to BL solution	Mole of PAC added to BL solution
A	50.10	1.43	100	143.5
	100.00	2.86	100	286.5
	150.09	4.30	100	430.0
B	25.10	0.72	200	143.5
	50.05	1.43	200	286.5
	75.00	2.15	200	430.0
C	15.06	0.43	200	86.3
	24.99	0.71	200	143.2
	35.06	1.00	200	200.9

2.2.2 Synthesis of SLS from Lignin

Sulfonation of the lignin was conducted in a three-neck flask reactor. The reactor was equipped with a condenser, a magnetic stirrer and a heater. Approximately 5 g of lignin powder was dissolved into 250 ml of solution of sodium bisulfite ($NaHSO_3$) 0.3 M, stirred and heated at 97 °C for 4 hours. Subsequently, the solution was filtrated to obtain unreacted lignin (solid) and filtrate (SLS and unreacted $NaHSO_3$). Distillation was then carried out at 100 °C to remove the water from the filtrate. In addition, the solid mixture of SLS and a certain amount of $NaHSO_3$ were then dissolved in 200 mL of methanol solution, followed by stirring for 30 minutes. The solution was filtered to separate the dissolved SLS into methanol (liquid) and $NaHSO_3$ (solid). The filtrate was then distilled at 70 °C to remove the methanol, obtaining a light brown SLS powder.

2.2.3 Formulation of SLS with PFAD Soap and Octanol

Formulation of SLS to obtain the surfactant mix was conducted by mixing SLS, octanol and palm fatty acid distillate (PFAD) in saline water. The amount of SLS and octanol was varied systematically to obtain the mixture with the lowest interfacial tension (IFT) values. The mixing was conducted with a magnetic stirrer at 70 °C for 2 hours, followed by filtration to remove solid impurities. Formulation of SLS with PFAD soap and octanol was conducted on mass basis. For instance, the composition of SLS:PFAD:octanol = 68:24:8 was obtained by mixing 0.204 g of SLS, 0.072 g of PFAD soap and 0.024 g of octanol, respectively, to give a total weight of 0.3 g. This mixture was then added to 30 ml of saline water to obtain 1 wt% surfactant solution.

2.2.4 IFT Measurements

Interfacial tension (IFT) was measured using a TX-500 Spinning Drop Tensiometer at the Department of Chemical Engineering, UGM. Initially, the SLS solution was diluted to 1 wt% solution with saline water. The SLS solution was inserted into a capillary pipe, which was then closed. As much as 0.3μL of crude oil was injected into a capillary pipe using a micrometer. The capillary tube filled with SLS solution and oil was rotated at 3000 rpm at a temperature of 50 °C for at least 1 hour before the IFT value was recorded.

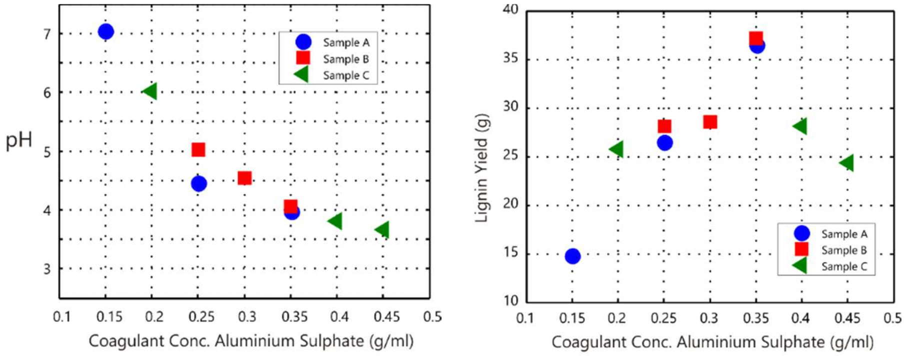
3 Results and Discussion

The extraction of lignin was initiated by CO_2 bubbling into the BL solution, which caused the pH to decrease. The decrease of pH may be due to the dissociation reaction of H^+ ion formation in the solution. The pH value of the BL solution from the initial pulp mill waste was 12.21, which subsequently dropped to ca. 8 after the bubbling step. To facilitate lignin precipitation, we treated our samples by adding two types of coagulants, namely aluminum sulphate and PAC; the results are presented here.

3.1 Influence of Aluminum Sulphate Concentration on the Final pH and Yield of Lignin

Figure 1 shows the final pH of BL solution and the lignin yield following the addition of aluminum sulphate as coagulant. We used 3 batches of samples (denoted as sample A, B and C) with an initial pH of ca. 8. Here, the volume of aluminum sulphate solution (at various concentrations) was kept constant at 100 ml and was added to 150 ml of BL solution. As can be seen from Figure 1(a), increasing the aluminum sulfate concentration gave a lower final pH. It can be inferred that the addition of coagulant resulted in more hydroxyl phenolic groups in the protonated lignin. As a result, a portion of the ionized phenolic groups was converted to non-ionized phenolic groups. The protonation reaction that occurs in the BL solution facilitates more H^+ ions, which decreases the pH of the solution. Figure 1(b) shows the influence of coagulant concentration on the lignin yield.

In general, the higher the concentration of coagulant the higher the lignin yield. Addition of coagulant concentration accelerates the formation of ionized hydroxyl phenolic groups and hence a larger lignin yield can be obtained. It is also interesting to note from Figure 1(b) that increasing the coagulant concentration up to 0.35 g/L gave an increase of the lignin yield reaching a maximum of 37 g lignin. Further increase of the coagulant concentration gave a lower lignin yield. This indicates an optimum coagulant concentration, which gave the highest yield at final pH 4 and a coagulant concentration of 0.35 g/L.



(a) (b)

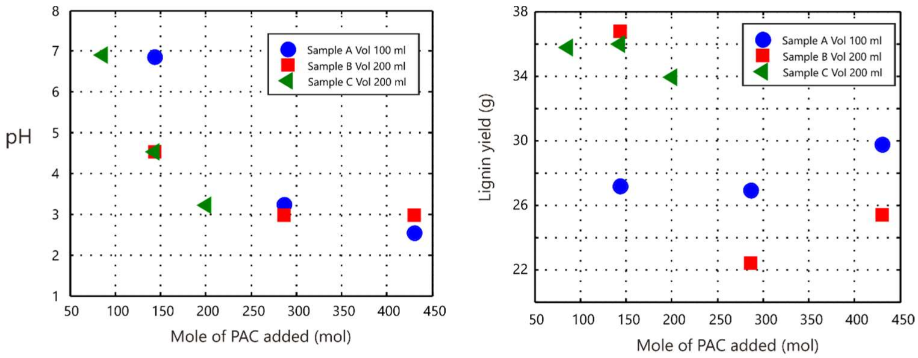
Figure 1 Influence of the coagulant concentration of aluminum sulphate on the final pH of the BL solution (a) and lignin yield (b) by using three samples denoted as sample A, B and C.

3.2 Influence of PAC Concentration on the Final pH and Yield of Lignin

The investigation of the influence of PAC addition on the lignin yield and the final pH was conducted by varying the volume of the PAC solution that was added to the BL solution, as described in Table 2. Figure 2 illustrates the influence of PAC on the final pH as well as the lignin yield as a function of the number of moles and the volume of the PAC solution.

As can be seen from Figure 2(a), the increase of PAC moles may lower the pH from ca. 7 to ca. 3. However, it is interesting to note that increasing the number of PAC moles beyond 200 moles had a negligible influence on the pH, as it tended to level out at pH 3. The influence of PAC on the lignin yield is presented in Figure 2(b). Generally, we observed that the lignin yield of the PAC was higher than that of the aluminum sulphate. The lignin yield varied between 22 and 37 g of lignin for 150 mL of BL solution. However, in spite of point scattering, we could also observe that the increase of the number of PAC moles generally tended to lower the lignin yield.

The PAC volume added to the BL solution was found to have a significant influence on the lignin yield at the same mole amount of PAC. For instance for 143 PAC moles, the dilute PAC solution of 0.7 M, as represented by samples B and C, gave a much higher yield than sample A (1.4 M). The maximum yield of PAC was obtained by using 0.72 M solution with a volume of 200 ml, which resulted in 37 g of lignin.



(a) (b)

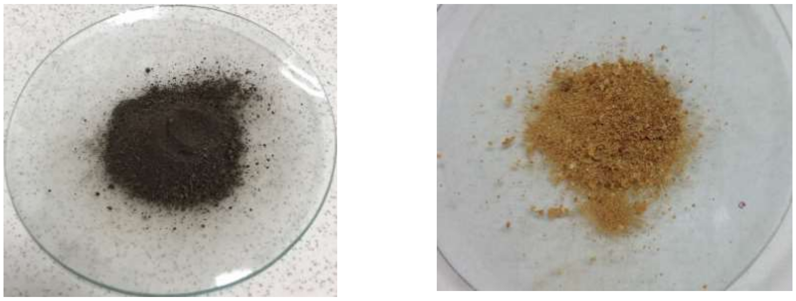
Figure 2 Influence of the number of PAC moles added on the final pH of the BL solution (a) and lignin yield (b). Sample A, B and C had different volumes of coagulant solution added to the BL solution.

3.3 Formulation of SLS with PFAD Soap and Octanol

Sulfonation of lignin aimed to insert sulfonate groups into the lignin in order to create hydrophilic groups. It is clear that there was a color change from lignin to SLS after sulfonation, as shown in Figure 3. Sulfonation of 5 g lignin typically gave 1.4 g of SLS powder, which indicates a lignin yield of approximately 28% (mass basis). In addition, our parallel work showed that the FTIR analyses of the lignin resulting from this method gave similar spectra to commercial lignin, which indicates the compatibility of lignin from BL with commercial lignin [19].

Formulation of SLS, octanol and PFAD was conducted by varying the ratio of each compound to obtain an ultralow IFT surfactant within the range of 10^{-3} mN/m. It is important to note that the formulation of SLS should maintain a high proportion of SLS as the main compound in the surfactant mix. Without formulation, our result showed that the IFT value of 1 wt% SLS solution was 0.7

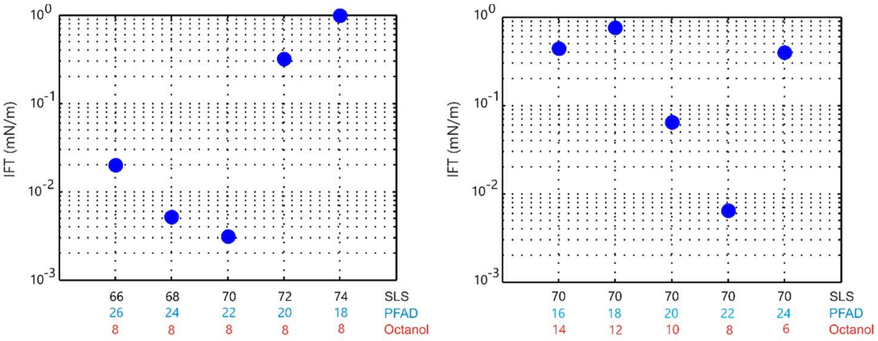
mN/m. This is considerably high for direct EOR application. The IFT value of the SLS solution is in agreement with Prakoso, *et al.* [7], who reported 0.2 mN/m.



(a) (b)

Figure 3 Appearance of the lignin powder extracted from kraft black liquor (a) and SLS powder (b)

Figure 4 shows the IFT values for various mixtures of SLS:PFAD:octanol in a semilog plot. Figure 4(a) shows the influence of SLS and PFAD on the surfactant mix. It is obvious that the IFT values were scattered and highly sensitive to small changes of SLS composition with a large IFT range, from 3.10^{-3} to 1.9 mN/m. Figure 4(b) similarly shows that varying the amount of octanol and PFAD gave IFT values from $6.5.10^{-3}$ to 0.76 mN/m. The scattering values of IFT indicate complex interactions among the surfactant mix, oil and water. The formulation is optimal when the affinity of the amphiphile(s) at the interface is exactly the same for the oil and water phases at a certain temperature [20].



(a) (b)

Figure 4 IFT values from the formulation of surfactant mix at various ratios of SLS:PFAD:octanol. The effect of varying the amount of SLS and PFAD at a constant octanol weight of 8 wt% (a) and the effect of varying the amount of PFAD and octanol at a constant SLS weight of 70 wt% (b).

It should be emphasized that the composition of 70:22:8 was measured 2 times and gave a consistent ultralow IFT value of $3.1.10^{-3}$ and $6.5.10^{-3}$ mN/m, respectively. It can be concluded that the mixture of 70:22:8 was optimal and fulfills the requirement for EOR surfactants. Hence, the formulation of SLS demonstrated in the present study was successful in obtaining a mixed-surfactant composition with an ultralow IFT value in the range of 10^{-3} mN/m. Our results showed that with proper formulation, SLS is a promising EOR surfactant candidate with an ultralow IFT value suitable for EOR application. It is also noteworthy that the use of PFAD as demonstrated here is expected to lower the surfactant cost compared to the use of formulas as for example in [10,11,14].

Further work, however, is needed to confirm the thermal stability of SLS surfactant, especially at higher temperatures, which characterize reservoirs in Indonesia. In addition, it is also important to conduct a flooding test in a lab-size facility to evaluate the performance of SLS to improve oil recovery as well as to investigate the influence of salinity on oil recovery [12,13]. Further, a study on a preliminary design of a pilot plant for SLS production could be an attractive path in order to evaluate the feasibility of SLS production with the present method on a larger scale.

4 Conclusions

Development of a low-cost surfactant from kraft black liquor solution through a novel method of lignin extraction as well as formulation of SLS surfactant to obtain ultralow IFT was presented in this paper. The isolation of lignin from black liquor was conducted by using 2 types of coagulants: poly aluminum chloride (PAC) and aluminum sulphate (Al2(SO4)3.14H2O). Bubbling of CO_2 for 2 h could decrease the pH of the BL solution from the initial pH of 12 to ca. 8. Addition of 100 ml of 0.35 gr/l aluminum sulphate solution could further decrease the pH to ca. 4 to obtain a maximum lignin yield of 37 gr from 150 ml of BL solution. Similarly, addition of 200 ml of dilute PAC solution of 0.7 M could decrease the pH to 4.5 with a maximum lignin yield of 36 gr from 150 ml of BL solution.

Sulfonation of lignin to obtain SLS was conducted using $NaHSO_3$ solution. The initial IFT value of the SLS solution was considerably high at 0.7 mN/m. After formulation it was found that the composition SLS:PFAD soap:octanol = 70:22:8 (wt%) gave an IFT value of $3.1\ 10^{-3}$ mN/m. This IFT fulfills the ultralow IFT requirement for EOR application. The development of a low-cost SLS surfactant as demonstrated here is promising, as it provides not only an environmentally-friendly method for lignin extraction but also an ultralow IFT surfactant that is suitable for the implementation of EOR at lower operation cost.

Acknowledgements

PT. Riau Andalan Pulp and Paper (RAPP) is greatly acknowledged for providing the black liquor from Pangkalan Kerinci Plant in Riau. This work was supported by the Department of Chemical Engineering, Faculty of Engineering, UGM. Mr. Suhardi is greatly acknowledged for his practical help in the lab.

References

[1] Republic of Indonesia, Presidential Regulation No. 22/2017, *National Energy General Plan*, accessed from http://jdih.esdm.go.id/peraturan/Perpres %2022%20Tahun%202017.pdf (17 October 2018).

[2] Sheng, J.J., *Modern Chemical Enhanced Oil Recovery: Theory and Practice*. United States, Elsevier, 2011.

[3] Calvo-Flores, F. G., Dobado, J. A., Isac-García, J. & Martín-Martínez, F. J., *Lignin and Lignans as Renewable Raw Materials: Chemistry, Technology and Applications*, United Kingdom: John Wiley & Sons, Ltd, 2015.

[4] DeBons, F.E. & Whittington, L.E., *Improved Oil Recovery Surfactants Based on Lignin*, J. Petrol. Sci. Eng., **7**(1-2), pp. 131-138, 1992.

[5] Azis, M.M., Rachmadi, H., Wintoko, J., Yuliansyah, A.T., Hasokowati, W., Purwono, S., Rochmadi & Murachman, B., *On the Use of Sodium Lignosulphonate for Enhance Oil Recovery*, IOP Conf. Ser. Earth Environ. Sci., **65**, 012030, 2017.

[6] Purwono, S. & Murachman, B., *Development of Non Petroleum Base Chemicals for Improving Oil Recovery in Indonesia*, SPE Asia Pacific Oil and Gas Conference and Exhibition, Jakarta, 17-19 April 2001.

[7] Prakoso, N.I., Purwono, S. and Rochmadi, *Synthesis and Application of Green Surfactant from Oil Palm Empty Fruit Bunches' Lignin for Enhanced Oil Recovery Studies*, Chem. Eng. Trans., **63**, pp. 739-744, 2019.

[8] Setiati, R., Siregar, S., Marhaendrajana, T. & Wahyuningrum, D., *Challenge Sodium Lignosulfonate Surfactants Synthesized from Bagasse as an Injection Fluid Based on Hydrophil liphophilic Balance*, IOP. Conf. Ser.: Mater. Sci. Eng., 434 012083, 2018.

[9] 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. & Nam, J-D., *An Eco-friendly and Efficient Route of Lignin Extraction from Black Liquor and a Lignin-based Copolyester Synthesis*, Polym. Bull., **68**(3), pp. 879-890, 2012.

[10] Ganie, K., Manan, M.A., Ibrahim, A. & Idris, A.K., *An Experimental Approach to Formulate Lignin-Based Surfactant for Enhanced Oil Recovery*, Int. J. of Chem. Eng., **2019**, 4120859, 2019.

[11] Sudarmoyo, Swadesi, B., Andini, A.N., Siregar, S., Kurnia, R., Buhari, A. and Budiaman, IGS, *Laboratory Study: The Development of a Sodium*

Lignosulfonate (SLS) Surfactant Formulation for Light Oil Reservoir to Improve Oil Recovery, AIP Conf. Proc. 1977, 030033, 2018.

[12] Chen. S., Zhou, Y., Liu, H., Yang, J., Wei, Y. and Zhang, J. *Synthesis and Physicochemical Investigation of Anionic-Nonionic Surfactants Based on Lignin for Application in Enhanced Oil Recovery*, Energy Fuels, **33**, pp. 6247-6257, 2019.

[13] Chen. S., Liu, H., Sun, H., Yan, X., Wang, G., Zhou, Y. and Zhang, J. *Synthesis and Physicochemical Performance Evaluation of Novel Sulphobetaine Zwitterionic Surfactants from Lignin for Enhanced Oil Recovery*, J. Mol. Liq., **249**, pp. 73-82, 2018.

[14] Kakoty, M. & Gogoi, S.B., *Evaluation of Surfactant Formulation for EOR in Some Depleted Oil Fields of Upper Assam,* in: H. Ameen, T. Sorour (Eds.), Sustain. Issues Environ. Geotech., Springer International Publishing, Cham, pp. 57-75, 2019.

[15] Darmawati, G.A., *Optimization of Lignin Isolation from Black Liquor of Paper Mill with Aluminum Sulfate Coagulant as Raw Material for Sodium Lignosulfonate (SLS),* Research Report of Coal Gas and Petroleum Technology Lab, Department of Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada, Yogyakarta, 2017. (Text in Indonesian)

[16] Fenyka, D.A., *The Effect of Poly Aluminum Chloride (PAC) Coagulant Concentration for Optimization of Lignin Isolation from Black Liquor of Paper as Raw Material for Sodium Lignosulphonate (SLS) Surfactant,* Research Report of Coal Gas and Petroleum Technology Lab, Department of Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada, Yogyakarta, 2017. (Text in Indonesian)

[17] Febrina, F., *Synthesis of Sodium Lignosulfonate (SLS) from Black Liquor and Formulation with Octanol and PFAD to Obtain Mix-Surfactants with Interfacial Tension (IFT) of 10^{-3} mN/m,* Research Report of Coal Gas and Petroleum Technology Lab, Department of Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada, Yogyakarta, 2017. (Text in Indonesian)

[18] Anindia, I., *Synthesis of Sodium Lignosulfonate (SLS) from Black Liquor and The Effect of Mix-surfactant Composition (SLS, PFAD and Octanol) to Obtain IFT of 10^{-3} mN/m (Variations of PFAD and Octanol)*, Research Report of Coal Gas and Petroleum Technology Lab, Department of Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada, Yogyakarta, 2017. (Text in Indonesian)

[19] Putri, N.A., Azis, M.M. & Purwono, S., *A Comparison of Sodium Lignosulfonate (SLS) Synthesis from Black Liquor Lignin and Commercial Lignin*, Mat. Sci. Forum, **948**, pp. 206-211, 2019.

[20] Salager, J-L, Forgiarini, A.M., Marquez, L., Manchego, L. and Bullon, J., *How to Attain an Ultralow Interfacial Tension and a Three-Phase*

Behavior with a Surfactant Formulation for Enhanced Oil Recovery: A Review. Part 2. Performance Improvement Trends from Winsor's Premise to Currently Proposed Inter- and Intra-Molecular Mixtures, J. Surf. Deterg., **16**, pp. 631-663, 2013.