

The Effect of Acid Concentration (H_2SO_4) on the Yield and Functional Group during Lignin Isolation of Biomass Waste Pulp and Paper Industry

Slamet Priyanto^{1*}, Anansya Putri Intan¹, Bambang Rianto¹, Tutuk Djoko Kusworo¹, Bambang Pramudono¹, Edi Untoro², and Puspa Ratu²

¹) Department of Chemical Engineering, Diponegoro University, Jl. Prof. Soedharto, Tembalang, Semarang, Jawa Tengah, Indonesia 50239

²) Ministry of Energy and Mineral Resources Education and Training Agency (ESDM) Akamigas Cepu Mineral Energy School

*) Corresponding author: slametpriyanto2013@gmail.com
Telp/Fax.: +62-746-0058

(Received: October 25, 2019 Accepted: November 28, 2019)

Abstract

The decline in oil production in Indonesia lately has been much discussed by industrial practitioners, especially from the petroleum industry. The decrease is due to the age of old drilling wells with high water cut (> 90%), so it is necessary to pursue a production method that can increase the production of these old wells. The EOR (Enhanced Oil Recovery) method is one way of extracting oil from oil wells that cannot be further retrieved by injecting materials that are not in the reservoir. One ingredient that can be injected is Sodium Ligno Sulfonate (SLS) surfactant derived from lignin. Lignin was obtained from the lignin isolation process from Black Liquor, which in this study came from the pulp and paper mill waste of PT. Indah Kiat, Pekanbaru, Sumatra, Indonesia. This study aims to determine the effect of variations in H_2SO_4 concentrations (concentrations of 15%, 20%, 25%, 30% w/w) on the yield of lignin isolation results, and to compare the functional groups between dirty lignin, clean lignin, and pure lignin using FT-IR. Based on the research results, it was found that the best lignin is lignin with an H_2SO_4 concentration of 20%, with the highest yield and the color of lignin produced tends to be similar to pure lignin. In addition, it was found that the peak of the net lignin group had more similarity with commercial lignin compared to crude lignin.

Keywords: lignin; black liquor; Enhanced Oil Recovery (EOR); FTIR

How to Cite This Article: Priyanto, S., Intan, A.P., Rianto, B., Kusworo, T.D., Pramudono, B., Untoro, E., and Ratu, P. (2019), The Effect of Acid Concentration (H_2SO_4) on the Yield and Functional Group during Lignin Isolation of Biomass Waste Pulp And Paper Industry, Reaktor, 19(4), 162-167, <http://dx.doi.org/10.14710/reaktor.19.4.162-167>.

INTRODUCTION

The decline in petroleum production in Indonesia is a big problem that is being discussed lately. The decrease was due to the age of old drilling

wells with high water cut (> 90%), so it is necessary to pursue a production method that increases the production of old wells. One of the efforts made is the Enhanced Oil Recovery (EOR) method, which is

performed by injecting chemicals that are not present in the reservoir. Materials that are often used include surfactants dissolved in injection water. Injection water is mixed with surfactants to reduce Inter Facial Tension (IFT) between oil and water (R & D Ministry of Energy and Mineral Resources, 2010). One type of surfactant used is Sodium Ligno Sulfate (SLS). This material was isolated from lignin of the Black Liquor pulp and paper biomass waste. Black Liquor used in this study was the results of the pulp and paper industry process (Syahbirin, 2009). Lignin content in Black Liquor can reach 22.9% (Junaedi, 2011).

Black Liquor pollutes the environment if it is discharged without a proper processing. So far, the pulp and paper factory of PT. Indah Kiat in Pekanbaru, Sumatra, Indonesia uses Black Liquor as a fuel for its steam boilers. In this study, Black Liquor was isolated and its lignin content was taken. The isolation method used is the sedimentation isolation method with H_2SO_4 acid to precipitate its solids (Ma'ruf *et al.*, 2017).

The Black Liquor used was obtained from Acacia Mangium Willd wood. Lignin is the largest component found in the remaining solution of the pulp cooker. Lignin in black kraft softwood is found in about 22.9% of dry solids (Junaedi, 2011), or 14.6% according to the study of Priyanto (2018). Lignin can be used as fuel if it is really dry (Syahbirin, 2009). Lignin can also be used as a surfactant (Lubis, 2007). This study aims to study the effect of the best concentration of sulfuric acid (H_2SO_4) to produce the largest oil yield and characterize the purified lignin compared to the spectrum produced by the spectrophotometric FTIR.

This research was expected to be an alternative diversification in replacing imported products of Lignin to increase surfactant from petroleum production, which was still dominant in Indonesia's domestic usage. Black Liquor produced by the pulp industry in Indonesia was only used as boiler fuel. High lignin concentrations in Black Liquor could be isolated and then synthesized with bisulfite compounds into surfactants that have high economic value, thereby reducing surfactant imports.

This research would answer the challenge of getting purified lignin from biomass waste.

MATERIALS AND METHODS

The raw material used was Black Liquor from PT. Indah Kiat Pulp and Paper Corporation, Pekanbaru, Riau, Sumatra, Indonesia. Aquadest was obtained from UPT Laboratory of Diponegoro University and Indrasari Chemical Shop Semarang. H_2SO_4 and NaOH were also purchased from Indrasari Stores. Commercial lignin was obtained from PT. Aldrick Yogyakarta, Indonesia.

The research flow chart can be seen in Figure 1. The study was conducted in a separation laboratory at the Department of Chemical Engineering, Faculty of Engineering, Diponegoro University. The steps of the research carried out in the following sequences.

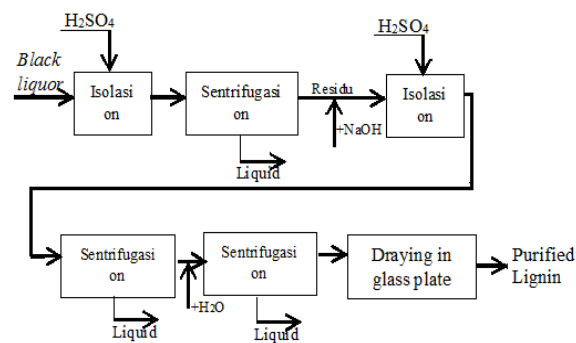


Figure 1. The Research Flow Chart

1. Isolation of Lignin

The lignin isolation method used refers to the method developed by Kim *et al.* (1987). First, Black Liquor from pulp and paper industry waste was dissolved with water in a beaker glass with a weight ratio of 1:1. Then the solution was slowly isolated with H_2SO_4 until the pH reaches 2 and the solution turned to brownish in color. Isolation was done by rapid stirring. If during the stirring the foam forms, stop the insulation and set the stirring to a low speed until the foam disappeared then continued isolation with rapid stirring again. The isolated solution was then separated using a centrifuge for 20 minutes at 3000 revolutions per minute. After centrifugation was complete, sediments in the form of solids which could be referred to as crude lignin, the remaining liquid in the form of degradation of organic substances and non-lignin substances were discarded.

To increase the purity of lignin, crude lignin was dissolved with 1 N NaOH until the pH becomes basic (10.5-11.5), then the solution was filtered using ordinary filter paper. After filtering was complete, the solution was isolated again using H_2SO_4 15% dropwise until the pH becomes 2.

The solution which had been acidified with H_2SO_4 was centrifuged again for 20 minutes at a speed of 3000 rpm. After centrifugation, the results of sedimentation in the form of solids were washed with distilled water until the pH reached a constant (neutral pH), and the filtrate was discarded. The solution was then centrifuged again for 20 minutes at 3000 revolutions per minute. After centrifugation, the result of sedimentation in the form of solids which could be called purified lignin was taken and dried on a glass plate at room temperature to dryness and the filtrate was discarded. Purified dried lignin was weighed. Then the purified lignin yield will be calculated using the formula:

$$yield_{purified\ lignin} = \frac{w_{purified\ lignin}}{w_{Black\ Liquor}} \times 100 \quad (1)$$

The above steps were repeated for other acid concentration variables, 20, 25, 30% w/w.

2. Observation of The Role Group of The Lignin

After obtaining crude lignin and purified lignin, characterization was compared to commercial lignin,

observed the role of groups in the spectrum using FT-IR spectrophotometry (Fourier Transform Infra Red Spectroscopy).

RESULTS AND DISCUSSIONS

Effect of Variation of Acid Concentration (H₂SO₄) on Yield Isolation of Lignin Is Obtained Table 1. Isolation of lignin from Black Liquor is best using sulfuric acid (H₂SO₄), especially for precipitation of lignin. This was consistent with the opinion of Kim *et al.* (1987) which states that the use of H₂SO₄ in lignin isolation is better than using HCl because the resulting lignin contains metal cations such as Na⁺ which was lower than the isolation using HCl. According to Damat (1989) to isolate lignin from the remaining solution of the pulp cooker, sulfuric acid (H₂SO₄) should be used because it was economically cheaper. The use of sulfuric acid will also degrade non-lignin organic substances.

The acid would precipitate lignin from Black Liquor because lignin was not soluble in acidic solutions. The concentrations used in the isolation of lignin varied, namely concentrations of H₂SO₄ 15%, 20%, 25%, and 30% w/w. The acid concentration used should be between 5 and 20% (Lubis *et al.*, 2007) to prevent the partial acidification process from achieving uniform acidification.

The resulting lignin was in the form of lignin powder. In this experiment, it was found that the best lignin was at a 20% H₂SO₄ concentration. This was indicated by the amount of lignin solid (yield) formed by lignin isolation, which was 22.98%. The results of this experiment were the same as the results of research conducted by Lubis (2007) and Syahbirin (2009) where the acid concentration that produces the most lignin solids was at a concentration of H₂SO₄ 20%.

In principle, the higher the degree of acidity the easier it was to degrade lignin from the non-lignin components contained in the substance to be isolated. But if the solution was too acidic the greater the lignin damage factor. The results of isolation of lignin with H₂SO₄ 20% correlation have a yield greater than other concentrations. This was because the increased concentration of non-lignin organic compounds dissolved in acids such as polysaccharides contained in Black Liquor was easily degraded so that more lignin is produced (Pramudono, 2012). According to Fengel and Wegener (1995) polysaccharides were the most common contaminants in lignin isolation. The content of other polysaccharides was very dependent on the process of isolation, the type of wood and the process of purification of lignin.

Low lignin content at low H₂SO₄ concentration indicates that the results of lignin isolation still contain a lot of non-lignin content. According to Damat (1989), the non-lignin content which is a lot of lignin solids as the result of isolation shows that the degradation of polysaccharides and their separation from non-lignin content is still not perfect.

Table 1. Lignin Yields in Various Acid concentrations

Lignin	Yield (%)			
	H ₂ SO ₄ 15%	H ₂ SO ₄ 20%	H ₂ SO ₄ 25%	H ₂ SO ₄ 30%
Crude Lignin	50.12	52.43	48.87	47.86
Purified Lignin	21.54	22.98	16.75	20.77

Polysaccharide degradation can occur under strong acid conditions. Damat (1987) states that in addition to the addition of acids to the isolation process, the low pH of lignin is due to the presence of more acidic non-lignin components, such as formic acid, acetic acid, and lactic acid.

Based on Figure 2, there is a significant difference in the color of purified lignin, purified lignin with a variation of 20% H₂SO₄ concentration has a lighter color compared to purified lignin with other variations of H₂SO₄ concentration. Therefore, based on the color, purified lignin with a variation of 20% H₂SO₄ concentration results from the best, besides that the yield is also the highest of 52.43%. Functional groups in crude lignin, purified lignin, and commercial lignin. Lignin isolates were produced from the best isolation conditions and produced the greatest yield, then further identified by the FTIR spectrophotometer.

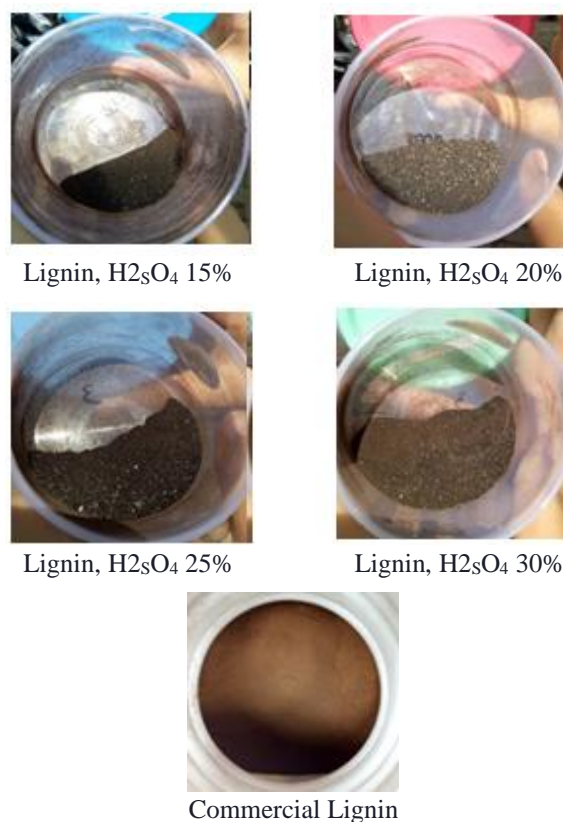


Figure 2. Purified Lignin from lignin isolation with variations in H₂SO₄ concentrations of 15%, 20%, 25%, 30%, and Commercial Lignin

Table 2. FTIR spectrum for Crude Lignin, Purified Lignin and Commercial Lignin

No	Purified Lignin (cm ⁻¹)	Crude Lignin (cm ⁻¹)	Commercial Lignin (cm ⁻¹)	Position (cm ⁻¹ *)	Group Role *)
1	3422	3402.5	3416	3540-3400	OH
2	2930.5	2945.5	2930.5	3000 - 2842	C-H metyl and metylen
3	2844	2837.5	2854.5	2940 – 2820	OH on metyl and metylen
4	1715	-	-	1715-1710	C=O and aromatic ring
5	1598.53	-	1591.5	1605-1600	Vibrasion aromatic ring
6	1504	-	1517	1515-1505	Vibrasion aromatic ring
7	1470.5	1465	1465.5	1470-1460	Deformasion C-H (asimetric)
8	-	1430	1430	1430-1425	Vibrasion aromatic
9	-	-	-	1330-1325	Vibrasion siringil
10	-	-	1276.5	1270-1275	Vibrasion guaiasil
11	921	923.5	-	915-925	C-H; aromatic group

*) according to Hergert (1971) in Lubis (2007); S.Y. Lin and C.W. Dence (1993)

The best isolation condition was kraft lignin isolate which was isolated from kraft black leachate type using 20% H₂SO₄ concentration. The lignin kraft isolate compared to the standard lignin used is commercial lignin kraft. The purpose of the functional group analysis is to determine the functional groups that exist in lignin from the results of isolation and standard lignin used.

The results of the identification of the functional groups of lignin isolates by FTIR showed spectrophotometer absorption patterns, which were most similar to commercial lignin kraft. The results of

the identification of the two lignins can be seen in Figure 3 and Table 2. Based on Figure 3, the functional group identification results with purified lignin FTIR and crude lignin with commercial lignin show absorption patterns in areas of wave numbers similar to commercial kraft lignin with the brand of Aldrich Chemistry as a reference. It can be seen that the groups contained in purified lignin had more similarities than the groups contained in crude lignin.

In Table 2 it could be seen that the crude lignin and purified lignin and the commercial lignin kraft were in the FT-IR spectrophotometer absorption band.

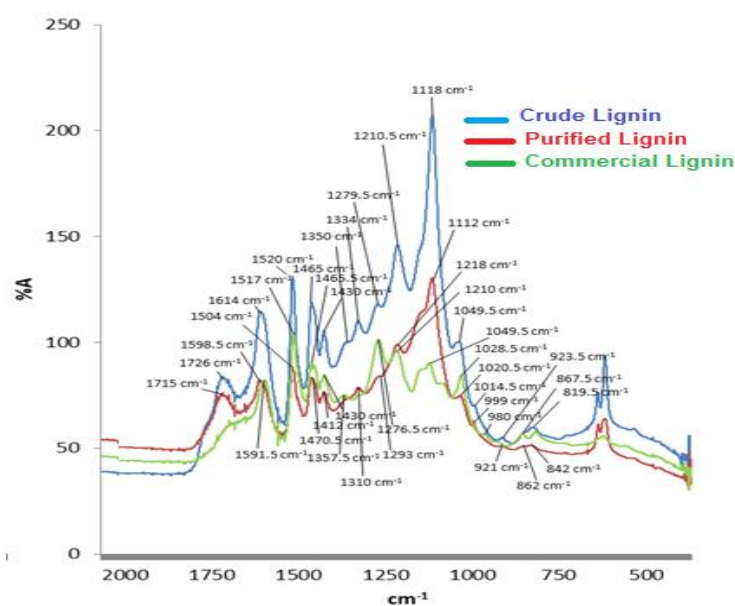


Figure 3. FTIR spectrum for Crude Lignin, Purified Lignin and Commercial Lignin

The absorption band in the range 3540 - 3400 cm⁻¹ was a stretch of the -OH group owned by purified lignin, crude lignin, and purified lignin, indicating that the lignin still contains a water component. In the range of absorption band 1715-1710 cm⁻¹, it was seen that the crude lignin and purified lignin did not have a stretch of C = O not conjugated with the aromatic ring while the net lignin had a stretch of C = O not conjugated with the aromatic ring. Lubis (2007) explained that the range of C = O is not conjugated with an aromatic ring was a circular carbon chain (C6) with a bond of C = O is not conjugated.

Purified lignin and commercial lignin both contain vibrations of aromatic rings in the range 1500 - 1600 cm⁻¹, but not possessed by dirty lignin. However, in the range of absorption bands, 1270-1275 cm⁻¹ is only owned by pure lignin, which should also be owned by clean lignin and dirty lignin. In the range of absorption bands indicate that lignin contains the presence of guaiasil which is one of the constituents of lignin.

Acacia Mangium Willd was a type of broadleaf wood. Compounding precepts of broadleaf wood lignin include siringil groups and guaiasil groups. But based on the identification of the functional groups of lignin isolates with FTIR showed different results. Sugesty (2012), stated that purified lignin and crude lignin did not contain the syringyl ring group and the guaiasil group. However, the purified lignin identified only contained guaiasil groups and did not contain siringil groups. According to Lubis (2007), it can be concluded that the commercial kraft lignin used is lignin derived from needle wood. Based on Santoso's research (2003) lignin which tends to contain guaiasil groups was mostly contained in needle wood.

Fengel (1995) stated that the wavenumber shift might occur due to the influence of the boundary structure (bordering) on the aromatic core contained in the material being analyzed. Although the infrared spectrum was a characteristic of compounds whose structure was known with certainty, there were many uncertainties when interpreting IR lignin spectra. This was mainly due to large variations in the structure and composition of lignin, which is depending on the origin of the sample and special isolation procedures.

CONCLUSIONS

The highest acid concentration (H₂SO₄) was 20% w/w with the yield of lignin obtained at 22.98% for purified lignin and 52.43% for crude lignin. Functional groups contained in purified lignin have more similarities with commercial lignin compared to crude lignin.

ACKNOWLEDGEMENT

This study was supported by Directorate of Research and Community Service, Directorate General of Research and Development, Ministry of Research, Technology and High Education, Diponegoro

University, Dean of Engineering Faculty, Fiscal Year 2018, No: 2689/UN7.3.3/PG/2018.

REFERENCES

- Energy and Mineral Resources Research and Development Agency. 2012. Making Surfactants for Oil-Pressing Applications with Chemical Injection. (Badan Penelitian dan Pengembangan Energi dan Sumber Daya Mineral. 2012. *Pembuatan Surfaktan untuk Aplikasi Pendesakan Minyak dengan Injeksi Kimia*). <http://www.litbang.esdm.go.id/berita/pembuatan-surfaktan-untuk-aplikasi-pendesakan-minyak-dengan-injeksi-kimia>. (9 November 2016).
- Damat. 1989. Isolation of Lignin from Pulp Mill Cooking Solution Remaining by Using H₂SO₄ and HCl. Department of Agricultural Industrial Technology, Faculty of Agricultural Technology, Bogor Agricultural University. Bogor. (*Isolasi Lignin dari Larutan Sisa Pemasak Pabrik Pulp dengan Menggunakan H₂SO₄ dan HCl*. Jurusan Teknologi Industri Pertanian, Fakultas Teknologi Pertanian, Institut Pertanian Bogor. Bogor).
- Fengel D, Wegener G. 1995. Wood: Chemistry, Ultrastructure, and Reactions. Sastrohamidjojo H, translator. Yogyakarta: University Gajah Mada Press. Translation from: Wood: Chemistry, Ultrastructure, Reaction. (*Kayu: Kimia, Ultrastruktur, dan Reaksi-Reaksi*. Sastrohamidjojo H, penerjemah. Yogyakarta: UGM Press. Terjemahan dari: *Wood: Chemistry, Ultrastructure, Reaction*).
- Hergert, H. L. 1971. *Infrared Spectra in Lignins: Occurrence, Formation, Structure and Reactions* (Sarkanen, K.V. and Ludwig, C.H., Eds). Wiley-Interscience, New York. Pp. 267-297. *dalam* Fengel, D. dan G. Wegener. 1995. *Kayu: Kimia, Ultrastruktur dan Reaksi*. Gajah Mada Press University. Yogyakarta.
- Junaedi Ahmad, *et al.*, 2011. Pulp Data and Statistics in Indonesia. Ministry of Forestry, Forestry Research and Development Agency. Bangkinang. (*Data dan Statistika Pulp di Indonesia*. Kementerian Kehutanan, Badan Penelitian dan Pengembangan Kehutanan. Bangkinang).
- Kim H, Hill MK, Friche AL. 1987. *Preparation of Kraft Lignin from Black Liquor*. Tappi Journal 70 (12): 112-116.
- Lin, S. Y. dan C. W. Dence. 1992. *Methods in Lignin Chemistry*. State University of New York: New York.
- Lubis A.A., Isolation of Lignin From Black Liquor Process Cooking Soda Pulp And Pulp Sulphate (Kraft), Cooking Process of Soda and Pulp Sulfate Pulp (Kraft), Faculty of Agriculture, IPB, Bogor, 2007.

Ma'ruf, Pramudono, B, and Aryanti N., Optimization of Lignin Extraction from Rice Husk by Alkaline Hydrogen Peroxide Using Response Surface Methodology *Rasayan J. Chem.*, 2017, 10(2), 407.

Pramudono, B., Aji, H.A., Priyanto, S., Kusworo, T.D., Suherman, Ma'ruf, A., Untoro, E., Ratu, P. 2017. *Optimization of Sodium Lignosulfonate (SLS) Synthesis from Waste Biomass of Pulp and Paper Mill Using Response Surface Methodology.*

Priyanto, S., Pramudono, B., Kusworo, T. D., Suherman, Aji, H.A., Untoro, E., Ratu, P., Synthesis Study of Surfactants Sodium Ligno Sulphonate (SLS) from Biomass Waste Using Fourier Transform Infra

Red (FTIR), MATEC Web of Conferences, 2018, **156**, 03030

Syahbirin, Gustini. 2009. Utilization of Kraft Lignin from the Black Liquor Pulp Plant for the Manufacture of Sodium Lignosulfonate and Sulfonate Hydroxymethyl Phenol Lignin Sulfuric Acid as Dispersing Material. IPB Postgraduate School (*Pemanfaatan Lignin Kraft Dari Black Liquor Pabrik Pulp Untuk Pembuatan Natrium Lignosulfonat dan Sulfonat Hidroksimetil Fenol Lignin Asam Sulfat Sebagai Bahan Pendispersi.* Sekolah Pascasarjana IPB), Bogor.

Sugesty, S., 2012, Analyzing Lignin Klason from Various Raw Materials. Cellulose and Paper Symposium, *J. Chem Eng*, 18, 1, 41