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Infra Red Evaluation of Sodium Lignosulfonate Surfactant (SLS)

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Abstract:
Bagasse is a waste of sugar cane liquid extraction process, after the sugar manufacturing process. The bagasse still contains29.46 % of lignin component. Sodium lignosulfonate is a product of lignin sulfonationisolation process by sodium bisulfite as sulfonation agent. The advantage of lignosulfonateover synthetic surfactant and petroleum-based surfactant is that it is not toxic and it is derived from renewable natural materials. Lignosulfonate is one type of anionic surfactant that can be used as injection fluid in enhanced oil recovery technique in the upstreamoil industry.In this research, the result of the sulfonation process of lignocellulose from bagasse was characterized by Fourier Transform Infra-Red (FTIR) spectroscopy method to determine the typical functional groups in the lignosulfonate structure, which identified that thesulfonate has a chemical formula of $C\text{-}SO_2\text{-}O\text{-}C$. In this research, we used the data from Aldrich and Patricia as thecommercial lignosulfonate references. Compared with thereference, the value of sulfonate SLS appeared at the wavenumber of 1384.64 cm^{-1}, where sulfonate component was formed at the wavenumber of 1365 cm^{-1} (Aldrich) or 1350 cm^{-1} (Patricia).The conclusion of this research is thatbagasse can be processed into surfactant sodium lignosulfonate, using sodium bisulphate, which have sulfonate component appearing at the wavenumber of 1384.64 cm^{-1} that matches with standard lignosulfonate. From the FTIR test,, we have identifiedthree mainlignin components ,i.e, Fenolic, Alifatic and Keton, and four main lignosulfonate component ,i.e., Alkena, Sulfate, carboxylic Acids and Ester.

Keywords: *bagasse, lignin, lignosulfonate, SLS surfactant*

1. Introduction
Nowadays, the sodium lignosulfonate surfactant used in the upstream oil industry is surfactant made of petroleum and is better known as petroleum sulfonate. Because of the downturn situation of petroleum industry, any of the related part of petroleum product will be affected, such as the price of surfactant petroleum sulfonate, which is fluctuating. Therefore, it is interesting to search an alternative raw materials, i.e. bagasse which is a mill residual waste from sugar factory. Bagasse is used as animal food for most farmers and as fuel at sugar factory. Based on the research done (Arora, 1976, Samsuri, 2007), bagasse contains 13-24% of lignin components, so it can be considered to process lignin to become lignosulfonate as an alternative raw material from the existing plantations .
There are two kinds of processes that yieldSodium Lignosulfonate Surfactant (SLS), i.e., lignin isolation process and sulfonation process. Lignin isolationprocess used sodium hydroxide as reagent whilst sulfonation process used sodium bisulfite as reagent. Because the main ingredient is reagent, the result of isolation and sulfonation processes are called Sodium Lignosulfonate Surfactant (SLS) . Further, to test the validity of the result, the product should be tested through FTIR (Fourier Transform Infra Red) which shows the component spectrum inside the SLS. The result, then will be compared with SLS which has been commercially used.

2. Sodium Lignosulfonate Surfactant (SLSSurfactant) Bagasse
Sodium lignosulfonate surfactant is one of the lignosulfonate components which is obtained after the lignin sulfonation process with bisulfite ion. This process is called sulfonation in which reagent sodium bisulfite is used. Lignin separated from bagasse through lignin isolation process (Heradewi, 2007).

2.1. Definition of Sodium Lignosulfonate Surfactant
SLS is one of lignosulfonate components that is made from lignin based raw material with sodium hydroxide and sodium bisulfite reagents, so it is called Sodium Lignosulfonate Surfactant. Sulfonate is known with the formula $R\text{-}SO_3Na$ as the simplification of sulfat $R\text{-}O\text{-}SO_3Na$ (Fujimoto, 1985).R is the group of carbon atom aromatic $C_8 – C_{22}$which constitutes the group of hydrophilic whilst group of hydrophobic consists of carbosilat, sulfonate, fosfat or other acid. Surfactant SLS is categorized as surfactant anionic because it has a group of sulfonate and salt ($\text{-}NaSO_3\text{-}$) which constitutes anion (head) and group of hidrocarbon as the tail.

2.2. Sulfonation Process

Sulfonation is the process to create lignosulfonate through the chemical reaction between bisulfite ion and lignin ion. The resulting product is known as SLS Surfactant (Sodium Lignosulfonate Surfactant). Sulfonation process is started by separating lignin from the bagasse. The bagasse that has been sieved should be put on the flask and be directly refluxed inside sodium hidroxyde solvent wtih 2% concentration during five hours. The result of NaOH reflux is filtered, diluted, and acidized with sulfuric acid (H_2SO_4 98%) titration until pH=2 and set for at least eight hours until the sediment appears, then it should be filtered and dried in the oven at 70 ^oC. The obtained sediment is lignin. The lignin was further processed by using sodium bisulfit through sulfonation process for five hours at 100 ^oC. The result is processed through oven drying and heating until it formed brown powder . This powder is surfactant sodium lignosulfonate. The sulfonation results are validated by FTIR (Fourier Transform Infra Red), LCMS (Liquid Chromatograph Mass Spectrum) and NMR (Neutron Magnetic Resonance).

2.3. Standard Sodium Lignosulfonate Surfactant

SLS Surfactant which has been commercially used is the standard sulfonate product of Patricia and Aldrich (Patricia, 2009). As for lignin,the standard product used is Aldrich and Kraft (Chakar, 2004). In general, the components inside lignin are Fenolic, Alifatic, Keton, Arena, Amine and Alkylproducts, as shown in table below.

No.	Component	Standard	Aldrich	Kraft
1.	Fenolic O–H	3200 – 3550	3436.62	3414
2.	Alifatic –CH–	2900	2930.17	2926.01
3.	Keton C=O	1400 – 1450	1444.68	1460.89
4.	Arena –C=C–	1500 – 1600	1599.14	1614.42
5.	Amine C–N	1000–1250	-	-
6.	Alkyl C–H	600 – 700	-	-

Table 1: Wave number of lignin standard

The component in the sulfonate structure are alkenes, sulfate, carboxylic acids and ester, as shown in the table below.

No.	Component of standard lignosulfonate	Wave number (cm^{-1})	
		Patricia	Aldrich
1.	Alkena	1630 – 1680	1608.34
2.	Sulfate	1350	1365
3.	Carboxylic Acids	1000 – 1300	1187.94
4.	Ester	500 –540	499.831

Table 2: Wave number of lignosulfonate standart

The data on table 1 and 2 are the standard used to compare the lignin and sulfonate results from bagasse.

3. The Methods of Process Bagasse to Sodium Lignosulfonate Surfactant

The material used for sulfonation process are bagasse powder, distilled water, caustic soda (NaOH)**,** sulphuric acid (H_2SO_4) and sodium bisulfite ($NaHSO_3$). And the tools that used for sulfonation process are sieve shaker, reflux, hot plate magnetic stirrer and oven. Sodium lignosulfonate is a product oflignin sulfonate isolation process by sodium bisulfite as sulfonation agent.The process of hydrolisis and sulfonation bagasse :

1. Put the bagasse inside neck flask, add natrium hydroxide until the bagasse submerged, be heated during five hours to T = 100°C
2. Separate filtrate of reflux NaOH, and dilute with water with 1:1 comparison
3. Titrate H_2SO_4, until pH = 2
4. Deposit the result of solvent titration H_2SO_4, minimum eigth hours
5. Filter and dry the sediment with oven or evaporator
6. Get the lignin composition through the result of FTIR tests
7. Put the lignin inside neck flask and add sodium bisulfite and heat during five hours in T = 100°C
8. Dry the sulfonation result with oven drying & heating until it gets the form like powder
9. Run FTIR tests to identify the component and lignosulfonate structure

4. Result and Discussion

Based on the result of the lignin isolation and lignin sulfonation into sodium lignosulfonate surfactantexperiment, the FTIR test was done to obtain the component of lignin and SLS Surfactant. Figure 1 below shows bagasse, figure 2 shows the lignin from bagasse, the result of isolation process, and figure 3 shows SLS surfactant, the result of sulfonation process (SetiatiR, 2016)

Figure 1: Bagasse

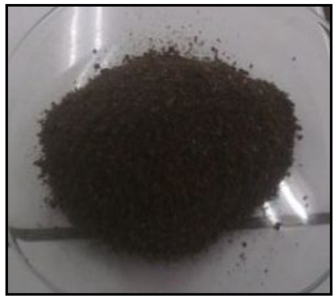
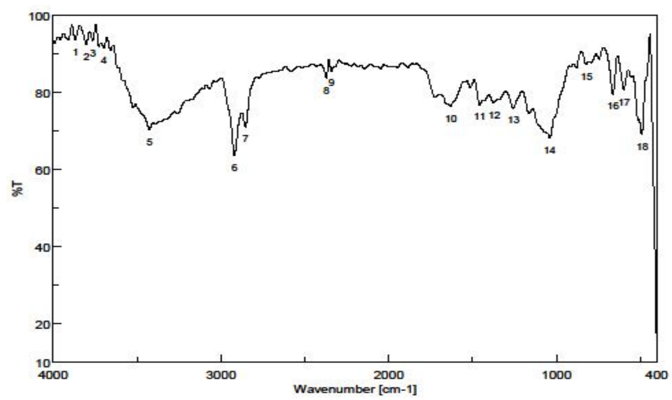


Figure 2: Lignin from Bagasse

Figure 3: SLS Surfactant from bagasse

4.1. The Result of Isolation Lignin from Bagasse



Result of Peak Picking

No.	Position	Intensity	No.	Position	Intensity
1	3868.5	93.4744	2	3802.94	92.3465
3	3764.37	93.3341	4	3698.8	91.5135
5	3424.96	70.2881	6	2919.7	63.5146
7	2854.13	71.0283	8	2372.01	83.6101
9	2341.16	85.5117	10	1631.48	76.2943
11	1457.92	76.7195	12	1373.07	77.1791
13	1257.36	75.8991	14	1041.37	68.0563
15	821.527	87.1722	16	663.393	79.4446
17	597.825	80.5994	18	489.831	69.0579

[Comment]

Sample Name	hampas tebu
Comment	
User	
Division	
Company	Institut Teknologi Bandung

[Measurement Information]

Model Name	FT/IR-4200typeA
Serial Number	B012261018

Figure 4: The result FTIR of bagasse

Figure 4 shows that the components of bagasse before the lignin isolation with a reagent sodium hydroxide.Figure 5 provides more clearly difference between the absorption peak of bagasse before hydrolisis process and lignin itself. There are main components of bagasse which have the spectrum of functional groups. Some of the components contained in the bagasse include phenolic (at a wavenumber of 3424.96 cm^{-1}), aliphatic (2919.7 cm^{-1}), ketones (1457.92 cm^{-1}), arena (1631.48 cm^{-1}), amine (1041.37 cm^{-1}) and alkyl (663.393 cm^{-1}) beside the other components that appear at wavenumbers of 2300 cm^{-1}, 1200 cm^{-1}, 800 cm^{1} and 489 cm^{-1}.

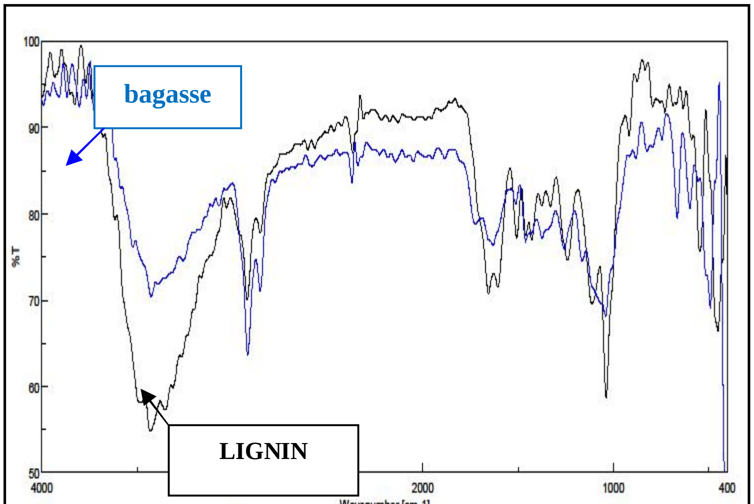


Figure 5. Overlay FTIR of bagasse and lignin's bagasse

The result of the FTIR lignin bagasse test is then compared with the standard lignin spectrum and commercial lignin product of Aldrich and Kraft, as shown in the Table 3 below.

No.	Component of Lignin	Wave number (cm^{-1})			
		Standard Lignin	Lignin (bagasse)	Comercial Lignin (Aldrich)	Comercial Lignin (Kraft)
1.	Phenolic O–H	3200 – 3550	3400	3436.62	3414
2.	Alifatik –CH– and aromatik	2900	2910	2930.17	2926.01
3.	Keton C=O	1400 – 1450	1450	1444.68	1460.89
4.	Arena –C=C–	1500 – 1600	-	1599.14	1614.42
5.	Amine C – N	1000 – 1250	1100	-	-
6.	Alkyl C–H	600 – 700	650	-	-

Table 3: Spectrum comparison of lignin bagasse and standard lignin

The bagasse lignin is compared with the standard lignin and the commercial lignin such as the ones belong to Aldrich and Kraft. Based on the analysis and identification on the FTIR spectrum of lignin from isolation or commercial lignin, it is shown that lignin of isolation process from bagasse has many similar functions with commercial lignin standard from Aldrich and Kraft. The similarities are grouped into stretching vibration–CH– alifatic and aromatic with wavenumber around 2900 cm^{-1}. The result of Spectrum IR isolation from bagasse has many similar stretching vibrations –CH– alifatic and aromatic with wave number of 2919.7 cm^{-1}, whilst commercial lignin Aldrich and commercial lignin Kraft have wave number of 2930.17 cm^{-1} and 2926.01 cm^{-1} respectively.The peak picking for group of stretching vibration–C=C– with the wave number between 1500 – 1600 cm^{-1} at the IR spectrum lignin bagasse with at 1511.92 cm^{-1}wave number, and appears IR spectrum lignin Aldrich at 1599.14 cm^{-1} wave number and lignin Kraft at 1614.42 cm^{1} wave number .The peak picking for group of stretching vibration O–H phenolic with 3200 – 3550 cm^{-1}wave number, founded to spectrum IR lignin bagasse at 3405.67 cm^{-1} wave number, spectrum IR lignin Aldrich at 3436.62 cm^{-1} wave number and lignin Kraft at 3414 cm-^{1}wave number. Therefore, FTIR spectrum of lignin bagasse is slightly different with FTIR spectrum commercial lignin product of Aldrich and Kraft, mainly at the peak picking for group of stretching vibration–CH– alifatic and aromatic, stretching vibration –C=C– and stretching vibration O–H phenolic. Based on the analysis of FTIR spectrum from all of the research variables, such us, the size of mesh bagasse and NaOH concentrate in lignin isolation process, it can be found that lignin with best rendement value was gained through hydrolisis process bagasse by using NaOH 2%.

4.2. The result of sulfonation lignin.

In figure 5explain the results of infra-redfor SLS Surfactant are component with a wavenumber of 3484.1 cm^{-1}, 2923.56 cm^{-1}, 2352.73 cm^{-1}, 2051.89 cm^{-1}, 1635.34 cm^{-1}, 1511.92 cm^{-1}, 1384.64 cm^{-1}, 1253.5 cm^{-1}, 1114.65 cm^{-1}, 705.819 cm^{-1}, 620.956 cm^{-1}, 588.254 cm^{-1}, 462.832 cm^{-1}. Based on standard components of lignin, there are only four main components component lignosulfonate such as Alkena, Sulfate, carboxylic Acids and Ester. The curve of component SLS surfactant are a peak picking primer on the1635.34 cm^{-1}wave number as stretching vibration Alkena, at 1384.64 cm^{-1} wave number as stretching vibration Sulfat, with 1114.65 cm^{-1}wave number as stretching vibration Carbocylic Acids, at 462.832 cm^{-1} wave numberas stretching vibration Ester as seen in the figure 6.

From figure 7, there are several differences among the FTIR result of lignin and surfactant, in which the blue line curve represents FTIR Surfactant curve. From the result of the infra-red test, it appears that there has been peak picking of surfactant curve (blue curve) compared to lignin curve (black curve). There is a curve difference through3-peak picking curves which proved that the lignin surfactant components consist of alkena, sulfate and carboxylic acid. The result of infrared spectrum of SLS Surfactant from bagasse has been compared with standard SLS Surfactant of Aldrich and Patricia products as shown in the Table 4 below. From the result of infra-red test, wave number spectrum which read as “fingerprint” for some peak picking especially sulfat at 1384.64 cm^{-1} wave number in which the sulfate has peak picking range within 1350 – 1450 cm^{-1} wave number. The appearance of the peak picking indicates that Sodium Lignosulfonate Surfactant has achieved a complete process, which can be seen on Table 4.

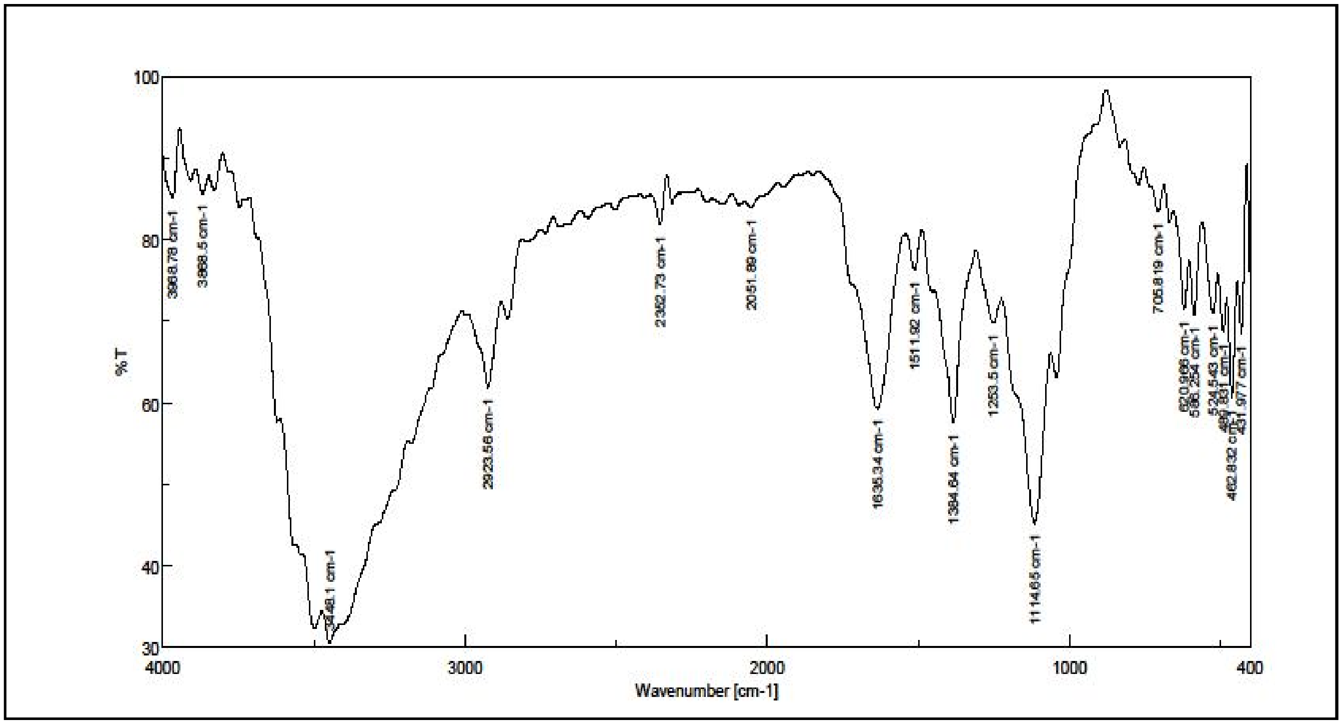


Figure 6: The result FTIR of SLS Surfactant from Bagasse

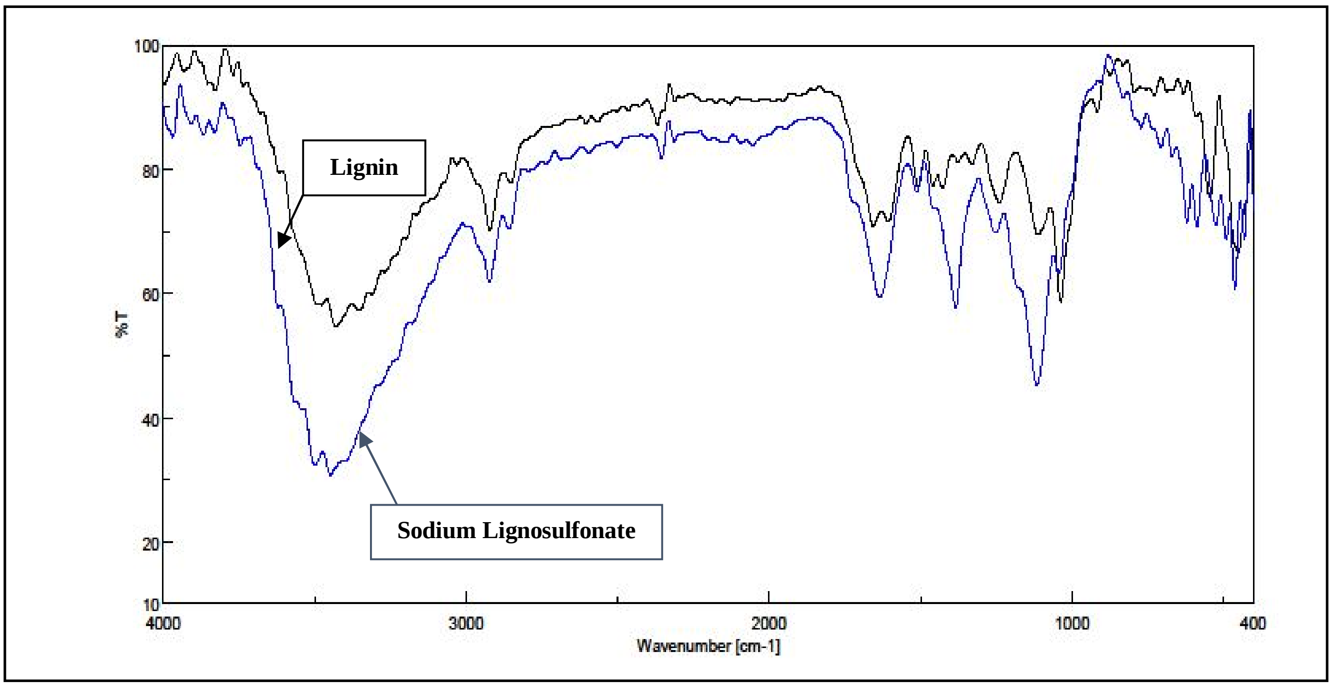


Figure 7: Overlay Result of FTIR between Lignin and SLS Surfactant from bagasse

No.	Components	Wave number (cm^{-1})		
		SLS Surfactant(bagasse)	Standar (Aldrich)	Standar (Patricia)
1.	Alkena C=C	1635.34	1608.34	1630 –1680
2.	Sulfate S=O	1384.64	1365	1350
3.	Carboxylic Acids C=O	1114.65	1187.94	1000 – 1300
4.	Ester S–OR	462.832	499.831	500 –540

Table 4. Comparison spectrum lignosulfonate bagasse and lignosulfonate standart (Patricia and Aldrich)

5. Conclusions

Based on the study using infra red evaluation test, it can be concluded that:

1. The identification process was based on well conducted experiments and thorough observation on the samples used. .
2. The identification process showed that the lignin matched with the standard lignin components and that it contained three main components, i.e.,Phenolic, Alifatic, and Keton.
3. The same identification process showed that surfactant sulfonation process yielded sulphonate that matched surfactant standard components and that it containedfour main components,i.e., Alkena, Sulfate, Carboxylic Acids, and Ester.

6. References

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