

# **BUKTI KORESPONDENSI AUTHOR**

**JOURNAL RENEWBLE MATERIAL**

**Quartile 2, SJR 0,38**



**Sri Hidayati**

**Sebagai Syarat Pengajuan Guru Besar**

**JURUSAN TEKNOLOGI HASIL PERTANIAN**

**FAKULTAS PERTANIAN**

**UNIVERSITAS LAMPUNG**

**2023**

## JOURNAL RENEWBLE MATERIAL (<https://www.techscience.com/journal/jrm>)

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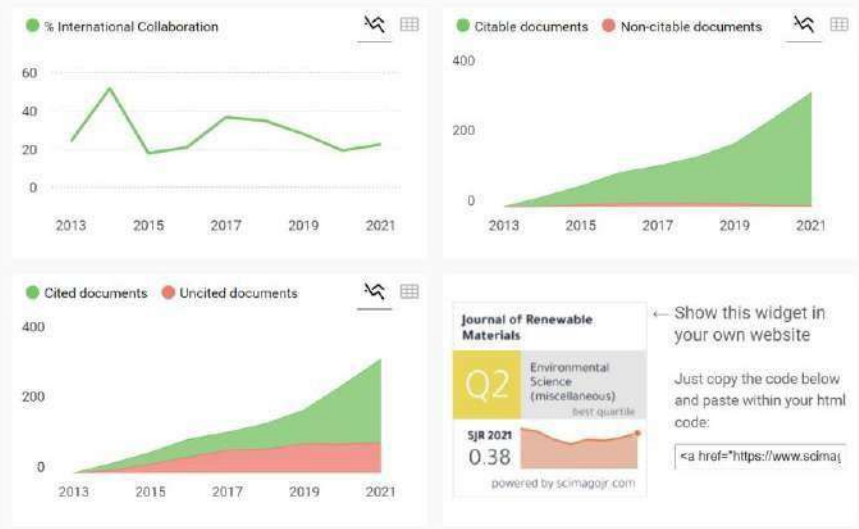
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### Characterization of Formacell Lignin Derived from Black Liquor as a Potential Green Additive for Advanced Biocomposites

Sri Hidayati<sup>1,7</sup>, Eugenia Fonny Budiyo<sup>1</sup>, Hadi Saputra<sup>1</sup>, Sutopo Hadi<sup>1</sup>, Apri Heri Iswanto<sup>2,3</sup>, Nissa Nurfaejri Solihat<sup>4</sup>, Petar Antov<sup>5</sup>, Lee Seng Hua<sup>6,7</sup>, Widyia Fatrisari<sup>4,8</sup>, Mohd. Sapuan Salit<sup>9</sup>

DOI: 10.32804/jrm.2023.027579

(This article belongs to this Special Issue: [Advances in Eco-friendly Wood-Based Composites: Design, Manufacturing, Properties and Applications](#))

**Abstract** Black liquor is obtained as a by-product of the pulping process, which is used to convert biomass into pulp by removing lignin, hemicelluloses and other extractives from wood to free cellulose fibers. Lignin represents a major constituent in black liquor, with quantities varying from 20% to 30%, which a very low share is used for manufacturing value-added products, while the rest is mainly burned for energy purposes, thus underestimating its great potential as a raw material. Therefore, it is essential to establish new isolation and extraction methods to increase lignin valorization in the development of bio-based chemicals. The aim... [More >](#)

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<b>8. Proof Submitted</b>	<b>18 Januari 2023</b>
<b>9. Finnaly Proof</b>	<b>28 Januari 2023</b>
<b>10. Publish</b>	<b>10 April 2023</b>



sri hidayati <srihidayati.unila@gmail.com>

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## [jrm] Validate Your Account

1 message

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**JRM Editorial** <noreply@tspsubmission.com>  
Reply-To: JRM Editorial <jrm@techscience.com>  
To: Sri Hidayati <srihidayati.unila@gmail.com>

Fri, Nov 4, 2022 at 1:18 PM

Sri Hidayati

You have created an account with Journal of Renewable Materials, but before you can start using it, you need to validate your email account. To do this, simply follow the link below:

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Thank you,  
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sri hidayati &lt;srihidayati.unila@gmail.com&gt;

---

**[jrm] ID:27579 Submission Acknowledgement**

1 message

**JRM Editorial** <noreply@tspsubmission.com>

Fri, Nov 4, 2022 at 4:24 PM

To: Sri Hidayati &lt;srihidayati.unila@gmail.com&gt;

Dear Sri Hidayati,

Thank you for submitting the manuscript, "Characterization of Formacell Lignin Derived from Black Liquor as a Potential Green Additive for Advanced Biocomposites " to Journal of Renewable Materials. With the online journal management system that we are using, you will be able to track its progress through the editorial process by logging in to the journal web site:

Submission URL: <https://www.tspsubmission.com/index.php/jrm/authorDashboard/submission/27579>

Username: sri\_hidayati71

If you have any questions, please contact me. Thank you for considering this journal as a venue for your work.

JRM Editorial

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sri hidayati &lt;srihidayati.unila@gmail.com&gt;

**[jrm] ID: 27579: Editor Decision Revision Request**

2 messages

**JRM Editorial** <admin4@tspsubmission.com>

Wed, Nov 30, 2022 at 9:08 AM

To: "Dr. Sri Hidayati" <srihidayati.unila@gmail.com>, Eugenia Fony Budiyanoto <eugenefonny@gmail.com>, Hadi Saputra <hadiggm97@gmail.com>, Sutopo Hadi <sutopo.hadi@fmipa.unila.ac.id>, "Dr. Apri Heri Iswanto" <apri@usu.ac.id>, Mrs Nissa Nurfaejrin Solihat <niss001@brin.go.id>, "Prof. Dr. Petar Antov" <p.antov@ltu.bg>, "Dr. Lee Seng Hua" <leesenghua@hotmail.com>, "Dr. Widya Fatriasari" <widy003@brin.go.id>, "Prof. Mohd. Sapuan Salit" <sapuan@upm.edu.my>

Dear Dr. Sri Hidayati, Eugenia Fony Budiyanoto, Hadi Saputra, Sutopo Hadi, Dr. Apri Heri Iswanto, Mrs Nissa Nurfaejrin Solihat, Prof. Dr. Petar Antov, Dr. Lee Seng Hua, Dr. Widya Fatriasari, Prof. Mohd. Sapuan Salit,

The review of your submission to Journal of Renewable Materials, "Characterization of Formacell Lignin Derived from Black Liquor as a Potential Green Additive for Advanced Biocomposites".

ID: 27579

has been completed. Although we found that your paper has merit, it is not acceptable to publish in its present form. We invite you to revise your paper to address reviewers' comments as fully as possible. Please revise the manuscript according to the reviewers' comments and upload the revised file within **one month**.

When you submit your revision, please upload the following 3 files:

1. Your rebuttal;
2. Your revised paper with track change (**highlighted in yellow**);
3. Your clean revised paper.

**Please find the reviewer's comments at the end of this message. Also, in track-change version, please have all the revised part highlighted in yellow in the text.**

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Thank you very much for your contributions to Journal of Renewable Materials.

Sincerely,

-----  
Reviewer J:

The manuscript entitled "Characterization of Formacell Lignin Derived from Black Liquor as a Potential Green Additive for Advanced Biocomposites" reported a study on lignin isolation and characterization using KOH and EtOH precipitation methods. The authors investigated the structural difference of the lignin that obtained by different concentration of KOH or EtOH. However, I do not recommend the manuscript for publication base on this shape.



1. The experimental description is not clear. Did the lignin obtained by continuously added different concentration of KOH or EtOH in one experiment, or they were independent experiments?
2. The molecular weight and hydroxyl groups (including phenyl) content are very important for the lignin structure, but the authors did not mention these properties.
3. Some discussions are not correct or lack of supporting. For example the authors claimed that the different content of OMe by different KOH was because of the replacement or removal of OMe during the process. However, as we know that OMe is highly stable under room temperature. I don't think such condition was able to cleave the OMe in lignin.
4. The authors claim that the main mechanism of lignin depolymerization involves  $\alpha$ -O-4 cleavage, which is not true at all.

Recommendation: Major Revision

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Reviewer L:

The manuscript entitled " Characterization of Formacell Lignin Derived from Black Liquor as a Potential Green Additive for Advanced Biocomposites" reports on determining the effect of KOH or ethanol concentration as an isolation agent on lignin yields and the chemical characteristics of lignin isolated from form a black cell liquor of oil palm empty fruit bunch (OPEFB). Lignin was isolated using KOH with various concentrations ranging from 5% to 15% (w/v). Ethanol was also used to precipitate lignin from black liquor at concentrations varying from 5% to 30% (v/v). The results obtained showed that the addition of KOH solution at 12.5% and 15% c oncentrations resulted in better lignin yield and chemical properties of lignin, i.e., pH values of 3.86 and 4.27, lignin yield of 12.78 and 14.95, methoxyl content of 11.33 and 10.13, and lignin equivalent weights of 476.25 and 427.03, respectively.

This is nice work, and the following corrections are needed prior to acceptance:

- "Black liquor used in this research is a by-product of the formacell pulping of OPEFB, as reported by Hidayati et al. [35]" -Please brief about the cited work in a bit more detail for readers

- [The formacell pulping was conducted in the autoclave at a liquor-to-particle ratio of 15:1 for 1 h at 130 °C] -Any specific reasons for this ratio?

- Figure 1 should be of better quality

- Different peaks in figure 2-3 should be marked

- Conclusion should be re-written to highlight the future perspective

- Introduction can be strengthened to highly the importance of sustainable materials by having a look at relevant references such as <https://www.sciencedirect.com/science/article/pii/S0960852422015887>.

Recommendation: Major Revision

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sri hidayati &lt;srihidayati.unila@gmail.com&gt;

---

**JRM-27579-additional review comments**

1 message

**gabriel.cao@techscience.com** <gabriel.cao@techscience.com>

Wed, Nov 30, 2022 at 9:23 AM

To: "srihidayati.unila" <srihidayati.unila@gmail.com>, eugenefonny <eugenefonny@gmail.com>, hadiggm97 <hadiggm97@gmail.com>, "sutopo.hadi" <sutopo.hadi@fmipa.unila.ac.id>, apri <apri@usu.ac.id>, niss001 <niss001@brin.go.id>, "p.antov" <p.antov@ltu.bg>, leesenghua <leesenghua@hotmail.com>, widy003 <widy003@brin.go.id>, sapuan <sapuan@upm.edu.my>

Dear authors,

With regard to your manuscript-27579, we have sent an revision request letter to you.

Apart from the reviewers' comments, there are also some comments from our editors:

-Please try to lower the self-citations below 5;

-Please revise your manuscript according to our JRM-template.

Look forward to your kind reply.

Best regards,  
Gabriel Cao

---

**Journal of Renewable Materials**

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---

**Revision ID: 27579**

1 message

---

**sri hidayati** <srihidayati.unila@gmail.com>

Mon, Dec 12, 2022 at 10:20 AM

To: admin4@tspsubmission.com

Dear Editor and reviewers




Authors thanks for the opportunity to revise the manuscript. We are very appreciative of all of the comments and suggestions that useful for improving the quality of the manuscript. We have tried our best to address your comment point by point on your valuable concern. All of the revised parts have been presented in yellow highlight. We expect by this revised version, the manuscript can be reconsidered to fit with a high standard of the journal of renewable materials

Best Regards  
On behalf of the Authors

Dr. Sri Hidayati

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**3 attachments**

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## Authors Response

Dear Editor and Reviewers

Authors thanks for the opportunity to revise the manuscript. We are very appreciative of all of the comments and suggestions that useful for improving the quality of the manuscript. We have tried our best to address your comment point by point on your valuable concern. All of the revised parts have been presented in yellow highlight. We expect by this revised version, the manuscript can be reconsidered to fit with a high standard of the journal of renewable materials

### Reviewer J

The manuscript entitled “Characterization of Formacell Lignin Derived from Black Liquor as a Potential Green Additive for Advanced Biocomposites” reported a study on lignin isolation and characterization using KOH and EtOH precipitation methods. The authors investigated the structural difference of the lignin obtained by different concentrations of KOH or EtOH. However, I do not recommend the manuscript for publication based on this shape.

Author’s response

Thank you for your insight, we are appreciated your valuable time in reviewing the manuscript. We tried to revise the manuscript and respond in detail to your comments and suggestion. We hope that the revision of the manuscript can help improve the clarity and revising miss leading in the initial manuscript

1. The experimental description is not clear. Did the lignin obtained by continuously added different concentration of KOH or EtOH in one experiment, or they were independent experiments?

Author’s response:

Thank you for your comments; the research is divided into two parts, the first of which is the lignin isolation with EtOH and the second with KOH. We attempted to compare chemical agents for lignin isolation based primarily on yield and lignin characteristics. In the method section, we add additional sentences to provide clear information (please check lines 103-106)

2. The molecular weight and hydroxyl groups (including phenyl) content are very important for the lignin structure, but the authors did not mention these properties.

Author’s response:

Because of the proposed lignin utilisation as a resin for wood biocomposites, the phenolic hydroxyl content was not examined in this study. According to Ghorbani, M. et al. (2016), the methoxyl content of lignin as formaldehyde resins is an important parameter because a high methoxyl content inhibits lignin reactivity during resin use. Furthermore, according to the proposed pathway of Yin et al (2020), the removal of the methoxy group in lignin by KOH

solution created a higher hydroxyl group of lignin. As a result, the authors believe that one of the analyses, either methoxyl or hydroxyl, will suffice to understand the lignin properties.

In this study, the equivalent weight of lignin was examined as a method for determining the molecular weight of lignin.

3. Some discussions are not correct or lack of supporting. For example, the authors claimed that the different content of OMe by different KOH was because of the replacement or removal of OMe during the process. However, as we know that OMe is highly stable under room temperature. I don't think such condition was able to cleave the OMe in lignin.

Author's response:

The explanation about reducing OMe content by increasing KOH has been revised for clarity as follows (lines 221-226): "Furthermore, according to [the pathway proposed by Yin et al.](#), the removal of the methoxy group in lignin created a higher hydroxyl group of lignin by KOH solution. The presence of potassium in lignin isolation decreased the methoxyl content due to cleavage C $\alpha$ —C $\beta$  through C $\beta$ —O bond. This cleavage leads to the removal of side chains such as methoxy. The mechanism of this reaction has been proved by Yin et al. [47]"

4. The authors claim that the main mechanism of lignin depolymerization involves  $\alpha$ -O-4 cleavage, which is not true at all.

Author's response:

Thank you for the suggestion. The information about lignin depolymerization involving  $\alpha$ -O-4 has been removed.

Reviewer L:

The manuscript entitled " Characterization of Formacell Lignin Derived from Black Liquor as a Potential Green Additive for Advanced Biocomposites" reports on determining the effect of KOH or ethanol concentration as an isolation agent on lignin yields and the chemical characteristics of lignin isolated from form a black cell liquor of oil palm empty fruit bunch (OPEFB). Lignin was isolated using KOH with various concentrations ranging from 5% to 15% (w/v). Ethanol was also used to precipitate lignin from black liquor at concentrations varying from 5% to 30% (v/v). The results obtained showed that the addition of KOH solution at 12.5% and 15% concentrations resulted in better lignin yield and chemical properties of lignin, i.e., pH values of 3.86 and 4.27, lignin yield of 12.78 and 14.95, methoxyl content of 11.33 and 10.13, and lignin equivalent weights of 476.25 and 427.03, respectively.

This is nice work, and the following corrections are needed prior to acceptance:

Author's response

Thank you for your positive comments. We have tried to revise the manuscript by considering all of your comments and suggestion

1. "Black liquor used in this research is a by-product of the formacell pulping of OPEFB, as reported by Hidayati et al. [35]" -Please brief about the cited work in a bit more detail for readers

Author's response:

Thank you for your comments. A brief detailed method has been added in the experimental section (2.2 Pulping process), especially in the formacell pulping of OPEFB based on our previous paper. Please check additional sentences in lines 94-100.

2. The formacell pulping was conducted in the autoclave at a liquor-to-particle ratio of 15:1 for 1 h at 130 °C] -Any specific reasons for this ratio?

Author's response

The ratio of liquor to OPEFB particle ratio of 15: 1 has been used based on our initial experimental trial in the laboratory considering the volumetric of OPEFB as typical of nonwoodybiomass. In this ratio, the OPEFB particle can be immersed completely in the chemical liquor. This information has been added in lines 95-98.

3. Figure 1 should be of better quality

Author's response:

Figure 1 has been revised and upgraded to a better-quality presentation in 600 dpi.(see line 117-119).

4. Different peaks in figure 2-3 should be marked

Author's response:

Figures 2 and 3 have been marked by letters a and b to present the different peaks that can be identified. Please see line 301, 311-313

5. Conclusion should be re-written to highlight the future perspective

Author's response:

The conclusion has been revised by adding a future perspective of study mainly future perspective lignin for biocomposite application. Please see line 364-369.

6. Introduction can be strengthened to highly the importance of sustainable materials by having a look at relevant references such as <https://www.sciencedirect.com/science/article/pii/S0960852422015887>.

Author's response:

We agree with the reviewer's suggestion thus the introduction has been strengthened by adding some relevant literature such as mentioned. Please see lines 30-33.

### **Editor's comments**

With regard to your manuscript-27579, we have sent a revision request letter to you. Apart from the reviewers' comments, there are also some comments from our editors:

1. Please try to lower the self-citations below 5;

Author's response:

Thank you for your constructive feedback; we have reduced the self-citation to less than 5 in the revised manuscript version. The number of papers published by the author that have been cited in the revised version is four.

2. Please revise your manuscript according to our JRM-template.

Author's response

The manuscript has been revised carefully according to JRM-template



29 DOI: XXXXX

30

31 **ARTICLE**

32 **Characterization of Formacell Lignin Derived from Black Liquor as a**  
33 **Potential Green Additive for Advanced Biocomposites**

34 **Sri Hidayati<sup>1\*</sup>, Eugenia Fonny Budiyo<sup>1</sup>, Hadi Saputra<sup>1</sup>, Sutopo Hadi<sup>1</sup>, Apri Heri**  
35 **Iswanto<sup>2,3</sup>, Nissa Nurfaejrin Solihat<sup>4</sup>, Petar Antov<sup>5</sup>, Lee Seng Hua<sup>6,7</sup>, Widya Fatriasari<sup>4,8</sup>,**  
36 **Mohd. Sapuan Salit<sup>9</sup>**

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38 Brojonegoro No. 1 Bandar Lampung, Indonesia

39 <sup>2</sup>Department of Forest Product, Faculty of Forestry, Universitas Sumatera Utara. Kampus USU Padang Bulan, Medan  
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41 <sup>3</sup>JATI-Sumatran Forestry Analysis Study Center, Jl. Tridharma Ujung No.1, Kampus USU, Medan, North Sumatra,  
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46 <sup>6</sup>Department of Wood Industry, Faculty of Applied Sciences, Universiti Teknologi MARA (UiTM), Cawangan Pahang  
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51 45363, Indonesia

52 <sup>9</sup>Advanced engineering Materials and Composites Research Centre, Department of Mechanical and Manufacturing  
53 Engineering, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

54 \*Corresponding Author: [srihidayati.unila@gmail.com](mailto:srihidayati.unila@gmail.com)

55 Received: XXXX Accepted: XXXX





**ABSTRACT**

Black liquor is obtained as a by-product of the pulping process, used to convert biomass into pulp by removing lignin, hemicelluloses and other extractives from wood to free cellulose fibers. Lignin represents a major constituent in black liquor with quantities varying from 20% to 30%, of which a very low share is used for manufacturing value-added products, while the rest is mainly burned for energy purposes, thus underestimating its great potential as a raw material. Therefore, it is essential to establish new isolation and extraction methods to increase lignin valorization in the development of bio-based chemicals. The aim of this research work was to determine the effect of KOH or ethanol concentration as an isolation agent on lignin yields and the chemical characteristics of lignin isolated from formacell black liquor of oil palm empty fruit bunch (OPEFB). Isolation of lignin was carried out using KOH with various concentrations ranging from 5% to 15% (w/v). Ethanol was also used to precipitate lignin from black liquor at concentrations varying from 5% to 30% (v/v). The results obtained showed that the addition of KOH solution at 12.5% and 15% concentrations resulted in better lignin yield and chemical properties of lignin, i.e., pH values of 3.86 and 4.27, lignin yield of 12.78 and 14.95, methoxylcontent of 11.33 and 10.13, and lignin equivalent weights of 476.25 and 427.03, respectively. Due to its phenolic structure and rich functional groups that are favorable for modifications, lignin has the potential to be used as green additive in the development of advanced biocomposite products in various applications to replace current fossil fuel-based material, ranging from fillers, fire retardants, formaldehyde scavengers, carbon fibers, aerogels, and wood adhesives.

**KEYWORDS**

formacell black liquor; lignin properties; KOH; ethanol; oil palm empty fruit bunch; advanced biocomposite

56

57

**58 1 Introduction**

59 Global challenges such as food security and environmental threats can be treated by applying the  
60 circular bioeconomy principles, including sustainable conversion of biomass components into  
61 bio-based products as green alternatives to their petroleum-based counterparts, thus closing the  
62 material resource loops [1]. Black liquor (BL) is liquid waste left over from cooking pulp, aimed  
63 at removing lignin, hemicelluloses, and other extractable constituents from wood in order to free  
64 the cellulose fibers. Lignin is the main organic substance in BL, reaching 45% dry weight [2].  
65 About 150 billion tons of BL are released from the pulp and paper industry, where every 1 ton of  
66 pulp production will produce 7 tons of BL [3]. Taking into account the increased production of  
67 bioethanol, this availability is projected to reach 225 million tons annually in 2030 [4-6].  
68 However, only 2-5% of BL has been valorized into biomaterial [7] and the rest for energy  
69 purposes [8-10]. Hence, it is important to develop new techniques aimed at increasing the  
70 valorization of lignin as a renewable feedstock in various value-added industrial applications.  
71 Lignin is a complex polyphenol compound with a complex three-dimensional chemical structure  
72 that is difficult to decompose naturally, so it has the potential to cause water pollution if  
73 discharged into the environment [11]. Lignin has a highly aromatic structure that is stable to heat  
74 and has high carbon content. In addition, lignin contains various functional groups, e.g., aliphatic,  
75 phenolic, methoxyl, and carbonyl hydroxyl groups, allowing its modification. Thus, it can be used  
76 in many functional applications such as biomass-based fuels, adhesives, flame retardants,

77 dispersants, and surfactant formulations, as antioxidants in plastics and rubbers, dyes, synthetic  
78 floors, thermosets, paints, food packaging, filler in adhesives, seed coatings, automotive devices,  
79 3D printing, and fuels for highway maintenance [12-17]. However, the utilization of lignin is still  
80 limited on an industrial scale due to the inhomogeneity of structure.

81 A lignin component is a phenylpropane unit with several different methoxy groups [18].  
82 Chemical structures of lignin are identified by the presence of polypropene units such as p-  
83 hydroxyphenyl (or p-coumaryl alcohol), guaiacyl (or coniferyl alcohol), and syringyl (or sinapyl  
84 alcohol), and their percentage vary depending on the botanical origin. Polypropene units can be  
85 chemically bonded in different bonding patterns where the  $\beta$ -O-4 aryl glycerol ether bond is the  
86 primary linkage [19]. However, the technical lignin's structure differs from the native lignin and  
87 depends on the pulping method used. Besides, the source of raw materials and isolation method,  
88 including the type of chemical used and temperature, play critical roles in the physicochemical  
89 properties of lignin [20].

90 Lignin can be extracted in powder form from BL with proper chemical treatment and  
91 screening process [21]. Precipitation of lignin in the BL occurs due to the condensation reaction  
92 on the lignin constituent units, which were initially soluble and will be polymerized and form  
93 large molecules [22]. Base, acid, and organic solvents are common solutions to isolate lignin  
94 from BL. The process of lignin separation using organic solvents is known as the alcell or  
95 organosolv process [23]. This method is popular for breaking down lignin fractions [24]. The  
96 benefits of this method include obtaining lignin with a low molecular weight that is free of sulfur,  
97 and its application can be improved through fractionation or chemical modification [25] but  
98 organosolv fractionation is laborious work [26]; hence, acid and base deposition methods are  
99 more feasible. However, this method depends on the pH of the liquor, residence time, and  
100 temperature [22]. Some acids such as  $H_2SO_4$ , phosphoric acid ( $H_3PO_4$ ), or HCl have been  
101 reported in isolating lignin from base BL, such as from the kraft process [27]. Meanwhile, lignin  
102 from formacell BL, BL derived from acetic acid, or formic acid as cooking liquid can be released  
103 by different alkalis, especially KOH,  $Ca(OH)_2$ , and NaOH [20]. KOH, a strong base, is stronger  
104 than NaOH and its use is expected to result in higher lignin yield.

105 Based on Miller et al. [28], a strong base (e.g., NaOH and KOH) provides a higher result in  
106 lignin yield than a weak base, and it would be a promising technique for depolymerizing lignin.  
107 The concentration of base is important to measure because it will influence selectivity, chemical-  
108 physical properties, and lignin yield [20, 29]. Recently, Hidayati et al evaluated the effect of  
109 NaOH concentration on lignin properties [20] while the disadvantage of NaOH was  
110 monoaromatic re-condensation led to the higher molecular weight of lignin [30]. Consequently,  
111 an alternative base such as KOH and ethanol is needed to overcome this problem. To date, no one  
112 reported lignin isolation from formacell BL using different concentrations of KOH and ethanol.  
113 Therefore, this study aimed to determine the effect of KOH and ethanol concentrations on the  
114 yield and chemical characteristics of lignin isolated from formacell black liquor of oil palm empty  
115 fruit bunch (OPEFB).

## 116 2 Material and Methods

**117 2.1 Materials**

118 Black liquor used in this research is a by-product of the formacell pulping of OPEFB, as  
119 reported by Hidayati et al. [31]. The pulping conditions are presented in detail in the next section.  
120 . OPEFB was obtained from PTPN Business Unit VII Central Lampung Bekri, Indonesia.  
121 Meanwhile, KOH, NaCl, NaOH, HCl, and ethanol were supplied by Merck (Darmstadt,  
122 Germany).

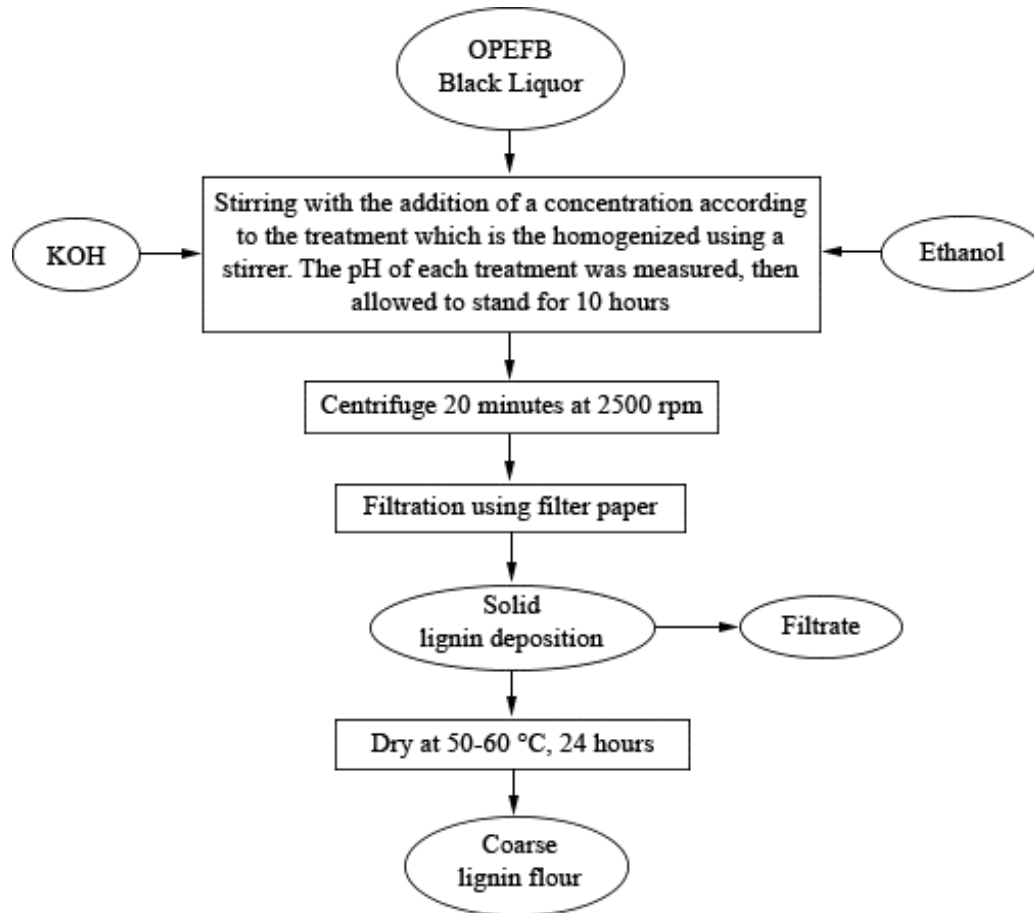
**123 2.2 Pulping process**

124 The formacell pulping was conducted in the autoclave at a liquor-to-particle ratio of 15:1  
125 for 1 h at 130 °C. The ratio of liquor to OPEFB particle ratio of 15:1 was used based on our initial  
126 experimental trials in the laboratory considering the volumetric of OPEFB as a typical example of  
127 non-woody biomass. In this ratio, the OPEFB particles can be immersed completely in the  
128 chemical liquor. The ratio solvent of acetic acid and formic acid was 85:15 with the addition of  
129 HCl of 0.5% as the catalyst. The cooking liquor was collected after filtration and washing the  
130 completed softened OPEFB with fresh water at room temperature. This formacell BL was used  
131 for the next step.

**132 2.3 Lignin isolation**

133 The formacell BL obtained from the pulping process of 100 mL contained a total solid  
134 content of around 25.10%. There are two methods for lignin isolation from formacell BL of  
135 OPEFB. The first one, i.e. the isolation of lignin from BL was conducted using KOH with a  
136 concentration of 2.5%; 5%; 7.5%; 10%; 12.5%; and 15% (w/v). The second isolation technique  
137 used ethanol at concentrations of 5%, 10%, 15%, 20%, 25 and 30% (v/v). As much as 100 mL of  
138 the KOH or ethanol solution was added into 100 mL BL, then stirred and measured the pH of the  
139 liquor was. The solution was allowed to stand for 10 hours, then centrifugated for 20 minutes at  
140 2500 rpm, and then separated using filter paper. The precipitated lignin was then oven-dried at  
141 50-60 °C for 24 h. Dried lignin was crushed manually to produce fine lignin powder (Fig. 1). The  
142 experiment was conducted in triplicate.

143 The data were calculated and presented in average and standard deviation tables and  
144 graphs. Observations made were pH value, the yield of lignin, lignin methoxyl content, the  
145 equivalent weight of lignin, analysis of lignin with Fourier Transform Infra-Red spectroscopy  
146 (FTIR) spectrophotometer (Cary 630 FTIR, Agilent, Australia), and lignin morphology using a  
147 scanning electron microscope (SEM) (JEOL JSM 6510 LA, Japan).



148

149

**Figure 1:** Flowchart of lignin isolation process using KOH/Ethanol.

#### 150 **2.4 Lignin Yield**

151 Lignin yield was calculated based on the method according to Kim [32], as presented in  
 152 Equation 1.

$$153 \quad \text{Lignin Yield (\%)} = \frac{a}{b} \times 100\% \quad (1)$$

154 **Notation :** a = weight of isolated lignin;

155 b = weight of lignin in black liquor

#### 156 **2.5 Methoxyl content of lignin**

157 The methoxyl content of lignin was determined by using the ASTM 15120-81 method  
 158 [33]. As much as 0.5 g of lignin was added to 5 mL of ethanol, following addition to 100 mL of  
 159 distilled water containing 1 g of NaCl, and made in the form of suspension. Neutralization was  
 160 performed using 0.1 N NaOH, given 6 drops of phenolphthalein (pp) indicator, then 25 mL of  
 161 0.25 N NaOH was added and homogenized in a closed state for 30 minutes at room temperature.  
 162 After that, 25 mL of 0.25 N HCl was added and titrated with 0.1 N NaOH until the end of the lasting  
 163 color change (at least 30 seconds). The methoxyl content of lignin was calculated according to  
 164 Equation 2 as follows.

$$\text{Methoxyl (\%)} = \frac{\text{ml NaOH} \times \text{N NaOH} \times 3.1}{\text{Berat sampel (gram)}} \times 100\% \quad (2)$$

## 166 **2.6 Lignin Equivalent Weight**

167 Isolated lignin equivalent weight was calculated using the method of Santoso [34]. 0.5 g  
168 lignin was put into 250 mL Erlenmeyer and moistened with 5 mL ethanol. The mixture is spiked  
169 with 1 g of NaCl which is then added with 100 mL of distilled water and 6 drops of phenolphthalein  
170 indicator. The solution was then titrated with 0.1 N NaOH until pH 7.5. The equivalent weight of  
171 isolated lignin was calculated by using Equation 3.

$$\text{Equivalent Weight} = \frac{1000 \times \text{gram sample}}{(\text{mLN}) \text{NaOH}} \quad (3)$$

## 173 **2.7 FT-IR analysis of isolated lignin**

174 As much as 1 mg isolated lignins were added with 150 mg KBr, pelletized, and then the  
175 samples were analyzed by FT-IR spectrophotometer (Cary 630 FTIR Agilent). The analysis was  
176 set at a wavenumber of  $4000 \text{ cm}^{-1}$  to  $400 \text{ cm}^{-1}$  (wavelength of 2.5–25  $\mu\text{m}$ ).

## 177 **2.7 SEM analysis**

178 Morphology of isolated lignin was carried out using Scanning Electron Microscope (SEM)  
179 (JEOL JSM 6510 LA) with 1000 x magnification.

# 180 **3 Results and Discussion**

## 181 **3.1 pH of the liquor**

182 The pH of black liquor from formacell pulping OPEFB is  $0.59 \pm 0.01$ , indicating that the  
183 liquor is acidic; thus, base or ethanol can be used to precipitate lignin from BL. To speed up the  
184 reaction, solvents such as acetic acid and formic acid are used in the formacell pulping process,  
185 along with HCl as a catalyst [31]. This process causes the pH of the formacell black liquor to  
186 become very acidic. Zhuang et al. [35] stated that formic acid and acetic acid could delignify  
187 lignin because of their acidic nature, so they can degrade lignin well. In another study, a  
188 combination of formic acid, acetic acid, and water achieved more than 50% lignin  
189 depolymerization in biomass [36]. The pH of the BL will be affected by the addition of KOH  
190 solution. According to the research, the pH value obtained from formacell pulping added with  
191 KOH solution ranged from  $2.43 \pm 0.07$  to  $4.27 \pm 0.35$  (Table 1), while the addition of ethanol  
192 concentrations can slightly increase the pH value from  $1.0 \pm 0.01$  to  $1.29 \pm 0.03$ . According to the  
193 findings, KOH has a greater effect on increasing pH than ethanol due to the strong base property  
194 of KOH.

195 The pH steadily increased as an upsurging concentration of KOH, where the lowest pH,  
196  $2.43 \pm 0.07$ , was obtained from 2.5% KOH, and the highest was a pH of  $4.27 \pm 0.35$  from KOH  
197 15%. Increasing the concentration of KOH solution causes more  $\text{OH}^-$  ions in the black liquor so  
198 that the pH of the solution becomes more alkaline. It can also be explained that KOH is a strong  
199 base. The stronger the base, the more  $\text{OH}^-$  ions are released, increasing the pH of the solution  
200 and making it more alkaline. Ethanol has a higher pKa than KOH, indicating a weaker acid.

201 Unlike KOH, increasing the ethanol concentration slightly increased the pH, with the lowest  
202 being 1 and the highest being 1.29 after adding 5% and 30%, as shown in Table 1.

203 **Table 1:** Effect of KOH and ethanol concentrations on pH, yield, methoxyl content, and an  
204 equivalent weight of isolated lignin.

Treatment	pH	Yield (%)	Lignin methoxyl (%)	Equivalent Weight
KOH concentration (%)				
2.5	2.43±0.07	3.57±0.38	13.06±0.9	1372.94±26.73
5.0	2.94±0.06	4.85±1.12	12.94±1.31	655.73±45.16
7.5	3.21±0.1	8.63±1.41	12.81±0.84	528.74±54.44
10	3.61±0.15	11.20±2.69	12.36±0.9	510.33±49.05
12.5	3.86±0.15	12.78±0.78	11.33±0.4	476.25±34.61
15	4.27±0.35	14.95±1.10	10.13±1.42	427.03±44.20
Ethanol concentration (%)				
5	1.00±0.01	1.95±0.18	17.03±0.42	449.88±48.47
10	1.08±0.06	2.27±0.317	16.45±1.44	624.67±59.2
15	1.15±0.07	1.69±0.091	15.05±1.03	767.97±56.6
20	1.20±0.047	1.77±0.207	14.47±1.17	896.95±64.15
25	1.22±0.056	1.44±0.174	13.14±1.78	1521.16±72.10
30	1.29±0.03	1.08±0.179	11.99±1.20	2123.02±70.72

205

206

### 207 **3.2 Lignin yield**

208 The lignin yield from adding KOH solution at various concentrations in isolation of BL  
209 ranged from  $3.57 \pm 0.38$  to  $14.95 \pm 1.10$  (Table 1). In comparison, ethanol isolation resulted in  
210 lower lignin yields of about  $0.51 \pm 0.00$  to  $1.06 \pm 0.00$ . The highest lignin yield was produced at a  
211 concentration of 15% KOH solution ( $14.95\% \pm 1.10$ ). Increasing the concentration of KOH  
212 solution caused the lignin yield to increase. It can be affected by the increasing concentration of  
213 an alkaline solution (KOH) that facilitates easier breaking of lignin bonds with other compounds,  
214 and a condensation reaction occurs in the lignin constituent units [37]. It is also supported by  
215 Sundin's [38] who stated that lignin deposition from BL due to the protonation of phenol groups  
216 on lignin molecules caused by the addition of  $\text{OH}^-$  ions from KOH. It reduces the electrostatic  
217 force between lignin molecules, resulting in the deposition of lignin (reduced solubility). The  
218 more  $\text{OH}^-$  ions, the more lignin deposits will form. The deposit lignin increase occurred because  
219 of an increase in ionic strength and protonation. The protonation of the phenolic group in lignin  
220 leads the lignin nucleus to form aggregates when the pKa value of lignin is reached [39].

221 The lignin yield with KOH liquor treatment is higher than that of NaOH, as reported by  
222 Hidayati et al. [20]. Lignin was isolated from formacell black liquor of OPEFB by using NaOH,  
223 producing lignin yields ranging from 1.48% to 5.67%. It might be caused by the stronger base of

224 KOH than NaOH. As seen in the periodic system, the metal Na<sup>+</sup> and K<sup>+</sup> are included in Group 1A.  
225 This is also related to the lower nature of alkali metal bases; the stronger, the lower the metal, the  
226 more easily reduced. Besides pH, temperature and ionic strength also affect lignin solubility. The  
227 molecular weight distribution in lignins is related to yield [40]. Both molecular weight and the  
228 ratio of phenols to aromatic units contribute to the solubility of lignin [40]. The changes in lignin  
229 yield in isolation by adding ethanol concentration are very low. The very low electronegativity of  
230 ethanol can suggest it is due to the presence of carbon compounds that cannot precipitate lignin  
231 properly. In the absence of sulfide, delignification was slower in the Alcell process.

232 As opposed to KOH precipitation, increasing ethanol concentrations leads to almost 0%  
233 lignin recovery. This result was in agreement with the precipitation of lignin from *Miscanthus x*  
234 *giganteus*, where after the addition of 75% of ethanol, there was no lignin precipitated [41]. In the  
235 low concentration of ethanol, lignin precipitation is carried out by diluting liquor with water, and  
236 the solubility of lignin decreases, resulting in more lignin being recovered. In other words, when  
237 the water content in the ethanol is limited, most of the lignin is soluble in the system, and hence  
238 the aggregate is not formed.

239

### 240 **3.3 Methoxyl content in lignin**

241 Methoxyl is one of the chemical groups in lignin for identifying one of the characteristics of  
242 lignin. The methoxyl group in each type of lignin has different content because of the different  
243 structures of lignin types. Determining methoxyl contents gives information about the average C9  
244 units in lignin, and eventually, the unsaturated side chain and average oxygen content can be  
245 calculated [42]. The methoxyl content in KOH lignin ranged from 10.13% ± 1.92 to 12.94% ±  
246 0.90, whereas the use of ethanol concentrations results in methoxyl contents between 11.99 ±  
247 0.02 to 17.03 ± 0.5 (Table 1). The highest methoxyl content in lignin was acquired from isolated  
248 lignin by adding a 2.5% KOH solution. Increasing the concentration of KOH and ethanol solution  
249 leads to a decrease in the methoxyl content of isolated lignins. This may be due to the use of  
250 KOH as a strong base as a precipitating solution, which allows some methoxyl groups to degrade  
251 and transform into other compounds. This decrease in methoxyl content can be influenced by the  
252 disruption of structural stability in lignin caused by the addition of KOH. Furthermore, according  
253 to the pathway proposed by Yin et al., the removal of the methoxy group in lignin created a  
254 higher hydroxyl group of lignin by KOH solution. The presence of potassium in lignin isolation  
255 decreased the methoxyl content due to cleavage C $\alpha$ —C $\beta$  through C $\beta$ —O bond. This cleavage  
256 leads to the removal of side chains such as methoxy. The mechanism of this reaction has been  
257 proved by Yin et al. [43].

258 The various methoxyl content in lignin depends on the source of lignin and the  
259 delignification process used. Generally, high methoxyl content will inhibit lignin reactivity during  
260 use in the resin field. Lignin has phenolic hydroxyl groups that are typically linked to nearby  
261 phenyl propane units, allowing lignin to connect with formaldehyde in a way analogous to phenol  
262 and formaldehyde [44]. Molecular weight and lignin purity are important factors during the  
263 production of biocarbon fibers [44, 45].

264 In the case of lignin application as an adhesive raw material, the low methoxyl content is  
265 more beneficial because it will increase the reactivity of aromatic nuclei in lignin [46]. It will  
266 facilitate the reaction of methylation or hydroxymethylation with adhesive-forming reactants such  
267 as NaOH and formaldehyde, hinting at the ease of gel formation. Recently, Gendron et al.  
268 compared four types of lignin for green adhesive, where the lowest methoxyl content of lignin  
269 had the highest water solubility and shear resistance as an adhesive [47].

270 The lignin standard of Indulin AT has a methoxyl content of around 13.5% - 14.5% [48], so  
271 the methoxyl contents in isolated lignin in this study are still lower. Meanwhile, compared to  
272 methoxyl content by Hidayati et al. [20] with a value of 14.61% - 20.77% by using NaOH as  
273 precipitating solution, the results of this study are also lower. These results are probably  
274 influenced by the use of KOH, which is classified as a strong base with a higher reactivity than  
275 NaOH, as seen from the periodic system. The influence of harsh chemicals and temperature  
276 during isolation causes the structure of lignin to undergo many changes, including the methoxyl  
277 group. The methoxyl group is degraded and transformed into other degradation compounds such  
278 as aromatic hydrocarbon and phenolic types, resulting in lower methoxyl content [49].

### 279 **3.4 The equivalent weight of lignin**

280 The determination of the equivalent weight of lignin is intended to determine the  
281 molecular weight of lignin to identify lignin degradation and condensation reactions. The  
282 molecular weight of lignin is an important property that influences biomass recalcitrance and  
283 lignin value. Determination of the molecular weight of lignin in the original biomass depends on  
284 the source of the raw material used, chemicals used for isolation, and purification methods [50,  
285 51]. Based on the results, the equivalent weight of lignin from the KOH solution ranged from  
286  $427.03 \pm 74.20$  to  $1372.94 \pm 269.73$ , whereas the addition of ethanol concentration resulted in  
287 molecular weights ranging from  $449.88 \pm 1.9$  to  $2123.03 \pm 27.5$  (Table 1).

288 Increasing the concentration of KOH solution resulted in a decrease in lignin equivalent  
289 weight so that the lowest value at 15% KOH solution concentration was  $427.03 \pm 74.20$ . This  
290 might be attributed to the increasing addition of a KOH solution as a strong base will degrade a  
291 portion of lignin into a derivative compound with shorter chains. It can degrade lignin resulting in  
292 a low equivalent weight. According to Patil et al., there are two routes for lignin depolymerization:  
293 harsh and moderate, resulting in different lignin structures [52]. The average molecular weight of  
294 lignin decreases with increasing precipitation of lignin yield by KOH. It was shown that  
295 increasing the amount of lignin with lower molecular weight deposited a high yield of lignin.  
296 Lignin is degraded into smaller fragments so that there are more phenolic groups with lower  
297 molecular weights [53]. The product's molecular weight can be lowered by increasing salt  
298 concentration [54, 55].

299 According to Gellerstedt [56], the termination of methyl aryl ether bonds from the aromatic  
300 ring of lignin resulted in decreased methoxyl content and low molecular weight of lignin due to  
301 the lignin degradation process. Based on several previous studies, lignin molecular weight values  
302 were obtained, namely 2500 - 14,000 [57], and 1327.64 - 1787.23 [20]. In contrast, the equivalent



303 weight of Indulin AT reached 3357 - 3366 [58]. This shows that the equivalent weight value of  
304 lignin varies greatly.

305 Lignin that has a high molecular weight can be used as a matrix in polyolefin composites,  
306 because a higher molecular mass of lignin has a better affinity with the matrix [59], while lignin  
307 with a lower molecular weight can be used for the development of phenol-formaldehyde resins,  
308 antioxidants, adhesives, and paints due to their higher reactivity than high molecular weight  
309 lignin [59].

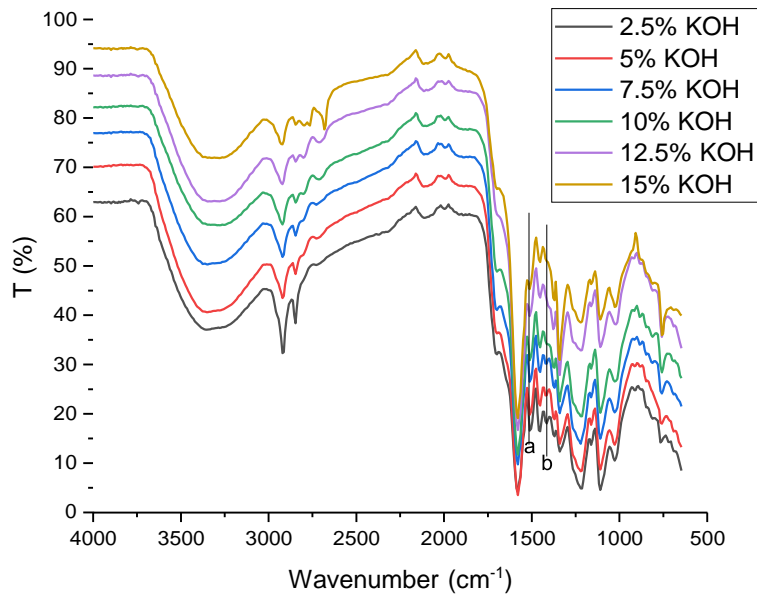
310 Differences in elemental composition, functional group types, proportions, and molecular  
311 weight in lignin molecules provide opportunities to use lignin in a variety of value-added  
312 applications. Some factors that influence the molecular weight of lignin are the diversity of lignin  
313 isolation procedures, macromolecular degradation during isolation, the effect of condensation  
314 mainly on acidic conditions, the apparent polydispersity of dissolved lignin, inadequate  
315 determination methods used to characterize the isolated lignin, and uncertainties in the properties  
316 of lignin. Because lignin is heterogeneous and inconstant, characterizing native lignin is also  
317 difficult [60].

318 The molecular weight of lignin is very important in the development of such polymeric  
319 products; similarly, low-molecular-weight lignin isolated from wheat straw by acetic acid pulping  
320 is an ideal feedstock for adhesive manufacturing [61]. Doherty et al. [62] stated that lignin from  
321 the soda process of wheat plants ranges from 1700 with a methoxyl content of 16. The organosolv  
322 pulping process at bagasse produces a molecular weight of around 2000 and a methoxyl content  
323 of 15.1. Lignin produced in the isolation process using alcohol or alcell process has a low  
324 molecular weight ( $M_w < 900$ ) with low polydispersity, no sulfur, and low ash content, although  
325 the value depends on the analytical method. There is also a molecular weight of  $2580 \text{ g mol}^{-1}$   
326 with a polydispersity of 4.3. Sameni et al. compared four types of lignin from different isolation  
327 methods, where the highest  $M_w$  (13488) was obtained from the steam explosion process with a  
328 methoxyl content of 0.69. Meanwhile, with the same methoxyl content, the lowest  $M_w$  (2565)  
329 was derived from the kraft process [57]. Yun et al. reported that organosolv fractionation from  
330 native lignin decreased its molecular weight from 5070 to 1810 [23].

### 331 **3.6 Lignin Analysis with FT-IR Spectrophotometer**

332 FTIR was performed to analyze differences in the functional groups of lignin in the sample  
333 (Fig. 2 and 3). FTIR spectra analysis showed that the peak in the aromatic ring vibrations  
334 decreased with the absorption band at  $1446 \text{ cm}^{-1}$  (a) and  $1408 \text{ cm}^{-1}$  (b), especially in the  
335 treatment using the highest concentration of KOH (Figure 2) and ethanol (Figure 3). There are  
336 similarities in the wavelength of  $3500 \text{ cm}^{-1}$  to  $31090 \text{ cm}^{-1}$  which refer to the presence of  
337 hydrogen bonds in the hydroxyl group (alcohol and phenolic). A wavelength absorption of  $1587$   
338  $\text{cm}^{-1}$  and  $1513 \text{ cm}^{-1}$  indicates the aromatic lignin skeletal vibration [60]. Wavenumbers at  $1460$   
339  $\text{cm}^{-1}$  to  $1420 \text{ cm}^{-1}$  are associated with stretching wavelengths of CH (methyl and methylene) and  
340 CH deformation with aromatic ring stretching fields [63]. The peaks observed in the range of  
341  $1220 \text{ cm}^{-1}$  to  $1270 \text{ cm}^{-1}$  in all spectra may refer to the C-H deformation vibrations of the guaiacyl  
342 [64]. The bands at  $1300 \text{ cm}^{-1}$  (syringyl) and  $1200 \text{ cm}^{-1}$  (guaiacyl) indicate the presence of both

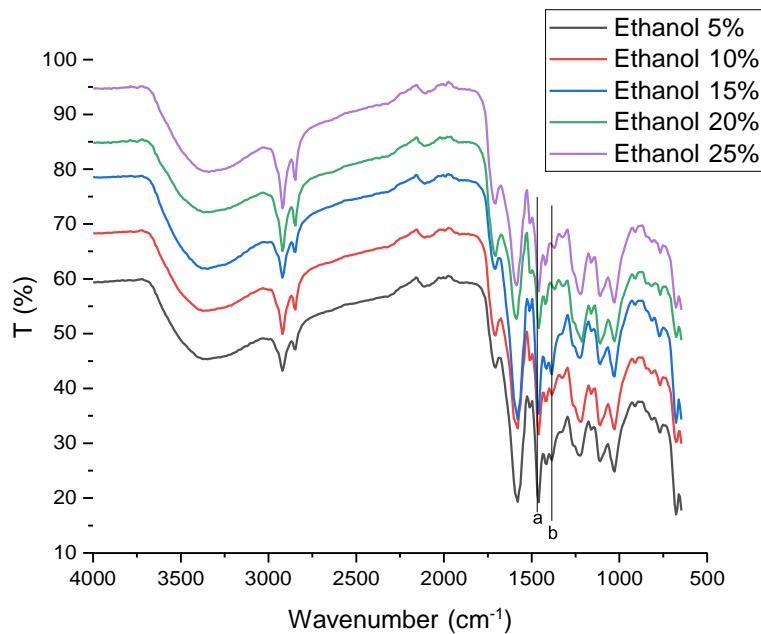
343 syringyl and guaiacyl in lignin's chemical structure as the unique peaks of lignin precursor [65].  
344 A similar peak was also found in kraft lignin isolated from *Acacia mangium* black liquor [27]. In  
345 general, peaks in Fig. 2 and 3 show that the treatment using KOH had a sharper peak than that of  
346 ethanol treatment. However, no difference in the peaks resulting from these two treatments was  
347 determined. Hidayati et al. [20] reported the experiment in isolated lignin from formacell black  
348 liquor of OPEFB using NaOH with the wave number of isolated lignin for guaiacyl lignin at  
349 around  $1273.02\text{ cm}^{-1}$ .



350

351

**Figure 2:** The FT-IR spectra of lignin using KOH isolation



**Figure 3:** The FT-IR spectra of lignin using ethanol isolation

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### 355 **3.7 Morphological observation**

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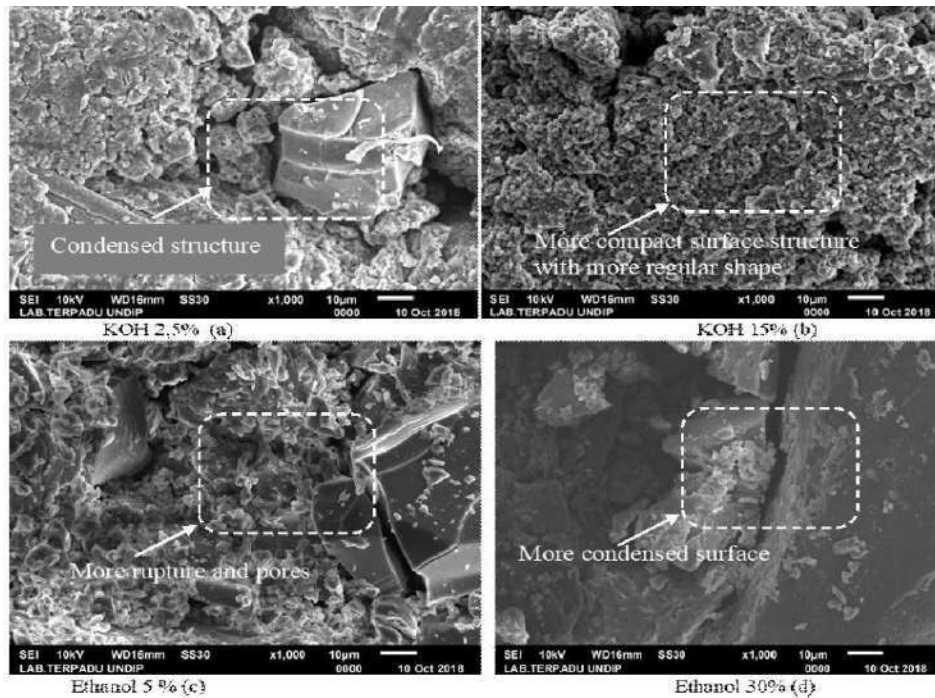
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Scanning Electron Microscope (SEM) was used to observe the size and morphology of lignin. In this study, SEM images were taken from the lowest and the highest concentration of KOH and ethanol as representative lignin morphology. As seen in Fig. 4, increasing the concentration of KOH acid from 2.5% to 15% showed differences in lignin morphology. Lignin isolation using 15% KOH (Fig. 4b) produced a more compact formation and morphology compared to lignin produced by isolation using 2.5% KOH concentration (Fig. 4a). In stark contrast, in treatment using ethanol appears that treatment with a 5% ethanol concentration resulted in a more condensed form and morphology than those using a 30% concentration. This result was in accordance with the findings reported by Solihat et al. [27] and Hamzah et al., [41] where increasing ethanol concentration created more rupture and amorphous lignin surface.



366

367 **Figure 4:** Morphological images of isolated lignin (a) KOH 2.5%, (b) KOH 15%, (c) ethanol 5%,  
 368 (d) ethanol 30% with 1000 x magnification

369

### 370 **3.8 Prospective Application of Formacell Lignin as Advanced Biocomposite Products**

371 The lignin molecule contains a variety of active functional groups, including aliphatic  
 372 hydroxyl (Al-OH), phenolic hydroxyl (Ph-OH), carboxyl (-COOH), carbonyl (-C=O), and  
 373 methoxy groups (-OCH<sub>3</sub>), which determine its properties, chemistry, and reactivity of lignin.  
 374 Lignin's chemical properties enable it and its derivatives to be used as high-value materials. The  
 375 lignin molecule can be used in a variety of value-added applications due to differences in  
 376 molecular weight, elemental composition, and the types and proportions of functional groups.  
 377 Currently, Saražin et al. investigated the potency of organosolv lignin-based non-isocyanate  
 378 polyurethane for wood adhesive and the result demonstrated satisfactory mechanical properties  
 379 [66] and its curing kinetics for interior furniture showed that it was more suitable than urea-  
 380 formaldehyde (UF) adhesive [67]. Sulfur-free lignin is produced by isolating lignin from the  
 381 formacell process. Most value-added applications prefer lignin with a lower percentage of sulfur  
 382 and ash. For example, sulfur-free lignin is preferred for use in aerogel composites. Joul et al.  
 383 reacted lignin isolated by organic acid with 5-methylresorcinol-formaldehyde to create aerogel  
 384 and according to the data, formacell lignin had good reactivity to create a high surface area of  
 385 aerogel [68]. According to Talabi et al., lignin with rich hydroxyl carbon, low molecular weight,  
 386 and less in the methoxyl group was suitable for lignin-based-formaldehyde resin with a 73%  
 387 graphitization level [69], and hence formacell lignin with higher KOH and ethanol concentrations  
 388 are appropriate for this application. Meanwhile, the high molecular weight of lignin is preferred  
 389 as a matrix in carbon fiber composites because it improves the mechanical performance of the  
 390 fiber.

391

**392 4 Conclusions**

393 A strong base, such as KOH, was used to successfully isolate lignin from oil palm empty  
394 fruit bunch formacell BL (OPEFB). Some identified lignin peaks can be found in the FTIR  
395 spectra, with no significant difference between lignins isolated with KOH and ethanol. The  
396 addition of KOH solution at 12.5 and 15% concentrations is the more effective method for  
397 isolating lignin from formacell BL. At this condition, isolated lignins have pH values of 3.86 and  
398 4.27, lignin yield of 2.78 and 14.95%, methoxyl content of 11.33 and 10.13, and lignin equivalent  
399 weights of 476.25 and 427.03, respectively. The lignin produced by the isolation process using  
400 KOH and ethanol was characterized by the low methoxy content and low molecular weight that  
401 created its higher reactivity. According to these properties, lignin derived from formacell is  
402 suitable for developing green, bio-based additives in biocomposite applications such as wood  
403 adhesives from non-isocyanate polyurethane, coatings, lignin-based-formaldehyde resins,  
404 formaldehyde scavengers, composite fillers, and other value-added industrial applications.

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31 **ARTICLE**

32 **Characterization of Formacell Lignin Derived from Black Liquor as a**  
33 **Potential Green Additive for Advanced Biocomposites**

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**ABSTRACT**

Black liquor is obtained as a by-product of the pulping process, used to convert biomass into pulp by removing lignin, hemicelluloses and other extractives from wood to free cellulose fibers. Lignin represents a major constituent in black liquor with quantities varying from 20% to 30%, of which a very low share is used for manufacturing value-added products, while the rest is mainly burned for energy purposes, thus underestimating its great potential as a raw material. Therefore, it is essential to establish new isolation and extraction methods to increase lignin valorization in the development of bio-based chemicals. The aim of this research work was to determine the effect of KOH or ethanol concentration as an isolation agent on lignin yields and the chemical characteristics of lignin isolated from formacell black liquor of oil palm empty fruit bunch (OPEFB). Isolation of lignin was carried out using KOH with various concentrations ranging from 5% to 15% (w/v). Ethanol was also used to precipitate lignin from black liquor at concentrations varying from 5% to 30% (v/v). The results obtained showed that the addition of KOH solution at 12.5% and 15% concentrations resulted in better lignin yield and chemical properties of lignin, i.e., pH values of 3.86 and 4.27, lignin yield of 12.78 and 14.95, methoxylcontent of 11.33 and 10.13, and lignin equivalent weights of 476.25 and 427.03, respectively. Due to its phenolic structure and rich functional groups that are favorable for modifications, lignin has the potential to be used as green additive in the development of advanced biocomposite products in various applications to replace current fossil fuel-based material, ranging from fillers, fire retardants, formaldehyde scavengers, carbon fibers, aerogels, and wood adhesives.

**KEYWORDS**

formacell black liquor; lignin properties; KOH; ethanol; oil palm empty fruit bunch; advanced biocomposite

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**58 1 Introduction**

59 Global challenges such as food security and environmental threats can be treated by applying the  
60 circular bioeconomy principles, including sustainable conversion of biomass components into  
61 bio-based products as green alternatives to their petroleum-based counterparts, thus closing the  
62 material resource loops [1]. Black liquor (BL) is liquid waste left over from cooking pulp, aimed  
63 at removing lignin, hemicelluloses, and other extractable constituents from wood in order to free  
64 the cellulose fibers. Lignin is the main organic substance in BL, reaching 45% dry weight [2].  
65 About 150 billion tons of BL are released from the pulp and paper industry, where every 1 ton of  
66 pulp production will produce 7 tons of BL [3]. Taking into account the increased production of  
67 bioethanol, this availability is projected to reach 225 million tons annually in 2030 [4-6].  
68 However, only 2-5% of BL has been valorized into biomaterial [7] and the rest for energy  
69 purposes [8-10]. Hence, it is important to develop new techniques aimed at increasing the  
70 valorization of lignin as a renewable feedstock in various value-added industrial applications.  
71 Lignin is a complex polyphenol compound with a complex three-dimensional chemical structure  
72 that is difficult to decompose naturally, so it has the potential to cause water pollution if  
73 discharged into the environment [11]. Lignin has a highly aromatic structure that is stable to heat  
74 and has high carbon content. In addition, lignin contains various functional groups, e.g., aliphatic,  
75 phenolic, methoxyl, and carbonyl hydroxyl groups, allowing its modification. Thus, it can be used  
76 in many functional applications such as biomass-based fuels, adhesives, flame retardants,

77 dispersants, and surfactant formulations, as antioxidants in plastics and rubbers, dyes, synthetic  
78 floors, thermosets, paints, food packaging, filler in adhesives, seed coatings, automotive devices,  
79 3D printing, and fuels for highway maintenance [12-17]. However, the utilization of lignin is still  
80 limited on an industrial scale due to the inhomogeneity of structure.

81 A lignin component is a phenylpropane unit with several different methoxy groups [18].  
82 Chemical structures of lignin are identified by the presence of polypropene units such as p-  
83 hydroxyphenyl (or p-coumaryl alcohol), guaiacyl (or coniferyl alcohol), and syringyl (or sinapyl  
84 alcohol), and their percentage vary depending on the botanical origin. Polypropene units can be  
85 chemically bonded in different bonding patterns where the  $\beta$ -O-4 aryl glycerol ether bond is the  
86 primary linkage [19]. However, the technical lignin's structure differs from the native lignin and  
87 depends on the pulping method used. Besides, the source of raw materials and isolation method,  
88 including the type of chemical used and temperature, play critical roles in the physicochemical  
89 properties of lignin [20].

90 Lignin can be extracted in powder form from BL with proper chemical treatment and  
91 screening process [21]. Precipitation of lignin in the BL occurs due to the condensation reaction  
92 on the lignin constituent units, which were initially soluble and will be polymerized and form  
93 large molecules [22]. Base, acid, and organic solvents are common solutions to isolate lignin  
94 from BL. The process of lignin separation using organic solvents is known as the alcell or  
95 organosolv process [23]. This method is popular for breaking down lignin fractions [24]. The  
96 benefits of this method include obtaining lignin with a low molecular weight that is free of sulfur,  
97 and its application can be improved through fractionation or chemical modification [25] but  
98 organosolv fractionation is laborious work [26]; hence, acid and base deposition methods are  
99 more feasible. However, this method depends on the pH of the liquor, residence time, and  
100 temperature [22]. Some acids such as  $H_2SO_4$ , phosphoric acid ( $H_3PO_4$ ), or HCl have been  
101 reported in isolating lignin from base BL, such as from the kraft process [27]. Meanwhile, lignin  
102 from formacell BL, BL derived from acetic acid, or formic acid as cooking liquid can be released  
103 by different alkalis, especially KOH,  $Ca(OH)_2$ , and NaOH [20]. KOH, a strong base, is stronger  
104 than NaOH and its use is expected to result in higher lignin yield.

105 Based on Miller et al. [28], a strong base (e.g., NaOH and KOH) provides a higher result in  
106 lignin yield than a weak base, and it would be a promising technique for depolymerizing lignin.  
107 The concentration of base is important to measure because it will influence selectivity, chemical-  
108 physical properties, and lignin yield [20, 29]. Recently, Hidayati et al evaluated the effect of  
109 NaOH concentration on lignin properties [20] while the disadvantage of NaOH was  
110 monoaromatic re-condensation led to the higher molecular weight of lignin [30]. Consequently,  
111 an alternative base such as KOH and ethanol is needed to overcome this problem. To date, no one  
112 reported lignin isolation from formacell BL using different concentrations of KOH and ethanol.  
113 Therefore, this study aimed to determine the effect of KOH and ethanol concentrations on the  
114 yield and chemical characteristics of lignin isolated from formacell black liquor of oil palm empty  
115 fruit bunch (OPEFB).

## 116 2 Material and Methods

## 117 **2.1 Materials**

118 Black liquor used in this research is a by-product of the formacell pulping of OPEFB, as  
119 reported by Hidayati et al. [31]. **The pulping conditions are presented in details in the next**  
120 **section.** OPEFB was obtained from PTPN Business Unit VII Central Lampung Bekri, Indonesia.  
121 Meanwhile, KOH, NaCl, NaOH, HCl, and ethanol were supplied by Merck (Darmstadt,  
122 Germany).

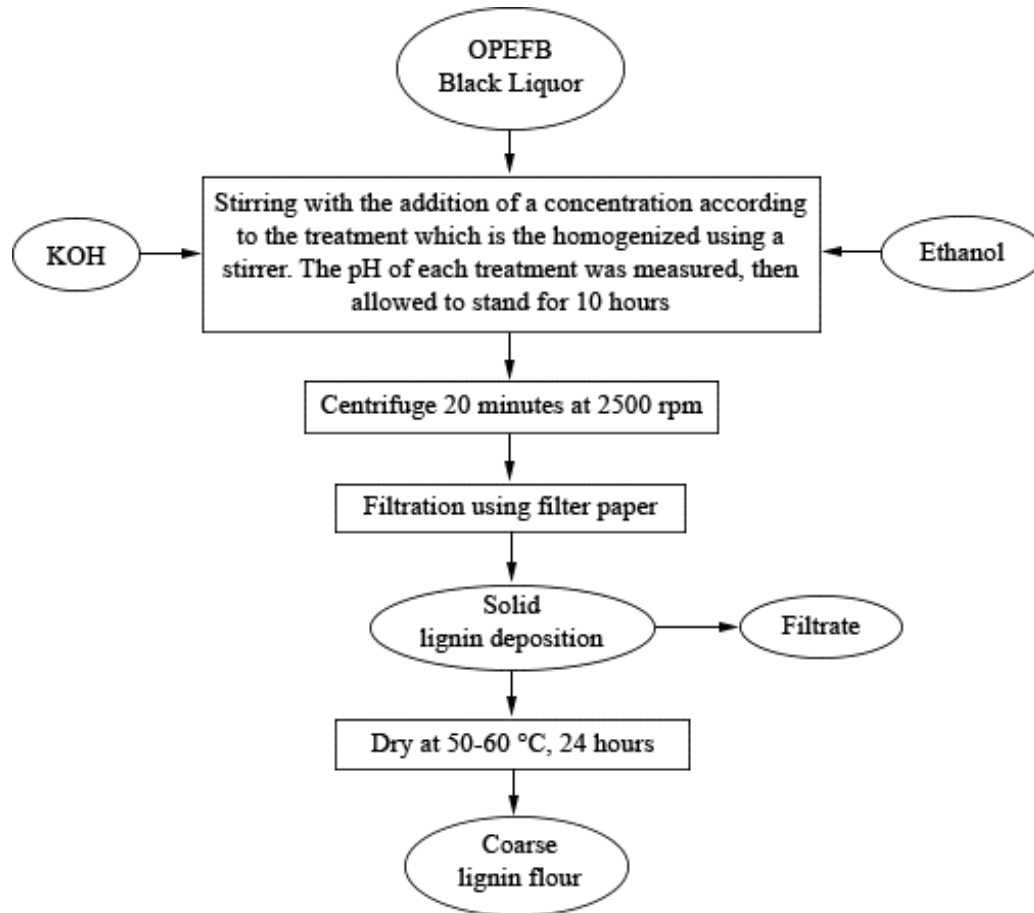
## 123 **2.2 Pulping process**

124 The formacell pulping was conducted in the autoclave at a liquor-to-particle ratio of 15:1  
125 for 1 h at 130 °C. **The ratio of liquor to OPEFB particle ratio of 15:1 was used based on our initial**  
126 **experimental trials in the laboratory considering the volumetric of OPEFB as a typical example of**  
127 **non-woody biomass. In this ratio, the OPEFB particles can be immersed completely in the**  
128 **chemical liquor.** The ratio solvent of acetic acid and formic acid was 85:15 with the addition of  
129 HCl of 0.5% as the catalyst. The cooking liquor was collected after filtration and washing the  
130 completed softened OPEFB with fresh water at room temperature. This formacell BL was used  
131 for the next step.

## 132 **2.3 Lignin isolation**

133 The formacell BL obtained from the pulping process of 100 mL contained a total solid  
134 content of around 25.10%. **There are two methods for lignin isolation from formacell BL of**  
135 **OPEFB. The first one, i.e. the isolation of lignin from BL was conducted using KOH with a**  
136 **concentration of 2.5%; 5%; 7.5%; 10%; 12.5%; and 15% (w/v). The second isolation technique**  
137 **used ethanol at concentrations of 5%, 10%, 15%, 20%, 25 and 30% (v/v).** As much as 100 mL of  
138 the KOH or ethanol solution was added into 100 mL BL, then stirred and measured the pH of the  
139 liquor was. The solution was allowed to stand for 10 hours, then centrifugated for 20 minutes at  
140 2500 rpm, and then separated using filter paper. The precipitated lignin was then oven-dried at  
141 50-60 °C for 24 h. Dried lignin was crushed manually to produce fine lignin powder (Fig. 1). The  
142 experiment was conducted in triplicate.

143 The data were calculated and presented in average and standard deviation tables and  
144 graphs. Observations made were pH value, the yield of lignin, lignin methoxyl content, the  
145 equivalent weight of lignin, analysis of lignin with Fourier Transform Infra-Red spectroscopy  
146 (FTIR) spectrophotometer (Cary 630 FTIR, Agilent, Australia), and lignin morphology using a  
147 scanning electron microscope (SEM) (JEOL JSM 6510 LA, Japan).



148

149

**Figure 1:** Flowchart of lignin isolation process using KOH/Ethanol.

#### 150 2.4 Lignin Yield

151 Lignin yield was calculated based on the method according to Kim [32], as presented in  
 152 Equation 1.

$$153 \quad \text{Lignin Yield (\%)} = \frac{a}{b} \times 100\% \quad (1)$$

154 **Notation :** a = weight of isolated lignin;

155 b = weight of lignin in black liquor

#### 156 2.5 Methoxyl content of lignin

157 The methoxyl content of lignin was determined by using the ASTM 15120-81 method  
 158 [33]. As much as 0.5 g of lignin was added to 5 mL of ethanol, following addition to 100 mL of  
 159 distilled water containing 1 g of NaCl, and made in the form of suspension. Neutralization was  
 160 performed using 0.1 N NaOH, given 6 drops of phenolphthalein (pp) indicator, then 25 mL of  
 161 0.25 N NaOH was added and homogenized in a closed state for 30 minutes at room temperature.  
 162 After that, 25 mL of 0.25 N HCl was added and titrated with 0.1 N NaOH until the end of the  
 163 lasting color change (at least 30 seconds). The methoxyl content of lignin was calculated according  
 164 to Equation 2 as follows.

$$\text{Methoxyl (\%)} = \frac{\text{ml NaOH} \times \text{N NaOH} \times 3.1}{\text{Berat sampel (gram)}} \times 100\% \quad (2)$$

## 166 **2.6 Lignin Equivalent Weight**

167 Isolated lignin equivalent weight was calculated using the method of Santoso [34]. 0.5 g  
168 lignin was put into 250 mL Erlenmeyer and moistened with 5 mL ethanol. The mixture is spiked  
169 with 1 g of NaCl which is then added with 100 mL of distilled water and 6 drops of phenolphthalein  
170 indicator. The solution was then titrated with 0.1 N NaOH until pH 7.5. The equivalent weight of  
171 isolated lignin was calculated by using Equation 3.

$$\text{Equivalent Weight} = \frac{1000 \times \text{gram sample}}{(\text{mLN}) \text{NaOH}} \quad (3)$$

## 173 **2.7 FT-IR analysis of isolated lignin**

174 As much as 1 mg isolated lignins were added with 150 mg KBr, pelletized, and then the  
175 samples were analyzed by FT-IR spectrophotometer (Cary 630 FTIR Agilent). The analysis was  
176 set at a wavenumber of  $4000 \text{ cm}^{-1}$  to  $400 \text{ cm}^{-1}$  (wavelength of 2.5–25  $\mu\text{m}$ ).

## 177 **2.7 SEM analysis**

178 Morphology of isolated lignin was carried out using Scanning Electron Microscope (SEM)  
179 (JEOL JSM 6510 LA) with 1000 x magnification.

# 180 **3 Results and Discussion**

## 181 **3.1 pH of liquor**

182 The pH of black liquor from formacell pulping OPEFB is  $0.59 \pm 0.01$ , indicating that the  
183 liquor is acidic; thus, base or ethanol can be used to precipitate lignin from BL. To speed up the  
184 reaction, solvents such as acetic acid and formic acid are used in the formacell pulping process,  
185 along with HCl as a catalyst [31]. This process causes the pH of the formacell black liquor to  
186 become very acidic. Zhuang et al. [35] stated that formic acid and acetic acid could delignify  
187 lignin because of their acidic nature, so they can degrade lignin well. In another study, a  
188 combination of formic acid, acetic acid, and water achieved more than 50% lignin  
189 depolymerization in biomass [36]. The pH of the BL will be affected by the addition of KOH  
190 solution. According to the research, the pH value obtained from formacell pulping added with  
191 KOH solution ranged from  $2.43 \pm 0.07$  to  $4.27 \pm 0.35$  (Table 1), while the addition of ethanol  
192 concentrations can slightly increase the pH value from  $1.0 \pm 0.01$  to  $1.29 \pm 0.03$ . According to the  
193 findings, KOH has a greater effect on increasing pH than ethanol due to the strong base property  
194 of KOH.

195 The pH steadily increased as an upsurging concentration of KOH, where the lowest pH,  
196  $2.43 \pm 0.07$ , was obtained from 2.5% KOH, and the highest was a pH of  $4.27 \pm 0.35$  from KOH  
197 15%. Increasing the concentration of KOH solution causes more  $\text{OH}^-$  ions in the black liquor so  
198 that the pH of the solution becomes more alkaline. It can also be explained that KOH is a strong  
199 base. The stronger the base, the more  $\text{OH}^-$  ions are released, increasing the pH of the solution  
200 and making it more alkaline. Ethanol has a higher pKa than KOH, indicating a weaker acid.

201 Unlike KOH, increasing the ethanol concentration slightly increased the pH, with the lowest  
202 being 1 and the highest being 1.29 after adding 5% and 30%, as shown in Table 1.

203 **Table 1:** Effect of KOH and ethanol concentrations on pH, yield, methoxyl content, and an  
204 equivalent weight of isolated lignin.

Treatment	pH	Yield (%)	Lignin methoxyl (%)	Equivalent Weight
KOH concentration (%)				
2.5	2.43±0.07	3.57±0.38	13.06±0.9	1372.94±26.73
5.0	2.94±0.06	4.85±1.12	12.94±1.31	655.73±45.16
7.5	3.21±0.1	8.63±1.41	12.81±0.84	528.74±54.44
10	3.61±0.15	11.20±2.69	12.36±0.9	510.33±49.05
12.5	3.86±0.15	12.78±0.78	11.33±0.4	476.25±34.61
15	4.27±0.35	14.95±1.10	10.13±1.42	427.03±44.20
Ethanol concentration (%)				
5	1.00±0.01	1.95±0.18	17.03±0.42	449.88±48.47
10	1.08±0.06	2.27±0.317	16.45±1.44	624.67±59.2
15	1.15±0.07	1.69±0.091	15.05±1.03	767.97±56.6
20	1.20±0.047	1.77±0.207	14.47±1.17	896.95±64.15
25	1.22±0.056	1.44±0.174	13.14±1.78	1521.16±72.10
30	1.29±0.03	1.08±0.179	11.99±1.20	2123.02±70.72

205

206

### 207 **3.2 Lignin yield**

208 The lignin yield from adding KOH solution at various concentrations in isolation of BL  
209 ranged from  $3.57 \pm 0.38$  to  $14.95 \pm 1.10$  (Table 1). In comparison, ethanol isolation resulted in  
210 lower lignin yields of about  $0.51 \pm 0.00$  to  $1.06 \pm 0.00$ . The highest lignin yield was produced at a  
211 concentration of 15% KOH solution ( $14.95\% \pm 1.10$ ). Increasing the concentration of KOH  
212 solution caused the lignin yield to increase. It can be affected by the increasing concentration of  
213 an alkaline solution (KOH) that facilitates easier breaking of lignin bonds with other compounds,  
214 and a condensation reaction occurs in the lignin constituent units [37]. It is also supported by  
215 Sundin's [38] who stated that lignin deposition from BL due to the protonation of phenol groups  
216 on lignin molecules caused by the addition of  $\text{OH}^-$  ions from KOH. It reduces the electrostatic  
217 force between lignin molecules, resulting in the deposition of lignin (reduced solubility). The  
218 more  $\text{OH}^-$  ions, the more lignin deposits will form. The deposit lignin increase occurred because  
219 of an increase in ionic strength and protonation. The protonation of the phenolic group in lignin  
220 leads the lignin nucleus to form aggregates when the pKa value of lignin is reached [39].

221 The lignin yield with KOH liquor treatment is higher than that of NaOH, as reported by  
222 Hidayati et al. [20]. Lignin was isolated from formacell black liquor of OPEFB by using NaOH,  
223 producing lignin yields ranging from 1.48% to 5.67%. It might be caused by the stronger base of



224 KOH than NaOH. As seen in the periodic system, the metal  $\text{Na}^+$  and  $\text{K}^+$  are included in Group 1A.  
225 This is also related to the lower nature of alkali metal bases; the stronger, the lower the metal, the  
226 more easily reduced. Besides pH, temperature and ionic strength also affect lignin solubility. The  
227 molecular weight distribution in lignins is related to yield [40]. Both molecular weight and the  
228 ratio of phenols to aromatic units contribute to the solubility of lignin [40]. The changes in lignin  
229 yield in isolation by adding ethanol concentration are very low. The very low electronegativity of  
230 ethanol can suggest it is due to the presence of carbon compounds that cannot precipitate lignin  
231 properly. In the absence of sulfide, delignification was slower in the Alcell process.

232 As opposed to KOH precipitation, increasing ethanol concentrations leads to almost 0%  
233 lignin recovery. This result was in agreement with the precipitation of lignin from *Miscanthus x*  
234 *giganteus*, where after the addition of 75% of ethanol, there was no lignin precipitated [41]. In the  
235 low concentration of ethanol, lignin precipitation is carried out by diluting liquor with water, and  
236 the solubility of lignin decreases, resulting in more lignin being recovered. In other words, when  
237 the water content in the ethanol is limited, most of the lignin is soluble in the system, and hence  
238 the aggregate is not formed.

239

### 240 **3.3 Methoxyl content in lignin**

241 Methoxyl is one of the chemical groups in lignin for identifying one of the characteristics of  
242 lignin. The methoxyl group in each type of lignin has different content because of the different  
243 structures of lignin types. Determining methoxyl contents gives information about the average C9  
244 units in lignin, and eventually, the unsaturated side chain and average oxygen content can be  
245 calculated [42]. The methoxyl content in KOH lignin ranged from  $10.13\% \pm 1.92$  to  $12.94\% \pm$   
246  $0.90$ , whereas the use of ethanol concentrations results in methoxyl contents between  $11.99 \pm$   
247  $0.02$  to  $17.03 \pm 0.5$  (Table 1). The highest methoxyl content in lignin was acquired from isolated  
248 lignin by adding a 2.5% KOH solution. Increasing the concentration of KOH and ethanol solution  
249 leads to a decrease in the methoxyl content of isolated lignins. This may be due to the use of  
250 KOH as a strong base as a precipitating solution, which allows some methoxyl groups to degrade  
251 and transform into other compounds. This decrease in methoxyl content can be influenced by the  
252 disruption of structural stability in lignin caused by the addition of KOH. Furthermore, according  
253 to the pathway proposed by Yin et al., the removal of the methoxy group in lignin created a  
254 higher hydroxyl group of lignin by KOH solution. The presence of potassium in lignin isolation  
255 decreased the methoxyl content due to cleavage  $\text{C}\alpha\text{—C}\beta$  through  $\text{C}\beta\text{—O}$  bond. This cleavage  
256 leads to the removal of side chains such as methoxy. The mechanism of this reaction has been  
257 proved by Yin et al. [43].

258 The various methoxyl content in lignin depends on the source of lignin and the  
259 delignification process used. Generally, high methoxyl content will inhibit lignin reactivity during  
260 use in the resin field. Lignin has phenolic hydroxyl groups that are typically linked to nearby  
261 phenyl propane units, allowing lignin to connect with formaldehyde in a way analogous to phenol  
262 and formaldehyde [44]. Molecular weight and lignin purity are important factors during the  
263 production of biocarbon fibers [44, 45].

264 In the case of lignin application as an adhesive raw material, the low methoxyl content is  
265 more beneficial because it will increase the reactivity of aromatic nuclei in lignin [46]. It will  
266 facilitate the reaction of methylation or hydroxymethylation with adhesive-forming reactants such  
267 as NaOH and formaldehyde, hinting at the ease of gel formation. Recently, Gendron et al.  
268 compared four types of lignin for green adhesive, where the lowest methoxyl content of lignin  
269 had the highest water solubility and shear resistance as an adhesive [47].

270 The lignin standard of Indulin AT has a methoxyl content of around 13.5% - 14.5% [48], so  
271 the methoxyl contents in isolated lignin in this study are still lower. Meanwhile, compared to  
272 methoxyl content by Hidayati et al. [20] with a value of 14.61% - 20.77% by using NaOH as  
273 precipitating solution, the results of this study are also lower. These results are probably  
274 influenced by the use of KOH, which is classified as a strong base with a higher reactivity than  
275 NaOH, as seen from the periodic system. The influence of harsh chemicals and temperature  
276 during isolation causes the structure of lignin to undergo many changes, including the methoxyl  
277 group. The methoxyl group is degraded and transformed into other degradation compounds such  
278 as aromatic hydrocarbon and phenolic types, resulting in lower methoxyl content [49].

### 279 **3.4 The equivalent weight of lignin**

280 The determination of the equivalent weight of lignin is intended to determine the  
281 molecular weight of lignin to identify lignin degradation and condensation reactions. The  
282 molecular weight of lignin is an important property that influences biomass recalcitrance and  
283 lignin value. Determination of the molecular weight of lignin in the original biomass depends on  
284 the source of the raw material used, chemicals used for isolation, and purification methods [50,  
285 51]. Based on the results, the equivalent weight of lignin from the KOH solution ranged from  
286  $427.03 \pm 74.20$  to  $1372.94 \pm 269.73$ , whereas the addition of ethanol concentration resulted in  
287 molecular weights ranging from  $449.88 \pm 1.9$  to  $2123.03 \pm 27.5$  (Table 1).

288 Increasing the concentration of KOH solution resulted in a decrease in lignin equivalent  
289 weight so that the lowest value at 15% KOH solution concentration was  $427.03 \pm 74.20$ . This  
290 might be attributed to the increasing addition of a KOH solution as a strong base will degrade a  
291 portion of lignin into a derivative compound with shorter chains. It can degrade lignin resulting in  
292 a low equivalent weight. According to Patil et al., there are two routes for lignin depolymerization:  
293 harsh and moderate, resulting in different lignin structures [52]. The average molecular weight of  
294 lignin decreases with increasing precipitation of lignin yield by KOH. It was shown that  
295 increasing the amount of lignin with lower molecular weight deposited a high yield of lignin.  
296 Lignin is degraded into smaller fragments so that there are more phenolic groups with lower  
297 molecular weights [53]. The product's molecular weight can be lowered by increasing salt  
298 concentration [54, 55].

299 According to Gellerstedt [56], the termination of methyl aryl ether bonds from the aromatic  
300 ring of lignin resulted in decreased methoxyl content and low molecular weight of lignin due to  
301 the lignin degradation process. Based on several previous studies, lignin molecular weight values  
302 were obtained, namely 2500 - 14,000 [57], and 1327.64 - 1787.23 [20]. In contrast, the equivalent

303 weight of Indulin AT reached 3357 - 3366 [58]. This shows that the equivalent weight value of  
304 lignin varies greatly.

305 Lignin that has a high molecular weight can be used as a matrix in polyolefin composites,  
306 because a higher molecular mass of lignin has a better affinity with the matrix [59], while lignin  
307 with a lower molecular weight can be used for the development of phenol-formaldehyde resins,  
308 antioxidants, adhesives, and paints due to their higher reactivity than high molecular weight  
309 lignin [59].

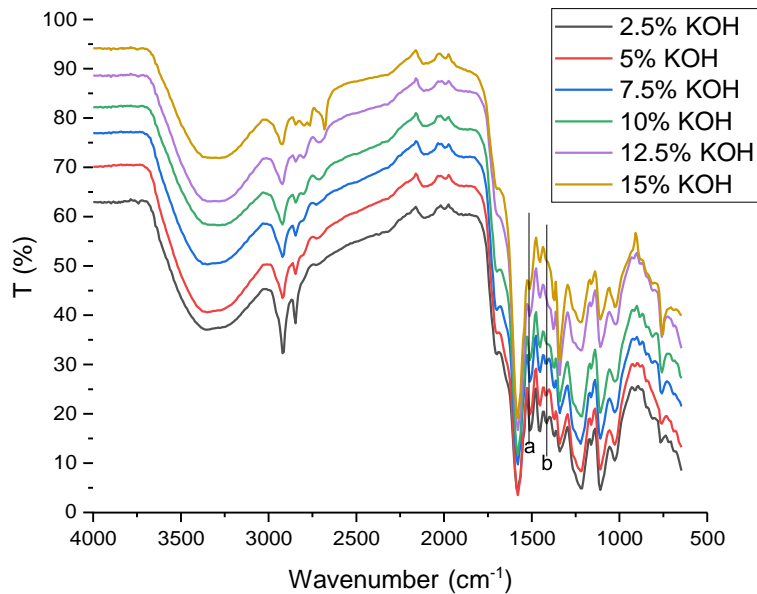
310 Differences in elemental composition, functional group types, proportions, and molecular  
311 weight in lignin molecules provide opportunities to use lignin in a variety of value-added  
312 applications. Some factors that influence the molecular weight of lignin are the diversity of lignin  
313 isolation procedures, macromolecular degradation during isolation, the effect of condensation  
314 mainly on acidic conditions, the apparent polydispersity of dissolved lignin, inadequate  
315 determination methods used to characterize the isolated lignin, and uncertainties in the properties  
316 of lignin. Because lignin is heterogeneous and inconstant, characterizing native lignin is also  
317 difficult [60].

318 The molecular weight of lignin is very important in the development of such polymeric  
319 products; similarly, low-molecular-weight lignin isolated from wheat straw by acetic acid pulping  
320 is an ideal feedstock for adhesive manufacturing [61]. Doherty et al. [62] stated that lignin from  
321 the soda process of wheat plants ranges from 1700 with a methoxyl content of 16. The organosolv  
322 pulping process at bagasse produces a molecular weight of around 2000 and a methoxyl content  
323 of 15.1. Lignin produced in the isolation process using alcohol or alcell process has a low  
324 molecular weight ( $M_w < 900$ ) with low polydispersity, no sulfur, and low ash content, although  
325 the value depends on the analytical method. There is also a molecular weight of  $2580 \text{ g mol}^{-1}$   
326 with a polydispersity of 4.3. Sameni et al. compared four types of lignin from different isolation  
327 methods, where the highest  $M_w$  (13488) was obtained from the steam explosion process with a  
328 methoxyl content of 0.69. Meanwhile, with the same methoxyl content, the lowest  $M_w$  (2565)  
329 was derived from the kraft process [57]. Yun et al. reported that organosolv fractionation from  
330 native lignin decreased its molecular weight from 5070 to 1810 [23].

### 331 **3.6 Lignin Analysis with FT-IR Spectrophotometer**

332 FTIR was performed to analyze differences in the functional groups of lignin in the sample  
333 (Fig. 2 and 3). FTIR spectra analysis showed that the peak in the aromatic ring vibrations  
334 decreased with the absorption band at  $1446 \text{ cm}^{-1}$  (a) and  $1408 \text{ cm}^{-1}$  (b), especially in the  
335 treatment using the highest concentration of KOH (Figure 2) and ethanol (Figure 3). There are  
336 similarities in the wavelength of  $3500 \text{ cm}^{-1}$  to  $31090 \text{ cm}^{-1}$  which refer to the presence of  
337 hydrogen bonds in the hydroxyl group (alcohol and phenolic). A wavelength absorption of  $1587$   
338  $\text{cm}^{-1}$  and  $1513 \text{ cm}^{-1}$  indicates the aromatic lignin skeletal vibration [60]. Wavenumbers at  $1460$   
339  $\text{cm}^{-1}$  to  $1420 \text{ cm}^{-1}$  are associated with stretching wavelengths of CH (methyl and methylene) and  
340 CH deformation with aromatic ring stretching fields [63]. The peaks observed in the range of  
341  $1220 \text{ cm}^{-1}$  to  $1270 \text{ cm}^{-1}$  in all spectra may refer to the C-H deformation vibrations of the guaiacyl  
342 [64]. The bands at  $1300 \text{ cm}^{-1}$  (syringyl) and  $1200 \text{ cm}^{-1}$  (guaiacyl) indicate the presence of both

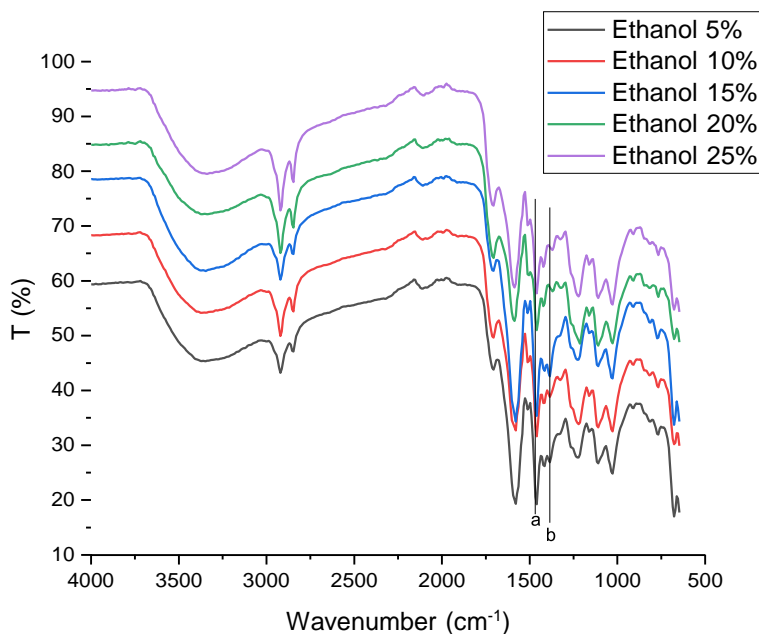
343 syringyl and guaiacyl in lignin's chemical structure as the unique peaks of lignin precursor [65].  
344 A similar peak was also found in kraft lignin isolated from *Acacia mangium* black liquor [27]. In  
345 general, peaks in Fig. 2 and 3 show that the treatment using KOH had a sharper peak than that of  
346 ethanol treatment. However, no difference in the peaks resulting from these two treatments was  
347 determined. Hidayati et al. [20] reported the experiment in isolated lignin from formacell black  
348 liquor of OPEFB using NaOH with the wave number of isolated lignin for guaiacyl lignin at  
349 around  $1273.02\text{ cm}^{-1}$ .



350

351

**Figure 2:** The FT-IR spectra of lignin using KOH isolation



**Figure 3:** The FT-IR spectra of lignin using ethanol isolation

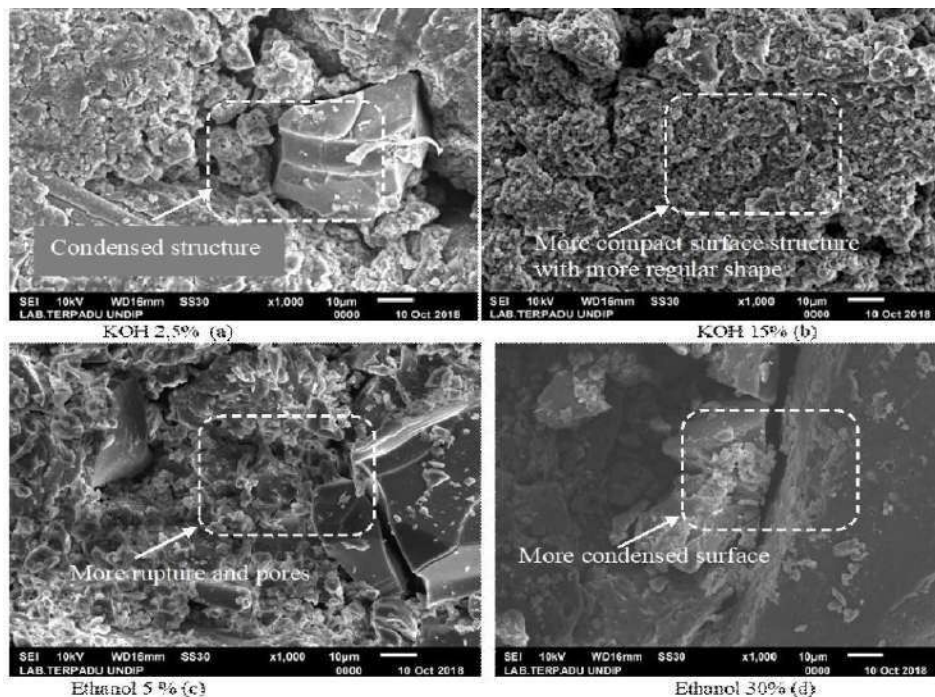
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### 355 **3.7 Morphological observation**

356 Scanning Electron Microscope (SEM) was used to observe the size and morphology of lignin.  
357 In this study, SEM images were taken from the lowest and the highest concentration of KOH and  
358 ethanol as representative lignin morphology. As seen in Fig. 4, increasing the concentration of  
359 KOH acid from 2.5% to 15% showed differences in lignin morphology. Lignin isolation using 15%  
360 KOH (Fig. 4b) produced a more compact formation and morphology compared to lignin  
361 produced by isolation using 2.5% KOH concentration (Fig. 4a). In stark contrast, in treatment  
362 using ethanol appears that treatment with a 5% ethanol concentration resulted in a more  
363 condensed form and morphology than those using a 30% concentration. This result was in  
364 accordance with the findings reported by Solihat et al. [27] and Hamzah et al., [41] where  
365 increasing ethanol concentration created more rupture and amorphous lignin surface.



366

367 **Figure 4:** Morphological images of isolated lignin (a) KOH 2.5%, (b) KOH 15%, (c) ethanol 5%,  
 368 (d) ethanol 30% with 1000 x magnification

369

### 370 *3.8 Prospective Application of Formacell Lignin as Advanced Biocomposite Products*

371 The lignin molecule contains a variety of active functional groups, including aliphatic  
 372 hydroxyl (Al-OH), phenolic hydroxyl (Ph-OH), carboxyl (-COOH), carbonyl (-C=O), and  
 373 methoxy groups (-OCH<sub>3</sub>), which determine its properties, chemistry, and reactivity of lignin.  
 374 Lignin's chemical properties enable it and its derivatives to be used as high-value materials. The  
 375 lignin molecule can be used in a variety of value-added applications due to differences in  
 376 molecular weight, elemental composition, and the types and proportions of functional groups.  
 377 Currently, Saražin et al. investigated the potency of organosolv lignin-based non-isocyanate  
 378 polyurethane for wood adhesive and the result demonstrated satisfactory mechanical properties  
 379 [66] and its curing kinetics for interior furniture showed that it was more suitable than urea-  
 380 formaldehyde (UF) adhesive [67]. Sulfur-free lignin is produced by isolating lignin from the  
 381 formacell process. Most value-added applications prefer lignin with a lower percentage of sulfur  
 382 and ash. For example, sulfur-free lignin is preferred for use in aerogel composites. Joul et al.  
 383 reacted lignin isolated by organic acid with 5-methylresorcinol-formaldehyde to create aerogel  
 384 and according to the data, formacell lignin had good reactivity to create a high surface area of  
 385 aerogel [68]. According to Talabi et al., lignin with rich hydroxyl carbon, low molecular weight,  
 386 and less in the methoxyl group was suitable for lignin-based-formaldehyde resin with a 73%  
 387 graphitization level [69], and hence formacell lignin with higher KOH and ethanol concentrations  
 388 are appropriate for this application. Meanwhile, the high molecular weight of lignin is preferred  
 389 as a matrix in carbon fiber composites because it improves the mechanical performance of the  
 390 fiber.

391

**392 4 Conclusions**

393 A strong base, such as KOH, was used to successfully isolate lignin from oil palm empty  
394 fruit bunch formacell BL (OPEFB). Some identified lignin peaks can be found in the FTIR  
395 spectra, with no significant difference between lignins isolated with KOH and ethanol. The  
396 addition of KOH solution at 12.5 and 15% concentrations is the more effective method for  
397 isolating lignin from formacell BL. At this condition, isolated lignins have pH values of 3.86 and  
398 4.27, lignin yield of 2.78 and 14.95%, methoxyl content of 11.33 and 10.13, and lignin equivalent  
399 weights of 476.25 and 427.03, respectively. **The lignin produced by the isolation process using  
400 KOH and ethanol was characterized by the low methoxy content and a low molecular weight that  
401 created its higher reactivity. According to these properties, lignin derived from formacell is  
402 suitable for developing green, bio-based additives in biocomposite applications such as wood  
403 adhesives from non-isocyanate polyurethane, coatings, lignin-based-formaldehyde resins,  
404 formaldehyde scavengers, composite fillers, and other value-added industrial applications.**

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2 messages

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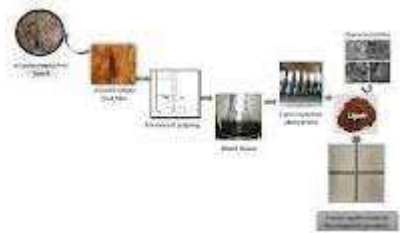
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31 **ARTICLE**

32 **Characterization of Formacell Lignin Derived from Black Liquor as a**  
33 **Potential Green Additive for Advanced Biocomposites**

34 **Sri Hidayati<sup>1\*</sup>, Eugenia Fonny Budiyo<sup>1</sup>, Hadi Saputra<sup>1</sup>, Sutopo Hadi<sup>1</sup>, Apri Heri**  
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**ABSTRACT**

Black liquor is obtained as a by-product of the pulping process, used to convert biomass into pulp by removing lignin, hemicelluloses and other extractives from wood to free cellulose fibers. Lignin represents a major constituent in black liquor with quantities varying from 20% to 30%, of which a very low share is used for manufacturing value-added products, while the rest is mainly burned for energy purposes, thus underestimating its great potential as a raw material. Therefore, it is essential to establish new isolation and extraction methods to increase lignin valorization in the development of bio-based chemicals. The aim of this research work was to determine the effect of KOH or ethanol concentration as an isolation agent on lignin yields and the chemical characteristics of lignin isolated from formacell black liquor of oil palm empty fruit bunch (OPEFB). Isolation of lignin was carried out using KOH with various concentrations ranging from 5% to 15% (w/v). Ethanol was also used to precipitate lignin from black liquor at concentrations varying from 5% to 30% (v/v). The results obtained showed that the addition of KOH solution at 12.5% and 15% concentrations resulted in better lignin yield and chemical properties of lignin, i.e., pH values of 3.86 and 4.27, lignin yield of 12.78 and 14.95%, methoxyl content of 11.33 and 10.13%, and lignin equivalent weights of 476.25 and 427.03, respectively. Due to its phenolic structure and rich functional groups that are favorable for modifications, lignin has the potential to be used as green additive in the development of advanced biocomposite products in various applications to replace current fossil fuel-based material, ranging from fillers, fire retardants, formaldehyde scavengers, carbon fibers, aerogels, and wood adhesives.

**KEYWORDS**

formacell black liquor; lignin properties; KOH; ethanol; oil palm empty fruit bunch; advanced biocomposite

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**58 1 Introduction**

59 Global challenges such as food security and environmental threats can be treated by applying the  
60 circular bioeconomy principles, including sustainable conversion of biomass components into  
61 bio-based products as green alternatives to their petroleum-based counterparts, thus closing the  
62 material resource loops [1]. Black liquor (BL) is liquid waste left over from cooking pulp, aimed  
63 at removing lignin, hemicelluloses, and other extractable constituents from wood in order to free  
64 the cellulose fibers. Lignin is the main organic substance in BL, reaching 45% dry weight [2].  
65 About 150 billion tons of BL are released from the pulp and paper industry, where every 1 ton of  
66 pulp production will produce 7 tons of BL [3]. Taking into account the increased production of  
67 bioethanol, this availability is projected to reach 225 million tons annually in 2030 [4-6].  
68 However, only 2-5% of BL has been valorized into biomaterial [7] and the rest for energy  
69 purposes [8-10]. Hence, it is important to develop new techniques aimed at increasing the  
70 valorization of lignin as a renewable feedstock in various value-added industrial applications.  
71 Lignin is a complex polyphenol compound with a complex three-dimensional chemical structure  
72 that is difficult to decompose naturally, so it has the potential to cause water pollution if  
73 discharged into the environment [11]. Lignin has a highly aromatic structure that is stable to heat  
74 and has high carbon content. In addition, lignin contains various functional groups, e.g., aliphatic,  
75 phenolic, methoxyl, and carbonyl hydroxyl groups, allowing its modification. Thus, it can be used  
76 in many functional applications such as biomass-based fuels, adhesives, flame retardants,

77 dispersants, and surfactant formulations, as antioxidants in plastics and rubbers, dyes, synthetic  
78 floors, thermosets, paints, food packaging, filler in adhesives, seed coatings, automotive devices,  
79 3D printing, and fuels for highway maintenance [12-17]. However, the utilization of lignin is still  
80 limited on an industrial scale due to the inhomogeneity of structure.

81 A lignin component is a phenylpropane unit with several different methoxy groups [18].  
82 Chemical structures of lignin are identified by the presence of polypropene units such as p-  
83 hydroxyphenyl (or p-coumaryl alcohol), guaiacyl (or coniferyl alcohol), and syringyl (or sinapyl  
84 alcohol), and their percentage vary depending on the botanical origin. Polypropene units can be  
85 chemically bonded in different bonding patterns where the  $\beta$ -O-4 aryl glycerol ether bond is the  
86 primary linkage [19]. However, the technical lignin's structure differs from the native lignin and  
87 depends on the pulping method used. Besides, the source of raw materials and isolation method,  
88 including the type of chemical used and temperature, play critical roles in the physicochemical  
89 properties of lignin [20].

90 Lignin can be extracted in powder form from BL with proper chemical treatment and  
91 screening process [21]. Precipitation of lignin in the BL occurs due to the condensation reaction  
92 on the lignin constituent units, which were initially soluble and will be polymerized and form  
93 large molecules [22]. Base, acid, and organic solvents are common solutions to isolate lignin  
94 from BL. The process of lignin separation using organic solvents is known as the alcell or  
95 organosolv process [23]. This method is popular for breaking down lignin fractions [24]. The  
96 benefits of this method include obtaining lignin with a low molecular weight that is free of sulfur,  
97 and its application can be improved through fractionation or chemical modification [25] but  
98 organosolv fractionation is laborious work [26]; hence, acid and base deposition methods are  
99 more feasible. However, this method depends on the pH of the liquor, residence time, and  
100 temperature [22]. Some acids such as  $H_2SO_4$ , phosphoric acid ( $H_3PO_4$ ), or HCl have been  
101 reported in isolating lignin from base BL, such as from the kraft process [27]. Meanwhile, lignin  
102 from formacell BL, BL derived from acetic acid, or formic acid as cooking liquid can be released  
103 by different alkalis, especially KOH,  $Ca(OH)_2$ , and NaOH [20]. KOH, a strong base, is stronger  
104 than NaOH and its use is expected to result in higher lignin yield.

105 Based on Miller et al. [28], a strong base (e.g., NaOH and KOH) provides a higher result in  
106 lignin yield than a weak base, and it would be a promising technique for depolymerizing lignin.  
107 The concentration of base is important to measure because it will influence selectivity, chemical-  
108 physical properties, and lignin yield [20, 29]. Recently, Hidayati et al. evaluated the effect of  
109 NaOH concentration on lignin properties [20] while the disadvantage of NaOH was  
110 monoaromatic re-condensation led to the higher molecular weight of lignin [30]. Consequently,  
111 an alternative base such as KOH and ethanol is needed to overcome this problem. To date, no one  
112 reported lignin isolation from formacell BL using different concentrations of KOH and ethanol.  
113 Therefore, this study aimed to determine the effect of KOH and ethanol concentrations on the  
114 yield and chemical characteristics of lignin isolated from formacell BL of oil palm empty fruit  
115 bunch (OPEFB).

## 116 2 Material and Methods

**117 2.1 Materials**

118 Black liquor used in this research is a by-product of the formacell pulping of OPEFB, as  
119 reported by Hidayati et al. [31]. The pulping conditions are presented in detail in the next section.  
120 OPEFB was obtained from PTPN Business Unit VII Central Lampung Bekri, Indonesia.  
121 Meanwhile, KOH, NaCl, NaOH, HCl, and ethanol were supplied by Merck (Darmstadt,  
122 Germany).

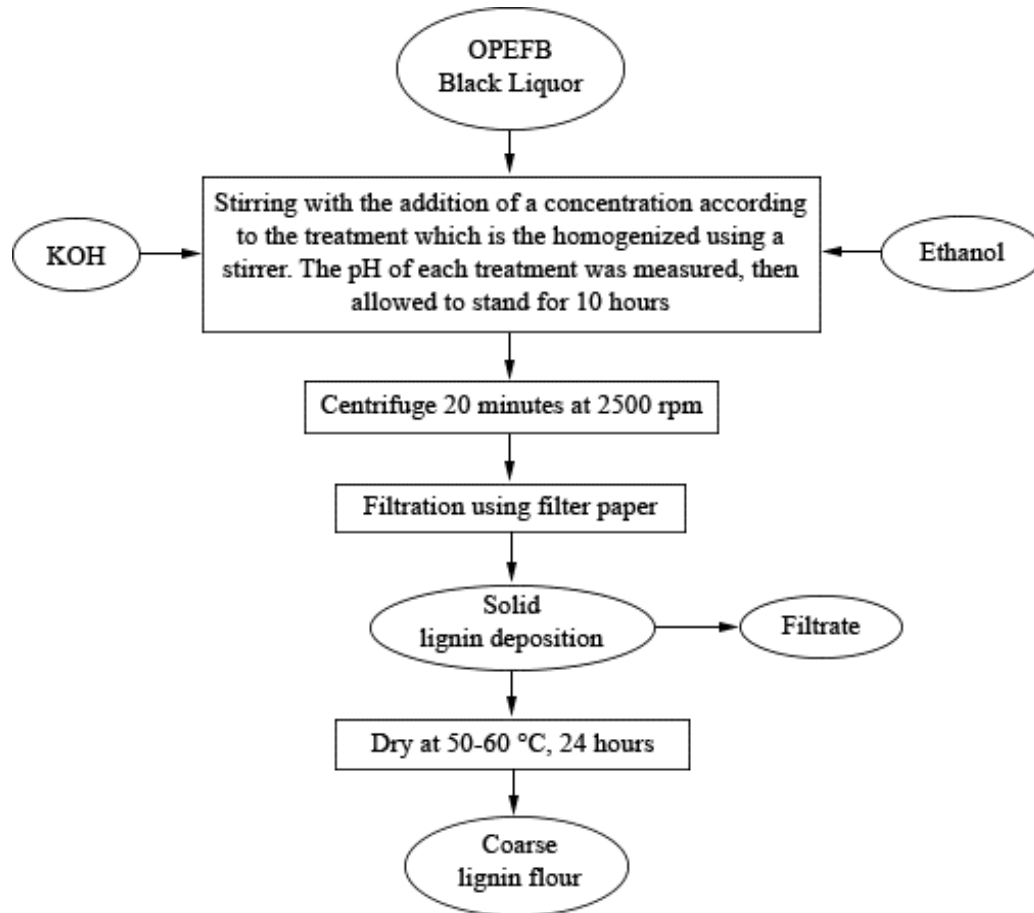
**123 2.2 Pulping process**

124 The formacell pulping was conducted in the autoclave at a liquor-to-particle ratio of 15:1  
125 for 1 h at 130 °C. This ratio of liquor to OPEFB particle ratio was used based on our initial  
126 experimental trials in the laboratory considering the volumetric of OPEFB as a typical example of  
127 non-woody biomass. In this ratio, the OPEFB particles can be immersed completely in the  
128 chemical liquor. The ratio solvent of acetic acid and formic acid was 85:15 with the addition of  
129 HCl of 0.5% as the catalyst. The cooking liquor was collected after filtration and washing the  
130 completed softened OPEFB with fresh water at room temperature. This formacell BL was used  
131 for the next step.

**132 2.3 Lignin isolation**

133 The formacell BL obtained from the pulping process of 100 mL contained a total solid  
134 content of around 25.10%. There are two methods for lignin isolation from formacell BL of  
135 OPEFB. The first one, i.e. the isolation of lignin from BL was conducted using KOH with a  
136 concentration of 2.5%; 5%; 7.5%; 10%; 12.5%; and 15% (w/v). The second isolation technique  
137 used ethanol at concentrations of 5%, 10%, 15%, 20%, 25 and 30% (v/v). As much as 100 mL of  
138 the KOH or ethanol solution was added into 100 mL BL, then stirred and measured the pH of the  
139 liquor was. The solution was allowed to stand for 10 hours, then centrifugated for 20 minutes at  
140 2500 rpm, and then separated using filter paper. The precipitated lignin was then oven-dried at  
141 50-60 °C for 24 h. Dried lignin was crushed manually to produce fine lignin powder (Fig. 1). The  
142 experiment was conducted in triplicate.

143 The data were calculated and presented in average and standard deviation tables and  
144 graphs. Observations made were pH value, the yield of lignin, lignin methoxyl content, the  
145 equivalent weight of lignin, analysis of lignin with Fourier Transform Infra-Red spectroscopy  
146 (FTIR) spectrophotometer (Cary 630 FTIR, Agilent, Australia), and lignin morphology using a  
147 scanning electron microscope (SEM) (JEOL JSM 6510 LA, Japan).



148

149

**Figure 1:** Flowchart of lignin isolation process using KOH/Ethanol.

#### 150 **2.4 Lignin Yield**

151 Lignin yield was calculated based on the method according to Kim [32], as presented in  
 152 Equation 1.

$$153 \quad \text{Lignin Yield (\%)} = \frac{a}{b} \times 100\% \quad (1)$$

154 **Notation :** a = weight of isolated lignin;

155 b = weight of lignin in black liquor

#### 156 **2.5 Methoxyl content of lignin**

157 The methoxyl content of lignin was determined by using the ASTM 15120-81 method  
 158 [33]. As much as 0.5 g of lignin was added to 5 mL of ethanol, following addition to 100 mL of  
 159 distilled water containing 1 g of NaCl, and made in the form of suspension. Neutralization was  
 160 performed using 0.1 N NaOH, given 6 drops of phenolphthalein (pp) indicator, and then 25 mL of  
 161 0.25 N NaOH was added and homogenized in a closed state for 30 minutes at room temperature.  
 162 After that, 25 mL of 0.25 N HCl was added and titrated with 0.1 N NaOH until the end of the  
 163 lasting color change (at least 30 seconds). The methoxyl content of lignin was calculated according  
 164 to Equation 2 as follows.

$$165 \quad \text{Methoxyl (\%)} = \frac{\text{ml NaOH} \times N \text{ NaOH} \times 3.1}{\text{Berat sampel (gram)}} \times 100\% \quad (2)$$

## 166 **2.6 Lignin Equivalent Weight**

167 Isolated lignin equivalent weight was calculated using the method of Santoso [34]. 0.5 g  
 168 lignin was put into 250 mL Erlenmeyer and moistened with 5 mL ethanol. The mixture is spiked  
 169 with 1 g of NaCl which is then added with 100 mL of distilled water and 6 drops of phenolphthalein  
 170 indicator. The solution was then titrated with 0.1 N NaOH until pH 7.5. The equivalent weight of  
 171 isolated lignin was calculated by using Equation 3.

$$172 \quad \text{Equivalent Weight} = \frac{1000 \times \text{gram sample}}{(\text{mLN}) \text{NaOH}} \quad (3)$$

## 173 **2.7 FT-IR analysis of isolated lignin**

174 As much as 1 mg isolated lignin was added with 150 mg KBr, pelletized, and then the  
 175 samples were analyzed by FT-IR spectrophotometer (Cary 630 FTIR Agilent). The analysis was  
 176 set at a wavenumber of 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup> (wavelength of 2.5–25 μm).

## 177 **2.7 SEM analysis**

178 Morphology of isolated lignin was carried out using Scanning Electron Microscope (SEM)  
 179 (JEOL JSM 6510 LA) with 1000 x magnification.

# 180 **3 Results and Discussion**

## 181 **3.1 pH of the black liquor**

182 The pH of BL from formacell pulping OPEFB is 0.59 ± 0.01, indicating that the liquor is  
 183 acidic; thus, base or ethanol can be used to precipitate lignin from BL. To speed up the reaction,  
 184 solvents such as acetic acid and formic acid are used in the formacell pulping process, along with  
 185 HCl as a catalyst [31]. This process causes the pH of the formacell BL to become very acidic.  
 186 Zhuang et al. [35] stated that formic acid and acetic acid could delignify lignin because of their  
 187 acidic nature, so they can degrade lignin well. In another study, a combination of formic acid,  
 188 acetic acid, and water achieved more than 50% lignin depolymerization in biomass [36]. The pH  
 189 of the BL will be affected by the addition of KOH solution. According to the research, the pH  
 190 value obtained from formacell pulping added with KOH solution ranged from 2.43 ± 0.07 to 4.27  
 191 ± 0.35 (Table 1), while the addition of ethanol concentrations can slightly increase the pH value  
 192 from 1.0 ± 0.01 to 1.29 ± 0.03. According to the findings, KOH has a greater effect on increasing  
 193 pH than ethanol due to the strong base property of KOH.

194 The pH steadily increased as an up-surgin concentration of KOH, where the lowest pH,  
 195 2.43 ± 0.07, was obtained from 2.5% KOH, and the highest was a pH of 4.27 ± 0.35 from KOH  
 196 15%. Increasing the concentration of KOH solution causes more OH<sup>-</sup> ions in the BL so that the  
 197 pH of the solution becomes more alkaline. It can also be explained that KOH is a strong base. The  
 198 stronger the base, the more OH ions are released, increasing the pH of the solution and making it  
 199 more alkaline. Ethanol has a higher pKa than KOH, indicating a weaker acid. Unlike KOH,

200 increasing the ethanol concentration slightly increased the pH, with the lowest being 1 and the  
201 highest being 1.29 after adding 5% and 30%, as shown in Table 1.

202 **Table 1:** Effect of KOH and ethanol concentrations on pH, yield, methoxyl content, and an  
203 equivalent weight of isolated lignin.

Treatment	pH	Yield (%)	Lignin methoxyl (%)	Equivalent Weight
KOH concentration (%)				
2.5	2.43±0.07	3.57±0.38	13.06±0.9	1372.94±26.73
5.0	2.94±0.06	4.85±1.12	12.94±1.31	655.73±45.16
7.5	3.21±0.1	8.63±1.41	12.81±0.84	528.74±54.44
10	3.61±0.15	11.20±2.69	12.36±0.9	510.33±49.05
12.5	3.86±0.15	12.78±0.78	11.33±0.4	476.25±34.61
15	4.27±0.35	14.95±1.10	10.13±1.42	427.03±44.20
Ethanol concentration (%)				
5	1.00±0.01	1.95±0.18	17.03±0.42	449.88±48.47
10	1.08±0.06	2.27±0.317	16.45±1.44	624.67±59.2
15	1.15±0.07	1.69±0.091	15.05±1.03	767.97±56.6
20	1.20±0.047	1.77±0.207	14.47±1.17	896.95±64.15
25	1.22±0.056	1.44±0.174	13.14±1.78	1521.16±72.10
30	1.29±0.03	1.08±0.179	11.99±1.20	2123.02±70.72

204

205

### 206 **3.2 Lignin yield**

207 The lignin yield from adding KOH solution at various concentrations in isolation of BL  
208 ranged from  $3.57 \pm 0.38$  to  $14.95 \pm 1.10$  (Table 1). In comparison, ethanol isolation resulted in  
209 lower lignin yields of about  $0.51 \pm 0.00$  to  $1.06 \pm 0.00$ . The highest lignin yield was produced at a  
210 concentration of 15% KOH solution ( $14.95\% \pm 1.10$ ). Increasing the concentration of KOH  
211 solution caused the lignin yield to increase. It can be affected by the increasing concentration of  
212 an alkaline solution (KOH) that facilitates easier breaking of lignin bonds with other compounds,  
213 and a condensation reaction occurs in the lignin constituent units [37]. It is also supported by  
214 Sundin [38] who stated that lignin deposition from BL due to the protonation of phenol groups on  
215 lignin molecules caused by the addition of  $\text{OH}^-$  ions from KOH. It reduces the electrostatic force  
216 between lignin molecules, resulting in the deposition of lignin and reduced solubility. The more  
217  $\text{OH}^-$  ions, the more lignin deposits will form. The deposit lignin increase occurred because of an  
218 increase in ionic strength and protonation. The protonation of the phenolic group in lignin leads  
219 the lignin nucleus to form aggregates when the pKa value of lignin is reached [39].

220 The lignin yield with KOH liquor treatment is higher than that of NaOH, as reported by  
221 Hidayati et al. [20]. Lignin was isolated from formacell BL of OPEFB by using NaOH, producing  
222 lignin yields ranging from 1.48% to 5.67%. It might be caused by the stronger base of KOH than

223 NaOH. As seen in the periodic system, the metal Na<sup>+</sup> and K<sup>+</sup> are included in Group 1A. This is  
224 also related to the lower nature of alkali metal bases; the stronger, the lower the metal, the more  
225 easily reduced. Besides pH, temperature and ionic strength also affect lignin solubility. The  
226 molecular weight distribution in lignins is related to yield [40]. Both molecular weight and the  
227 ratio of phenols to aromatic units contribute to the solubility of lignin [40]. The changes in lignin  
228 yield in isolation by adding ethanol concentration are very low. The very low electronegativity of  
229 ethanol can suggest **the presence of carbon compounds that cannot precipitate lignin properly**. In  
230 the absence of sulfide, delignification was slower in the Alcell process.

231 As opposed to KOH precipitation, increasing ethanol concentrations leads to almost 0%  
232 lignin recovery. This result was in agreement with the precipitation of lignin from *Miscanthus x*  
233 *giganteus*, where after the addition of 75% of ethanol, there was no lignin precipitated [41]. In the  
234 low concentration of ethanol, lignin precipitation is carried out by diluting liquor with water, and  
235 the solubility of lignin decreases, resulting in more lignin being recovered. In other words, when  
236 the water content in the ethanol is limited, most of the lignin is soluble in the system, and hence  
237 the aggregate is not formed.

238

### 239 **3.3 Methoxyl content in lignin**

240 Methoxyl is one of the chemical groups in lignin for identifying one of the characteristics of  
241 lignin. The methoxyl group in each type of lignin has different content because of the different  
242 structures of lignin types. Determining methoxyl contents gives information about the average C9  
243 units in lignin, and eventually, the unsaturated side chain and average oxygen content can be  
244 calculated [42]. The methoxyl content in KOH lignin ranged from 10.13% ± 1.92 to 12.94% ±  
245 0.90, whereas the use of ethanol concentrations results in methoxyl contents between 11.99 ±  
246 0.02 to 17.03 ± 0.5 (Table 1). The highest methoxyl content in lignin was acquired from isolated  
247 lignin by adding a 2.5% KOH solution. Increasing the concentration of KOH and ethanol solution  
248 leads to a decrease in the methoxyl content of isolated lignins. This may be due to the use of  
249 KOH as a strong base as a precipitating solution, which allows some methoxyl groups to degrade  
250 and transform into other compounds. This decrease in methoxyl content can be influenced by the  
251 disruption of structural stability in lignin caused by the addition of KOH. Furthermore, according  
252 to the pathway proposed by Yin et al., the removal of the methoxy group in lignin created a  
253 higher hydroxyl group of lignin by KOH solution. The presence of potassium in lignin isolation  
254 decreased the methoxyl content due to cleavage C $\alpha$ —C $\beta$  through C $\beta$ —O bond. This cleavage  
255 leads to the removal of side chains such as methoxy<sup>1</sup>. The mechanism of this reaction has been  
256 proved by Yin et al. [43].

257 The various methoxyl content in lignin depends on the source of lignin and the  
258 delignification process used. Generally, high methoxyl content will inhibit lignin reactivity during  
259 use in the resin field. Lignin has phenolic hydroxyl groups that are typically linked to nearby  
260 phenyl propane units, allowing lignin to connect with formaldehyde in a way analogous to phenol  
261 and formaldehyde [44]. Molecular weight and lignin purity are important factors during the  
262 production of biocarbon fibers [44, 45].



263 In the case of lignin application as an adhesive raw material, the low methoxyl content is  
264 more beneficial because it will increase the reactivity of aromatic nuclei in lignin [46]. It will  
265 facilitate the reaction of methylation or hydroxymethylation with adhesive-forming reactants such  
266 as NaOH and formaldehyde, hinting at the ease of gel formation. Recently, Gendron et al.  
267 compared four types of lignin for green adhesive, where the lowest methoxyl content of lignin  
268 had the highest water solubility and shear resistance as an adhesive [47].

269 The lignin standard of Indulin AT has a methoxyl content of around 13.5% - 14.5% [48], so  
270 the methoxyl contents in isolated lignin in this study are still lower. Meanwhile, compared to  
271 methoxyl content by Hidayati et al. [20] with a value of 14.61% - 20.77% by using NaOH as  
272 precipitating solution, the results of this study are also lower. These results are probably  
273 influenced by the use of KOH, which is classified as a strong base with a higher reactivity than  
274 NaOH, as seen from the periodic system. The influence of harsh chemicals and temperature  
275 during isolation causes the structure of lignin to undergo many changes, including the methoxyl  
276 group. The methoxyl group is degraded and transformed into other degradation compounds such  
277 as aromatic hydrocarbon and phenolic types, resulting in lower methoxyl content [49].

### 278 **3.4 The equivalent weight of lignin**

279 The determination of the equivalent weight of lignin is intended to determine the  
280 molecular weight of lignin to identify lignin degradation and condensation reactions. The  
281 molecular weight of lignin is an important property that influences biomass recalcitrance and  
282 lignin value. Determination of the molecular weight of lignin in the original biomass depends on  
283 the source of the raw material used, chemicals used for isolation, and purification methods [50,  
284 51]. Based on the results, the equivalent weight of lignin from the KOH solution ranged from  
285  $427.03 \pm 74.20$  to  $1372.94 \pm 269.73$ , whereas the addition of ethanol concentration resulted in  
286 molecular weights ranging from  $449.88 \pm 1.9$  to  $2123.03 \pm 27.5$  (Table 1).

287 Increasing the concentration of KOH solution resulted in a decrease in lignin equivalent  
288 weight so that the lowest value at 15% KOH solution concentration was  $427.03 \pm 74.20$ . This  
289 might be attributed to the increasing addition of a KOH solution as a strong base will degrade a  
290 portion of lignin into a derivative compound with shorter chains. It can degrade lignin resulting in  
291 a low equivalent weight. According to Patil et al., there are two routes for lignin depolymerization:  
292 harsh and moderate, resulting in different lignin structures [52]. The average molecular weight of  
293 lignin decreases with increasing precipitation of lignin yield by KOH. It was shown that  
294 increasing the amount of lignin with lower molecular weight deposited a high yield of lignin.  
295 Lignin is degraded into smaller fragments so that there are more phenolic groups with lower  
296 molecular weights [53]. The product's molecular weight can be lowered by increasing salt  
297 concentration [54, 55].

298 According to Gellerstedt [56], the termination of methyl aryl ether bonds from the aromatic  
299 ring of lignin resulted in decreased methoxyl content and low molecular weight of lignin due to  
300 the lignin degradation process. Based on several previous studies, lignin molecular weight values  
301 were obtained, namely 2500 - 14,000 [57], and 1327.64 - 1787.23 [20]. In contrast, the equivalent

302 weight of Indulin AT reached 3357 - 3366 [58]. This shows that the equivalent weight value of  
303 lignin varies greatly.

304 Lignin that has a high molecular weight can be used as a matrix in polyolefin composites,  
305 because a higher molecular mass of lignin has a better affinity with the matrix [59], while lignin  
306 with a lower molecular weight can be used for the development of phenol-formaldehyde resins,  
307 antioxidants, adhesives, and paints due to their higher reactivity than high molecular weight  
308 lignin [59].

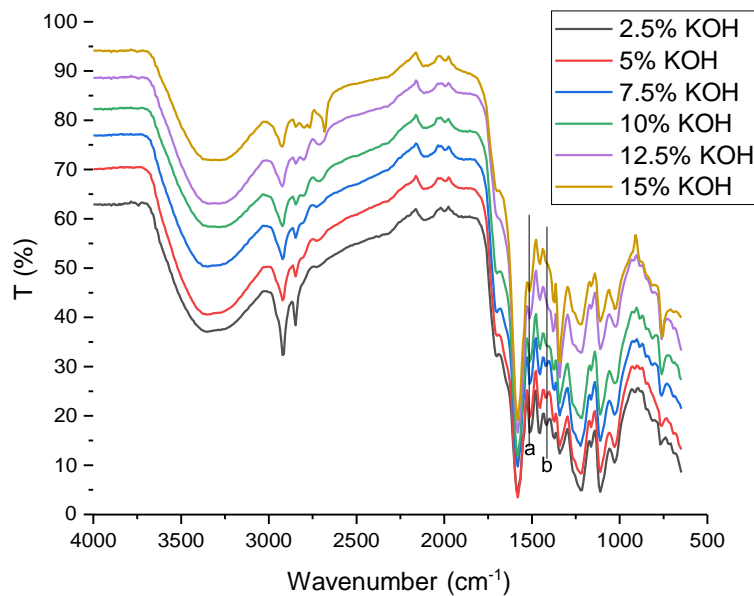
309 Differences in elemental composition, functional group types, proportions, and molecular  
310 weight in lignin molecules provide opportunities to use lignin in a variety of value-added  
311 applications. Some factors that influence the molecular weight of lignin are the diversity of lignin  
312 isolation procedures, macromolecular degradation during isolation, the effect of condensation  
313 mainly on acidic conditions, the apparent polydispersity of dissolved lignin, inadequate  
314 determination methods used to characterize the isolated lignin, and uncertainties in the properties  
315 of lignin. Because lignin is heterogeneous and inconstant, characterizing native lignin is also  
316 difficult [60].

317 The molecular weight of lignin is very important in the development of such polymeric  
318 products; similarly, low-molecular-weight lignin isolated from wheat straw by acetic acid pulping  
319 is an ideal feedstock for adhesive manufacturing [61]. Doherty et al. [62] stated that lignin from  
320 the soda process of wheat plants ranges from 1700 with a methoxyl content of 16. The organosolv  
321 pulping process at bagasse produces a molecular weight of around 2000 and a methoxyl content  
322 of 15.1. Lignin produced in the isolation process using alcohol or alcell process has a low  
323 molecular weight ( $M_w < 900$ ) with low polydispersity, no sulfur, and low ash content, although  
324 the value depends on the analytical method. There is also a molecular weight of  $2580 \text{ g mol}^{-1}$   
325 with a polydispersity of 4.3. Sameni et al. compared four types of lignin from different isolation  
326 methods, where the highest  $M_w$  (13488) was obtained from the steam explosion process with a  
327 methoxyl content of 0.69. Meanwhile, with the same methoxyl content, the lowest  $M_w$  (2565)  
328 was derived from the kraft process [57]. Yun et al. reported that organosolv fractionation from  
329 native lignin decreased its molecular weight from 5070 to 1810 [23].

### 330 **3.6 Lignin Analysis with FT-IR Spectrophotometer**

331 FTIR was performed to analyze differences in the functional groups of lignin in the sample  
332 (Fig. 2 and 3). FTIR spectra analysis showed that the peak in the aromatic ring vibrations  
333 decreased with the absorption band at  $1446 \text{ cm}^{-1}$  (a) and  $1408 \text{ cm}^{-1}$  (b), especially in the  
334 treatment using the highest concentration of KOH (Fig. 2) and ethanol (Fig. 3). There are  
335 similarities in the wavelength of  $3500 \text{ cm}^{-1}$  to  $31090 \text{ cm}^{-1}$  which refer to the presence of  
336 hydrogen bonds in the hydroxyl group (alcohol and phenolic). A wavelength absorption of  $1587$   
337  $\text{cm}^{-1}$  and  $1513 \text{ cm}^{-1}$  indicates the aromatic lignin skeletal vibration [60]. Wavenumbers at  $1460$   
338  $\text{cm}^{-1}$  to  $1420 \text{ cm}^{-1}$  are associated with stretching wavelengths of CH (methyl and methylene) and  
339 CH deformation with aromatic ring stretching fields [63]. The peaks observed in the range of  
340  $1220 \text{ cm}^{-1}$  to  $1270 \text{ cm}^{-1}$  in all spectra may refer to the C-H deformation vibrations of the guaiacyl  
341 [64]. The bands at  $1300 \text{ cm}^{-1}$  (syringyl) and  $1200 \text{ cm}^{-1}$  (guaiacyl) indicate the presence of both

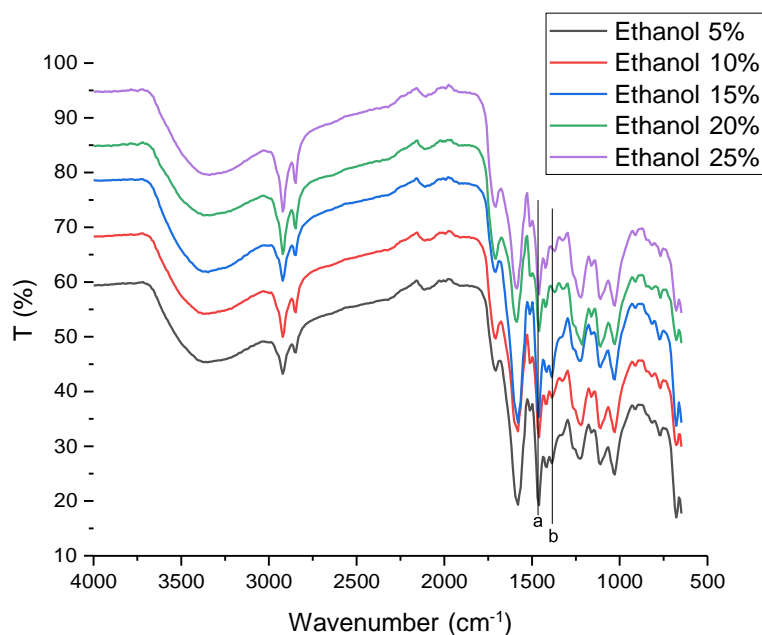
342 syringyl and guaiacyl in lignin's chemical structure as the unique peaks of lignin precursor [65].  
343 A similar peak was also found in kraft lignin isolated from *Acacia mangium* black liquor [27]. In  
344 general, peaks in Fig. 2 and 3 show that the treatment using KOH had a sharper peak than that of  
345 ethanol treatment. However, no difference in the peaks resulting from these two treatments was  
346 determined. Hidayati et al. [20] reported the experiment in isolated lignin from formacell BL of  
347 OPEFB using NaOH with the wave number of isolated lignin for guaiacyl lignin at around  
348  $1273.02\text{ cm}^{-1}$ .



349

350

**Figure 2:** The FT-IR spectra of lignin using KOH isolation



351

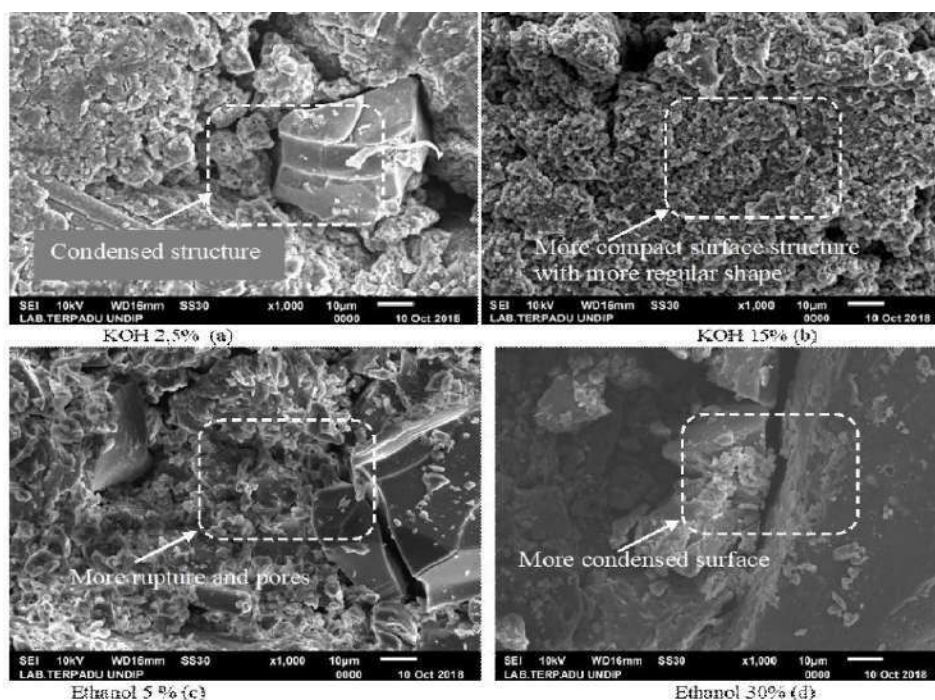
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**Figure 3:** The FT-IR spectra of lignin using ethanol isolation

353

354 **3.7 Morphological observation**

355 Scanning Electron Microscope (SEM) was used to observe the size and morphology of lignin.  
 356 In this study, SEM images were taken from the lowest and the highest concentration of KOH and  
 357 ethanol as representative lignin morphology. As seen in Fig. 4, increasing the concentration of  
 358 KOH acid from 2.5% to 15% showed differences in lignin morphology. Lignin isolation using 15%  
 359 KOH (Fig. 4b) produced a more compact formation and morphology compared to lignin  
 360 produced by isolation using 2.5% KOH concentration (Fig. 4a). In stark contrast, in treatment  
 361 using ethanol appears that treatment with a 5% ethanol concentration resulted in a more  
 362 condensed form and morphology than those using a 30% concentration. This result was in  
 363 accordance with the findings reported by Solihat et al. [27] and Hamzah et al. [41] where  
 364 increasing ethanol concentration created more rupture and amorphous lignin surface.



365

366 **Figure 4:** Morphological images of isolated lignin (a) KOH 2.5%, (b) KOH 15%, (c) ethanol 5%,  
 367 (d) ethanol 30% with 1000 x magnification

368

369 **3.8 Prospective Application of Formacell Lignin as Advanced Biocomposite Products**

370 The lignin molecule contains a variety of active functional groups, including aliphatic  
 371 hydroxyl (Al-OH), phenolic hydroxyl (Ph-OH), carboxyl (-COOH), carbonyl (-C=O), and  
 372 methoxy groups (-OCH<sub>3</sub>), which determine its properties, chemistry, and reactivity of lignin.  
 373 Lignin's chemical properties enable it and its derivatives to be used as high-value materials. The  
 374 lignin molecule can be used in a variety of value-added applications due to differences in  
 375 molecular weight, elemental composition, and the types and proportions of functional groups.  
 376 Currently, Saražin et al. investigated the potency of organosolv lignin-based non-isocyanate  
 377 polyurethane for wood adhesive and the result demonstrated satisfactory mechanical properties

378 [66] and its curing kinetics for interior furniture showed that it was more suitable than urea-  
379 formaldehyde (UF) adhesive [67]. Sulfur-free lignin is produced by isolating lignin from the  
380 formacell process. Most value-added applications prefer lignin with a lower percentage of sulfur  
381 and ash. For example, sulfur-free lignin is preferred for use in aerogel composites. Jõul et al.  
382 reacted lignin isolated by organic acid with 5-methylresorcinol-formaldehyde to create aerogel  
383 and according to the data, formacell lignin had good reactivity to create a high surface area of  
384 aerogel [68]. According to Talabi et al. lignin with rich hydroxyl carbon, low molecular weight,  
385 and less in the methoxyl group was suitable for lignin-based-formaldehyde resin with a 73%  
386 graphitization level [69], and hence formacell lignin with higher KOH and ethanol concentrations  
387 are appropriate for this application. Meanwhile, the high molecular weight of lignin is preferred  
388 as a matrix in carbon fiber composites because it improves the mechanical performance of the  
389 fiber.

390

#### 391 4 Conclusions

392 A strong base, such as KOH, was used to successfully isolate lignin from oil palm empty  
393 fruit bunch (OPEFB) formacell BL. Some identified lignin peaks can be found in the FTIR  
394 spectra, with no significant difference between lignins isolated with KOH and ethanol. The  
395 addition of KOH solution at 12.5 and 15% concentrations is the more effective method for  
396 isolating lignin from formacell BL. At this condition, isolated lignins have pH values of 3.86 and  
397 4.27, lignin yield of 2.78 and 14.95%, methoxyl content of 11.33 and 10.13%, and lignin  
398 equivalent weights of 476.25 and 427.03, respectively. The lignin produced by the isolation  
399 process using KOH and ethanol was characterized by the low methoxy content and a low  
400 molecular weight that created its higher reactivity. According to these properties, lignin derived  
401 from formacell is suitable for developing green, bio-based additives in biocomposite applications  
402 such as wood adhesives from non-isocyanate polyurethane, coatings, lignin-based-formaldehyde  
403 resins, formaldehyde scavengers, composite fillers, and other value-added industrial applications.

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415 **Conflicts of Interest:** The authors declare that they have no conflicts of interest to report  
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Abdelaziz, O.Y., Brink, D.P., Prothmann, J., Ravi, K., Sun, M., et al. (2016). Biological valorization of low molecular weight lignin. *Biotechnol Adv*, 34(8), 1318-1346.

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Thu, Jan 19, 2023 at 12:05 PM

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Gmail - [TSP\_JRM\_27579] - Proof submitted for your review

To: Sutopo Hadi <sutopo.hadi@fmipa.unila.ac.id>

[Quoted text hidden]

---

**sri hidayati** <srihidayati.unila@gmail.com>  
To: "pm@transforma.in" <pm@transforma.in>

Thu, Jan 19, 2023 at 4:10 PM


Dear: JRM editorial board

Sincerely,  
We hereby submit our revised paper. For your attention, we thank you very much

Greetings

Sri Hidayati  
[Quoted text hidden]

---

 **TSP\_JRM\_27579\_PA WF.pdf**  
2330K





sri hidayati <srihidayati.unila@gmail.com>

---

## [jrm] Validate Your Account

1 message

---

**JRM Editorial** <noreply@tspsubmission.com>  
Reply-To: JRM Editorial <jrm@techscience.com>  
To: Sri Hidayati <srihidayati.unila@gmail.com>

Fri, Nov 4, 2022 at 1:18 PM

Sri Hidayati

You have created an account with Journal of Renewable Materials, but before you can start using it, you need to validate your email account. To do this, simply follow the link below:

[https://www.tspsubmission.com/index.php/jrm/user/activateUser/sri\\_hidayati71/aYQWfV](https://www.tspsubmission.com/index.php/jrm/user/activateUser/sri_hidayati71/aYQWfV)

Thank you,  
JRM Editorial

---

### Journal of Renewable Materials

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Email: [jrm@techscience.com](mailto:jrm@techscience.com)



sri hidayati <srihidayati.unila@gmail.com>

---

## [jrm] ID:27579 Submission Acknowledgement

1 message

---

**JRM Editorial** <noreply@tspsubmission.com>  
To: Sri Hidayati <srihidayati.unila@gmail.com>

Fri, Nov 4, 2022 at 4:24 PM

Dear Sri Hidayati,

Thank you for submitting the manuscript, "Characterization of Formacell Lignin Derived from Black Liquor as a Potential Green Additive for Advanced Biocomposites " to Journal of Renewable Materials. With the online journal management system that we are using, you will be able to track its progress through the editorial process by logging in to the journal web site:

Submission URL: <https://www.tspsubmission.com/index.php/jrm/authorDashboard/submission/27579>

Username: sri\_hidayati71

If you have any questions, please contact me. Thank you for considering this journal as a venue for your work.

JRM Editorial

---

### Journal of Renewable Materials

2590 Windmill Ln #308, Henderson, NV 89074, USA

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Fax: +1 844 635 2598

Office Hours: 9:00-17:00 (UTC -8:00)

Email: [jrm@techscience.com](mailto:jrm@techscience.com)



sri hidayati &lt;srihidayati.unila@gmail.com&gt;

**[jrm] ID: 27579: Editor Decision Revision Request**

2 messages

**JRM Editorial** <admin4@tspsubmission.com>

Wed, Nov 30, 2022 at 9:08 AM

To: "Dr. Sri Hidayati" <srihidayati.unila@gmail.com>, Eugenia Fony Budiyanto <eugenefonny@gmail.com>, Hadi Saputra <hadiggm97@gmail.com>, Sutopo Hadi <sutopo.hadi@fmipa.unila.ac.id>, "Dr. Apri Heri Iswanto" <apri@usu.ac.id>, Mrs Nissa Nurfaejrin Solihat <niss001@brin.go.id>, "Prof. Dr. Petar Antov" <p.antov@ltu.bg>, "Dr. Lee Seng Hua" <leesenghua@hotmail.com>, "Dr. Widya Fatriasari" <widy003@brin.go.id>, "Prof. Mohd. Sapuan Salit" <sapuan@upm.edu.my>

Dear Dr. Sri Hidayati, Eugenia Fony Budiyanto, Hadi Saputra, Sutopo Hadi, Dr. Apri Heri Iswanto, Mrs Nissa Nurfaejrin Solihat, Prof. Dr. Petar Antov, Dr. Lee Seng Hua, Dr. Widya Fatriasari, Prof. Mohd. Sapuan Salit,

The review of your submission to Journal of Renewable Materials, "Characterization of Formacell Lignin Derived from Black Liquor as a Potential Green Additive for Advanced Biocomposites".

ID: 27579

has been completed. Although we found that your paper has merit, it is not acceptable to publish in its present form. We invite you to revise your paper to address reviewers' comments as fully as possible. Please revise the manuscript according to the reviewers' comments and upload the revised file within **one month**.

When you submit your revision, please upload the following 3 files:

1. Your rebuttal;
2. Your revised paper with track change (**highlighted in yellow**);
3. Your clean revised paper.

**Please find the reviewer's comments at the end of this message. Also, in track-change version, please have all the revised part highlighted in yellow in the text.**

When uploading your revision files, scrolling down the page, you will find a panel for Revisions. Use the **Revision Panel** to upload your revised manuscript.

Thank you very much for your contributions to Journal of Renewable Materials.

Sincerely,

-----  
Reviewer J:

The manuscript entitled "Characterization of Formacell Lignin Derived from Black Liquor as a Potential Green Additive for Advanced Biocomposites" reported a study on lignin isolation and characterization using KOH and EtOH precipitation methods. The authors investigated the structural difference of the lignin that obtained by different concentration of KOH or EtOH. However, I do not recommend the manuscript for publication base on this shape.

1. The experimental description is not clear. Did the lignin obtained by continuously added different concentration of KOH or EtOH in one experiment, or they were independent experiments?
2. The molecular weight and hydroxyl groups (including phenyl) content are very important for the lignin structure, but the authors did not mention these properties.
3. Some discussions are not correct or lack of supporting. For example the authors claimed that the different content of OMe by different KOH was because of the replacement or removal of OMe during the process. However, as we know that OMe is highly stable under room temperature. I don't think such condition was able to cleave the OMe in lignin.
4. The authors claim that the main mechanism of lignin depolymerization involves  $\alpha$ -O-4 cleavage, which is not true at all.

Recommendation: Major Revision

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-----

Reviewer L:

The manuscript entitled " Characterization of Formacell Lignin Derived from Black Liquor as a Potential Green Additive for Advanced Biocomposites" reports on determining the effect of KOH or ethanol concentration as an isolation agent on lignin yields and the chemical characteristics of lignin isolated from form a black cell liquor of oil palm empty fruit bunch (OPEFB). Lignin was isolated using KOH with various concentrations ranging from 5% to 15% (w/v). Ethanol was also used to precipitate lignin from black liquor at concentrations varying from 5% to 30% (v/v). The results obtained showed that the addition of KOH solution at 12.5% and 15% c oncentrations resulted in better lignin yield and chemical properties of lignin, i.e., pH values of 3.86 and 4.27, lignin yield of 12.78 and 14.95, methoxyl content of 11.33 and 10.13, and lignin equivalent weights of 476.25 and 427.03, respectively.

This is nice work, and the following corrections are needed prior to acceptance:

- "Black liquor used in this research is a by-product of the formacell pulping of OPEFB, as reported by Hidayati et al. [35]" -Please brief about the cited work in a bit more detail for readers

- [The formacell pulping was conducted in the autoclave at a liquor-to-particle ratio of 15:1 for 1 h at 130 °C] -Any specific reasons for this ratio?

- Figure 1 should be of better quality

- Different peaks in figure 2-3 should be marked

- Conclusion should be re-written to highlight the future perspective

- Introduction can be strengthened to highly the importance of sustainable materials by having a look at relevant references such as <https://www.sciencedirect.com/science/article/pii/S0960852422015887>.

Recommendation: Major Revision

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sri hidayati &lt;srihidayati.unila@gmail.com&gt;

---

**JRM-27579-additional review comments**

1 message

**gabriel.cao@techscience.com** <gabriel.cao@techscience.com>

Wed, Nov 30, 2022 at 9:23 AM

To: "srihidayati.unila" <srihidayati.unila@gmail.com>, eugenefonny <eugenefonny@gmail.com>, hadiggm97 <hadiggm97@gmail.com>, "sutopo.hadi" <sutopo.hadi@fmipa.unila.ac.id>, apri <apri@usu.ac.id>, niss001 <niss001@brin.go.id>, "p.antov" <p.antov@ltu.bg>, leesenghua <leesenghua@hotmail.com>, widy003 <widy003@brin.go.id>, sapuan <sapuan@upm.edu.my>

Dear authors,

With regard to your manuscript-27579, we have sent an revision request letter to you.

Apart from the reviewers' comments, there are also some comments from our editors:

-Please try to lower the self-citations below 5;

-Please revise your manuscript according to our JRM-template.

Look forward to your kind reply.

Best regards,  
Gabriel Cao

---

**Journal of Renewable Materials**

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2590 Windmill Ln, Henderson, NV 89074

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Email: [jrm@techscience.com](mailto:jrm@techscience.com)



sri hidayati &lt;srihidayati.unila@gmail.com&gt;

---

**Revision ID: 27579**

1 message

---

**sri hidayati** <srihidayati.unila@gmail.com>  
To: admin4@tspsubmission.com

Mon, Dec 12, 2022 at 10:20 AM

Dear Editor and reviewers




Authors thanks for the opportunity to revise the manuscript. We are very appreciative of all of the comments and suggestions that useful for improving the quality of the manuscript. We have tried our best to address your comment point by point on your valuable concern. All of the revised parts have been presented in yellow highlight. We expect by this revised version, the manuscript can be reconsidered to fit with a high standard of the journal of renewable materials

Best Regards  
On behalf of the Authors

Dr. Sri Hidayati

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**3 attachments**

-  **Response to editors and Reviewers WFNN\_PA\_Lee (2).docx**  
24K
-  **27579-Manuscript-NNSWF\_PA\_LSH 09122022 NNS clean.docx**  
1048K
-  **27579-Manuscript-NNSWF\_PA\_LSH 09122022 NNS.docx**  
1049K

## Authors Response

Dear Editor and Reviewers

Authors thanks for the opportunity to revise the manuscript. We are very appreciative of all of the comments and suggestions that useful for improving the quality of the manuscript. We have tried our best to address your comment point by point on your valuable concern. All of the revised parts have been presented in yellow highlight. We expect by this revised version, the manuscript can be reconsidered to fit with a high standard of the journal of renewable materials

### Reviewer J

The manuscript entitled “Characterization of Formacell Lignin Derived from Black Liquor as a Potential Green Additive for Advanced Biocomposites” reported a study on lignin isolation and characterization using KOH and EtOH precipitation methods. The authors investigated the structural difference of the lignin obtained by different concentrations of KOH or EtOH. However, I do not recommend the manuscript for publication based on this shape.

Author’s response

Thank you for your insight, we are appreciated your valuable time in reviewing the manuscript. We tried to revise the manuscript and respond in detail to your comments and suggestion. We hope that the revision of the manuscript can help improve the clarity and revising miss leading in the initial manuscript

1. The experimental description is not clear. Did the lignin obtained by continuously added different concentration of KOH or EtOH in one experiment, or they were independent experiments?

Author’s response:

Thank you for your comments; the research is divided into two parts, the first of which is the lignin isolation with EtOH and the second with KOH. We attempted to compare chemical agents for lignin isolation based primarily on yield and lignin characteristics. In the method section, we add additional sentences to provide clear information (please check lines 103-106)

2. The molecular weight and hydroxyl groups (including phenyl) content are very important for the lignin structure, but the authors did not mention these properties.

Author’s response:

Because of the proposed lignin utilisation as a resin for wood biocomposites, the phenolic hydroxyl content was not examined in this study. According to Ghorbani, M. et al. (2016), the methoxyl content of lignin as formaldehyde resins is an important parameter because a high methoxyl content inhibits lignin reactivity during resin use. Furthermore, according to the proposed pathway of Yin et al (2020), the removal of the methoxy group in lignin by KOH

solution created a higher hydroxyl group of lignin. As a result, the authors believe that one of the analyses, either methoxyl or hydroxyl, will suffice to understand the lignin properties.

In this study, the equivalent weight of lignin was examined as a method for determining the molecular weight of lignin.

3. Some discussions are not correct or lack of supporting. For example, the authors claimed that the different content of OMe by different KOH was because of the replacement or removal of OMe during the process. However, as we know that OMe is highly stable under room temperature. I don't think such condition was able to cleave the OMe in lignin.

Author's response:

The explanation about reducing OMe content by increasing KOH has been revised for clarity as follows (lines 221-226): "Furthermore, according to [the pathway proposed by Yin et al.](#), the removal of the methoxy group in lignin created a higher hydroxyl group of lignin by KOH solution. The presence of potassium in lignin isolation decreased the methoxyl content due to cleavage C $\alpha$ —C $\beta$  through C $\beta$ —O bond. This cleavage leads to the removal of side chains such as methoxy. The mechanism of this reaction has been proved by Yin et al. [47]"

4. The authors claim that the main mechanism of lignin depolymerization involves  $\alpha$ -O-4 cleavage, which is not true at all.

Author's response:

Thank you for the suggestion. The information about lignin depolymerization involving  $\alpha$ -O-4 has been removed.



Reviewer L:

The manuscript entitled " Characterization of Formacell Lignin Derived from Black Liquor as a Potential Green Additive for Advanced Biocomposites" reports on determining the effect of KOH or ethanol concentration as an isolation agent on lignin yields and the chemical characteristics of lignin isolated from form a black cell liquor of oil palm empty fruit bunch (OPEFB). Lignin was isolated using KOH with various concentrations ranging from 5% to 15% (w/v). Ethanol was also used to precipitate lignin from black liquor at concentrations varying from 5% to 30% (v/v). The results obtained showed that the addition of KOH solution at 12.5% and 15% concentrations resulted in better lignin yield and chemical properties of lignin, i.e., pH values of 3.86 and 4.27, lignin yield of 12.78 and 14.95, methoxyl content of 11.33 and 10.13, and lignin equivalent weights of 476.25 and 427.03, respectively.

This is nice work, and the following corrections are needed prior to acceptance:

Author's response

Thank you for your positive comments. We have tried to revise the manuscript by considering all of your comments and suggestion

1. "Black liquor used in this research is a by-product of the formacell pulping of OPEFB, as reported by Hidayati et al. [35]" -Please brief about the cited work in a bit more detail for readers

Author's response:

Thank you for your comments. A brief detailed method has been added in the experimental section (2.2 Pulping process), especially in the formacell pulping of OPEFB based on our previous paper. Please check additional sentences in lines 94-100.

2. The formacell pulping was conducted in the autoclave at a liquor-to-particle ratio of 15:1 for 1 h at 130 °C] -Any specific reasons for this ratio?

Author's response

The ratio of liquor to OPEFB particle ratio of 15: 1 has been used based on our initial experimental trial in the laboratory considering the volumetric of OPEFB as typical of nonwoodybiomass. In this ratio, the OPEFB particle can be immersed completely in the chemical liquor. This information has been added in lines 95-98.

3. Figure 1 should be of better quality

Author's response:

Figure 1 has been revised and upgraded to a better-quality presentation in 600 dpi.(see line 117-119).

4. Different peaks in figure 2-3 should be marked

Author's response:

Figures 2 and 3 have been marked by letters a and b to present the different peaks that can be identified. Please see line 301, 311-313

5. Conclusion should be re-written to highlight the future perspective

Author's response:

The conclusion has been revised by adding a future perspective of study mainly future perspective lignin for biocomposite application. Please see line 364-369.

6. Introduction can be strengthened to highly the importance of sustainable materials by having a look at relevant references such as <https://www.sciencedirect.com/science/article/pii/S0960852422015887>.

Author's response:

We agree with the reviewer's suggestion thus the introduction has been strengthened by adding some relevant literature such as mentioned. Please see lines 30-33.

### **Editor's comments**

With regard to your manuscript-27579, we have sent a revision request letter to you. Apart from the reviewers' comments, there are also some comments from our editors:

1. Please try to lower the self-citations below 5;

Author's response:

Thank you for your constructive feedback; we have reduced the self-citation to less than 5 in the revised manuscript version. The number of papers published by the author that have been cited in the revised version is four.

2. Please revise your manuscript according to our JRM-template.

Author's response

The manuscript has been revised carefully according to JRM-template



29 DOI: XXXXX

30

31 **ARTICLE**

32 **Characterization of Formacell Lignin Derived from Black Liquor as a**  
33 **Potential Green Additive for Advanced Biocomposites**

34 **Sri Hidayati<sup>1\*</sup>, Eugenia Fonny Budiyanto<sup>1</sup>, Hadi Saputra<sup>1</sup>, Sutopo Hadi<sup>1</sup>, Apri Heri**  
35 **Iswanto<sup>2,3</sup>, Nissa Nurfajrin Solihat<sup>4</sup>, Petar Antov<sup>5</sup>, Lee Seng Hua<sup>6,7</sup>, Widya Fatriasari<sup>4,8</sup>,**  
36 **Mohd. Sapan Salit<sup>9</sup>**

37 <sup>1</sup>Agricultural Product Technology Department, Faculty of Agriculture, The University of Lampung, Jl. Sumantri  
38 Brojonegoro No. 1 Bandar Lampung, Indonesia

39 <sup>2</sup>Department of Forest Product, Faculty of Forestry, Universitas Sumatera Utara. Kampus USU Padang Bulan, Medan  
40 20155, North Sumatra, Indonesia

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42 Indonesia

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44 46 Cibinong 16911, Indonesia

45 <sup>5</sup>Faculty of Forest Industry, University of Forestry, 1797 Sofia, Bulgaria

46 <sup>6</sup>Department of Wood Industry, Faculty of Applied Sciences, Universiti Teknologi MARA (UiTM), Cawangan Pahang  
47 Kampus Jengka, Lintasan Semarak, Bandar Jengka, 26400 Bandar Tun Razak, Malaysia

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51 45363, Indonesia

52 <sup>9</sup>Advanced engineering Materials and Composites Research Centre, Department of Mechanical and Manufacturing  
53 Engineering, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

54 \*Corresponding Author: [srihidayati.unila@gmail.com](mailto:srihidayati.unila@gmail.com)

55 Received: XXXX Accepted: XXXX



**ABSTRACT**

Black liquor is obtained as a by-product of the pulping process, used to convert biomass into pulp by removing lignin, hemicelluloses and other extractives from wood to free cellulose fibers. Lignin represents a major constituent in black liquor with quantities varying from 20% to 30%, of which a very low share is used for manufacturing value-added products, while the rest is mainly burned for energy purposes, thus underestimating its great potential as a raw material. Therefore, it is essential to establish new isolation and extraction methods to increase lignin valorization in the development of bio-based chemicals. The aim of this research work was to determine the effect of KOH or ethanol concentration as an isolation agent on lignin yields and the chemical characteristics of lignin isolated from formacell black liquor of oil palm empty fruit bunch (OPEFB). Isolation of lignin was carried out using KOH with various concentrations ranging from 5% to 15% (w/v). Ethanol was also used to precipitate lignin from black liquor at concentrations varying from 5% to 30% (v/v). The results obtained showed that the addition of KOH solution at 12.5% and 15% concentrations resulted in better lignin yield and chemical properties of lignin, i.e., pH values of 3.86 and 4.27, lignin yield of 12.78 and 14.95, methoxylcontent of 11.33 and 10.13, and lignin equivalent weights of 476.25 and 427.03, respectively. Due to its phenolic structure and rich functional groups that are favorable for modifications, lignin has the potential to be used as green additive in the development of advanced biocomposite products in various applications to replace current fossil fuel-based material, ranging from fillers, fire retardants, formaldehyde scavengers, carbon fibers, aerogels, and wood adhesives.

**KEYWORDS**

formacell black liquor; lignin properties; KOH; ethanol; oil palm empty fruit bunch; advanced biocomposite

56

57

**58 1 Introduction**

59 Global challenges such as food security and environmental threats can be treated by applying the  
60 circular bioeconomy principles, including sustainable conversion of biomass components into  
61 bio-based products as green alternatives to their petroleum-based counterparts, thus closing the  
62 material resource loops [1]. Black liquor (BL) is liquid waste left over from cooking pulp, aimed  
63 at removing lignin, hemicelluloses, and other extractable constituents from wood in order to free  
64 the cellulose fibers. Lignin is the main organic substance in BL, reaching 45% dry weight [2].  
65 About 150 billion tons of BL are released from the pulp and paper industry, where every 1 ton of  
66 pulp production will produce 7 tons of BL [3]. Taking into account the increased production of  
67 bioethanol, this availability is projected to reach 225 million tons annually in 2030 [4-6].  
68 However, only 2-5% of BL has been valorized into biomaterial [7] and the rest for energy  
69 purposes [8-10]. Hence, it is important to develop new techniques aimed at increasing the  
70 valorization of lignin as a renewable feedstock in various value-added industrial applications.  
71 Lignin is a complex polyphenol compound with a complex three-dimensional chemical structure  
72 that is difficult to decompose naturally, so it has the potential to cause water pollution if  
73 discharged into the environment [11]. Lignin has a highly aromatic structure that is stable to heat  
74 and has high carbon content. In addition, lignin contains various functional groups, e.g., aliphatic,  
75 phenolic, methoxyl, and carbonyl hydroxyl groups, allowing its modification. Thus, it can be used  
76 in many functional applications such as biomass-based fuels, adhesives, flame retardants,

77 dispersants, and surfactant formulations, as antioxidants in plastics and rubbers, dyes, synthetic  
78 floors, thermosets, paints, food packaging, filler in adhesives, seed coatings, automotive devices,  
79 3D printing, and fuels for highway maintenance [12-17]. However, the utilization of lignin is still  
80 limited on an industrial scale due to the inhomogeneity of structure.

81 A lignin component is a phenylpropane unit with several different methoxy groups [18].  
82 Chemical structures of lignin are identified by the presence of polypropene units such as p-  
83 hydroxyphenyl (or p-coumaryl alcohol), guaiacyl (or coniferyl alcohol), and syringyl (or sinapyl  
84 alcohol), and their percentage vary depending on the botanical origin. Polypropene units can be  
85 chemically bonded in different bonding patterns where the  $\beta$ -O-4 aryl glycerol ether bond is the  
86 primary linkage [19]. However, the technical lignin's structure differs from the native lignin and  
87 depends on the pulping method used. Besides, the source of raw materials and isolation method,  
88 including the type of chemical used and temperature, play critical roles in the physicochemical  
89 properties of lignin [20].

90 Lignin can be extracted in powder form from BL with proper chemical treatment and  
91 screening process [21]. Precipitation of lignin in the BL occurs due to the condensation reaction  
92 on the lignin constituent units, which were initially soluble and will be polymerized and form  
93 large molecules [22]. Base, acid, and organic solvents are common solutions to isolate lignin  
94 from BL. The process of lignin separation using organic solvents is known as the alcell or  
95 organosolv process [23]. This method is popular for breaking down lignin fractions [24]. The  
96 benefits of this method include obtaining lignin with a low molecular weight that is free of sulfur,  
97 and its application can be improved through fractionation or chemical modification [25] but  
98 organosolv fractionation is laborious work [26]; hence, acid and base deposition methods are  
99 more feasible. However, this method depends on the pH of the liquor, residence time, and  
100 temperature [22]. Some acids such as  $H_2SO_4$ , phosphoric acid ( $H_3PO_4$ ), or HCl have been  
101 reported in isolating lignin from base BL, such as from the kraft process [27]. Meanwhile, lignin  
102 from formacell BL, BL derived from acetic acid, or formic acid as cooking liquid can be released  
103 by different alkalis, especially KOH,  $Ca(OH)_2$ , and NaOH [20]. KOH, a strong base, is stronger  
104 than NaOH and its use is expected to result in higher lignin yield.

105 Based on Miller et al. [28], a strong base (e.g., NaOH and KOH) provides a higher result in  
106 lignin yield than a weak base, and it would be a promising technique for depolymerizing lignin.  
107 The concentration of base is important to measure because it will influence selectivity, chemical-  
108 physical properties, and lignin yield [20, 29]. Recently, Hidayati et al evaluated the effect of  
109 NaOH concentration on lignin properties [20] while the disadvantage of NaOH was  
110 monoaromatic re-condensation led to the higher molecular weight of lignin [30]. Consequently,  
111 an alternative base such as KOH and ethanol is needed to overcome this problem. To date, no one  
112 reported lignin isolation from formacell BL using different concentrations of KOH and ethanol.  
113 Therefore, this study aimed to determine the effect of KOH and ethanol concentrations on the  
114 yield and chemical characteristics of lignin isolated from formacell black liquor of oil palm empty  
115 fruit bunch (OPEFB).

## 116 2 Material and Methods

**117 2.1 Materials**

118 Black liquor used in this research is a by-product of the formacell pulping of OPEFB, as  
119 reported by Hidayati et al. [31]. The pulping conditions are presented in detail in the next section.  
120 . OPEFB was obtained from PTPN Business Unit VII Central Lampung Bekri, Indonesia.  
121 Meanwhile, KOH, NaCl, NaOH, HCl, and ethanol were supplied by Merck (Darmstadt,  
122 Germany).

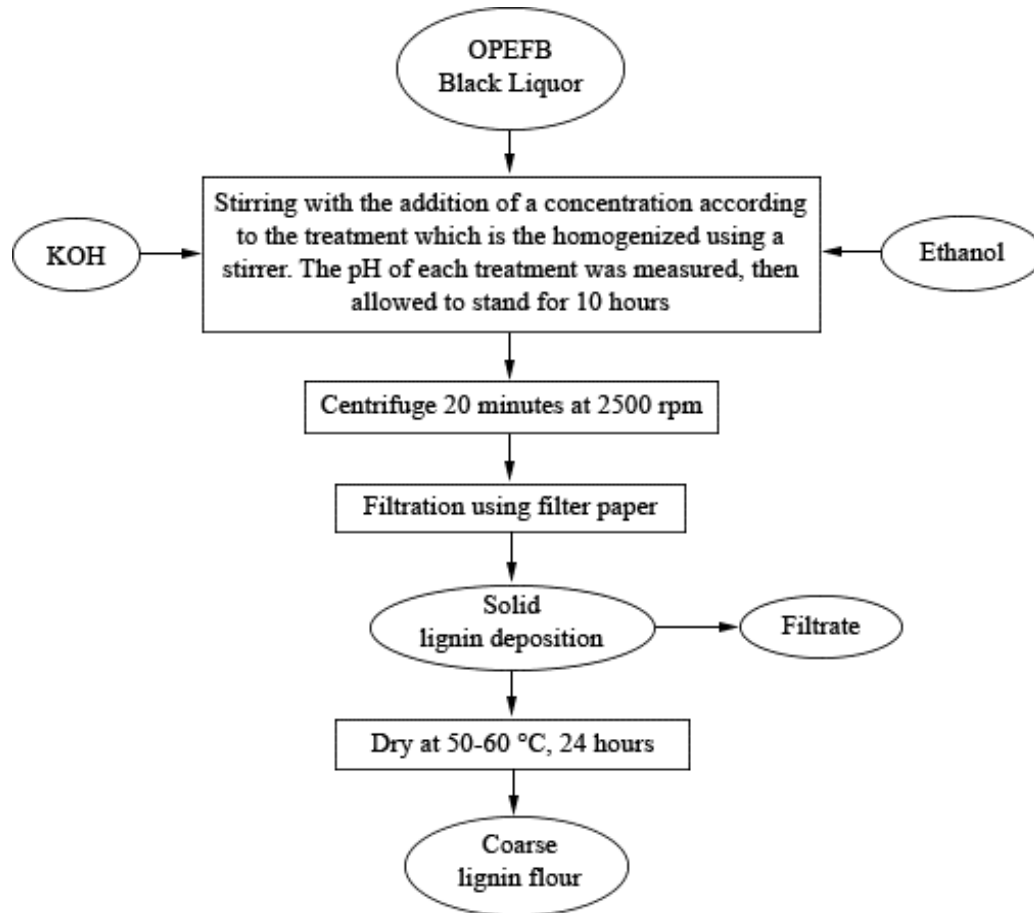
**123 2.2 Pulping process**

124 The formacell pulping was conducted in the autoclave at a liquor-to-particle ratio of 15:1  
125 for 1 h at 130 °C. The ratio of liquor to OPEFB particle ratio of 15:1 was used based on our initial  
126 experimental trials in the laboratory considering the volumetric of OPEFB as a typical example of  
127 non-woody biomass. In this ratio, the OPEFB particles can be immersed completely in the  
128 chemical liquor. The ratio solvent of acetic acid and formic acid was 85:15 with the addition of  
129 HCl of 0.5% as the catalyst. The cooking liquor was collected after filtration and washing the  
130 completed softened OPEFB with fresh water at room temperature. This formacell BL was used  
131 for the next step.

**132 2.3 Lignin isolation**

133 The formacell BL obtained from the pulping process of 100 mL contained a total solid  
134 content of around 25.10%. There are two methods for lignin isolation from formacell BL of  
135 OPEFB. The first one, i.e. the isolation of lignin from BL was conducted using KOH with a  
136 concentration of 2.5%; 5%; 7.5%; 10%; 12.5%; and 15% (w/v). The second isolation technique  
137 used ethanol at concentrations of 5%, 10%, 15%, 20%, 25 and 30% (v/v). As much as 100 mL of  
138 the KOH or ethanol solution was added into 100 mL BL, then stirred and measured the pH of the  
139 liquor was. The solution was allowed to stand for 10 hours, then centrifugated for 20 minutes at  
140 2500 rpm, and then separated using filter paper. The precipitated lignin was then oven-dried at  
141 50-60 °C for 24 h. Dried lignin was crushed manually to produce fine lignin powder (Fig. 1). The  
142 experiment was conducted in triplicate.

143 The data were calculated and presented in average and standard deviation tables and  
144 graphs. Observations made were pH value, the yield of lignin, lignin methoxyl content, the  
145 equivalent weight of lignin, analysis of lignin with Fourier Transform Infra-Red spectroscopy  
146 (FTIR) spectrophotometer (Cary 630 FTIR, Agilent, Australia), and lignin morphology using a  
147 scanning electron microscope (SEM) (JEOL JSM 6510 LA, Japan).



148

149

**Figure 1:** Flowchart of lignin isolation process using KOH/Ethanol.

#### 150 **2.4 Lignin Yield**

151 Lignin yield was calculated based on the method according to Kim [32], as presented in  
 152 Equation 1.

$$153 \quad \text{Lignin Yield (\%)} = \frac{a}{b} \times 100\% \quad (1)$$

154 **Notation :** a = weight of isolated lignin;

155 b = weight of lignin in black liquor

#### 156 **2.5 Methoxyl content of lignin**

157 The methoxyl content of lignin was determined by using the ASTM 15120-81 method  
 158 [33]. As much as 0.5 g of lignin was added to 5 mL of ethanol, following addition to 100 mL of  
 159 distilled water containing 1 g of NaCl, and made in the form of suspension. Neutralization was  
 160 performed using 0.1 N NaOH, given 6 drops of phenolphthalein (pp) indicator, then 25 mL of  
 161 0.25 N NaOH was added and homogenized in a closed state for 30 minutes at room temperature.  
 162 After that, 25 mL of 0.25 N HCl was added and titrated with 0.1 N NaOH until the end of the lasting  
 163 color change (at least 30 seconds). The methoxyl content of lignin was calculated according to  
 164 Equation 2 as follows.

$$\text{Methoxyl (\%)} = \frac{\text{ml NaOH} \times \text{N NaOH} \times 3.1}{\text{Berat sampel (gram)}} \times 100\% \quad (2)$$

## 166 **2.6 Lignin Equivalent Weight**

167 Isolated lignin equivalent weight was calculated using the method of Santoso [34]. 0.5 g  
168 lignin was put into 250 mL Erlenmeyer and moistened with 5 mL ethanol. The mixture is spiked  
169 with 1 g of NaCl which is then added with 100 mL of distilled water and 6 drops of phenolphthalein  
170 indicator. The solution was then titrated with 0.1 N NaOH until pH 7.5. The equivalent weight of  
171 isolated lignin was calculated by using Equation 3.

$$\text{Equivalent Weight} = \frac{1000 \times \text{gram sample}}{(\text{mLN})\text{NaOH}} \quad (3)$$

## 173 **2.7 FT-IR analysis of isolated lignin**

174 As much as 1 mg isolated lignins were added with 150 mg KBr, pelletized, and then the  
175 samples were analyzed by FT-IR spectrophotometer (Cary 630 FTIR Agilent). The analysis was  
176 set at a wavenumber of  $4000 \text{ cm}^{-1}$  to  $400 \text{ cm}^{-1}$  (wavelength of 2.5–25  $\mu\text{m}$ ).

## 177 **2.7 SEM analysis**

178 Morphology of isolated lignin was carried out using Scanning Electron Microscope (SEM)  
179 (JEOL JSM 6510 LA) with 1000 x magnification.

# 180 **3 Results and Discussion**

## 181 **3.1 pH of the liquor**

182 The pH of black liquor from formacell pulping OPEFB is  $0.59 \pm 0.01$ , indicating that the  
183 liquor is acidic; thus, base or ethanol can be used to precipitate lignin from BL. To speed up the  
184 reaction, solvents such as acetic acid and formic acid are used in the formacell pulping process,  
185 along with HCl as a catalyst [31]. This process causes the pH of the formacell black liquor to  
186 become very acidic. Zhuang et al. [35] stated that formic acid and acetic acid could delignify  
187 lignin because of their acidic nature, so they can degrade lignin well. In another study, a  
188 combination of formic acid, acetic acid, and water achieved more than 50% lignin  
189 depolymerization in biomass [36]. The pH of the BL will be affected by the addition of KOH  
190 solution. According to the research, the pH value obtained from formacell pulping added with  
191 KOH solution ranged from  $2.43 \pm 0.07$  to  $4.27 \pm 0.35$  (Table 1), while the addition of ethanol  
192 concentrations can slightly increase the pH value from  $1.0 \pm 0.01$  to  $1.29 \pm 0.03$ . According to the  
193 findings, KOH has a greater effect on increasing pH than ethanol due to the strong base property  
194 of KOH.

195 The pH steadily increased as an upsurging concentration of KOH, where the lowest pH,  
196  $2.43 \pm 0.07$ , was obtained from 2.5% KOH, and the highest was a pH of  $4.27 \pm 0.35$  from KOH  
197 15%. Increasing the concentration of KOH solution causes more  $\text{OH}^-$  ions in the black liquor so  
198 that the pH of the solution becomes more alkaline. It can also be explained that KOH is a strong  
199 base. The stronger the base, the more  $\text{OH}^-$  ions are released, increasing the pH of the solution  
200 and making it more alkaline. Ethanol has a higher pKa than KOH, indicating a weaker acid.



201 Unlike KOH, increasing the ethanol concentration slightly increased the pH, with the lowest  
202 being 1 and the highest being 1.29 after adding 5% and 30%, as shown in Table 1.

203 **Table 1:** Effect of KOH and ethanol concentrations on pH, yield, methoxyl content, and an  
204 equivalent weight of isolated lignin.

Treatment	pH	Yield (%)	Lignin methoxyl (%)	Equivalent Weight
KOH concentration (%)				
2.5	2.43±0.07	3.57±0.38	13.06±0.9	1372.94±26.73
5.0	2.94±0.06	4.85±1.12	12.94±1.31	655.73±45.16
7.5	3.21±0.1	8.63±1.41	12.81±0.84	528.74±54.44
10	3.61±0.15	11.20±2.69	12.36±0.9	510.33±49.05
12.5	3.86±0.15	12.78±0.78	11.33±0.4	476.25±34.61
15	4.27±0.35	14.95±1.10	10.13±1.42	427.03±44.20
Ethanol concentration (%)				
5	1.00±0.01	1.95±0.18	17.03±0.42	449.88±48.47
10	1.08±0.06	2.27±0.317	16.45±1.44	624.67±59.2
15	1.15±0.07	1.69±0.091	15.05±1.03	767.97±56.6
20	1.20±0.047	1.77±0.207	14.47±1.17	896.95±64.15
25	1.22±0.056	1.44±0.174	13.14±1.78	1521.16±72.10
30	1.29±0.03	1.08±0.179	11.99±1.20	2123.02±70.72

205

206

### 207 **3.2 Lignin yield**

208 The lignin yield from adding KOH solution at various concentrations in isolation of BL  
209 ranged from  $3.57 \pm 0.38$  to  $14.95 \pm 1.10$  (Table 1). In comparison, ethanol isolation resulted in  
210 lower lignin yields of about  $0.51 \pm 0.00$  to  $1.06 \pm 0.00$ . The highest lignin yield was produced at a  
211 concentration of 15% KOH solution ( $14.95\% \pm 1.10$ ). Increasing the concentration of KOH  
212 solution caused the lignin yield to increase. It can be affected by the increasing concentration of  
213 an alkaline solution (KOH) that facilitates easier breaking of lignin bonds with other compounds,  
214 and a condensation reaction occurs in the lignin constituent units [37]. It is also supported by  
215 Sundin's [38] who stated that lignin deposition from BL due to the protonation of phenol groups  
216 on lignin molecules caused by the addition of  $\text{OH}^-$  ions from KOH. It reduces the electrostatic  
217 force between lignin molecules, resulting in the deposition of lignin (reduced solubility). The  
218 more  $\text{OH}^-$  ions, the more lignin deposits will form. The deposit lignin increase occurred because  
219 of an increase in ionic strength and protonation. The protonation of the phenolic group in lignin  
220 leads the lignin nucleus to form aggregates when the pKa value of lignin is reached [39].

221 The lignin yield with KOH liquor treatment is higher than that of NaOH, as reported by  
222 Hidayati et al. [20]. Lignin was isolated from formacell black liquor of OPEFB by using NaOH,  
223 producing lignin yields ranging from 1.48% to 5.67%. It might be caused by the stronger base of

224 KOH than NaOH. As seen in the periodic system, the metal Na<sup>+</sup> and K<sup>+</sup> are included in Group 1A.  
225 This is also related to the lower nature of alkali metal bases; the stronger, the lower the metal, the  
226 more easily reduced. Besides pH, temperature and ionic strength also affect lignin solubility. The  
227 molecular weight distribution in lignins is related to yield [40]. Both molecular weight and the  
228 ratio of phenols to aromatic units contribute to the solubility of lignin [40]. The changes in lignin  
229 yield in isolation by adding ethanol concentration are very low. The very low electronegativity of  
230 ethanol can suggest it is due to the presence of carbon compounds that cannot precipitate lignin  
231 properly. In the absence of sulfide, delignification was slower in the Alcell process.

232 As opposed to KOH precipitation, increasing ethanol concentrations leads to almost 0%  
233 lignin recovery. This result was in agreement with the precipitation of lignin from *Miscanthus x*  
234 *giganteus*, where after the addition of 75% of ethanol, there was no lignin precipitated [41]. In the  
235 low concentration of ethanol, lignin precipitation is carried out by diluting liquor with water, and  
236 the solubility of lignin decreases, resulting in more lignin being recovered. In other words, when  
237 the water content in the ethanol is limited, most of the lignin is soluble in the system, and hence  
238 the aggregate is not formed.

239

### 240 **3.3 Methoxyl content in lignin**

241 Methoxyl is one of the chemical groups in lignin for identifying one of the characteristics of  
242 lignin. The methoxyl group in each type of lignin has different content because of the different  
243 structures of lignin types. Determining methoxyl contents gives information about the average C9  
244 units in lignin, and eventually, the unsaturated side chain and average oxygen content can be  
245 calculated [42]. The methoxyl content in KOH lignin ranged from 10.13% ± 1.92 to 12.94% ±  
246 0.90, whereas the use of ethanol concentrations results in methoxyl contents between 11.99 ±  
247 0.02 to 17.03 ± 0.5 (Table 1). The highest methoxyl content in lignin was acquired from isolated  
248 lignin by adding a 2.5% KOH solution. Increasing the concentration of KOH and ethanol solution  
249 leads to a decrease in the methoxyl content of isolated lignins. This may be due to the use of  
250 KOH as a strong base as a precipitating solution, which allows some methoxyl groups to degrade  
251 and transform into other compounds. This decrease in methoxyl content can be influenced by the  
252 disruption of structural stability in lignin caused by the addition of KOH. Furthermore, according  
253 to the pathway proposed by Yin et al., the removal of the methoxy group in lignin created a  
254 higher hydroxyl group of lignin by KOH solution. The presence of potassium in lignin isolation  
255 decreased the methoxyl content due to cleavage C $\alpha$ —C $\beta$  through C $\beta$ —O bond. This cleavage  
256 leads to the removal of side chains such as methoxy. The mechanism of this reaction has been  
257 proved by Yin et al. [43].

258 The various methoxyl content in lignin depends on the source of lignin and the  
259 delignification process used. Generally, high methoxyl content will inhibit lignin reactivity during  
260 use in the resin field. Lignin has phenolic hydroxyl groups that are typically linked to nearby  
261 phenyl propane units, allowing lignin to connect with formaldehyde in a way analogous to phenol  
262 and formaldehyde [44]. Molecular weight and lignin purity are important factors during the  
263 production of biocarbon fibers [44, 45].

264 In the case of lignin application as an adhesive raw material, the low methoxyl content is  
265 more beneficial because it will increase the reactivity of aromatic nuclei in lignin [46]. It will  
266 facilitate the reaction of methylation or hydroxymethylation with adhesive-forming reactants such  
267 as NaOH and formaldehyde, hinting at the ease of gel formation. Recently, Gendron et al.  
268 compared four types of lignin for green adhesive, where the lowest methoxyl content of lignin  
269 had the highest water solubility and shear resistance as an adhesive [47].

270 The lignin standard of Indulin AT has a methoxyl content of around 13.5% - 14.5% [48], so  
271 the methoxyl contents in isolated lignin in this study are still lower. Meanwhile, compared to  
272 methoxyl content by Hidayati et al. [20] with a value of 14.61% - 20.77% by using NaOH as  
273 precipitating solution, the results of this study are also lower. These results are probably  
274 influenced by the use of KOH, which is classified as a strong base with a higher reactivity than  
275 NaOH, as seen from the periodic system. The influence of harsh chemicals and temperature  
276 during isolation causes the structure of lignin to undergo many changes, including the methoxyl  
277 group. The methoxyl group is degraded and transformed into other degradation compounds such  
278 as aromatic hydrocarbon and phenolic types, resulting in lower methoxyl content [49].

### 279 **3.4 The equivalent weight of lignin**

280 The determination of the equivalent weight of lignin is intended to determine the  
281 molecular weight of lignin to identify lignin degradation and condensation reactions. The  
282 molecular weight of lignin is an important property that influences biomass recalcitrance and  
283 lignin value. Determination of the molecular weight of lignin in the original biomass depends on  
284 the source of the raw material used, chemicals used for isolation, and purification methods [50,  
285 51]. Based on the results, the equivalent weight of lignin from the KOH solution ranged from  
286  $427.03 \pm 74.20$  to  $1372.94 \pm 269.73$ , whereas the addition of ethanol concentration resulted in  
287 molecular weights ranging from  $449.88 \pm 1.9$  to  $2123.03 \pm 27.5$  (Table 1).

288 Increasing the concentration of KOH solution resulted in a decrease in lignin equivalent  
289 weight so that the lowest value at 15% KOH solution concentration was  $427.03 \pm 74.20$ . This  
290 might be attributed to the increasing addition of a KOH solution as a strong base will degrade a  
291 portion of lignin into a derivative compound with shorter chains. It can degrade lignin resulting in  
292 a low equivalent weight. According to Patil et al., there are two routes for lignin depolymerization:  
293 harsh and moderate, resulting in different lignin structures [52]. The average molecular weight of  
294 lignin decreases with increasing precipitation of lignin yield by KOH. It was shown that  
295 increasing the amount of lignin with lower molecular weight deposited a high yield of lignin.  
296 Lignin is degraded into smaller fragments so that there are more phenolic groups with lower  
297 molecular weights [53]. The product's molecular weight can be lowered by increasing salt  
298 concentration [54, 55].

299 According to Gellerstedt [56], the termination of methyl aryl ether bonds from the aromatic  
300 ring of lignin resulted in decreased methoxyl content and low molecular weight of lignin due to  
301 the lignin degradation process. Based on several previous studies, lignin molecular weight values  
302 were obtained, namely 2500 - 14,000 [57], and 1327.64 - 1787.23 [20]. In contrast, the equivalent

303 weight of Indulin AT reached 3357 - 3366 [58]. This shows that the equivalent weight value of  
304 lignin varies greatly.

305 Lignin that has a high molecular weight can be used as a matrix in polyolefin composites,  
306 because a higher molecular mass of lignin has a better affinity with the matrix [59], while lignin  
307 with a lower molecular weight can be used for the development of phenol-formaldehyde resins,  
308 antioxidants, adhesives, and paints due to their higher reactivity than high molecular weight  
309 lignin [59].

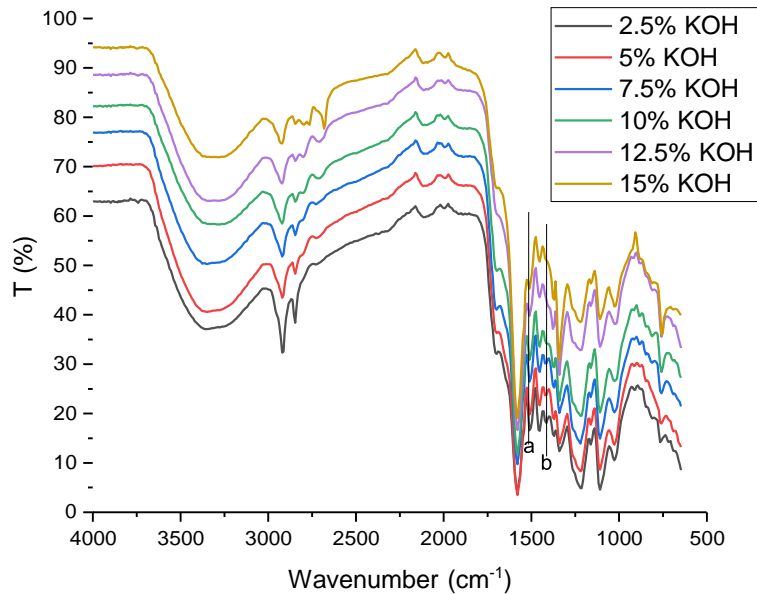
310 Differences in elemental composition, functional group types, proportions, and molecular  
311 weight in lignin molecules provide opportunities to use lignin in a variety of value-added  
312 applications. Some factors that influence the molecular weight of lignin are the diversity of lignin  
313 isolation procedures, macromolecular degradation during isolation, the effect of condensation  
314 mainly on acidic conditions, the apparent polydispersity of dissolved lignin, inadequate  
315 determination methods used to characterize the isolated lignin, and uncertainties in the properties  
316 of lignin. Because lignin is heterogeneous and inconstant, characterizing native lignin is also  
317 difficult [60].

318 The molecular weight of lignin is very important in the development of such polymeric  
319 products; similarly, low-molecular-weight lignin isolated from wheat straw by acetic acid pulping  
320 is an ideal feedstock for adhesive manufacturing [61]. Doherty et al. [62] stated that lignin from  
321 the soda process of wheat plants ranges from 1700 with a methoxyl content of 16. The organosolv  
322 pulping process at bagasse produces a molecular weight of around 2000 and a methoxyl content  
323 of 15.1. Lignin produced in the isolation process using alcohol or alcell process has a low  
324 molecular weight ( $M_w < 900$ ) with low polydispersity, no sulfur, and low ash content, although  
325 the value depends on the analytical method. There is also a molecular weight of  $2580 \text{ g mol}^{-1}$   
326 with a polydispersity of 4.3. Sameni et al. compared four types of lignin from different isolation  
327 methods, where the highest  $M_w$  (13488) was obtained from the steam explosion process with a  
328 methoxyl content of 0.69. Meanwhile, with the same methoxyl content, the lowest  $M_w$  (2565)  
329 was derived from the kraft process [57]. Yun et al. reported that organosolv fractionation from  
330 native lignin decreased its molecular weight from 5070 to 1810 [23].

### 331 **3.6 Lignin Analysis with FT-IR Spectrophotometer**

332 FTIR was performed to analyze differences in the functional groups of lignin in the sample  
333 (Fig. 2 and 3). FTIR spectra analysis showed that the peak in the aromatic ring vibrations  
334 decreased with the absorption band at  $1446 \text{ cm}^{-1}$  (a) and  $1408 \text{ cm}^{-1}$  (b), especially in the  
335 treatment using the highest concentration of KOH (Figure 2) and ethanol (Figure 3). There are  
336 similarities in the wavelength of  $3500 \text{ cm}^{-1}$  to  $31090 \text{ cm}^{-1}$  which refer to the presence of  
337 hydrogen bonds in the hydroxyl group (alcohol and phenolic). A wavelength absorption of  $1587$   
338  $\text{cm}^{-1}$  and  $1513 \text{ cm}^{-1}$  indicates the aromatic lignin skeletal vibration [60]. Wavenumbers at  $1460$   
339  $\text{cm}^{-1}$  to  $1420 \text{ cm}^{-1}$  are associated with stretching wavelengths of CH (methyl and methylene) and  
340 CH deformation with aromatic ring stretching fields [63]. The peaks observed in the range of  
341  $1220 \text{ cm}^{-1}$  to  $1270 \text{ cm}^{-1}$  in all spectra may refer to the C-H deformation vibrations of the guaiacyl  
342 [64]. The bands at  $1300 \text{ cm}^{-1}$  (syringyl) and  $1200 \text{ cm}^{-1}$  (guaiacyl) indicate the presence of both

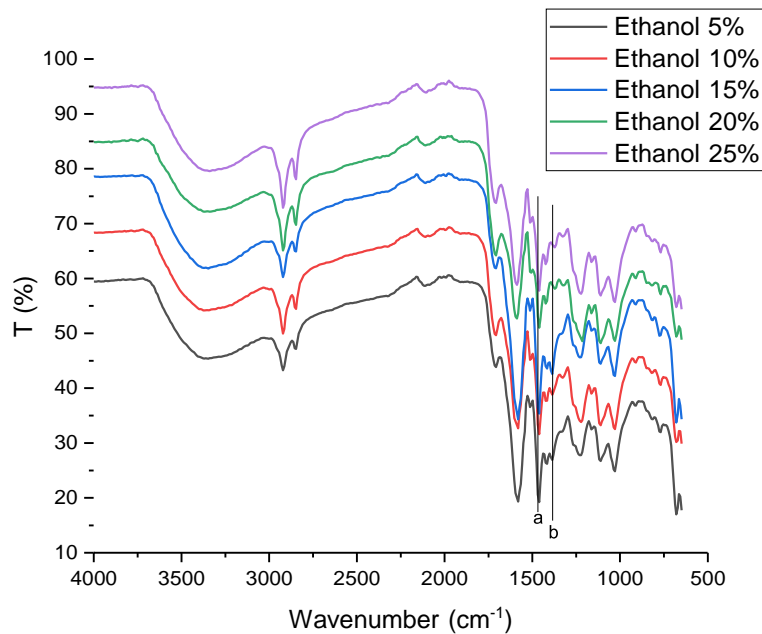
343 syringyl and guaiacyl in lignin's chemical structure as the unique peaks of lignin precursor [65].  
344 A similar peak was also found in kraft lignin isolated from *Acacia mangium* black liquor [27]. In  
345 general, peaks in Fig. 2 and 3 show that the treatment using KOH had a sharper peak than that of  
346 ethanol treatment. However, no difference in the peaks resulting from these two treatments was  
347 determined. Hidayati et al. [20] reported the experiment in isolated lignin from formacell black  
348 liquor of OPEFB using NaOH with the wave number of isolated lignin for guaiacyl lignin at  
349 around  $1273.02\text{ cm}^{-1}$ .



350

351

**Figure 2:** The FT-IR spectra of lignin using KOH isolation



**Figure 3:** The FT-IR spectra of lignin using ethanol isolation

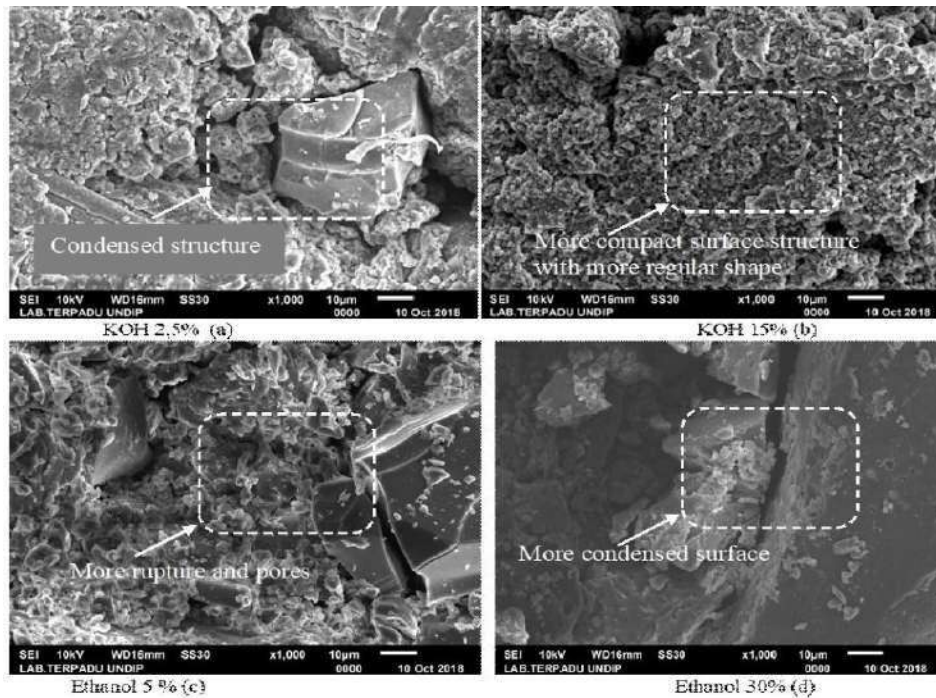
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### 355 **3.7 Morphological observation**

356 Scanning Electron Microscope (SEM) was used to observe the size and morphology of lignin.  
357 In this study, SEM images were taken from the lowest and the highest concentration of KOH and  
358 ethanol as representative lignin morphology. As seen in Fig. 4, increasing the concentration of  
359 KOH acid from 2.5% to 15% showed differences in lignin morphology. Lignin isolation using 15%  
360 KOH (Fig. 4b) produced a more compact formation and morphology compared to lignin  
361 produced by isolation using 2.5% KOH concentration (Fig. 4a). In stark contrast, in treatment  
362 using ethanol appears that treatment with a 5% ethanol concentration resulted in a more  
363 condensed form and morphology than those using a 30% concentration. This result was in  
364 accordance with the findings reported by Solihat et al. [27] and Hamzah et al., [41] where  
365 increasing ethanol concentration created more rupture and amorphous lignin surface.



366

367 **Figure 4:** Morphological images of isolated lignin (a) KOH 2.5%, (b) KOH 15%, (c) ethanol 5%,  
 368 (d) ethanol 30% with 1000 x magnification

369

### 370 **3.8 Prospective Application of Formacell Lignin as Advanced Biocomposite Products**

371 The lignin molecule contains a variety of active functional groups, including aliphatic  
 372 hydroxyl (Al-OH), phenolic hydroxyl (Ph-OH), carboxyl (-COOH), carbonyl (-C=O), and  
 373 methoxy groups (-OCH<sub>3</sub>), which determine its properties, chemistry, and reactivity of lignin.  
 374 Lignin's chemical properties enable it and its derivatives to be used as high-value materials. The  
 375 lignin molecule can be used in a variety of value-added applications due to differences in  
 376 molecular weight, elemental composition, and the types and proportions of functional groups.  
 377 Currently, Saražin et al. investigated the potency of organosolv lignin-based non-isocyanate  
 378 polyurethane for wood adhesive and the result demonstrated satisfactory mechanical properties  
 379 [66] and its curing kinetics for interior furniture showed that it was more suitable than urea-  
 380 formaldehyde (UF) adhesive [67]. Sulfur-free lignin is produced by isolating lignin from the  
 381 formacell process. Most value-added applications prefer lignin with a lower percentage of sulfur  
 382 and ash. For example, sulfur-free lignin is preferred for use in aerogel composites. Jõul et al.  
 383 reacted lignin isolated by organic acid with 5-methylresorcinol-formaldehyde to create aerogel  
 384 and according to the data, formacell lignin had good reactivity to create a high surface area of  
 385 aerogel [68]. According to Talabi et al., lignin with rich hydroxyl carbon, low molecular weight,  
 386 and less in the methoxyl group was suitable for lignin-based-formaldehyde resin with a 73%  
 387 graphitization level [69], and hence formacell lignin with higher KOH and ethanol concentrations  
 388 are appropriate for this application. Meanwhile, the high molecular weight of lignin is preferred  
 389 as a matrix in carbon fiber composites because it improves the mechanical performance of the  
 390 fiber.

391

**392 4 Conclusions**

393 A strong base, such as KOH, was used to successfully isolate lignin from oil palm empty  
394 fruit bunch formacell BL (OPEFB). Some identified lignin peaks can be found in the FTIR  
395 spectra, with no significant difference between lignins isolated with KOH and ethanol. The  
396 addition of KOH solution at 12.5 and 15% concentrations is the more effective method for  
397 isolating lignin from formacell BL. At this condition, isolated lignins have pH values of 3.86 and  
398 4.27, lignin yield of 2.78 and 14.95%, methoxyl content of 11.33 and 10.13, and lignin equivalent  
399 weights of 476.25 and 427.03, respectively. The lignin produced by the isolation process using  
400 KOH and ethanol was characterized by the low methoxy content and low molecular weight that  
401 created its higher reactivity. According to these properties, lignin derived from formacell is  
402 suitable for developing green, bio-based additives in biocomposite applications such as wood  
403 adhesives from non-isocyanate polyurethane, coatings, lignin-based-formaldehyde resins,  
404 formaldehyde scavengers, composite fillers, and other value-added industrial applications.

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31 **ARTICLE**

32 **Characterization of Formacell Lignin Derived from Black Liquor as a**  
33 **Potential Green Additive for Advanced Biocomposites**

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**ABSTRACT**

Black liquor is obtained as a by-product of the pulping process, used to convert biomass into pulp by removing lignin, hemicelluloses and other extractives from wood to free cellulose fibers. Lignin represents a major constituent in black liquor with quantities varying from 20% to 30%, of which a very low share is used for manufacturing value-added products, while the rest is mainly burned for energy purposes, thus underestimating its great potential as a raw material. Therefore, it is essential to establish new isolation and extraction methods to increase lignin valorization in the development of bio-based chemicals. The aim of this research work was to determine the effect of KOH or ethanol concentration as an isolation agent on lignin yields and the chemical characteristics of lignin isolated from formacell black liquor of oil palm empty fruit bunch (OPEFB). Isolation of lignin was carried out using KOH with various concentrations ranging from 5% to 15% (w/v). Ethanol was also used to precipitate lignin from black liquor at concentrations varying from 5% to 30% (v/v). The results obtained showed that the addition of KOH solution at 12.5% and 15% concentrations resulted in better lignin yield and chemical properties of lignin, i.e., pH values of 3.86 and 4.27, lignin yield of 12.78 and 14.95, methoxylcontent of 11.33 and 10.13, and lignin equivalent weights of 476.25 and 427.03, respectively. Due to its phenolic structure and rich functional groups that are favorable for modifications, lignin has the potential to be used as green additive in the development of advanced biocomposite products in various applications to replace current fossil fuel-based material, ranging from fillers, fire retardants, formaldehyde scavengers, carbon fibers, aerogels, and wood adhesives.

**KEYWORDS**

formacell black liquor; lignin properties; KOH; ethanol; oil palm empty fruit bunch; advanced biocomposite

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**58 1 Introduction**

59 Global challenges such as food security and environmental threats can be treated by applying the  
60 circular bioeconomy principles, including sustainable conversion of biomass components into  
61 bio-based products as green alternatives to their petroleum-based counterparts, thus closing the  
62 material resource loops [1]. Black liquor (BL) is liquid waste left over from cooking pulp, aimed  
63 at removing lignin, hemicelluloses, and other extractable constituents from wood in order to free  
64 the cellulose fibers. Lignin is the main organic substance in BL, reaching 45% dry weight [2].  
65 About 150 billion tons of BL are released from the pulp and paper industry, where every 1 ton of  
66 pulp production will produce 7 tons of BL [3]. Taking into account the increased production of  
67 bioethanol, this availability is projected to reach 225 million tons annually in 2030 [4-6].  
68 However, only 2-5% of BL has been valorized into biomaterial [7] and the rest for energy  
69 purposes [8-10]. Hence, it is important to develop new techniques aimed at increasing the  
70 valorization of lignin as a renewable feedstock in various value-added industrial applications.  
71 Lignin is a complex polyphenol compound with a complex three-dimensional chemical structure  
72 that is difficult to decompose naturally, so it has the potential to cause water pollution if  
73 discharged into the environment [11]. Lignin has a highly aromatic structure that is stable to heat  
74 and has high carbon content. In addition, lignin contains various functional groups, e.g., aliphatic,  
75 phenolic, methoxyl, and carbonyl hydroxyl groups, allowing its modification. Thus, it can be used  
76 in many functional applications such as biomass-based fuels, adhesives, flame retardants,

77 dispersants, and surfactant formulations, as antioxidants in plastics and rubbers, dyes, synthetic  
78 floors, thermosets, paints, food packaging, filler in adhesives, seed coatings, automotive devices,  
79 3D printing, and fuels for highway maintenance [12-17]. However, the utilization of lignin is still  
80 limited on an industrial scale due to the inhomogeneity of structure.

81 A lignin component is a phenylpropane unit with several different methoxy groups [18].  
82 Chemical structures of lignin are identified by the presence of polypropene units such as p-  
83 hydroxyphenyl (or p-coumaryl alcohol), guaiacyl (or coniferyl alcohol), and syringyl (or sinapyl  
84 alcohol), and their percentage vary depending on the botanical origin. Polypropene units can be  
85 chemically bonded in different bonding patterns where the  $\beta$ -O-4 aryl glycerol ether bond is the  
86 primary linkage [19]. However, the technical lignin's structure differs from the native lignin and  
87 depends on the pulping method used. Besides, the source of raw materials and isolation method,  
88 including the type of chemical used and temperature, play critical roles in the physicochemical  
89 properties of lignin [20].

90 Lignin can be extracted in powder form from BL with proper chemical treatment and  
91 screening process [21]. Precipitation of lignin in the BL occurs due to the condensation reaction  
92 on the lignin constituent units, which were initially soluble and will be polymerized and form  
93 large molecules [22]. Base, acid, and organic solvents are common solutions to isolate lignin  
94 from BL. The process of lignin separation using organic solvents is known as the alcell or  
95 organosolv process [23]. This method is popular for breaking down lignin fractions [24]. The  
96 benefits of this method include obtaining lignin with a low molecular weight that is free of sulfur,  
97 and its application can be improved through fractionation or chemical modification [25] but  
98 organosolv fractionation is laborious work [26]; hence, acid and base deposition methods are  
99 more feasible. However, this method depends on the pH of the liquor, residence time, and  
100 temperature [22]. Some acids such as  $H_2SO_4$ , phosphoric acid ( $H_3PO_4$ ), or HCl have been  
101 reported in isolating lignin from base BL, such as from the kraft process [27]. Meanwhile, lignin  
102 from formacell BL, BL derived from acetic acid, or formic acid as cooking liquid can be released  
103 by different alkalis, especially KOH,  $Ca(OH)_2$ , and NaOH [20]. KOH, a strong base, is stronger  
104 than NaOH and its use is expected to result in higher lignin yield.

105 Based on Miller et al. [28], a strong base (e.g., NaOH and KOH) provides a higher result in  
106 lignin yield than a weak base, and it would be a promising technique for depolymerizing lignin.  
107 The concentration of base is important to measure because it will influence selectivity, chemical-  
108 physical properties, and lignin yield [20, 29]. Recently, Hidayati et al evaluated the effect of  
109 NaOH concentration on lignin properties [20] while the disadvantage of NaOH was  
110 monoaromatic re-condensation led to the higher molecular weight of lignin [30]. Consequently,  
111 an alternative base such as KOH and ethanol is needed to overcome this problem. To date, no one  
112 reported lignin isolation from formacell BL using different concentrations of KOH and ethanol.  
113 Therefore, this study aimed to determine the effect of KOH and ethanol concentrations on the  
114 yield and chemical characteristics of lignin isolated from formacell black liquor of oil palm empty  
115 fruit bunch (OPEFB).

## 116 2 Material and Methods

## 117 **2.1 Materials**

118 Black liquor used in this research is a by-product of the formacell pulping of OPEFB, as  
119 reported by Hidayati et al. [31]. The pulping conditions are presented in details in the next  
120 section. OPEFB was obtained from PTPN Business Unit VII Central Lampung Bekri, Indonesia.  
121 Meanwhile, KOH, NaCl, NaOH, HCl, and ethanol were supplied by Merck (Darmstadt,  
122 Germany).

## 123 **2.2 Pulping process**

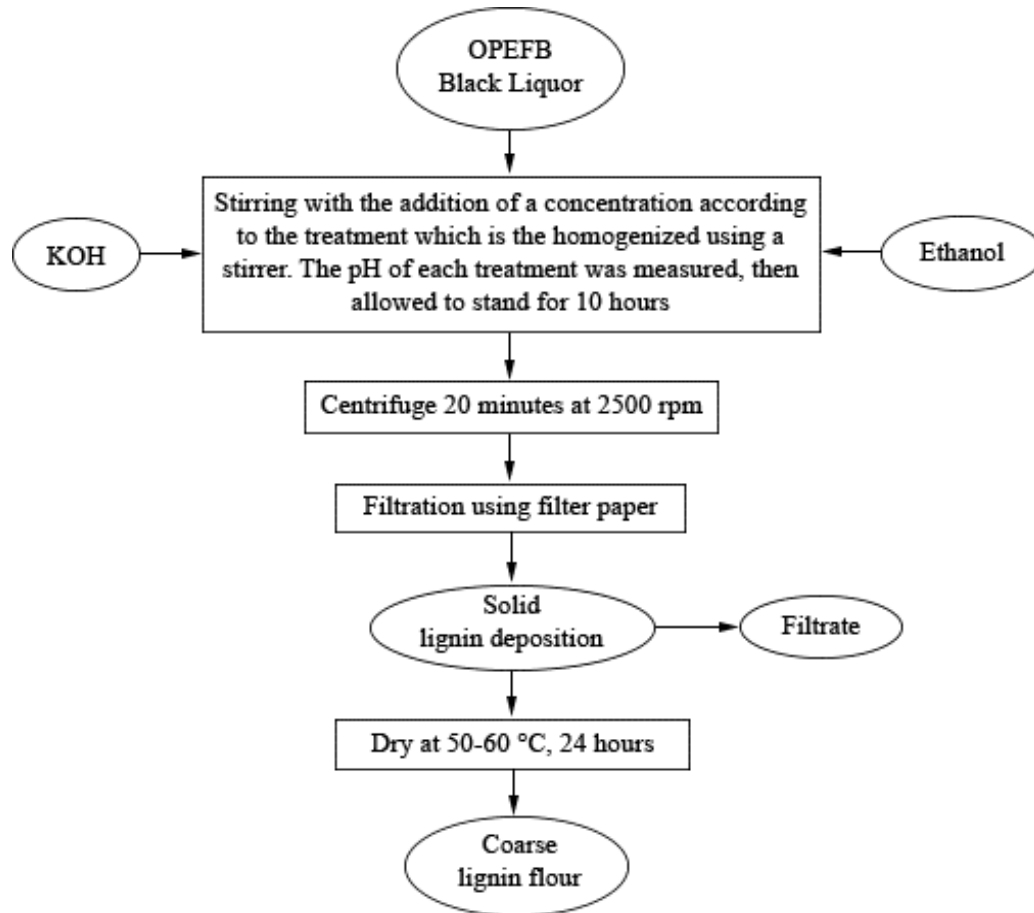
124 The formacell pulping was conducted in the autoclave at a liquor-to-particle ratio of 15:1  
125 for 1 h at 130 °C. The ratio of liquor to OPEFB particle ratio of 15:1 was used based on our initial  
126 experimental trials in the laboratory considering the volumetric of OPEFB as a typical example of  
127 non-woody biomass. In this ratio, the OPEFB particles can be immersed completely in the  
128 chemical liquor. The ratio solvent of acetic acid and formic acid was 85:15 with the addition of  
129 HCl of 0.5% as the catalyst. The cooking liquor was collected after filtration and washing the  
130 completed softened OPEFB with fresh water at room temperature. This formacell BL was used  
131 for the next step.

## 132 **2.3 Lignin isolation**

133 The formacell BL obtained from the pulping process of 100 mL contained a total solid  
134 content of around 25.10%. There are two methods for lignin isolation from formacell BL of  
135 OPEFB. The first one, i.e. the isolation of lignin from BL was conducted using KOH with a  
136 concentration of 2.5%; 5%; 7.5%; 10%; 12.5%; and 15% (w/v). The second isolation technique  
137 used ethanol at concentrations of 5%, 10%, 15%, 20%, 25 and 30% (v/v). As much as 100 mL of  
138 the KOH or ethanol solution was added into 100 mL BL, then stirred and measured the pH of the  
139 liquor was. The solution was allowed to stand for 10 hours, then centrifugated for 20 minutes at  
140 2500 rpm, and then separated using filter paper. The precipitated lignin was then oven-dried at  
141 50-60 °C for 24 h. Dried lignin was crushed manually to produce fine lignin powder (Fig. 1). The  
142 experiment was conducted in triplicate.

143 The data were calculated and presented in average and standard deviation tables and  
144 graphs. Observations made were pH value, the yield of lignin, lignin methoxyl content, the  
145 equivalent weight of lignin, analysis of lignin with Fourier Transform Infra-Red spectroscopy  
146 (FTIR) spectrophotometer (Cary 630 FTIR, Agilent, Australia), and lignin morphology using a  
147 scanning electron microscope (SEM) (JEOL JSM 6510 LA, Japan).





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**Figure 1:** Flowchart of lignin isolation process using KOH/Ethanol.

#### 150 2.4 Lignin Yield

151 Lignin yield was calculated based on the method according to Kim [32], as presented in  
 152 Equation 1.

$$153 \quad \text{Lignin Yield (\%)} = \frac{a}{b} \times 100\% \quad (1)$$

154 **Notation :** a = weight of isolated lignin;

155 b = weight of lignin in black liquor

#### 156 2.5 Methoxyl content of lignin

157 The methoxyl content of lignin was determined by using the ASTM 15120-81 method  
 158 [33]. As much as 0.5 g of lignin was added to 5 mL of ethanol, following addition to 100 mL of  
 159 distilled water containing 1 g of NaCl, and made in the form of suspension. Neutralization was  
 160 performed using 0.1 N NaOH, given 6 drops of phenolphthalein (pp) indicator, then 25 mL of  
 161 0.25 N NaOH was added and homogenized in a closed state for 30 minutes at room temperature.  
 162 After that, 25 mL of 0.25 N HCl was added and titrated with 0.1 N NaOH until the end of the  
 163 lasting color change (at least 30 seconds). The methoxyl content of lignin was calculated according  
 164 to Equation 2 as follows.

$$\text{Methoxyl (\%)} = \frac{\text{ml NaOH} \times \text{N NaOH} \times 3.1}{\text{Berat sampel (gram)}} \times 100\% \quad (2)$$

## 166 **2.6 Lignin Equivalent Weight**

167 Isolated lignin equivalent weight was calculated using the method of Santoso [34]. 0.5 g  
168 lignin was put into 250 mL Erlenmeyer and moistened with 5 mL ethanol. The mixture is spiked  
169 with 1 g of NaCl which is then added with 100 mL of distilled water and 6 drops of phenolphthalein  
170 indicator. The solution was then titrated with 0.1 N NaOH until pH 7.5. The equivalent weight of  
171 isolated lignin was calculated by using Equation 3.

$$\text{Equivalent Weight} = \frac{1000 \times \text{gram sample}}{(\text{mLN}) \text{NaOH}} \quad (3)$$

## 173 **2.7 FT-IR analysis of isolated lignin**

174 As much as 1 mg isolated lignins were added with 150 mg KBr, pelletized, and then the  
175 samples were analyzed by FT-IR spectrophotometer (Cary 630 FTIR Agilent). The analysis was  
176 set at a wavenumber of  $4000 \text{ cm}^{-1}$  to  $400 \text{ cm}^{-1}$  (wavelength of 2.5–25  $\mu\text{m}$ ).

## 177 **2.7 SEM analysis**

178 Morphology of isolated lignin was carried out using Scanning Electron Microscope (SEM)  
179 (JEOL JSM 6510 LA) with 1000 x magnification.

# 180 **3 Results and Discussion**

## 181 **3.1 pH of liquor**

182 The pH of black liquor from formacell pulping OPEFB is  $0.59 \pm 0.01$ , indicating that the  
183 liquor is acidic; thus, base or ethanol can be used to precipitate lignin from BL. To speed up the  
184 reaction, solvents such as acetic acid and formic acid are used in the formacell pulping process,  
185 along with HCl as a catalyst [31]. This process causes the pH of the formacell black liquor to  
186 become very acidic. Zhuang et al. [35] stated that formic acid and acetic acid could delignify  
187 lignin because of their acidic nature, so they can degrade lignin well. In another study, a  
188 combination of formic acid, acetic acid, and water achieved more than 50% lignin  
189 depolymerization in biomass [36]. The pH of the BL will be affected by the addition of KOH  
190 solution. According to the research, the pH value obtained from formacell pulping added with  
191 KOH solution ranged from  $2.43 \pm 0.07$  to  $4.27 \pm 0.35$  (Table 1), while the addition of ethanol  
192 concentrations can slightly increase the pH value from  $1.0 \pm 0.01$  to  $1.29 \pm 0.03$ . According to the  
193 findings, KOH has a greater effect on increasing pH than ethanol due to the strong base property  
194 of KOH.

195 The pH steadily increased as an upsurging concentration of KOH, where the lowest pH,  
196  $2.43 \pm 0.07$ , was obtained from 2.5% KOH, and the highest was a pH of  $4.27 \pm 0.35$  from KOH  
197 15%. Increasing the concentration of KOH solution causes more  $\text{OH}^-$  ions in the black liquor so  
198 that the pH of the solution becomes more alkaline. It can also be explained that KOH is a strong  
199 base. The stronger the base, the more  $\text{OH}^-$  ions are released, increasing the pH of the solution  
200 and making it more alkaline. Ethanol has a higher pKa than KOH, indicating a weaker acid.

201 Unlike KOH, increasing the ethanol concentration slightly increased the pH, with the lowest  
202 being 1 and the highest being 1.29 after adding 5% and 30%, as shown in Table 1.

203 **Table 1:** Effect of KOH and ethanol concentrations on pH, yield, methoxyl content, and an  
204 equivalent weight of isolated lignin.

Treatment	pH	Yield (%)	Lignin methoxyl (%)	Equivalent Weight
KOH concentration (%)				
2.5	2.43±0.07	3.57±0.38	13.06±0.9	1372.94±26.73
5.0	2.94±0.06	4.85±1.12	12.94±1.31	655.73±45.16
7.5	3.21±0.1	8.63±1.41	12.81±0.84	528.74±54.44
10	3.61±0.15	11.20±2.69	12.36±0.9	510.33±49.05
12.5	3.86±0.15	12.78±0.78	11.33±0.4	476.25±34.61
15	4.27±0.35	14.95±1.10	10.13±1.42	427.03±44.20
Ethanol concentration (%)				
5	1.00±0.01	1.95±0.18	17.03±0.42	449.88±48.47
10	1.08±0.06	2.27±0.317	16.45±1.44	624.67±59.2
15	1.15±0.07	1.69±0.091	15.05±1.03	767.97±56.6
20	1.20±0.047	1.77±0.207	14.47±1.17	896.95±64.15
25	1.22±0.056	1.44±0.174	13.14±1.78	1521.16±72.10
30	1.29±0.03	1.08±0.179	11.99±1.20	2123.02±70.72

205

206

### 207 **3.2 Lignin yield**

208 The lignin yield from adding KOH solution at various concentrations in isolation of BL  
209 ranged from  $3.57 \pm 0.38$  to  $14.95 \pm 1.10$  (Table 1). In comparison, ethanol isolation resulted in  
210 lower lignin yields of about  $0.51 \pm 0.00$  to  $1.06 \pm 0.00$ . The highest lignin yield was produced at a  
211 concentration of 15% KOH solution ( $14.95\% \pm 1.10$ ). Increasing the concentration of KOH  
212 solution caused the lignin yield to increase. It can be affected by the increasing concentration of  
213 an alkaline solution (KOH) that facilitates easier breaking of lignin bonds with other compounds,  
214 and a condensation reaction occurs in the lignin constituent units [37]. It is also supported by  
215 Sundin's [38] who stated that lignin deposition from BL due to the protonation of phenol groups  
216 on lignin molecules caused by the addition of  $\text{OH}^-$  ions from KOH. It reduces the electrostatic  
217 force between lignin molecules, resulting in the deposition of lignin (reduced solubility). The  
218 more  $\text{OH}^-$  ions, the more lignin deposits will form. The deposit lignin increase occurred because  
219 of an increase in ionic strength and protonation. The protonation of the phenolic group in lignin  
220 leads the lignin nucleus to form aggregates when the pKa value of lignin is reached [39].

221 The lignin yield with KOH liquor treatment is higher than that of NaOH, as reported by  
222 Hidayati et al. [20]. Lignin was isolated from formacell black liquor of OPEFB by using NaOH,  
223 producing lignin yields ranging from 1.48% to 5.67%. It might be caused by the stronger base of

224 KOH than NaOH. As seen in the periodic system, the metal  $\text{Na}^+$  and  $\text{K}^+$  are included in Group 1A.  
225 This is also related to the lower nature of alkali metal bases; the stronger, the lower the metal, the  
226 more easily reduced. Besides pH, temperature and ionic strength also affect lignin solubility. The  
227 molecular weight distribution in lignins is related to yield [40]. Both molecular weight and the  
228 ratio of phenols to aromatic units contribute to the solubility of lignin [40]. The changes in lignin  
229 yield in isolation by adding ethanol concentration are very low. The very low electronegativity of  
230 ethanol can suggest it is due to the presence of carbon compounds that cannot precipitate lignin  
231 properly. In the absence of sulfide, delignification was slower in the Alcell process.

232 As opposed to KOH precipitation, increasing ethanol concentrations leads to almost 0%  
233 lignin recovery. This result was in agreement with the precipitation of lignin from *Miscanthus x*  
234 *giganteus*, where after the addition of 75% of ethanol, there was no lignin precipitated [41]. In the  
235 low concentration of ethanol, lignin precipitation is carried out by diluting liquor with water, and  
236 the solubility of lignin decreases, resulting in more lignin being recovered. In other words, when  
237 the water content in the ethanol is limited, most of the lignin is soluble in the system, and hence  
238 the aggregate is not formed.

239

### 240 **3.3 Methoxyl content in lignin**

241 Methoxyl is one of the chemical groups in lignin for identifying one of the characteristics of  
242 lignin. The methoxyl group in each type of lignin has different content because of the different  
243 structures of lignin types. Determining methoxyl contents gives information about the average C9  
244 units in lignin, and eventually, the unsaturated side chain and average oxygen content can be  
245 calculated [42]. The methoxyl content in KOH lignin ranged from  $10.13\% \pm 1.92$  to  $12.94\% \pm$   
246  $0.90$ , whereas the use of ethanol concentrations results in methoxyl contents between  $11.99 \pm$   
247  $0.02$  to  $17.03 \pm 0.5$  (Table 1). The highest methoxyl content in lignin was acquired from isolated  
248 lignin by adding a 2.5% KOH solution. Increasing the concentration of KOH and ethanol solution  
249 leads to a decrease in the methoxyl content of isolated lignins. This may be due to the use of  
250 KOH as a strong base as a precipitating solution, which allows some methoxyl groups to degrade  
251 and transform into other compounds. This decrease in methoxyl content can be influenced by the  
252 disruption of structural stability in lignin caused by the addition of KOH. Furthermore, according  
253 to the pathway proposed by Yin et al., the removal of the methoxy group in lignin created a  
254 higher hydroxyl group of lignin by KOH solution. The presence of potassium in lignin isolation  
255 decreased the methoxyl content due to cleavage  $\text{C}\alpha\text{—C}\beta$  through  $\text{C}\beta\text{—O}$  bond. This cleavage  
256 leads to the removal of side chains such as methoxy. The mechanism of this reaction has been  
257 proved by Yin et al. [43].

258 The various methoxyl content in lignin depends on the source of lignin and the  
259 delignification process used. Generally, high methoxyl content will inhibit lignin reactivity during  
260 use in the resin field. Lignin has phenolic hydroxyl groups that are typically linked to nearby  
261 phenyl propane units, allowing lignin to connect with formaldehyde in a way analogous to phenol  
262 and formaldehyde [44]. Molecular weight and lignin purity are important factors during the  
263 production of biocarbon fibers [44, 45].

264 In the case of lignin application as an adhesive raw material, the low methoxyl content is  
265 more beneficial because it will increase the reactivity of aromatic nuclei in lignin [46]. It will  
266 facilitate the reaction of methylation or hydroxymethylation with adhesive-forming reactants such  
267 as NaOH and formaldehyde, hinting at the ease of gel formation. Recently, Gendron et al.  
268 compared four types of lignin for green adhesive, where the lowest methoxyl content of lignin  
269 had the highest water solubility and shear resistance as an adhesive [47].

270 The lignin standard of Indulin AT has a methoxyl content of around 13.5% - 14.5% [48], so  
271 the methoxyl contents in isolated lignin in this study are still lower. Meanwhile, compared to  
272 methoxyl content by Hidayati et al. [20] with a value of 14.61% - 20.77% by using NaOH as  
273 precipitating solution, the results of this study are also lower. These results are probably  
274 influenced by the use of KOH, which is classified as a strong base with a higher reactivity than  
275 NaOH, as seen from the periodic system. The influence of harsh chemicals and temperature  
276 during isolation causes the structure of lignin to undergo many changes, including the methoxyl  
277 group. The methoxyl group is degraded and transformed into other degradation compounds such  
278 as aromatic hydrocarbon and phenolic types, resulting in lower methoxyl content [49].

### 279 **3.4 The equivalent weight of lignin**

280 The determination of the equivalent weight of lignin is intended to determine the  
281 molecular weight of lignin to identify lignin degradation and condensation reactions. The  
282 molecular weight of lignin is an important property that influences biomass recalcitrance and  
283 lignin value. Determination of the molecular weight of lignin in the original biomass depends on  
284 the source of the raw material used, chemicals used for isolation, and purification methods [50,  
285 51]. Based on the results, the equivalent weight of lignin from the KOH solution ranged from  
286  $427.03 \pm 74.20$  to  $1372.94 \pm 269.73$ , whereas the addition of ethanol concentration resulted in  
287 molecular weights ranging from  $449.88 \pm 1.9$  to  $2123.03 \pm 27.5$  (Table 1).

288 Increasing the concentration of KOH solution resulted in a decrease in lignin equivalent  
289 weight so that the lowest value at 15% KOH solution concentration was  $427.03 \pm 74.20$ . This  
290 might be attributed to the increasing addition of a KOH solution as a strong base will degrade a  
291 portion of lignin into a derivative compound with shorter chains. It can degrade lignin resulting in  
292 a low equivalent weight. According to Patil et al., there are two routes for lignin depolymerization:  
293 harsh and moderate, resulting in different lignin structures [52]. The average molecular weight of  
294 lignin decreases with increasing precipitation of lignin yield by KOH. It was shown that  
295 increasing the amount of lignin with lower molecular weight deposited a high yield of lignin.  
296 Lignin is degraded into smaller fragments so that there are more phenolic groups with lower  
297 molecular weights [53]. The product's molecular weight can be lowered by increasing salt  
298 concentration [54, 55].

299 According to Gellerstedt [56], the termination of methyl aryl ether bonds from the aromatic  
300 ring of lignin resulted in decreased methoxyl content and low molecular weight of lignin due to  
301 the lignin degradation process. Based on several previous studies, lignin molecular weight values  
302 were obtained, namely 2500 - 14,000 [57], and 1327.64 - 1787.23 [20]. In contrast, the equivalent

303 weight of Indulin AT reached 3357 - 3366 [58]. This shows that the equivalent weight value of  
304 lignin varies greatly.

305 Lignin that has a high molecular weight can be used as a matrix in polyolefin composites,  
306 because a higher molecular mass of lignin has a better affinity with the matrix [59], while lignin  
307 with a lower molecular weight can be used for the development of phenol-formaldehyde resins,  
308 antioxidants, adhesives, and paints due to their higher reactivity than high molecular weight  
309 lignin [59].

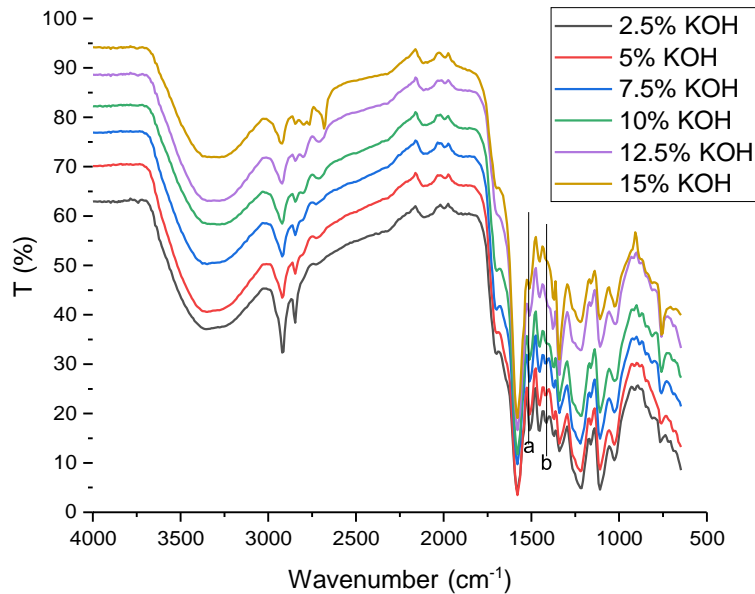
310 Differences in elemental composition, functional group types, proportions, and molecular  
311 weight in lignin molecules provide opportunities to use lignin in a variety of value-added  
312 applications. Some factors that influence the molecular weight of lignin are the diversity of lignin  
313 isolation procedures, macromolecular degradation during isolation, the effect of condensation  
314 mainly on acidic conditions, the apparent polydispersity of dissolved lignin, inadequate  
315 determination methods used to characterize the isolated lignin, and uncertainties in the properties  
316 of lignin. Because lignin is heterogeneous and inconstant, characterizing native lignin is also  
317 difficult [60].

318 The molecular weight of lignin is very important in the development of such polymeric  
319 products; similarly, low-molecular-weight lignin isolated from wheat straw by acetic acid pulping  
320 is an ideal feedstock for adhesive manufacturing [61]. Doherty et al. [62] stated that lignin from  
321 the soda process of wheat plants ranges from 1700 with a methoxyl content of 16. The organosolv  
322 pulping process at bagasse produces a molecular weight of around 2000 and a methoxyl content  
323 of 15.1. Lignin produced in the isolation process using alcohol or alcell process has a low  
324 molecular weight ( $M_w < 900$ ) with low polydispersity, no sulfur, and low ash content, although  
325 the value depends on the analytical method. There is also a molecular weight of  $2580 \text{ g mol}^{-1}$   
326 with a polydispersity of 4.3. Sameni et al. compared four types of lignin from different isolation  
327 methods, where the highest  $M_w$  (13488) was obtained from the steam explosion process with a  
328 methoxyl content of 0.69. Meanwhile, with the same methoxyl content, the lowest  $M_w$  (2565)  
329 was derived from the kraft process [57]. Yun et al. reported that organosolv fractionation from  
330 native lignin decreased its molecular weight from 5070 to 1810 [23].

### 331 **3.6 Lignin Analysis with FT-IR Spectrophotometer**

332 FTIR was performed to analyze differences in the functional groups of lignin in the sample  
333 (Fig. 2 and 3). FTIR spectra analysis showed that the peak in the aromatic ring vibrations  
334 decreased with the absorption band at  $1446 \text{ cm}^{-1}$  (a) and  $1408 \text{ cm}^{-1}$  (b), especially in the  
335 treatment using the highest concentration of KOH (Figure 2) and ethanol (Figure 3). There are  
336 similarities in the wavelength of  $3500 \text{ cm}^{-1}$  to  $31090 \text{ cm}^{-1}$  which refer to the presence of  
337 hydrogen bonds in the hydroxyl group (alcohol and phenolic). A wavelength absorption of  $1587$   
338  $\text{cm}^{-1}$  and  $1513 \text{ cm}^{-1}$  indicates the aromatic lignin skeletal vibration [60]. Wavenumbers at  $1460$   
339  $\text{cm}^{-1}$  to  $1420 \text{ cm}^{-1}$  are associated with stretching wavelengths of CH (methyl and methylene) and  
340 CH deformation with aromatic ring stretching fields [63]. The peaks observed in the range of  
341  $1220 \text{ cm}^{-1}$  to  $1270 \text{ cm}^{-1}$  in all spectra may refer to the C-H deformation vibrations of the guaiacyl  
342 [64]. The bands at  $1300 \text{ cm}^{-1}$  (syringyl) and  $1200 \text{ cm}^{-1}$  (guaiacyl) indicate the presence of both

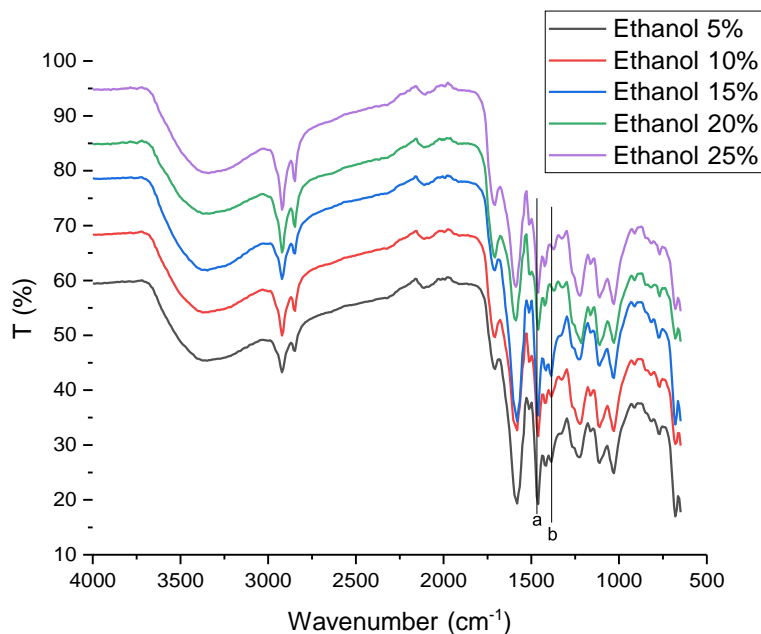
343 syringyl and guaiacyl in lignin's chemical structure as the unique peaks of lignin precursor [65].  
344 A similar peak was also found in kraft lignin isolated from *Acacia mangium* black liquor [27]. In  
345 general, peaks in Fig. 2 and 3 show that the treatment using KOH had a sharper peak than that of  
346 ethanol treatment. However, no difference in the peaks resulting from these two treatments was  
347 determined. Hidayati et al. [20] reported the experiment in isolated lignin from formacell black  
348 liquor of OPEFB using NaOH with the wave number of isolated lignin for guaiacyl lignin at  
349 around  $1273.02\text{ cm}^{-1}$ .



350

351

**Figure 2:** The FT-IR spectra of lignin using KOH isolation



**Figure 3:** The FT-IR spectra of lignin using ethanol isolation

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### 355 **3.7 Morphological observation**

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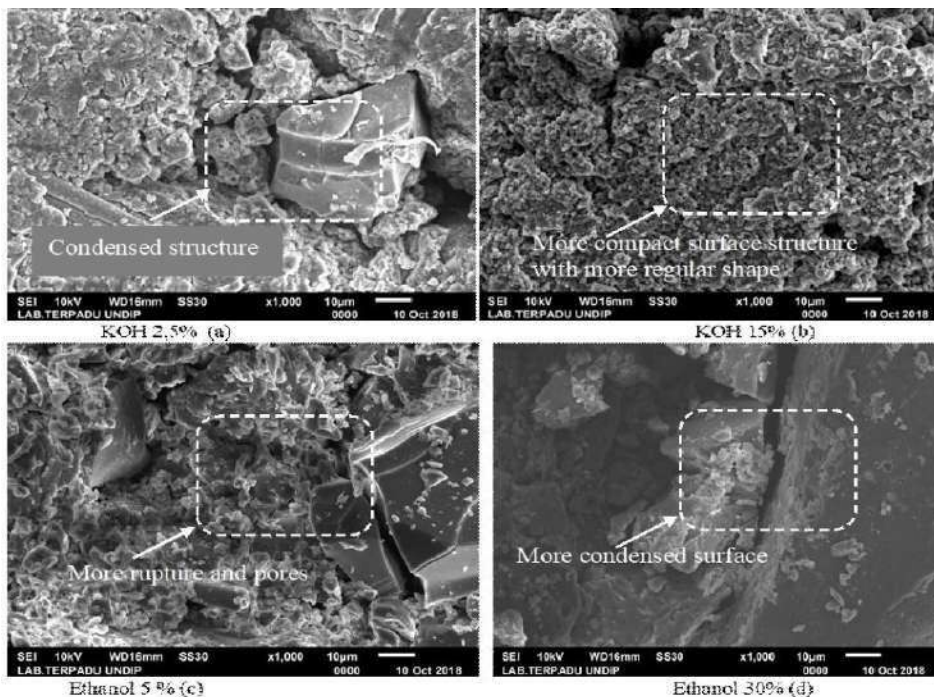
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Scanning Electron Microscope (SEM) was used to observe the size and morphology of lignin. In this study, SEM images were taken from the lowest and the highest concentration of KOH and ethanol as representative lignin morphology. As seen in Fig. 4, increasing the concentration of KOH acid from 2.5% to 15% showed differences in lignin morphology. Lignin isolation using 15% KOH (Fig. 4b) produced a more compact formation and morphology compared to lignin produced by isolation using 2.5% KOH concentration (Fig. 4a). In stark contrast, in treatment using ethanol appears that treatment with a 5% ethanol concentration resulted in a more condensed form and morphology than those using a 30% concentration. This result was in accordance with the findings reported by Solihat et al. [27] and Hamzah et al., [41] where increasing ethanol concentration created more rupture and amorphous lignin surface.





366

367 **Figure 4:** Morphological images of isolated lignin (a) KOH 2.5%, (b) KOH 15%, (c) ethanol 5%,  
 368 (d) ethanol 30% with 1000 x magnification

369

### 370 *3.8 Prospective Application of Formacell Lignin as Advanced Biocomposite Products*

371 The lignin molecule contains a variety of active functional groups, including aliphatic  
 372 hydroxyl (Al-OH), phenolic hydroxyl (Ph-OH), carboxyl (-COOH), carbonyl (-C=O), and  
 373 methoxy groups (-OCH<sub>3</sub>), which determine its properties, chemistry, and reactivity of lignin.  
 374 Lignin's chemical properties enable it and its derivatives to be used as high-value materials. The  
 375 lignin molecule can be used in a variety of value-added applications due to differences in  
 376 molecular weight, elemental composition, and the types and proportions of functional groups.  
 377 Currently, Saražin et al. investigated the potency of organosolv lignin-based non-isocyanate  
 378 polyurethane for wood adhesive and the result demonstrated satisfactory mechanical properties  
 379 [66] and its curing kinetics for interior furniture showed that it was more suitable than urea-  
 380 formaldehyde (UF) adhesive [67]. Sulfur-free lignin is produced by isolating lignin from the  
 381 formacell process. Most value-added applications prefer lignin with a lower percentage of sulfur  
 382 and ash. For example, sulfur-free lignin is preferred for use in aerogel composites. Joul et al.  
 383 reacted lignin isolated by organic acid with 5-methylresorcinol-formaldehyde to create aerogel  
 384 and according to the data, formacell lignin had good reactivity to create a high surface area of  
 385 aerogel [68]. According to Talabi et al., lignin with rich hydroxyl carbon, low molecular weight,  
 386 and less in the methoxyl group was suitable for lignin-based-formaldehyde resin with a 73%  
 387 graphitization level [69], and hence formacell lignin with higher KOH and ethanol concentrations  
 388 are appropriate for this application. Meanwhile, the high molecular weight of lignin is preferred  
 389 as a matrix in carbon fiber composites because it improves the mechanical performance of the  
 390 fiber.

391

**392 4 Conclusions**

393 A strong base, such as KOH, was used to successfully isolate lignin from oil palm empty  
394 fruit bunch formacell BL (OPEFB). Some identified lignin peaks can be found in the FTIR  
395 spectra, with no significant difference between lignins isolated with KOH and ethanol. The  
396 addition of KOH solution at 12.5 and 15% concentrations is the more effective method for  
397 isolating lignin from formacell BL. At this condition, isolated lignins have pH values of 3.86 and  
398 4.27, lignin yield of 2.78 and 14.95%, methoxyl content of 11.33 and 10.13, and lignin equivalent  
399 weights of 476.25 and 427.03, respectively. **The lignin produced by the isolation process using  
400 KOH and ethanol was characterized by the low methoxy content and a low molecular weight that  
401 created its higher reactivity. According to these properties, lignin derived from formacell is  
402 suitable for developing green, bio-based additives in biocomposite applications such as wood  
403 adhesives from non-isocyanate polyurethane, coatings, lignin-based-formaldehyde resins,  
404 formaldehyde scavengers, composite fillers, and other value-added industrial applications.**

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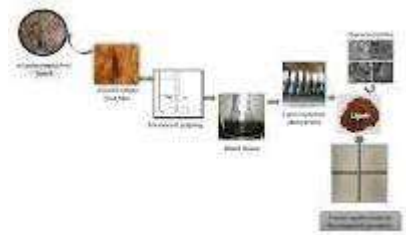
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31 **ARTICLE**

32 **Characterization of Formacell Lignin Derived from Black Liquor as a**  
33 **Potential Green Additive for Advanced Biocomposites**

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**ABSTRACT**

Black liquor is obtained as a by-product of the pulping process, used to convert biomass into pulp by removing lignin, hemicelluloses and other extractives from wood to free cellulose fibers. Lignin represents a major constituent in black liquor with quantities varying from 20% to 30%, of which a very low share is used for manufacturing value-added products, while the rest is mainly burned for energy purposes, thus underestimating its great potential as a raw material. Therefore, it is essential to establish new isolation and extraction methods to increase lignin valorization in the development of bio-based chemicals. The aim of this research work was to determine the effect of KOH or ethanol concentration as an isolation agent on lignin yields and the chemical characteristics of lignin isolated from formacell black liquor of oil palm empty fruit bunch (OPEFB). Isolation of lignin was carried out using KOH with various concentrations ranging from 5% to 15% (w/v). Ethanol was also used to precipitate lignin from black liquor at concentrations varying from 5% to 30% (v/v). The results obtained showed that the addition of KOH solution at 12.5% and 15% concentrations resulted in better lignin yield and chemical properties of lignin, i.e., pH values of 3.86 and 4.27, lignin yield of 12.78 and 14.95%, methoxyl content of 11.33 and 10.13%, and lignin equivalent weights of 476.25 and 427.03, respectively. Due to its phenolic structure and rich functional groups that are favorable for modifications, lignin has the potential to be used as green additive in the development of advanced biocomposite products in various applications to replace current fossil fuel-based material, ranging from fillers, fire retardants, formaldehyde scavengers, carbon fibers, aerogels, and wood adhesives.

**KEYWORDS**

formacell black liquor; lignin properties; KOH; ethanol; oil palm empty fruit bunch; advanced biocomposite

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57

**58 1 Introduction**

59 Global challenges such as food security and environmental threats can be treated by applying the  
60 circular bioeconomy principles, including sustainable conversion of biomass components into  
61 bio-based products as green alternatives to their petroleum-based counterparts, thus closing the  
62 material resource loops [1]. Black liquor (BL) is liquid waste left over from cooking pulp, aimed  
63 at removing lignin, hemicelluloses, and other extractable constituents from wood in order to free  
64 the cellulose fibers. Lignin is the main organic substance in BL, reaching 45% dry weight [2].  
65 About 150 billion tons of BL are released from the pulp and paper industry, where every 1 ton of  
66 pulp production will produce 7 tons of BL [3]. Taking into account the increased production of  
67 bioethanol, this availability is projected to reach 225 million tons annually in 2030 [4-6].  
68 However, only 2-5% of BL has been valorized into biomaterial [7] and the rest for energy  
69 purposes [8-10]. Hence, it is important to develop new techniques aimed at increasing the  
70 valorization of lignin as a renewable feedstock in various value-added industrial applications.  
71 Lignin is a complex polyphenol compound with a complex three-dimensional chemical structure  
72 that is difficult to decompose naturally, so it has the potential to cause water pollution if  
73 discharged into the environment [11]. Lignin has a highly aromatic structure that is stable to heat  
74 and has high carbon content. In addition, lignin contains various functional groups, e.g., aliphatic,  
75 phenolic, methoxyl, and carbonyl hydroxyl groups, allowing its modification. Thus, it can be used  
76 in many functional applications such as biomass-based fuels, adhesives, flame retardants,

77 dispersants, and surfactant formulations, as antioxidants in plastics and rubbers, dyes, synthetic  
78 floors, thermosets, paints, food packaging, filler in adhesives, seed coatings, automotive devices,  
79 3D printing, and fuels for highway maintenance [12-17]. However, the utilization of lignin is still  
80 limited on an industrial scale due to the inhomogeneity of structure.

81 A lignin component is a phenylpropane unit with several different methoxy groups [18].  
82 Chemical structures of lignin are identified by the presence of polypropene units such as p-  
83 hydroxyphenyl (or p-coumaryl alcohol), guaiacyl (or coniferyl alcohol), and syringyl (or sinapyl  
84 alcohol), and their percentage vary depending on the botanical origin. Polypropene units can be  
85 chemically bonded in different bonding patterns where the  $\beta$ -O-4 aryl glycerol ether bond is the  
86 primary linkage [19]. However, the technical lignin's structure differs from the native lignin and  
87 depends on the pulping method used. Besides, the source of raw materials and isolation method,  
88 including the type of chemical used and temperature, play critical roles in the physicochemical  
89 properties of lignin [20].

90 Lignin can be extracted in powder form from BL with proper chemical treatment and  
91 screening process [21]. Precipitation of lignin in the BL occurs due to the condensation reaction  
92 on the lignin constituent units, which were initially soluble and will be polymerized and form  
93 large molecules [22]. Base, acid, and organic solvents are common solutions to isolate lignin  
94 from BL. The process of lignin separation using organic solvents is known as the alcell or  
95 organosolv process [23]. This method is popular for breaking down lignin fractions [24]. The  
96 benefits of this method include obtaining lignin with a low molecular weight that is free of sulfur,  
97 and its application can be improved through fractionation or chemical modification [25] but  
98 organosolv fractionation is laborious work [26]; hence, acid and base deposition methods are  
99 more feasible. However, this method depends on the pH of the liquor, residence time, and  
100 temperature [22]. Some acids such as  $H_2SO_4$ , phosphoric acid ( $H_3PO_4$ ), or HCl have been  
101 reported in isolating lignin from base BL, such as from the kraft process [27]. Meanwhile, lignin  
102 from formacell BL, BL derived from acetic acid, or formic acid as cooking liquid can be released  
103 by different alkalis, especially KOH,  $Ca(OH)_2$ , and NaOH [20]. KOH, a strong base, is stronger  
104 than NaOH and its use is expected to result in higher lignin yield.

105 Based on Miller et al. [28], a strong base (e.g., NaOH and KOH) provides a higher result in  
106 lignin yield than a weak base, and it would be a promising technique for depolymerizing lignin.  
107 The concentration of base is important to measure because it will influence selectivity, chemical-  
108 physical properties, and lignin yield [20, 29]. Recently, Hidayati et al. evaluated the effect of  
109 NaOH concentration on lignin properties [20] while the disadvantage of NaOH was  
110 monoaromatic re-condensation led to the higher molecular weight of lignin [30]. Consequently,  
111 an alternative base such as KOH and ethanol is needed to overcome this problem. To date, no one  
112 reported lignin isolation from formacell BL using different concentrations of KOH and ethanol.  
113 Therefore, this study aimed to determine the effect of KOH and ethanol concentrations on the  
114 yield and chemical characteristics of lignin isolated from formacell BL of oil palm empty fruit  
115 bunch (OPEFB).

## 116 2 Material and Methods

**117 2.1 Materials**

118 Black liquor used in this research is a by-product of the formacell pulping of OPEFB, as  
119 reported by Hidayati et al. [31]. The pulping conditions are presented in detail in the next section.  
120 OPEFB was obtained from PTPN Business Unit VII Central Lampung Bekri, Indonesia.  
121 Meanwhile, KOH, NaCl, NaOH, HCl, and ethanol were supplied by Merck (Darmstadt,  
122 Germany).

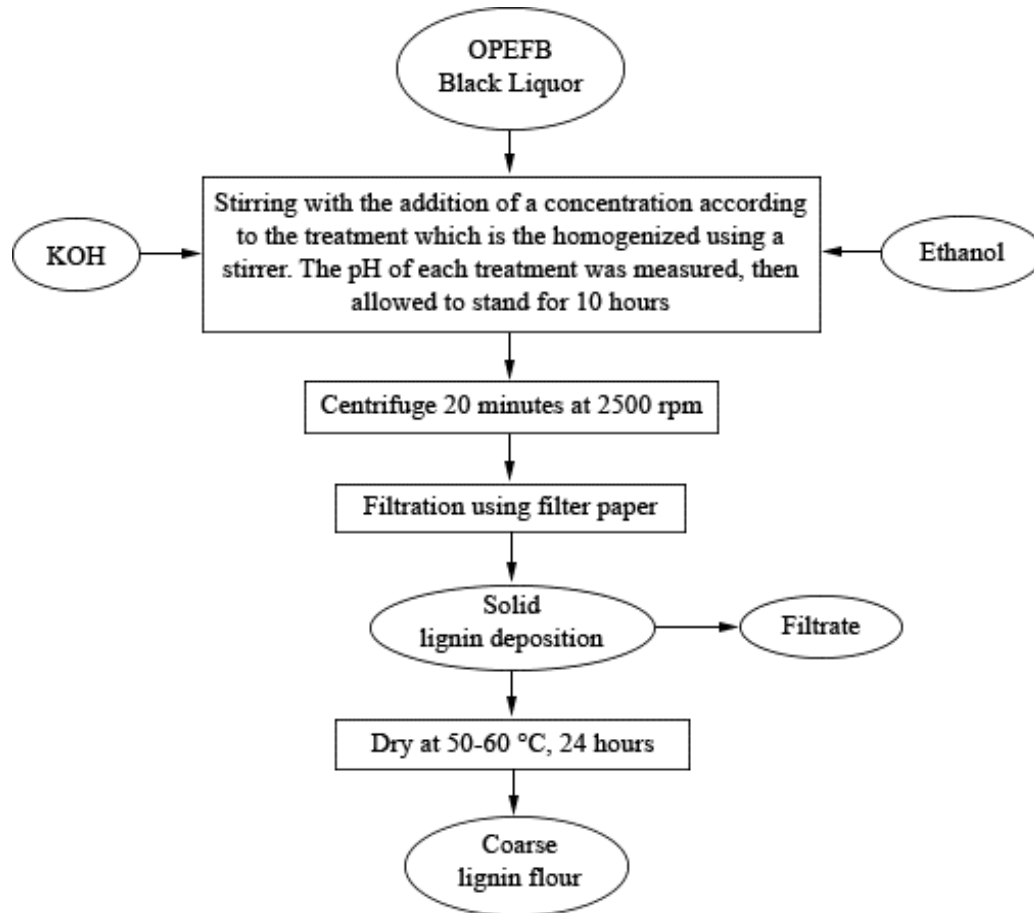
**123 2.2 Pulping process**

124 The formacell pulping was conducted in the autoclave at a liquor-to-particle ratio of 15:1  
125 for 1 h at 130 °C. This ratio of liquor to OPEFB particle ratio was used based on our initial  
126 experimental trials in the laboratory considering the volumetric of OPEFB as a typical example of  
127 non-woody biomass. In this ratio, the OPEFB particles can be immersed completely in the  
128 chemical liquor. The ratio solvent of acetic acid and formic acid was 85:15 with the addition of  
129 HCl of 0.5% as the catalyst. The cooking liquor was collected after filtration and washing the  
130 completed softened OPEFB with fresh water at room temperature. This formacell BL was used  
131 for the next step.

**132 2.3 Lignin isolation**

133 The formacell BL obtained from the pulping process of 100 mL contained a total solid  
134 content of around 25.10%. There are two methods for lignin isolation from formacell BL of  
135 OPEFB. The first one, i.e. the isolation of lignin from BL was conducted using KOH with a  
136 concentration of 2.5%; 5%; 7.5%; 10%; 12.5%; and 15% (w/v). The second isolation technique  
137 used ethanol at concentrations of 5%, 10%, 15%, 20%, 25 and 30% (v/v). As much as 100 mL of  
138 the KOH or ethanol solution was added into 100 mL BL, then stirred and measured the pH of the  
139 liquor was. The solution was allowed to stand for 10 hours, then centrifugated for 20 minutes at  
140 2500 rpm, and then separated using filter paper. The precipitated lignin was then oven-dried at  
141 50-60 °C for 24 h. Dried lignin was crushed manually to produce fine lignin powder (Fig. 1). The  
142 experiment was conducted in triplicate.

143 The data were calculated and presented in average and standard deviation tables and  
144 graphs. Observations made were pH value, the yield of lignin, lignin methoxyl content, the  
145 equivalent weight of lignin, analysis of lignin with Fourier Transform Infra-Red spectroscopy  
146 (FTIR) spectrophotometer (Cary 630 FTIR, Agilent, Australia), and lignin morphology using a  
147 scanning electron microscope (SEM) (JEOL JSM 6510 LA, Japan).



148

149

**Figure 1:** Flowchart of lignin isolation process using KOH/Ethanol.

#### 150 **2.4 Lignin Yield**

151 Lignin yield was calculated based on the method according to Kim [32], as presented in  
 152 Equation 1.

$$153 \quad \text{Lignin Yield (\%)} = \frac{a}{b} \times 100\% \quad (1)$$

154 **Notation :** a = weight of isolated lignin;

155 b = weight of lignin in black liquor

#### 156 **2.5 Methoxyl content of lignin**

157 The methoxyl content of lignin was determined by using the ASTM 15120-81 method  
 158 [33]. As much as 0.5 g of lignin was added to 5 mL of ethanol, following addition to 100 mL of  
 159 distilled water containing 1 g of NaCl, and made in the form of suspension. Neutralization was  
 160 performed using 0.1 N NaOH, given 6 drops of phenolphthalein (pp) indicator, and then 25 mL of  
 161 0.25 N NaOH was added and homogenized in a closed state for 30 minutes at room temperature.  
 162 After that, 25 mL of 0.25 N HCl was added and titrated with 0.1 N NaOH until the end of the  
 163 lasting color change (at least 30 seconds). The methoxyl content of lignin was calculated according  
 164 to Equation 2 as follows.



$$\text{Methoxyl (\%)} = \frac{\text{ml NaOH} \times \text{N NaOH} \times 3.1}{\text{Berat sampel (gram)}} \times 100\% \quad (2)$$

## 166 2.6 Lignin Equivalent Weight

167 Isolated lignin equivalent weight was calculated using the method of Santoso [34]. 0.5 g  
168 lignin was put into 250 mL Erlenmeyer and moistened with 5 mL ethanol. The mixture is spiked  
169 with 1 g of NaCl which is then added with 100 mL of distilled water and 6 drops of phenolphthalein  
170 indicator. The solution was then titrated with 0.1 N NaOH until pH 7.5. The equivalent weight of  
171 isolated lignin was calculated by using Equation 3.

$$\text{Equivalent Weight} = \frac{1000 \times \text{gram sample}}{(\text{mLN}) \text{NaOH}} \quad (3)$$

## 173 2.7 FT-IR analysis of isolated lignin

174 As much as 1 mg isolated lignin was added with 150 mg KBr, pelletized, and then the  
175 samples were analyzed by FT-IR spectrophotometer (Cary 630 FTIR Agilent). The analysis was  
176 set at a wavenumber of  $4000 \text{ cm}^{-1}$  to  $400 \text{ cm}^{-1}$  (wavelength of 2.5–25  $\mu\text{m}$ ).

## 177 2.7 SEM analysis

178 Morphology of isolated lignin was carried out using Scanning Electron Microscope (SEM)  
179 (JEOL JSM 6510 LA) with 1000 x magnification.

# 180 3 Results and Discussion

## 181 3.1 pH of the black liquor

182 The pH of BL from formacell pulping OPEFB is  $0.59 \pm 0.01$ , indicating that the liquor is  
183 acidic; thus, base or ethanol can be used to precipitate lignin from BL. To speed up the reaction,  
184 solvents such as acetic acid and formic acid are used in the formacell pulping process, along with  
185 HCl as a catalyst [31]. This process causes the pH of the formacell BL to become very acidic.  
186 Zhuang et al. [35] stated that formic acid and acetic acid could delignify lignin because of their  
187 acidic nature, so they can degrade lignin well. In another study, a combination of formic acid,  
188 acetic acid, and water achieved more than 50% lignin depolymerization in biomass [36]. The pH  
189 of the BL will be affected by the addition of KOH solution. According to the research, the pH  
190 value obtained from formacell pulping added with KOH solution ranged from  $2.43 \pm 0.07$  to  $4.27$   
191  $\pm 0.35$  (Table 1), while the addition of ethanol concentrations can slightly increase the pH value  
192 from  $1.0 \pm 0.01$  to  $1.29 \pm 0.03$ . According to the findings, KOH has a greater effect on increasing  
193 pH than ethanol due to the strong base property of KOH.

194 The pH steadily increased as an up-surgin concentration of KOH, where the lowest pH,  
195  $2.43 \pm 0.07$ , was obtained from 2.5% KOH, and the highest was a pH of  $4.27 \pm 0.35$  from KOH  
196 15%. Increasing the concentration of KOH solution causes more  $\text{OH}^-$  ions in the BL so that the  
197 pH of the solution becomes more alkaline. It can also be explained that KOH is a strong base. The  
198 stronger the base, the more OH ions are released, increasing the pH of the solution and making it  
199 more alkaline. Ethanol has a higher pKa than KOH, indicating a weaker acid. Unlike KOH,

200 increasing the ethanol concentration slightly increased the pH, with the lowest being 1 and the  
201 highest being 1.29 after adding 5% and 30%, as shown in Table 1.

202 **Table 1:** Effect of KOH and ethanol concentrations on pH, yield, methoxyl content, and an  
203 equivalent weight of isolated lignin.

Treatment	pH	Yield (%)	Lignin methoxyl (%)	Equivalent Weight
KOH concentration (%)				
2.5	2.43±0.07	3.57±0.38	13.06±0.9	1372.94±26.73
5.0	2.94±0.06	4.85±1.12	12.94±1.31	655.73±45.16
7.5	3.21±0.1	8.63±1.41	12.81±0.84	528.74±54.44
10	3.61±0.15	11.20±2.69	12.36±0.9	510.33±49.05
12.5	3.86±0.15	12.78±0.78	11.33±0.4	476.25±34.61
15	4.27±0.35	14.95±1.10	10.13±1.42	427.03±44.20
Ethanol concentration (%)				
5	1.00±0.01	1.95±0.18	17.03±0.42	449.88±48.47
10	1.08±0.06	2.27±0.317	16.45±1.44	624.67±59.2
15	1.15±0.07	1.69±0.091	15.05±1.03	767.97±56.6
20	1.20±0.047	1.77±0.207	14.47±1.17	896.95±64.15
25	1.22±0.056	1.44±0.174	13.14±1.78	1521.16±72.10
30	1.29±0.03	1.08±0.179	11.99±1.20	2123.02±70.72

204

205

### 206 **3.2 Lignin yield**

207 The lignin yield from adding KOH solution at various concentrations in isolation of BL  
208 ranged from  $3.57 \pm 0.38$  to  $14.95 \pm 1.10$  (Table 1). In comparison, ethanol isolation resulted in  
209 lower lignin yields of about  $0.51 \pm 0.00$  to  $1.06 \pm 0.00$ . The highest lignin yield was produced at a  
210 concentration of 15% KOH solution ( $14.95\% \pm 1.10$ ). Increasing the concentration of KOH  
211 solution caused the lignin yield to increase. It can be affected by the increasing concentration of  
212 an alkaline solution (KOH) that facilitates easier breaking of lignin bonds with other compounds,  
213 and a condensation reaction occurs in the lignin constituent units [37]. It is also supported by  
214 Sundin [38] who stated that lignin deposition from BL due to the protonation of phenol groups on  
215 lignin molecules caused by the addition of  $\text{OH}^-$  ions from KOH. It reduces the electrostatic force  
216 between lignin molecules, resulting in the deposition of lignin and reduced solubility. The more  
217  $\text{OH}^-$  ions, the more lignin deposits will form. The deposit lignin increase occurred because of an  
218 increase in ionic strength and protonation. The protonation of the phenolic group in lignin leads  
219 the lignin nucleus to form aggregates when the pKa value of lignin is reached [39].

220 The lignin yield with KOH liquor treatment is higher than that of NaOH, as reported by  
221 Hidayati et al. [20]. Lignin was isolated from formacell BL of OPEFB by using NaOH, producing  
222 lignin yields ranging from 1.48% to 5.67%. It might be caused by the stronger base of KOH than

223 NaOH. As seen in the periodic system, the metal Na<sup>+</sup> and K<sup>+</sup> are included in Group 1A. This is  
224 also related to the lower nature of alkali metal bases; the stronger, the lower the metal, the more  
225 easily reduced. Besides pH, temperature and ionic strength also affect lignin solubility. The  
226 molecular weight distribution in lignins is related to yield [40]. Both molecular weight and the  
227 ratio of phenols to aromatic units contribute to the solubility of lignin [40]. The changes in lignin  
228 yield in isolation by adding ethanol concentration are very low. The very low electronegativity of  
229 ethanol can suggest **the presence of carbon compounds that cannot precipitate lignin properly**. In  
230 the absence of sulfide, delignification was slower in the Alcell process.

231 As opposed to KOH precipitation, increasing ethanol concentrations leads to almost 0%  
232 lignin recovery. This result was in agreement with the precipitation of lignin from *Miscanthus x*  
233 *giganteus*, where after the addition of 75% of ethanol, there was no lignin precipitated [41]. In the  
234 low concentration of ethanol, lignin precipitation is carried out by diluting liquor with water, and  
235 the solubility of lignin decreases, resulting in more lignin being recovered. In other words, when  
236 the water content in the ethanol is limited, most of the lignin is soluble in the system, and hence  
237 the aggregate is not formed.

238

### 239 **3.3 Methoxyl content in lignin**

240 Methoxyl is one of the chemical groups in lignin for identifying one of the characteristics of  
241 lignin. The methoxyl group in each type of lignin has different content because of the different  
242 structures of lignin types. Determining methoxyl contents gives information about the average C9  
243 units in lignin, and eventually, the unsaturated side chain and average oxygen content can be  
244 calculated [42]. The methoxyl content in KOH lignin ranged from 10.13% ± 1.92 to 12.94% ±  
245 0.90, whereas the use of ethanol concentrations results in methoxyl contents between 11.99 ±  
246 0.02 to 17.03 ± 0.5 (Table 1). The highest methoxyl content in lignin was acquired from isolated  
247 lignin by adding a 2.5% KOH solution. Increasing the concentration of KOH and ethanol solution  
248 leads to a decrease in the methoxyl content of isolated lignins. This may be due to the use of  
249 KOH as a strong base as a precipitating solution, which allows some methoxyl groups to degrade  
250 and transform into other compounds. This decrease in methoxyl content can be influenced by the  
251 disruption of structural stability in lignin caused by the addition of KOH. Furthermore, according  
252 to the pathway proposed by Yin et al., the removal of the methoxy group in lignin created a  
253 higher hydroxyl group of lignin by KOH solution. The presence of potassium in lignin isolation  
254 decreased the methoxyl content due to cleavage C $\alpha$ —C $\beta$  through C $\beta$ —O bond. This cleavage  
255 leads to the removal of side chains such as methoxy<sup>1</sup>. The mechanism of this reaction has been  
256 proved by Yin et al. [43].

257 The various methoxyl content in lignin depends on the source of lignin and the  
258 delignification process used. Generally, high methoxyl content will inhibit lignin reactivity during  
259 use in the resin field. Lignin has phenolic hydroxyl groups that are typically linked to nearby  
260 phenyl propane units, allowing lignin to connect with formaldehyde in a way analogous to phenol  
261 and formaldehyde [44]. Molecular weight and lignin purity are important factors during the  
262 production of biocarbon fibers [44, 45].

263 In the case of lignin application as an adhesive raw material, the low methoxyl content is  
264 more beneficial because it will increase the reactivity of aromatic nuclei in lignin [46]. It will  
265 facilitate the reaction of methylation or hydroxymethylation with adhesive-forming reactants such  
266 as NaOH and formaldehyde, hinting at the ease of gel formation. Recently, Gendron et al.  
267 compared four types of lignin for green adhesive, where the lowest methoxyl content of lignin  
268 had the highest water solubility and shear resistance as an adhesive [47].

269 The lignin standard of Indulin AT has a methoxyl content of around 13.5% - 14.5% [48], so  
270 the methoxyl contents in isolated lignin in this study are still lower. Meanwhile, compared to  
271 methoxyl content by Hidayati et al. [20] with a value of 14.61% - 20.77% by using NaOH as  
272 precipitating solution, the results of this study are also lower. These results are probably  
273 influenced by the use of KOH, which is classified as a strong base with a higher reactivity than  
274 NaOH, as seen from the periodic system. The influence of harsh chemicals and temperature  
275 during isolation causes the structure of lignin to undergo many changes, including the methoxyl  
276 group. The methoxyl group is degraded and transformed into other degradation compounds such  
277 as aromatic hydrocarbon and phenolic types, resulting in lower methoxyl content [49].

### 278 **3.4 The equivalent weight of lignin**

279 The determination of the equivalent weight of lignin is intended to determine the  
280 molecular weight of lignin to identify lignin degradation and condensation reactions. The  
281 molecular weight of lignin is an important property that influences biomass recalcitrance and  
282 lignin value. Determination of the molecular weight of lignin in the original biomass depends on  
283 the source of the raw material used, chemicals used for isolation, and purification methods [50,  
284 51]. Based on the results, the equivalent weight of lignin from the KOH solution ranged from  
285  $427.03 \pm 74.20$  to  $1372.94 \pm 269.73$ , whereas the addition of ethanol concentration resulted in  
286 molecular weights ranging from  $449.88 \pm 1.9$  to  $2123.03 \pm 27.5$  (Table 1).

287 Increasing the concentration of KOH solution resulted in a decrease in lignin equivalent  
288 weight so that the lowest value at 15% KOH solution concentration was  $427.03 \pm 74.20$ . This  
289 might be attributed to the increasing addition of a KOH solution as a strong base will degrade a  
290 portion of lignin into a derivative compound with shorter chains. It can degrade lignin resulting in  
291 a low equivalent weight. According to Patil et al., there are two routes for lignin depolymerization:  
292 harsh and moderate, resulting in different lignin structures [52]. The average molecular weight of  
293 lignin decreases with increasing precipitation of lignin yield by KOH. It was shown that  
294 increasing the amount of lignin with lower molecular weight deposited a high yield of lignin.  
295 Lignin is degraded into smaller fragments so that there are more phenolic groups with lower  
296 molecular weights [53]. The product's molecular weight can be lowered by increasing salt  
297 concentration [54, 55].

298 According to Gellerstedt [56], the termination of methyl aryl ether bonds from the aromatic  
299 ring of lignin resulted in decreased methoxyl content and low molecular weight of lignin due to  
300 the lignin degradation process. Based on several previous studies, lignin molecular weight values  
301 were obtained, namely 2500 - 14,000 [57], and 1327.64 - 1787.23 [20]. In contrast, the equivalent

302 weight of Indulin AT reached 3357 - 3366 [58]. This shows that the equivalent weight value of  
303 lignin varies greatly.

304 Lignin that has a high molecular weight can be used as a matrix in polyolefin composites,  
305 because a higher molecular mass of lignin has a better affinity with the matrix [59], while lignin  
306 with a lower molecular weight can be used for the development of phenol-formaldehyde resins,  
307 antioxidants, adhesives, and paints due to their higher reactivity than high molecular weight  
308 lignin [59].

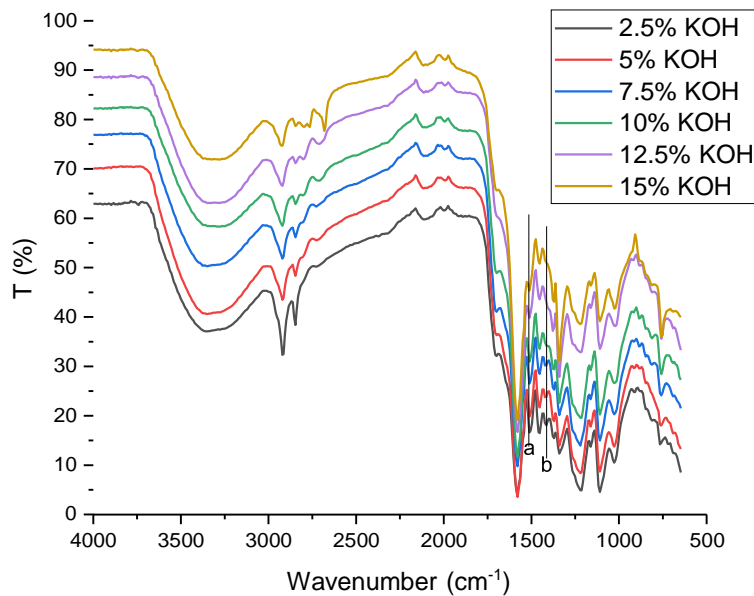
309 Differences in elemental composition, functional group types, proportions, and molecular  
310 weight in lignin molecules provide opportunities to use lignin in a variety of value-added  
311 applications. Some factors that influence the molecular weight of lignin are the diversity of lignin  
312 isolation procedures, macromolecular degradation during isolation, the effect of condensation  
313 mainly on acidic conditions, the apparent polydispersity of dissolved lignin, inadequate  
314 determination methods used to characterize the isolated lignin, and uncertainties in the properties  
315 of lignin. Because lignin is heterogeneous and inconstant, characterizing native lignin is also  
316 difficult [60].

317 The molecular weight of lignin is very important in the development of such polymeric  
318 products; similarly, low-molecular-weight lignin isolated from wheat straw by acetic acid pulping  
319 is an ideal feedstock for adhesive manufacturing [61]. Doherty et al. [62] stated that lignin from  
320 the soda process of wheat plants ranges from 1700 with a methoxyl content of 16. The organosolv  
321 pulping process at bagasse produces a molecular weight of around 2000 and a methoxyl content  
322 of 15.1. Lignin produced in the isolation process using alcohol or alcell process has a low  
323 molecular weight ( $M_w < 900$ ) with low polydispersity, no sulfur, and low ash content, although  
324 the value depends on the analytical method. There is also a molecular weight of  $2580 \text{ g mol}^{-1}$   
325 with a polydispersity of 4.3. Sameni et al. compared four types of lignin from different isolation  
326 methods, where the highest  $M_w$  (13488) was obtained from the steam explosion process with a  
327 methoxyl content of 0.69. Meanwhile, with the same methoxyl content, the lowest  $M_w$  (2565)  
328 was derived from the kraft process [57]. Yun et al. reported that organosolv fractionation from  
329 native lignin decreased its molecular weight from 5070 to 1810 [23].

### 330 **3.6 Lignin Analysis with FT-IR Spectrophotometer**

331 FTIR was performed to analyze differences in the functional groups of lignin in the sample  
332 (Fig. 2 and 3). FTIR spectra analysis showed that the peak in the aromatic ring vibrations  
333 decreased with the absorption band at  $1446 \text{ cm}^{-1}$  (a) and  $1408 \text{ cm}^{-1}$  (b), especially in the  
334 treatment using the highest concentration of KOH (Fig. 2) and ethanol (Fig. 3). There are  
335 similarities in the wavelength of  $3500 \text{ cm}^{-1}$  to  $31090 \text{ cm}^{-1}$  which refer to the presence of  
336 hydrogen bonds in the hydroxyl group (alcohol and phenolic). A wavelength absorption of  $1587$   
337  $\text{cm}^{-1}$  and  $1513 \text{ cm}^{-1}$  indicates the aromatic lignin skeletal vibration [60]. Wavenumbers at  $1460$   
338  $\text{cm}^{-1}$  to  $1420 \text{ cm}^{-1}$  are associated with stretching wavelengths of CH (methyl and methylene) and  
339 CH deformation with aromatic ring stretching fields [63]. The peaks observed in the range of  
340  $1220 \text{ cm}^{-1}$  to  $1270 \text{ cm}^{-1}$  in all spectra may refer to the C-H deformation vibrations of the guaiacyl  
341 [64]. The bands at  $1300 \text{ cm}^{-1}$  (syringyl) and  $1200 \text{ cm}^{-1}$  (guaiacyl) indicate the presence of both

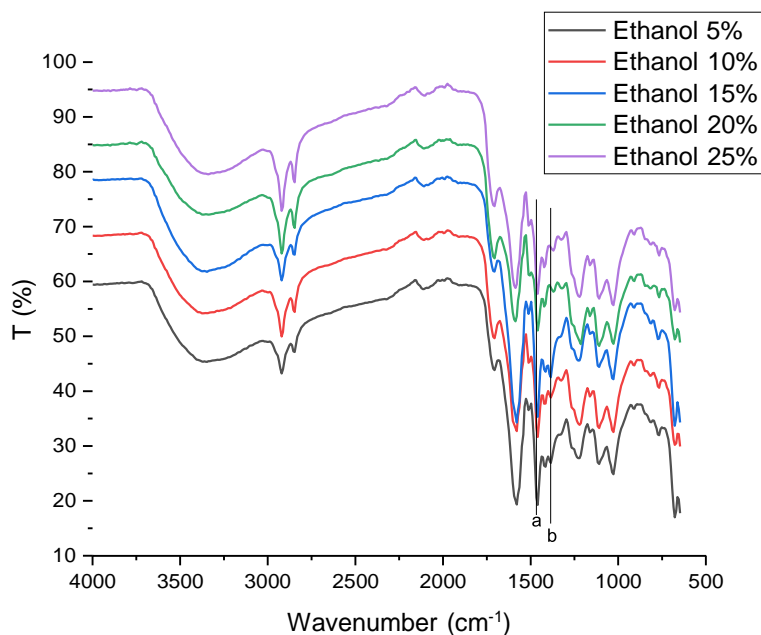
342 syringyl and guaiacyl in lignin's chemical structure as the unique peaks of lignin precursor [65].  
 343 A similar peak was also found in kraft lignin isolated from *Acacia mangium* black liquor [27]. In  
 344 general, peaks in Fig. 2 and 3 show that the treatment using KOH had a sharper peak than that of  
 345 ethanol treatment. However, no difference in the peaks resulting from these two treatments was  
 346 determined. Hidayati et al. [20] reported the experiment in isolated lignin from formacell BL of  
 347 OPEFB using NaOH with the wave number of isolated lignin for guaiacyl lignin at around  
 348  $1273.02\text{ cm}^{-1}$ .



349

350

**Figure 2:** The FT-IR spectra of lignin using KOH isolation



351

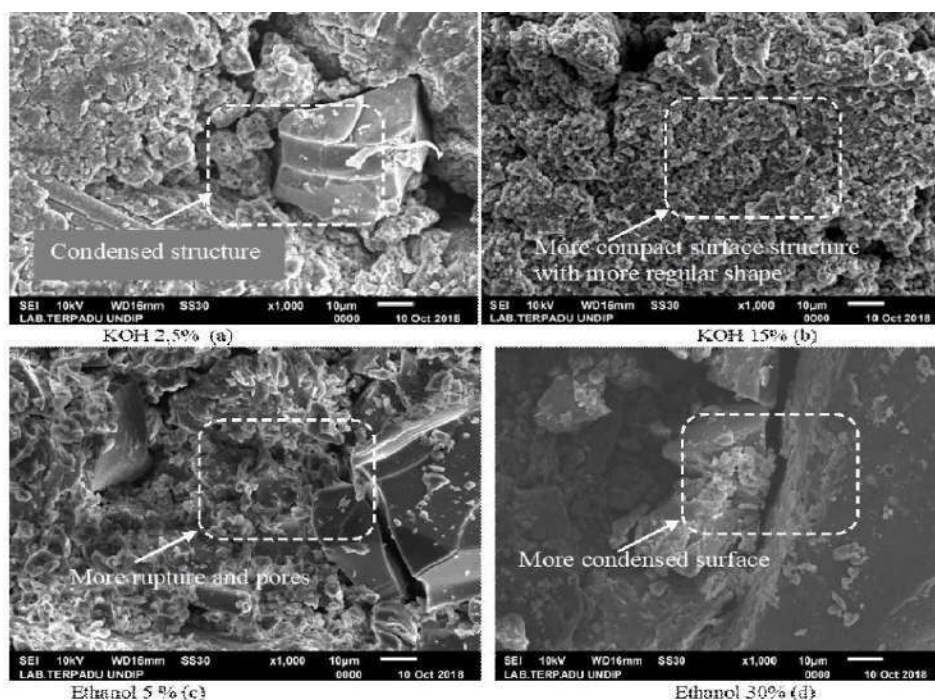
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**Figure 3:** The FT-IR spectra of lignin using ethanol isolation

353

354 **3.7 Morphological observation**

355 Scanning Electron Microscope (SEM) was used to observe the size and morphology of lignin.  
 356 In this study, SEM images were taken from the lowest and the highest concentration of KOH and  
 357 ethanol as representative lignin morphology. As seen in Fig. 4, increasing the concentration of  
 358 KOH acid from 2.5% to 15% showed differences in lignin morphology. Lignin isolation using 15%  
 359 KOH (Fig. 4b) produced a more compact formation and morphology compared to lignin  
 360 produced by isolation using 2.5% KOH concentration (Fig. 4a). In stark contrast, in treatment  
 361 using ethanol appears that treatment with a 5% ethanol concentration resulted in a more  
 362 condensed form and morphology than those using a 30% concentration. This result was in  
 363 accordance with the findings reported by Solihat et al. [27] and Hamzah et al. [41] where  
 364 increasing ethanol concentration created more rupture and amorphous lignin surface.



365

366 **Figure 4:** Morphological images of isolated lignin (a) KOH 2.5%, (b) KOH 15%, (c) ethanol 5%,  
 367 (d) ethanol 30% with 1000 x magnification

368

369 **3.8 Prospective Application of Formacell Lignin as Advanced Biocomposite Products**

370 The lignin molecule contains a variety of active functional groups, including aliphatic  
 371 hydroxyl (Al-OH), phenolic hydroxyl (Ph-OH), carboxyl (-COOH), carbonyl (-C=O), and  
 372 methoxy groups (-OCH<sub>3</sub>), which determine its properties, chemistry, and reactivity of lignin.  
 373 Lignin's chemical properties enable it and its derivatives to be used as high-value materials. The  
 374 lignin molecule can be used in a variety of value-added applications due to differences in  
 375 molecular weight, elemental composition, and the types and proportions of functional groups.  
 376 Currently, Saražin et al. investigated the potency of organosolv lignin-based non-isocyanate  
 377 polyurethane for wood adhesive and the result demonstrated satisfactory mechanical properties

378 [66] and its curing kinetics for interior furniture showed that it was more suitable than urea-  
379 formaldehyde (UF) adhesive [67]. Sulfur-free lignin is produced by isolating lignin from the  
380 formacell process. Most value-added applications prefer lignin with a lower percentage of sulfur  
381 and ash. For example, sulfur-free lignin is preferred for use in aerogel composites. Jõul et al.  
382 reacted lignin isolated by organic acid with 5-methylresorcinol-formaldehyde to create aerogel  
383 and according to the data, formacell lignin had good reactivity to create a high surface area of  
384 aerogel [68]. According to Talabi et al. lignin with rich hydroxyl carbon, low molecular weight,  
385 and less in the methoxyl group was suitable for lignin-based-formaldehyde resin with a 73%  
386 graphitization level [69], and hence formacell lignin with higher KOH and ethanol concentrations  
387 are appropriate for this application. Meanwhile, the high molecular weight of lignin is preferred  
388 as a matrix in carbon fiber composites because it improves the mechanical performance of the  
389 fiber.

390

#### 391 4 Conclusions

392 A strong base, such as KOH, was used to successfully isolate lignin from oil palm empty  
393 fruit bunch (OPEFB) formacell BL. Some identified lignin peaks can be found in the FTIR  
394 spectra, with no significant difference between lignins isolated with KOH and ethanol. The  
395 addition of KOH solution at 12.5 and 15% concentrations is the more effective method for  
396 isolating lignin from formacell BL. At this condition, isolated lignins have pH values of 3.86 and  
397 4.27, lignin yield of 2.78 and 14.95%, methoxyl content of 11.33 and 10.13%, and lignin  
398 equivalent weights of 476.25 and 427.03, respectively. The lignin produced by the isolation  
399 process using KOH and ethanol was characterized by the low methoxy content and a low  
400 molecular weight that created its higher reactivity. According to these properties, lignin derived  
401 from formacell is suitable for developing green, bio-based additives in biocomposite applications  
402 such as wood adhesives from non-isocyanate polyurethane, coatings, lignin-based-formaldehyde  
403 resins, formaldehyde scavengers, composite fillers, and other value-added industrial applications.

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ARTICLE

## Characterization of Formacell Lignin Derived from Black Liquor as a Potential Green Additive for Advanced Biocomposites

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### ABSTRACT

Black liquor is obtained as a by-product of the pulping process, which is used to convert biomass into pulp by removing lignin, hemicelluloses and other extractives from wood to free cellulose fibers. Lignin represents a major constituent in black liquor, with quantities varying from 20% to 30%, of which a very low share is used for manufacturing value-added products, while the rest is mainly burned for energy purposes, thus underestimating its great potential as a raw material. Therefore, it is essential to establish new isolation and extraction methods to increase lignin valorization in the development of bio-based chemicals. The aim of this research work was to determine the effect of KOH or ethanol concentration as an isolation agent on lignin yields and the chemical characteristics of lignin isolated from formacell black liquor of oil palm empty fruit bunch (OPEFB). Isolation of lignin was carried out using KOH with various concentrations ranging from 5% to 15% (w/v). Ethanol was also used to precipitate lignin from black liquor at concentrations varying from 5% to 30% (v/v). The results obtained showed that the addition of KOH solution at 12.5% and 15% concentrations resulted in better lignin yield and chemical properties of lignin, i.e., pH values of 3.86 and 4.27, lignin yield of 12.78% and 14.95%, methoxy content of 11.33% and 10.13%, and lignin equivalent weights of 476.25 and 427.03, respectively. Due to its phenolic structure and rich functional groups that are favorable for modifications, lignin has the potential to be used as a green additive in the development of advanced biocomposite products in various applications to replace current fossil fuel-based material, ranging from fillers, fire retardants, formaldehyde scavengers, carbon fibers, aerogels, and wood adhesives.



## KEYWORDS

Formacell black liquor; lignin properties; KOH; ethanol; oil palm empty fruit bunch; advanced biocomposite

## 1 Introduction

Global challenges such as food security and environmental threats can be treated by applying the circular bioeconomy principles, including sustainable conversion of biomass components into bio-based products as green alternatives to their petroleum-based counterparts, thus closing the material resource loops [1]. Black liquor (BL) is liquid waste left over from cooking pulp, aimed at removing lignin, hemicelluloses, and other extractable constituents from wood in order to free the cellulose fibers. Lignin is the main organic substance in BL, reaching 45% dry weight [2]. About 150 billion tons of BL are released from the pulp and paper industry, where every 1 ton of pulp production will produce 7 tons of BL [3]. Considering the increased production of bioethanol, this availability is projected to reach 225 million tons annually in 2030 [4–6]. However, only 2%–5% of BL has been valorized into biomaterial [7], and the rest for energy purposes [8–10]. Hence, it is important to develop new techniques aimed at increasing the valorization of lignin as a renewable feedstock in various value-added industrial applications. Lignin is a complex polyphenol compound with a complex three-dimensional chemical structure that is difficult to decompose naturally, so it has the potential to cause water pollution if discharged into the environment [11]. Lignin has a highly aromatic structure that is stable to heat and has high carbon content. In addition, lignin contains various functional groups, e.g., aliphatic, phenolic, methoxyl, and carbonyl hydroxyl groups, allowing its modification. Thus, it can be used in many functional applications such as biomass-based fuels, adhesives, flame retardants, dispersants, and surfactant formulations, as antioxidants in plastics and rubbers, dyes, synthetic floors, thermosets, paints, food packaging, filler in adhesives, seed coatings, automotive devices, 3D printing, and fuels for highway maintenance [12–17]. However, the utilization of lignin is still limited on an industrial scale due to the inhomogeneity of structure.

A lignin component is a phenylpropane unit with several different methoxy groups [18]. Chemical structures of lignin are identified by the presence of polypropene units such as p-hydroxyphenyl (or p-coumaryl alcohol), guaiacyl (or coniferyl alcohol), and syringyl (or sinapyl alcohol), and their percentage vary depending on the botanical origin. Polypropene units can be chemically bonded in different bonding patterns where the  $\beta$ -O-4 aryl glycerol ether bond is the primary linkage [19]. However, the technical lignin's structure differs from the native lignin and depends on the pulping method used. Besides, the source of raw materials and isolation method, including the type of chemical used and temperature, play critical roles in the physicochemical properties of lignin [20].

Lignin can be extracted in powder form from BL with proper chemical treatment and screening process [21]. Precipitation of lignin in the BL occurs due to the condensation reaction on the lignin constituent units, which were initially soluble and will be polymerized and form large molecules [22]. Base, acid, and organic solvents are common solutions to isolate lignin from BL. The process of lignin separation using organic solvents is known as the alcell or organosolv process [23]. This method is popular for breaking down lignin fractions [24]. The benefits of this method include obtaining lignin with a low molecular weight that is free of sulfur, and its application can be improved through fractionation or chemical modification [25], but organosolv fractionation is laborious work [26]; hence, acid and base deposition methods are more feasible. However, this method depends on the pH of the liquor, residence time, and temperature [22]. Some acids such as H<sub>2</sub>SO<sub>4</sub>, phosphoric acid (H<sub>3</sub>PO<sub>4</sub>), or HCl have been reported in isolating lignin from base BL, such as from the kraft process [27]. Meanwhile, lignin from formacell BL, BL derived from acetic acid, or formic acid as cooking liquid can be released by different alkalis, especially KOH,

$\text{Ca}(\text{OH})_2$ , and NaOH [20]. KOH, a strong base, is stronger than NaOH, and its use is expected to result in higher lignin yield.

Based on Miller et al. [28], a strong base (e.g., NaOH and KOH) provides a higher result in lignin yield than a weak base, and it would be a promising technique for depolymerizing lignin. The concentration of base is important to measure because it will influence selectivity, chemical-physical properties, and lignin yield [20,29]. Recently, Hidayati et al. evaluated the effect of NaOH concentration on lignin properties [20] while the disadvantage of NaOH was monoaromatic re-condensation led to the higher molecular weight of lignin [30]. Consequently, an alternative base such as KOH and ethanol is needed to overcome this problem. To date, no one reported lignin isolation from formacell BL using different concentrations of KOH and ethanol. Therefore, this study aimed to determine the effect of KOH and ethanol concentrations on the yield and chemical characteristics of lignin isolated from formacell BL of oil palm empty fruit bunch (OPEFB).

## 2 Material and Methods

### 2.1 Materials

Black liquor used in this research is a by-product of the formacell pulping of OPEFB, as reported by Hidayati et al. [31]. The pulping conditions are presented in detail in the next section. OPEFB was obtained from PTPN Business Unit VII Central Lampung Bekri, Indonesia. Meanwhile, KOH, NaCl, NaOH, HCl, and ethanol were supplied by Merck (Darmstadt, Germany).

### 2.2 Pulping Process

The formacell pulping was conducted in the autoclave at a liquor-to-particle ratio of 15:1 for 1 h at 130°C. This ratio of liquor to OPEFB particle ratio was used based on our initial experimental trials in the laboratory, considering the volumetric of OPEFB as a typical example of non-woody biomass. In this ratio, the OPEFB particles can be immersed completely in the chemical liquor. The ratio solvent of acetic acid and formic acid was 85:15 with the addition of HCl of 0.5% as the catalyst. The cooking liquor was collected after filtration and washing the completed softened OPEFB with fresh water at room temperature. This formacell BL was used for the next step.

### 2.3 Lignin Isolation

The formacell BL obtained from the pulping process of 100 mL contained a total solid content of around 25.10%. There are two methods for lignin isolation from formacell BL of OPEFB. The first one, i.e., the isolation of lignin from BL was conducted using KOH with a concentration of 2.5%; 5%; 7.5%; 10%; 12.5%; and 15% (w/v). The second isolation technique used ethanol at concentrations of 5%, 10%, 15%, 20%, 25% and 30% (v/v). As much as 100 mL of the KOH or ethanol solution was added into 100 mL BL, then stirred and measured the pH of the liquor was. The solution was allowed to stand for 10 h, then centrifugated for 20 min at 2500 rpm, and then separated using filter paper. The precipitated lignin was then oven-dried at 50°C–60°C for 24 h. Dried lignin was crushed manually to produce fine lignin powder (Fig. 1). The experiment was conducted in triplicate.

The data were calculated and presented in average and standard deviation tables and graphs. Observations made were pH value, the yield of lignin, lignin methoxyl content, the equivalent weight of lignin, analysis of lignin with Fourier Transform Infra-Red spectroscopy (FTIR) spectrophotometer (Cary 630 FTIR, Agilent, Australia), and lignin morphology using a scanning electron microscope (SEM) (JEOL JSM 6510 LA, Japan).

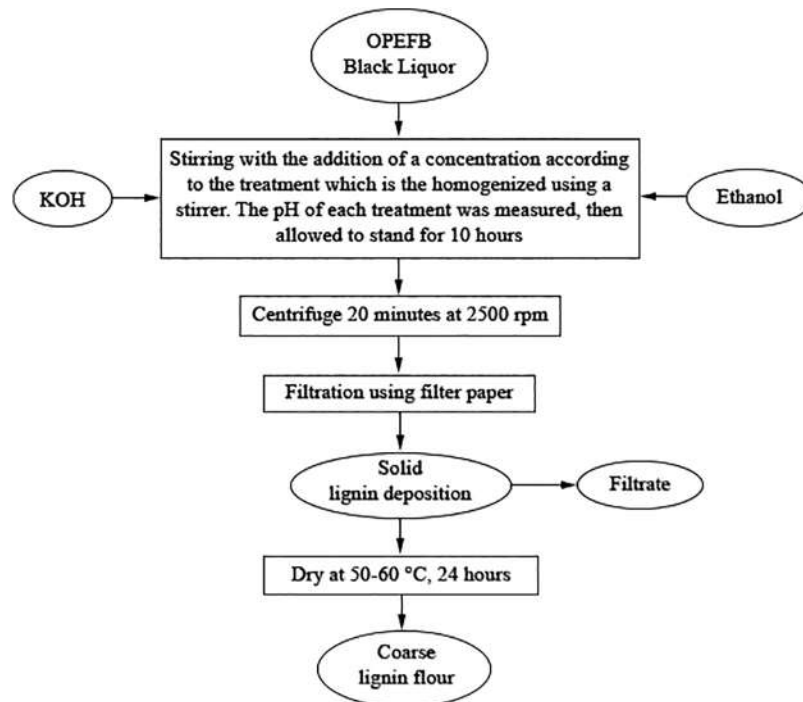


Figure 1: Flowchart of lignin isolation process using KOH/Ethanol

#### 2.4 Lignin Yield

Lignin yield was calculated based on the method according to Sluiter et al. [32], as presented in Eq. (1).

$$\text{Lignin Yield } \delta\% \text{ } \frac{a}{b} \times 100\% \quad (1)$$

Notation: a = weight of isolated lignin;

b = weight of lignin in black liquor.

#### 2.5 Methoxyl Content of Lignin

The methoxyl content of lignin was determined by using the ASTM 15120-81 method [33]. As much as 0.5 g of lignin was added to 5 mL of ethanol, following addition to 100 mL of distilled water containing 1 g of NaCl, and made in the form of suspension. Neutralization was performed using 0.1 N NaOH, given 6 drops of phenolphthalein (pp) indicator, and then 25 mL of 0.25 N NaOH was added and homogenized in a closed state for 30 min at room temperature. After that, 25 mL of 0.25 N HCl was added and titrated with 0.1 N NaOH until the end of the lasting color change (at least 30 s). The methoxyl content of lignin was calculated according to Eq. (2) as follows.

$$\text{Methoxyl } \delta\% \text{ } \frac{\text{ml NaOH} \times N \text{ NaOH} \times 3;1}{\text{Berat sampel } \delta\text{gram}} \times 100\% \quad (2)$$

#### 2.6 Lignin Equivalent Weight

Isolated lignin equivalent weight was calculated using the method of Brauns et al. [34]. 0.5 g lignin was put into 250 mL Erlenmeyer and moistened with 5 mL ethanol. The mixture is spiked with 1 g of NaCl which is then added with 100 mL of distilled water and 6 drops of phenolphthalein indicator. The solution was then titrated with 0.1 N NaOH until pH 7.5. The equivalent weight of isolated lignin was calculated by using Eq. (3).

$$\text{Equivalent Weight} = \frac{1000 \times \text{gram sample}}{\frac{1}{4} \delta mLN \text{NaOH}} \quad (3)$$

### 2.7 FT-IR Analysis of Isolated Lignin

As much as 1 mg isolated lignin was added with 150 mg KBr, pelletized, and then the samples were analyzed by FT-IR spectrophotometer (Cary 630 FTIR Agilent). The analysis was set at a wavenumber of 4000 to 400  $\text{cm}^{-1}$  (wavelength of 2.5–25  $\mu\text{m}$ ).

### 2.8 SEM Analysis

Morphology of isolated lignin was carried out using Scanning Electron Microscope (SEM) (JEOL JSM 6510 LA) with 1000  $\times$  magnification.

## 3 Results and Discussion

### 3.1 pH of the Black Liquor

The pH of BL from formacell pulping OPEFB is  $0.59 \pm 0.01$ , indicating that the liquor is acidic; thus, base or ethanol can be used to precipitate lignin from BL. To speed up the reaction, solvents such as acetic acid and formic acid are used in the formacell pulping process, along with HCl as a catalyst [31]. This process causes the pH of the formacell BL to become very acidic. Zhuang et al. [35] stated that formic acid and acetic acid could delignify lignin because of their acidic nature, so they can degrade lignin well. In another study, a combination of formic acid, acetic acid, and water achieved more than 50% lignin depolymerization in biomass [36]. The pH of the BL will be affected by the addition of KOH solution. According to the research, the pH value obtained from formacell pulping added with KOH solution ranged from  $2.43 \pm 0.07$  to  $4.27 \pm 0.35$  (Table 1), while the addition of ethanol concentrations can slightly increase the pH value from  $1.0 \pm 0.01$  to  $1.29 \pm 0.03$ . According to the findings, KOH has a greater effect on increasing pH than ethanol due to the strong base property of KOH.

Table 1: Effect of KOH and ethanol concentrations on pH, yield, methoxyl content, and an equivalent weight of isolated lignin

Treatment	pH	Yield (%)	Lignin methoxyl (%)	Equivalent weight
KOH concentration (%)				
2.5	$2.43 \pm 0.07$	$3.57 \pm 0.38$	$13.06 \pm 0.9$	$1372.94 \pm 26.73$
5.0	$2.94 \pm 0.06$	$4.85 \pm 1.12$	$12.94 \pm 1.31$	$655.73 \pm 45.16$
7.5	$3.21 \pm 0.1$	$8.63 \pm 1.41$	$12.81 \pm 0.84$	$528.74 \pm 54.44$
10	$3.61 \pm 0.15$	$11.20 \pm 2.69$	$12.36 \pm 0.9$	$510.33 \pm 49.05$
12.5	$3.86 \pm 0.15$	$12.78 \pm 0.78$	$11.33 \pm 0.4$	$476.25 \pm 34.61$
15	$4.27 \pm 0.35$	$14.95 \pm 1.10$	$10.13 \pm 1.42$	$427.03 \pm 44.20$
Ethanol concentration (%)				
5	$1.00 \pm 0.01$	$1.95 \pm 0.18$	$17.03 \pm 0.42$	$449.88 \pm 48.47$
10	$1.08 \pm 0.06$	$2.27 \pm 0.317$	$16.45 \pm 1.44$	$624.67 \pm 59.2$
15	$1.15 \pm 0.07$	$1.69 \pm 0.091$	$15.05 \pm 1.03$	$767.97 \pm 56.6$
20	$1.20 \pm 0.047$	$1.77 \pm 0.207$	$14.47 \pm 1.17$	$896.95 \pm 64.15$
25	$1.22 \pm 0.056$	$1.44 \pm 0.174$	$13.14 \pm 1.78$	$1521.16 \pm 72.10$
30	$1.29 \pm 0.03$	$1.08 \pm 0.179$	$11.99 \pm 1.20$	$2123.02 \pm 70.72$



The pH steadily increased as an up-surging concentration of KOH, where the lowest pH,  $2.43 \pm 0.07$ , was obtained from 2.5% KOH, and the highest was a pH of  $4.27 \pm 0.35$  from KOH 15%. Increasing the concentration of KOH solution causes more  $\text{OH}^-$  ions in the BL so that the pH of the solution becomes more alkaline. It can also be explained that KOH is a strong base. The stronger the base, the more OH ions are released, increasing the pH of the solution and making it more alkaline. Ethanol has a higher pKa than KOH, indicating a weaker acid. Unlike KOH, increasing the ethanol concentration slightly increased the pH, with the lowest being 1 and the highest being 1.29 after adding 5% and 30%, as shown in Table 1.

### 3.2 Lignin Yield

The lignin yield from adding KOH solution at various concentrations in isolation of BL ranged from  $3.57 \pm 0.38$  to  $14.95 \pm 1.10$  (Table 1). In comparison, ethanol isolation resulted in lower lignin yields of about  $0.51 \pm 0.00$  to  $1.06 \pm 0.00$ . The highest lignin yield was produced at a concentration of 15% KOH solution ( $14.95\% \pm 1.10$ ). Increasing the concentration of KOH solution caused the lignin yield to increase. It can be affected by the increasing concentration of an alkaline solution (KOH) that facilitates easier breaking of lignin bonds with other compounds, and a condensation reaction occurs in the lignin constituent units [37]. It is also supported by Sundin [38] who stated that lignin deposition from BL due to the protonation of phenol groups on lignin molecules caused by the addition of  $\text{OH}^-$  ions from KOH. It reduces the electrostatic force between lignin molecules, resulting in the deposition of lignin and reduced solubility. The more  $\text{OH}^-$  ions, the more lignin deposits will form. The deposit lignin increase occurred because of an increase in ionic strength and protonation. The protonation of the phenolic group in lignin leads the lignin nucleus to form aggregates when the pKa value of lignin is reached [39].

The lignin yield with KOH liquor treatment is higher than that of NaOH, as reported by Hidayati et al. [20]. Lignin was isolated from formacell BL of OPEFB by using NaOH, producing lignin yields ranging from 1.48% to 5.67%. It might be caused by the stronger base of KOH than NaOH. As seen in the periodic system, the metal  $\text{Na}^+$  and  $\text{K}^+$  are included in Group 1A. This is also related to the lower nature of alkali metal bases; the stronger, the lower the metal, the more easily reduced. Besides pH, temperature and ionic strength also affect lignin solubility. The molecular weight distribution in lignins is related to yield [40]. Both molecular weight and the ratio of phenols to aromatic units contribute to the solubility of lignin [40]. The changes in lignin yield in isolation by adding ethanol concentration are very low. The very low electronegativity of ethanol can suggest the presence of carbon compounds that cannot precipitate lignin properly. In the absence of sulfide, delignification was slower in the Alcell process.

As opposed to KOH precipitation, increasing ethanol concentrations leads to almost 0% lignin recovery. This result was in agreement with the precipitation of lignin from *Miscanthus x giganteus*, where after the addition of 75% of ethanol, there was no lignin precipitated [41]. In the low concentration of ethanol, lignin precipitation is carried out by diluting liquor with water, and the solubility of lignin decreases, resulting in more lignin being recovered. In other words, when the water content in the ethanol is limited, most of the lignin is soluble in the system, and hence the aggregate is not formed.

### 3.3 Methoxyl Content in Lignin

Methoxyl is one of the chemical groups in lignin for identifying one of the characteristics of lignin. The methoxyl group in each type of lignin has different content because of the different structures of lignin types. Determining methoxyl contents gives information about the average C9 units in lignin, and eventually, the unsaturated side chain and average oxygen content can be calculated [42]. The methoxyl content in KOH lignin ranged from  $10.13\% \pm 1.92$  to  $12.94\% \pm 0.90$ , whereas the use of ethanol concentrations results in methoxyl contents between  $11.99 \pm 0.02$  to  $17.03 \pm 0.5$  (Table 1). The highest methoxyl content in lignin was acquired from isolated lignin by adding a 2.5% KOH solution. Increasing the concentration of KOH

and ethanol solution leads to a decrease in the methoxyl content of isolated lignins. This may be due to the use of KOH as a strong base as a precipitating solution, which allows some methoxyl groups to degrade and transform into other compounds. This decrease in methoxyl content can be influenced by the disruption of structural stability in lignin caused by the addition of KOH. Furthermore, according to the pathway proposed by Yin et al. the removal of the methoxy group in lignin created a higher hydroxyl group of lignin by KOH solution. The presence of potassium in lignin isolation decreased the methoxyl content due to cleavage  $C\alpha-C\beta$  through  $C\beta-O$  bond. This cleavage leads to the removal of side chains such as methoxyl. The mechanism of this reaction has been proved by Yin et al. [43].

The various methoxyl content in lignin depends on the source of lignin and the delignification process used. Generally, high methoxyl content will inhibit lignin reactivity during use in the resin field. Lignin has phenolic hydroxyl groups that are typically linked to nearby phenyl propane units, allowing lignin to connect with formaldehyde in a way analogous to phenol and formaldehyde [44]. Molecular weight and lignin purity are important factors during the production of biocarbon fibers [44,45].

In the case of lignin application as an adhesive raw material, the low methoxyl content is more beneficial because it will increase the reactivity of aromatic nuclei in lignin [46]. It will facilitate the reaction of methylation or hydroxymethylation with adhesive-forming reactants such as NaOH and formaldehyde, hinting at the ease of gel formation. Recently, Gendron et al. compared four types of lignin for green adhesive, where the lowest methoxyl content of lignin had the highest water solubility and shear resistance as an adhesive [47].

The lignin standard of Indulin AT has a methoxyl content of around 13.5%–14.5% [48], so the methoxyl contents in isolated lignin in this study are still lower. Meanwhile, compared to methoxyl content by Hidayati et al. [20] with a value of 14.61%–20.77% by using NaOH as precipitating solution, the results of this study are also lower. These results are probably influenced by the use of KOH, which is classified as a strong base with a higher reactivity than NaOH, as seen from the periodic system. The influence of harsh chemicals and temperature during isolation causes the structure of lignin to undergo many changes, including the methoxyl group. The methoxyl group is degraded and transformed into other degradation compounds such as aromatic hydrocarbon and phenolic types, resulting in lower methoxyl content [49].

### 3.4 The Equivalent Weight of Lignin

The determination of the equivalent weight of lignin is intended to determine the molecular weight of lignin to identify lignin degradation and condensation reactions. The molecular weight of lignin is an important property that influences biomass recalcitrance and lignin value. Determination of the molecular weight of lignin in the original biomass depends on the source of the raw material used, chemicals used for isolation, and purification methods [50,51]. Based on the results, the equivalent weight of lignin from the KOH solution ranged from  $427.03 \pm 74.20$  to  $1372.94 \pm 269.73$ , whereas the addition of ethanol concentration resulted in molecular weights ranging from  $449.88 \pm 1.9$  to  $2123.03 \pm 27.5$  (Table 1).

Increasing the concentration of KOH solution resulted in a decrease in lignin equivalent weight, so the lowest value at 15% KOH solution concentration was  $427.03 \pm 74.20$ . This might be attributed to the increasing addition of a KOH solution as a strong base will degrade a portion of lignin into a derivative compound with shorter chains. It can degrade lignin resulting in a low equivalent weight. According to Patil et al. lignin depolymerization has two routes: harsh and moderate, resulting in different lignin structures [52]. The average molecular weight of lignin decreases with increasing precipitation of lignin yield by KOH. It was shown that increasing the amount of lignin with lower molecular weight deposited a high yield of lignin. Lignin is degraded into smaller fragments so that there are more phenolic groups with lower molecular weights [53]. Increasing salt concentration can lower the product's molecular weight [54,55].

According to Gellerstedt [56], the termination of methyl aryl ether bonds from the aromatic ring of lignin resulted in decreased methoxyl content and low molecular weight of lignin due to the lignin degradation process. Based on several previous studies, lignin molecular weight values were obtained, namely 2500–14,000 [57], and 1327.64–1787.23 [20]. In contrast, the equivalent weight of Indulin AT reached 3357–3366 [58]. This shows that the equivalent weight value of lignin varies greatly.

Lignin that has a high molecular weight can be used as a matrix in polyolefin composites, because a higher molecular mass of lignin has a better affinity with the matrix [59], while lignin with a lower molecular weight can be used for the development of phenol-formaldehyde resins, antioxidants, adhesives, and paints due to their higher reactivity than high molecular weight lignin [59].

Differences in elemental composition, functional group types, proportions, and molecular weight in lignin molecules provide opportunities to use lignin in a variety of value-added applications. Some factors that influence the molecular weight of lignin are the diversity of lignin isolation procedures, macromolecular degradation during isolation, the effect of condensation mainly on acidic conditions, the apparent polydispersity of dissolved lignin, inadequate determination methods used to characterize the isolated lignin, and uncertainties in the properties of lignin. Because lignin is heterogeneous and inconstant, characterizing native lignin is also difficult [60].

The molecular weight of lignin is very important in the development of such polymeric products; similarly, low-molecular-weight lignin isolated from wheat straw by acetic acid pulping is an ideal feedstock for adhesive manufacturing [61]. Doherty et al. [62] stated that lignin from the soda process of wheat plants ranges from 1700 with a methoxyl content of 16. The organosolv pulping process at bagasse produces a molecular weight of around 2000 and a methoxyl content of 15.1. Lignin produced in the isolation process using alcohol or alcell process has a low molecular weight ( $M_w < 900$ ) with low polydispersity, no sulfur, and low ash content, although the value depends on the analytical method. There is also a molecular weight of  $2580 \text{ g mol}^{-1}$  with a polydispersity of 4.3. Sameni et al. compared four types of lignin from different isolation methods, where the highest  $M_w$  (13488) was obtained from the steam explosion process with a methoxyl content of 0.69. Meanwhile, with the same methoxyl content, the lowest  $M_w$  (2565) was derived from the kraft process [57]. Yun et al. reported that organosolv fractionation from native lignin decreased its molecular weight from 5070 to 1810 [23].

### 3.5 Lignin Analysis with FT-IR Spectrophotometer

FTIR was performed to analyze differences in the functional groups of lignin in the sample (Figs. 2 and 3). FTIR spectra analysis showed that the peak in the aromatic ring vibrations decreased with the absorption band at  $1446 \text{ cm}^{-1}$  (a) and  $1408 \text{ cm}^{-1}$  (b), especially in the treatment using the highest concentration of KOH (Fig. 2) and ethanol (Fig. 3). There are similarities in the wavelength of  $3500$  to  $31090 \text{ cm}^{-1}$  which refer to the presence of hydrogen bonds in the hydroxyl group (alcohol and phenolic). A wavelength absorption of  $1587$  and  $1513 \text{ cm}^{-1}$  indicates the aromatic lignin skeletal vibration [60]. Wavenumbers at  $1460$  to  $1420 \text{ cm}^{-1}$  are associated with stretching wavelengths of CH (methyl and methylene) and CH deformation with aromatic ring stretching fields [63]. The peaks observed in the range of  $1220$  to  $1270 \text{ cm}^{-1}$  in all spectra may refer to the C-H deformation vibrations of the guaiacyl [64]. The bands at  $1300 \text{ cm}^{-1}$  (syringyl) and  $1200 \text{ cm}^{-1}$  (guaiacyl) indicate the presence of both syringyl and guaiacyl in lignin's chemical structure as the unique peaks of lignin precursor [65]. A similar peak was also found in kraft lignin isolated from *Acacia mangium* black liquor [27]. In general, peaks in Figs. 2 and 3 show that the treatment using KOH had a sharper peak than that of ethanol treatment. However, no difference in the peaks resulting from these two treatments was determined. Hidayati et al. [20] reported the experiment in isolated lignin from formacell BL of OPEFB using NaOH with the wave number of isolated lignin for guaiacyl lignin at around  $1273.02 \text{ cm}^{-1}$ .

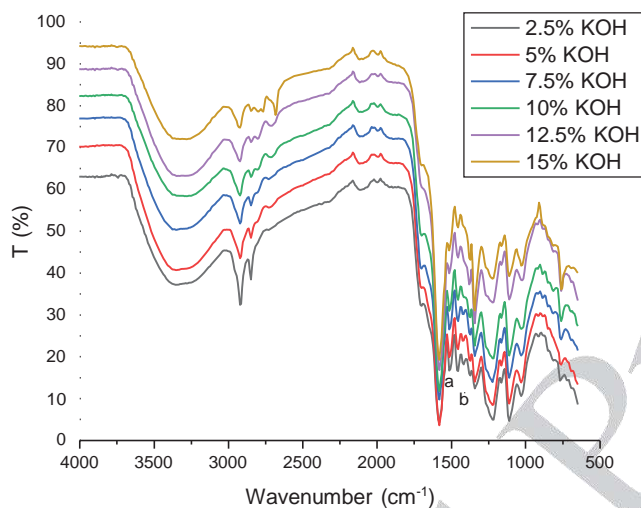


Figure 2: The FT-IR spectra of lignin using KOH isolation

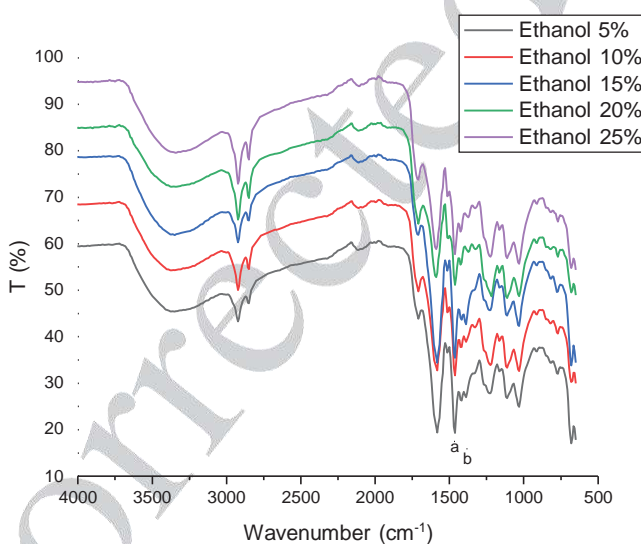


Figure 3: The FT-IR spectra of lignin using ethanol isolation

### 3.6 Morphological Observation

Scanning Electron Microscope (SEM) was used to observe the size and morphology of lignin. In this study, SEM images were taken from the lowest and the highest concentration of KOH and ethanol as representative lignin morphology. As seen in Fig. 4, increasing the concentration of KOH acid from 2.5% to 15% showed differences in lignin morphology. Lignin isolation using 15% KOH (Fig. 4b) produced a more compact formation and morphology compared to lignin produced by isolation using 2.5% KOH concentration (Fig. 4a). In stark contrast, in treatment using ethanol appears that treatment with a 5% ethanol concentration resulted in a more condensed form and morphology than those using a 30% concentration. This result was in accordance with the findings reported by Solihat et al. [27] and Hamzah et al. [41], where increasing ethanol concentration created more rupture and amorphous lignin surface.

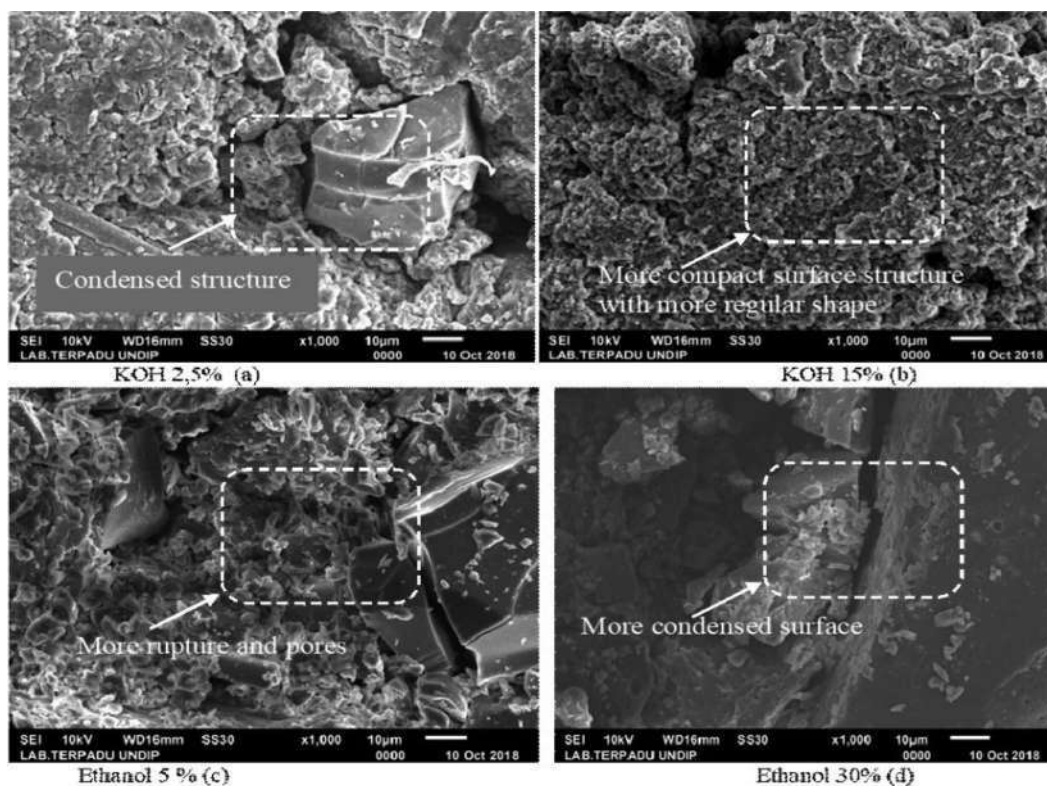


Figure 4: Morphological images of isolated lignin (a) KOH 2.5%, (b) KOH 15%, (c) ethanol 5%, (d) ethanol 30% with 1000 × magnification

### 3.7 Prospective Application of Formacell Lignin as Advanced Biocomposite Products

The lignin molecule contains a variety of active functional groups, including aliphatic hydroxyl (Al-OH), phenolic hydroxyl (Ph-OH), carboxyl (-COOH), carbonyl (-C=O), and methoxy groups (-OCH<sub>3</sub>), which determine its properties, chemistry, and reactivity of lignin. Lignin's chemical properties enable it and its derivatives to be used as high-value materials. The lignin molecule can be used in a variety of value-added applications due to differences in molecular weight, elemental composition, and the types and proportions of functional groups. Currently, Saražin et al. investigated the potency of organosolv lignin-based non-isocyanate polyurethane for wood adhesive and the result demonstrated satisfactory mechanical properties [66] and its curing kinetics for interior furniture showed that it was more suitable than urea-formaldehyde (UF) adhesive [67]. Sulfur-free lignin is produced by isolating lignin from the formacell process. Most value-added applications prefer lignin with a lower percentage of sulfur and ash. For example, sulfur-free lignin is preferred for use in aerogel composites. Jõul et al. reacted lignin isolated by organic acid with 5-methylresorcinol-formaldehyde to create aerogel and according to the data, formacell lignin had good reactivity to create a high surface area of aerogel [68]. According to Talabi et al. lignin with rich hydroxyl carbon, low molecular weight, and less in the methoxyl group was suitable for lignin-based-formaldehyde resin with a 73% graphitization level [69], and hence formacell lignin with higher KOH and ethanol concentrations are appropriate for this application. Meanwhile, the high molecular weight of lignin is preferred as a matrix in carbon fiber composites because it improves the mechanical performance of the fiber.

#### 4 Conclusions

A strong base, such as KOH, was used to successfully isolate lignin from oil palm empty fruit bunch (OPEFB) formacell BL. Some identified lignin peaks can be found in the FTIR spectra, with no significant difference between lignins isolated with KOH and ethanol. The addition of KOH solution at 12.5% and 15% concentrations is the more effective method for isolating lignin from formacell BL. At this condition, isolated lignins have pH values of 3.86 and 4.27, lignin yield of 2.78% and 14.95%, methoxyl content of 11.33% and 10.13%, and lignin equivalent weights of 476.25 and 427.03, respectively. The lignin produced by the isolation process using KOH and ethanol was characterized by the low methoxy content and a low molecular weight that created its higher reactivity. According to these properties, lignin derived from formacell is suitable for developing green, bio-based additives in biocomposite applications such as wood adhesives from non-isocyanate polyurethane, coatings, lignin-based-formaldehyde resins, formaldehyde scavengers, composite fillers, and other value-added industrial applications.

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ARTICLE

## Characterization of Formacell Lignin Derived from Black Liquor as a Potential Green Additive for Advanced Biocomposites

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### ABSTRACT

Black liquor is obtained as a by-product of the pulping process, which is used to convert biomass into pulp by removing lignin, hemicelluloses and other extractives from wood to free cellulose fibers. Lignin represents a major constituent in black liquor, with quantities varying from 20% to 30%, of which a very low share is used for manufacturing value-added products, while the rest is mainly burned for energy purposes, thus underestimating its great potential as a raw material. Therefore, it is essential to establish new isolation and extraction methods to increase lignin valorization in the development of bio-based chemicals. The aim of this research work was to determine the effect of KOH or ethanol concentration as an isolation agent on lignin yields and the chemical characteristics of lignin isolated from formacell black liquor of oil palm empty fruit bunch (OPEFB). Isolation of lignin was carried out using KOH with various concentrations ranging from 5% to 15% (w/v). Ethanol was also used to precipitate lignin from black liquor at concentrations varying from 5% to 30% (v/v). The results obtained showed that the addition of KOH solution at 12.5% and 15% concentrations resulted in better lignin yield and chemical properties of lignin, i.e., pH values of 3.86 and 4.27, lignin yield of 12.78% and 14.95%, methoxy content of 11.33% and 10.13%, and lignin equivalent weights of 476.25 and 427.03, respectively. Due to its phenolic structure and rich functional groups that are favorable for modifications, lignin has the potential to be used as a green additive in the development of advanced biocomposite products in various applications to replace current fossil fuel-based material, ranging from fillers, fire retardants, formaldehyde scavengers, carbon fibers, aerogels, and wood adhesives.





**KEYWORDS**

Formacell black liquor; lignin properties; KOH; ethanol; oil palm empty fruit bunch; advanced biocomposite

**1 Introduction**

Global challenges such as food security and environmental threats can be treated by applying the circular bioeconomy principles, including sustainable conversion of biomass components into bio-based products as green alternatives to their petroleum-based counterparts, thus closing the material resource loops [1]. Black liquor (BL) is liquid waste left over from cooking pulp, aimed at removing lignin, hemicelluloses, and other extractable constituents from wood in order to free the cellulose fibers. Lignin is the main organic substance in BL, reaching 45% dry weight [2]. About 150 billion tons of BL are released from the pulp and paper industry, where every 1 ton of pulp production will produce 7 tons of BL [3]. Considering the increased production of bioethanol, this availability is projected to reach 225 million tons annually in 2030 [4–6]. However, only 2%–5% of BL has been valorized into biomaterial [7], and the rest for energy purposes [8–10]. Hence, it is important to develop new techniques aimed at increasing the valorization of lignin as a renewable feedstock in various value-added industrial applications. Lignin is a complex polyphenol compound with a complex three-dimensional chemical structure that is difficult to decompose naturally, so it has the potential to cause water pollution if discharged into the environment [11]. Lignin has a highly aromatic structure that is stable to heat and has high carbon content. In addition, lignin contains various functional groups, e.g., aliphatic, phenolic, methoxyl, and carbonyl hydroxyl groups, allowing its modification. Thus, it can be used in many functional applications such as biomass-based fuels, adhesives, flame retardants, dispersants, and surfactant formulations, as antioxidants in plastics and rubbers, dyes, synthetic floors, thermosets, paints, food packaging, filler in adhesives, seed coatings, automotive devices, 3D printing, and fuels for highway maintenance [12–17]. However, the utilization of lignin is still limited on an industrial scale due to the inhomogeneity of structure.

A lignin component is a phenylpropane unit with several different methoxy groups [18]. Chemical structures of lignin are identified by the presence of polypropene units such as p-hydroxyphenyl (or p-coumaryl alcohol), guaiacyl (or coniferyl alcohol), and syringyl (or sinapyl alcohol), and their percentage vary depending on the botanical origin. Polypropene units can be chemically bonded in different bonding patterns where the  $\beta$ -O-4 aryl glycerol ether bond is the primary linkage [19]. However, the technical lignin's structure differs from the native lignin and depends on the pulping method used. Besides, the source of raw materials and isolation method, including the type of chemical used and temperature, play critical roles in the physicochemical properties of lignin [20].

Lignin can be extracted in powder form from BL with proper chemical treatment and screening process [21]. Precipitation of lignin in the BL occurs due to the condensation reaction on the lignin constituent units, which were initially soluble and will be polymerized and form large molecules [22]. Base, acid, and organic solvents are common solutions to isolate lignin from BL. The process of lignin separation using organic solvents is known as the alcell or organosolv process [23]. This method is popular for breaking down lignin fractions [24]. The benefits of this method include obtaining lignin with a low molecular weight that is free of sulfur, and its application can be improved through fractionation or chemical modification [25], but organosolv fractionation is laborious work [26]; hence, acid and base deposition methods are more feasible. However, this method depends on the pH of the liquor, residence time, and temperature [22]. Some acids such as H<sub>2</sub>SO<sub>4</sub>, phosphoric acid (H<sub>3</sub>PO<sub>4</sub>), or HCl have been reported in isolating lignin from base BL, such as from the kraft process [27]. Meanwhile, lignin from formacell BL, BL derived from acetic acid, or formic acid as cooking liquid can be released by different alkalis, especially KOH,

$\text{Ca(OH)}_2$ , and NaOH [20]. KOH, a strong base, is stronger than NaOH, and its use is expected to result in higher lignin yield.

Based on Miller et al. [28], a strong base (e.g., NaOH and KOH) provides a higher result in lignin yield than a weak base, and it would be a promising technique for depolymerizing lignin. The concentration of base is important to measure because it will influence selectivity, chemical-physical properties, and lignin yield [20,29]. Recently, Hidayati et al. evaluated the effect of NaOH concentration on lignin properties [20] while the disadvantage of NaOH was monoaromatic re-condensation led to the higher molecular weight of lignin [30]. Consequently, an alternative base such as KOH and ethanol is needed to overcome this problem. To date, no one reported lignin isolation from formacell BL using different concentrations of KOH and ethanol. Therefore, this study aimed to determine the effect of KOH and ethanol concentrations on the yield and chemical characteristics of lignin isolated from formacell BL of oil palm empty fruit bunch (OPEFB).

## 2 Material and Methods

### 2.1 Materials

Black liquor used in this research is a by-product of the formacell pulping of OPEFB, as reported by Hidayati et al. [31]. The pulping conditions are presented in detail in the next section. OPEFB was obtained from PTPN Business Unit VII Central Lampung Bekri, Indonesia. Meanwhile, KOH, NaCl, NaOH, HCl, and ethanol were supplied by Merck (Darmstadt, Germany).

### 2.2 Pulping Process

The formacell pulping was conducted in the autoclave at a liquor-to-particle ratio of 15:1 for 1 h at 130°C. This ratio of liquor to OPEFB particle ratio was used based on our initial experimental trials in the laboratory, considering the volumetric of OPEFB as a typical example of non-woody biomass. In this ratio, the OPEFB particles can be immersed completely in the chemical liquor. The ratio solvent of acetic acid and formic acid was 85:15 with the addition of HCl of 0.5% as the catalyst. The cooking liquor was collected after filtration and washing the completed softened OPEFB with fresh water at room temperature. This formacell BL was used for the next step.

### 2.3 Lignin Isolation

The formacell BL obtained from the pulping process of 100 mL contained a total solid content of around 25.10%. There are two methods for lignin isolation from formacell BL of OPEFB. The first one, i.e., the isolation of lignin from BL was conducted using KOH with a concentration of 2.5%; 5%; 7.5%; 10%; 12.5%; and 15% (w/v). The second isolation technique used ethanol at concentrations of 5%, 10%, 15%, 20%, 25% and 30% (v/v). As much as 100 mL of the KOH or ethanol solution was added into 100 mL BL, then stirred and measured the pH of the liquor was. The solution was allowed to stand for 10 h, then centrifugated for 20 min at 2500 rpm, and then separated using filter paper. The precipitated lignin was then oven-dried at 50°C–60°C for 24 h. Dried lignin was crushed manually to produce fine lignin powder (Fig. 1). The experiment was conducted in triplicate.

The data were calculated and presented in average and standard deviation tables and graphs. Observations made were pH value, the yield of lignin, lignin methoxyl content, the equivalent weight of lignin, analysis of lignin with Fourier Transform Infra-Red spectroscopy (FTIR) spectrophotometer (Cary 630 FTIR, Agilent, Australia), and lignin morphology using a scanning electron microscope (SEM) (JEOL JSM 6510 LA, Japan).

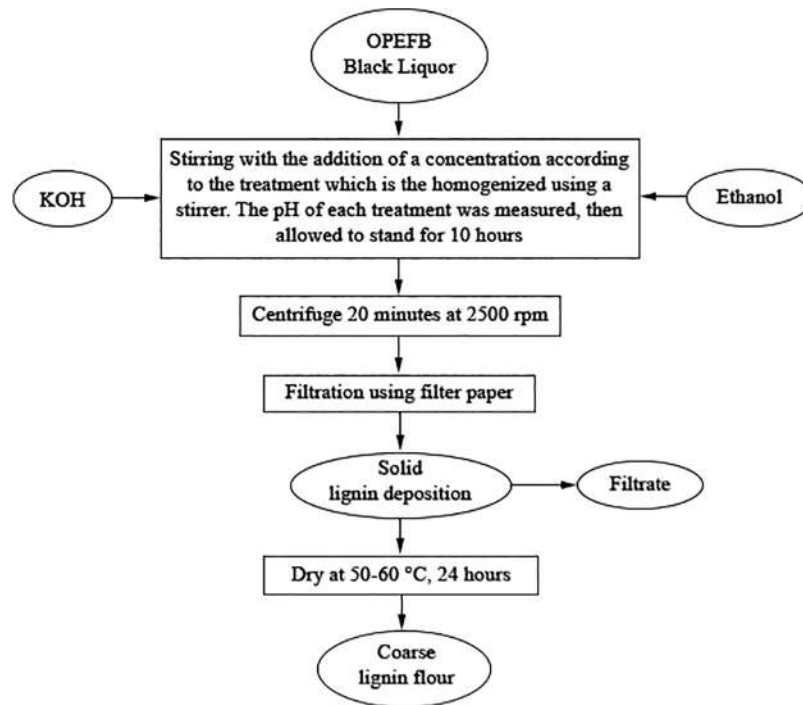


Figure 1: Flowchart of lignin isolation process using KOH/Ethanol

#### 2.4 Lignin Yield

Lignin yield was calculated based on the method according to Sluiter et al. [32], as presented in Eq. (1).

$$\text{Lignin Yield } \delta\% = \frac{a}{b} \times 100\% \quad (1)$$

Notation: a = weight of isolated lignin;

b = weight of lignin in black liquor.

#### 2.5 Methoxyl Content of Lignin

The methoxyl content of lignin was determined by using the ASTM 15120-81 method [33]. As much as 0.5 g of lignin was added to 5 mL of ethanol, following addition to 100 mL of distilled water containing 1 g of NaCl, and made in the form of suspension. Neutralization was performed using 0.1 N NaOH, given 6 drops of phenolphthalein (pp) indicator, and then 25 mL of 0.25 N NaOH was added and homogenized in a closed state for 30 min at room temperature. After that, 25 mL of 0.25 N HCl was added and titrated with 0.1 N NaOH until the end of the lasting color change (at least 30 s). The methoxyl content of lignin was calculated according to Eq. (2) as follows.

$$\text{Methoxyl } \delta\% = \frac{\text{ml NaOH} \times N \text{ NaOH} \times 3;1}{\text{Berat sampel } \delta\text{gram}} \times 100\% \quad (2)$$

#### 2.6 Lignin Equivalent Weight

Isolated lignin equivalent weight was calculated using the method of Brauns et al. [34]. 0.5 g lignin was put into 250 mL Erlenmeyer and moistened with 5 mL ethanol. The mixture is spiked with 1 g of NaCl which is then added with 100 mL of distilled water and 6 drops of phenolphthalein indicator. The solution was then titrated with 0.1 N NaOH until pH 7.5. The equivalent weight of isolated lignin was calculated by using Eq. (3).

$$\text{Equivalent Weight} = \frac{1000 \times \text{gram sample}}{\frac{1}{4} \delta mLNpNaOH} \quad (3)$$

### 2.7 FT-IR Analysis of Isolated Lignin

As much as 1 mg isolated lignin was added with 150 mg KBr, pelletized, and then the samples were analyzed by FT-IR spectrophotometer (Cary 630 FTIR Agilent). The analysis was set at a wavenumber of 4000 to 400  $\text{cm}^{-1}$  (wavelength of 2.5–25  $\mu\text{m}$ ).

### 2.8 SEM Analysis

Morphology of isolated lignin was carried out using Scanning Electron Microscope (SEM) (JEOL JSM 6510 LA) with 1000  $\times$  magnification.

## 3 Results and Discussion

### 3.1 pH of the Black Liquor

The pH of BL from formacell pulping OPEFB is  $0.59 \pm 0.01$ , indicating that the liquor is acidic; thus, base or ethanol can be used to precipitate lignin from BL. To speed up the reaction, solvents such as acetic acid and formic acid are used in the formacell pulping process, along with HCl as a catalyst [31]. This process causes the pH of the formacell BL to become very acidic. Zhuang et al. [35] stated that formic acid and acetic acid could delignify lignin because of their acidic nature, so they can degrade lignin well. In another study, a combination of formic acid, acetic acid, and water achieved more than 50% lignin depolymerization in biomass [36]. The pH of the BL will be affected by the addition of KOH solution. According to the research, the pH value obtained from formacell pulping added with KOH solution ranged from  $2.43 \pm 0.07$  to  $4.27 \pm 0.35$  (Table 1), while the addition of ethanol concentrations can slightly increase the pH value from  $1.0 \pm 0.01$  to  $1.29 \pm 0.03$ . According to the findings, KOH has a greater effect on increasing pH than ethanol due to the strong base property of KOH.

Table 1: Effect of KOH and ethanol concentrations on pH, yield, methoxyl content, and an equivalent weight of isolated lignin

Treatment	pH	Yield (%)	Lignin methoxyl (%)	Equivalent weight
KOH concentration (%)				
2.5	$2.43 \pm 0.07$	$3.57 \pm 0.38$	$13.06 \pm 0.9$	$1372.94 \pm 26.73$
5.0	$2.94 \pm 0.06$	$4.85 \pm 1.12$	$12.94 \pm 1.31$	$655.73 \pm 45.16$
7.5	$3.21 \pm 0.1$	$8.63 \pm 1.41$	$12.81 \pm 0.84$	$528.74 \pm 54.44$
10	$3.61 \pm 0.15$	$11.20 \pm 2.69$	$12.36 \pm 0.9$	$510.33 \pm 49.05$
12.5	$3.86 \pm 0.15$	$12.78 \pm 0.78$	$11.33 \pm 0.4$	$476.25 \pm 34.61$
15	$4.27 \pm 0.35$	$14.95 \pm 1.10$	$10.13 \pm 1.42$	$427.03 \pm 44.20$
Ethanol concentration (%)				
5	$1.00 \pm 0.01$	$1.95 \pm 0.18$	$17.03 \pm 0.42$	$449.88 \pm 48.47$
10	$1.08 \pm 0.06$	$2.27 \pm 0.317$	$16.45 \pm 1.44$	$624.67 \pm 59.2$
15	$1.15 \pm 0.07$	$1.69 \pm 0.091$	$15.05 \pm 1.03$	$767.97 \pm 56.6$
20	$1.20 \pm 0.047$	$1.77 \pm 0.207$	$14.47 \pm 1.17$	$896.95 \pm 64.15$
25	$1.22 \pm 0.056$	$1.44 \pm 0.174$	$13.14 \pm 1.78$	$1521.16 \pm 72.10$
30	$1.29 \pm 0.03$	$1.08 \pm 0.179$	$11.99 \pm 1.20$	$2123.02 \pm 70.72$

The pH steadily increased as an up-surging concentration of KOH, where the lowest pH,  $2.43 \pm 0.07$ , was obtained from 2.5% KOH, and the highest was a pH of  $4.27 \pm 0.35$  from KOH 15%. Increasing the concentration of KOH solution causes more  $\text{OH}^-$  ions in the BL so that the pH of the solution becomes more alkaline. It can also be explained that KOH is a strong base. The stronger the base, the more  $\text{OH}^-$  ions are released, increasing the pH of the solution and making it more alkaline. Ethanol has a higher pKa than KOH, indicating a weaker acid. Unlike KOH, increasing the ethanol concentration slightly increased the pH, with the lowest being 1 and the highest being 1.29 after adding 5% and 30%, as shown in Table 1.

### 3.2 Lignin Yield

The lignin yield from adding KOH solution at various concentrations in isolation of BL ranged from  $3.57 \pm 0.38$  to  $14.95 \pm 1.10$  (Table 1). In comparison, ethanol isolation resulted in lower lignin yields of about  $0.51 \pm 0.00$  to  $1.06 \pm 0.00$ . The highest lignin yield was produced at a concentration of 15% KOH solution ( $14.95\% \pm 1.10$ ). Increasing the concentration of KOH solution caused the lignin yield to increase. It can be affected by the increasing concentration of an alkaline solution (KOH) that facilitates easier breaking of lignin bonds with other compounds, and a condensation reaction occurs in the lignin constituent units [37]. It is also supported by Sundin [38] who stated that lignin deposition from BL due to the protonation of phenol groups on lignin molecules caused by the addition of  $\text{OH}^-$  ions from KOH. It reduces the electrostatic force between lignin molecules, resulting in the deposition of lignin and reduced solubility. The more  $\text{OH}^-$  ions, the more lignin deposits will form. The deposit lignin increase occurred because of an increase in ionic strength and protonation. The protonation of the phenolic group in lignin leads the lignin nucleus to form aggregates when the pKa value of lignin is reached [39].

The lignin yield with KOH liquor treatment is higher than that of NaOH, as reported by Hidayati et al. [20]. Lignin was isolated from formacell BL of OPEFB by using NaOH, producing lignin yields ranging from 1.48% to 5.67%. It might be caused by the stronger base of KOH than NaOH. As seen in the periodic system, the metal  $\text{Na}^+$  and  $\text{K}^+$  are included in Group 1A. This is also related to the lower nature of alkali metal bases; the stronger, the lower the metal, the more easily reduced. Besides pH, temperature and ionic strength also affect lignin solubility. The molecular weight distribution in lignins is related to yield [40]. Both molecular weight and the ratio of phenols to aromatic units contribute to the solubility of lignin [40]. The changes in lignin yield in isolation by adding ethanol concentration are very low. The very low electronegativity of ethanol can suggest the presence of carbon compounds that cannot precipitate lignin properly. In the absence of sulfide, delignification was slower in the Alcell process.

As opposed to KOH precipitation, increasing ethanol concentrations leads to almost 0% lignin recovery. This result was in agreement with the precipitation of lignin from *Miscanthus x giganteus*, where after the addition of 75% of ethanol, there was no lignin precipitated [41]. In the low concentration of ethanol, lignin precipitation is carried out by diluting liquor with water, and the solubility of lignin decreases, resulting in more lignin being recovered. In other words, when the water content in the ethanol is limited, most of the lignin is soluble in the system, and hence the aggregate is not formed.

### 3.3 Methoxyl Content in Lignin

Methoxyl is one of the chemical groups in lignin for identifying one of the characteristics of lignin. The methoxyl group in each type of lignin has different content because of the different structures of lignin types. Determining methoxyl contents gives information about the average C9 units in lignin, and eventually, the unsaturated side chain and average oxygen content can be calculated [42]. The methoxyl content in KOH lignin ranged from  $10.13\% \pm 1.92$  to  $12.94\% \pm 0.90$ , whereas the use of ethanol concentrations results in methoxyl contents between  $11.99 \pm 0.02$  to  $17.03 \pm 0.5$  (Table 1). The highest methoxyl content in lignin was acquired from isolated lignin by adding a 2.5% KOH solution. Increasing the concentration of KOH

and ethanol solution leads to a decrease in the methoxyl content of isolated lignins. This may be due to the use of KOH as a strong base as a precipitating solution, which allows some methoxyl groups to degrade and transform into other compounds. This decrease in methoxyl content can be influenced by the disruption of structural stability in lignin caused by the addition of KOH. Furthermore, according to the pathway proposed by Yin et al. the removal of the methoxy group in lignin created a higher hydroxyl group of lignin by KOH solution. The presence of potassium in lignin isolation decreased the methoxyl content due to cleavage  $C\alpha-C\beta$  through  $C\beta-O$  bond. This cleavage leads to the removal of side chains such as methoxyl. The mechanism of this reaction has been proved by Yin et al. [43].

The various methoxyl content in lignin depends on the source of lignin and the delignification process used. Generally, high methoxyl content will inhibit lignin reactivity during use in the resin field. Lignin has phenolic hydroxyl groups that are typically linked to nearby phenyl propane units, allowing lignin to connect with formaldehyde in a way analogous to phenol and formaldehyde [44]. Molecular weight and lignin purity are important factors during the production of biocarbon fibers [44,45].

In the case of lignin application as an adhesive raw material, the low methoxyl content is more beneficial because it will increase the reactivity of aromatic nuclei in lignin [46]. It will facilitate the reaction of methylation or hydroxymethylation with adhesive-forming reactants such as NaOH and formaldehyde, hinting at the ease of gel formation. Recently, Gendron et al. compared four types of lignin for green adhesive, where the lowest methoxyl content of lignin had the highest water solubility and shear resistance as an adhesive [47].

The lignin standard of Indulin AT has a methoxyl content of around 13.5%–14.5% [48], so the methoxyl contents in isolated lignin in this study are still lower. Meanwhile, compared to methoxyl content by Hidayati et al. [20] with a value of 14.61%–20.77% by using NaOH as precipitating solution, the results of this study are also lower. These results are probably influenced by the use of KOH, which is classified as a strong base with a higher reactivity than NaOH, as seen from the periodic system. The influence of harsh chemicals and temperature during isolation causes the structure of lignin to undergo many changes, including the methoxyl group. The methoxyl group is degraded and transformed into other degradation compounds such as aromatic hydrocarbon and phenolic types, resulting in lower methoxyl content [49].

### 3.4 The Equivalent Weight of Lignin

The determination of the equivalent weight of lignin is intended to determine the molecular weight of lignin to identify lignin degradation and condensation reactions. The molecular weight of lignin is an important property that influences biomass recalcitrance and lignin value. Determination of the molecular weight of lignin in the original biomass depends on the source of the raw material used, chemicals used for isolation, and purification methods [50,51]. Based on the results, the equivalent weight of lignin from the KOH solution ranged from  $427.03 \pm 74.20$  to  $1372.94 \pm 269.73$ , whereas the addition of ethanol concentration resulted in molecular weights ranging from  $449.88 \pm 1.9$  to  $2123.03 \pm 27.5$  (Table 1).

Increasing the concentration of KOH solution resulted in a decrease in lignin equivalent weight, so the lowest value at 15% KOH solution concentration was  $427.03 \pm 74.20$ . This might be attributed to the increasing addition of a KOH solution as a strong base will degrade a portion of lignin into a derivative compound with shorter chains. It can degrade lignin resulting in a low equivalent weight. According to Patil et al. lignin depolymerization has two routes: harsh and moderate, resulting in different lignin structures [52]. The average molecular weight of lignin decreases with increasing precipitation of lignin yield by KOH. It was shown that increasing the amount of lignin with lower molecular weight deposited a high yield of lignin. Lignin is degraded into smaller fragments so that there are more phenolic groups with lower molecular weights [53]. Increasing salt concentration can lower the product's molecular weight [54,55].

According to Gellerstedt [56], the termination of methyl aryl ether bonds from the aromatic ring of lignin resulted in decreased methoxyl content and low molecular weight of lignin due to the lignin degradation process. Based on several previous studies, lignin molecular weight values were obtained, namely 2500–14,000 [57], and 1327.64–1787.23 [20]. In contrast, the equivalent weight of Indulin AT reached 3357–3366 [58]. This shows that the equivalent weight value of lignin varies greatly.

Lignin that has a high molecular weight can be used as a matrix in polyolefin composites, because a higher molecular mass of lignin has a better affinity with the matrix [59], while lignin with a lower molecular weight can be used for the development of phenol-formaldehyde resins, antioxidants, adhesives, and paints due to their higher reactivity than high molecular weight lignin [59].

Differences in elemental composition, functional group types, proportions, and molecular weight in lignin molecules provide opportunities to use lignin in a variety of value-added applications. Some factors that influence the molecular weight of lignin are the diversity of lignin isolation procedures, macromolecular degradation during isolation, the effect of condensation mainly on acidic conditions, the apparent polydispersity of dissolved lignin, inadequate determination methods used to characterize the isolated lignin, and uncertainties in the properties of lignin. Because lignin is heterogeneous and inconstant, characterizing native lignin is also difficult [60].

The molecular weight of lignin is very important in the development of such polymeric products; similarly, low-molecular-weight lignin isolated from wheat straw by acetic acid pulping is an ideal feedstock for adhesive manufacturing [61]. Doherty et al. [62] stated that lignin from the soda process of wheat plants ranges from 1700 with a methoxyl content of 16. The organosolv pulping process at bagasse produces a molecular weight of around 2000 and a methoxyl content of 15.1. Lignin produced in the isolation process using alcohol or alcell process has a low molecular weight ( $M_w < 900$ ) with low polydispersity, no sulfur, and low ash content, although the value depends on the analytical method. There is also a molecular weight of  $2580 \text{ g mol}^{-1}$  with a polydispersity of 4.3. Sameni et al. compared four types of lignin from different isolation methods, where the highest  $M_w$  (13488) was obtained from the steam explosion process with a methoxyl content of 0.69. Meanwhile, with the same methoxyl content, the lowest  $M_w$  (2565) was derived from the kraft process [57]. Yun et al. reported that organosolv fractionation from native lignin decreased its molecular weight from 5070 to 1810 [23].

### 3.5 Lignin Analysis with FT-IR Spectrophotometer

FTIR was performed to analyze differences in the functional groups of lignin in the sample (Figs. 2 and 3). FTIR spectra analysis showed that the peak in the aromatic ring vibrations decreased with the absorption band at  $1446 \text{ cm}^{-1}$  (a) and  $1408 \text{ cm}^{-1}$  (b), especially in the treatment using the highest concentration of KOH (Fig. 2) and ethanol (Fig. 3). There are similarities in the wavelength of  $3500$  to  $31090 \text{ cm}^{-1}$  which refer to the presence of hydrogen bonds in the hydroxyl group (alcohol and phenolic). A wavelength absorption of  $1587$  and  $1513 \text{ cm}^{-1}$  indicates the aromatic lignin skeletal vibration [60]. Wavenumbers at  $1460$  to  $1420 \text{ cm}^{-1}$  are associated with stretching wavelengths of CH (methyl and methylene) and CH deformation with aromatic ring stretching fields [63]. The peaks observed in the range of  $1220$  to  $1270 \text{ cm}^{-1}$  in all spectra may refer to the C-H deformation vibrations of the guaiacyl [64]. The bands at  $1300 \text{ cm}^{-1}$  (syringyl) and  $1200 \text{ cm}^{-1}$  (guaiacyl) indicate the presence of both syringyl and guaiacyl in lignin's chemical structure as the unique peaks of lignin precursor [65]. A similar peak was also found in kraft lignin isolated from *Acacia mangium* black liquor [27]. In general, peaks in Figs. 2 and 3 show that the treatment using KOH had a sharper peak than that of ethanol treatment. However, no difference in the peaks resulting from these two treatments was determined. Hidayati et al. [20] reported the experiment in isolated lignin from formacell BL of OPEFB using NaOH with the wave number of isolated lignin for guaiacyl lignin at around  $1273.02 \text{ cm}^{-1}$ .

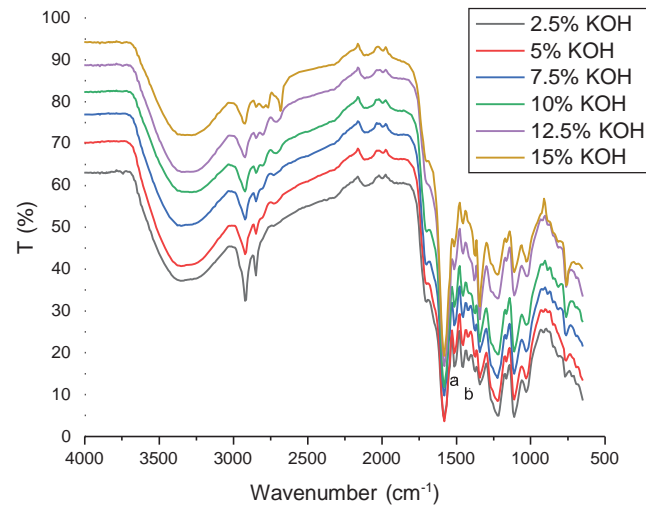


Figure 2: The FT-IR spectra of lignin using KOH isolation

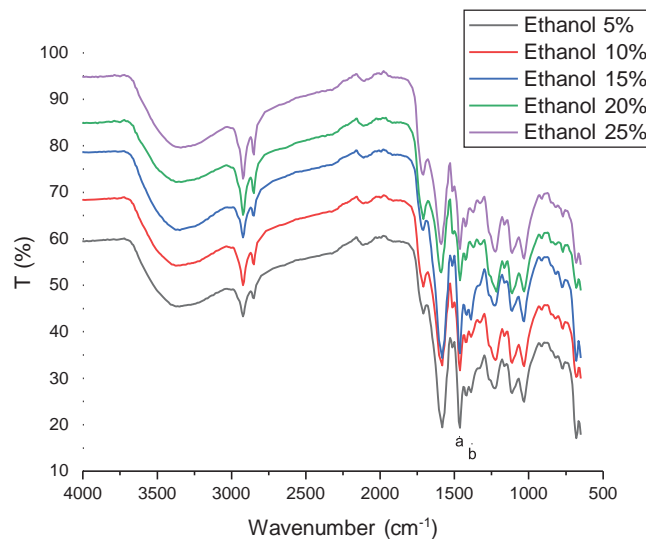


Figure 3: The FT-IR spectra of lignin using ethanol isolation

### 3.6 Morphological Observation

Scanning Electron Microscope (SEM) was used to observe the size and morphology of lignin. In this study, SEM images were taken from the lowest and the highest concentration of KOH and ethanol as representative lignin morphology. As seen in Fig. 4, increasing the concentration of KOH acid from 2.5% to 15% showed differences in lignin morphology. Lignin isolation using 15% KOH (Fig. 4b) produced a more compact formation and morphology compared to lignin produced by isolation using 2.5% KOH concentration (Fig. 4a). In stark contrast, in treatment using ethanol appears that treatment with a 5% ethanol concentration resulted in a more condensed form and morphology than those using a 30% concentration. This result was in accordance with the findings reported by Solihat et al. [27] and Hamzah et al. [41], where increasing ethanol concentration created more rupture and amorphous lignin surface.



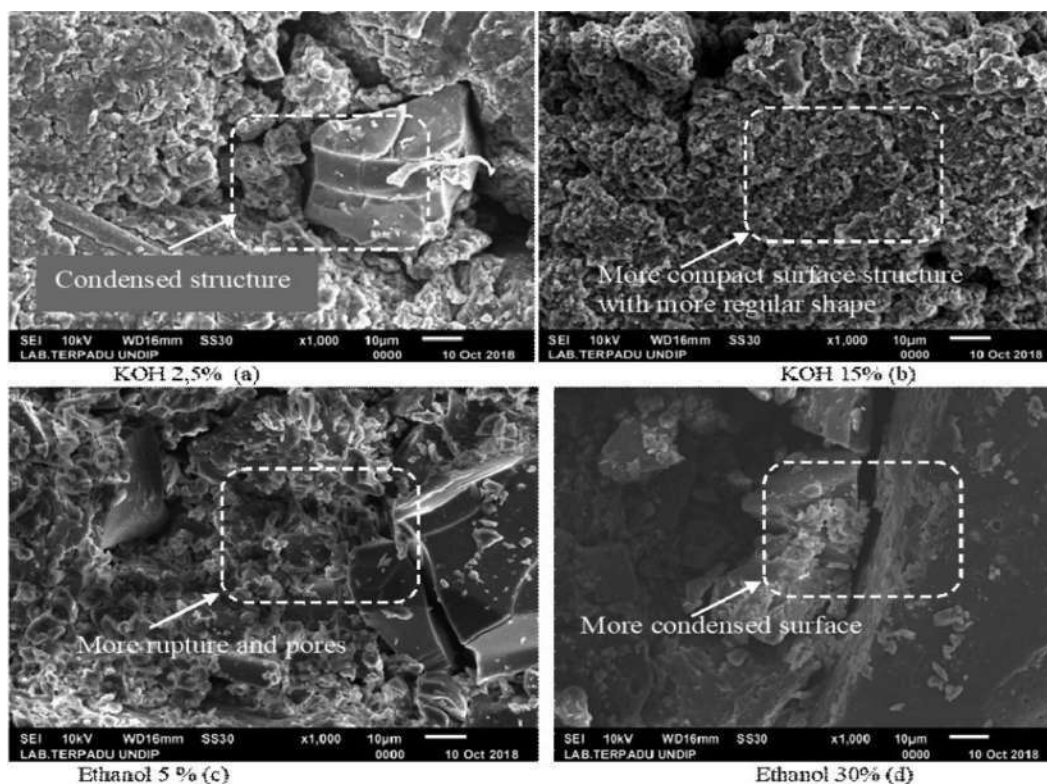


Figure 4: Morphological images of isolated lignin (a) KOH 2.5%, (b) KOH 15%, (c) ethanol 5%, (d) ethanol 30% with 1000 × magnification

### 3.7 Prospective Application of Formacell Lignin as Advanced Biocomposite Products

The lignin molecule contains a variety of active functional groups, including aliphatic hydroxyl (Al-OH), phenolic hydroxyl (Ph-OH), carboxyl (-COOH), carbonyl (-C=O), and methoxy groups (-OCH<sub>3</sub>), which determine its properties, chemistry, and reactivity of lignin. Lignin's chemical properties enable it and its derivatives to be used as high-value materials. The lignin molecule can be used in a variety of value-added applications due to differences in molecular weight, elemental composition, and the types and proportions of functional groups. Currently, Saražin et al. investigated the potency of organosolv lignin-based non-isocyanate polyurethane for wood adhesive and the result demonstrated satisfactory mechanical properties [66] and its curing kinetics for interior furniture showed that it was more suitable than urea-formaldehyde (UF) adhesive [67]. Sulfur-free lignin is produced by isolating lignin from the formacell process. Most value-added applications prefer lignin with a lower percentage of sulfur and ash. For example, sulfur-free lignin is preferred for use in aerogel composites. Jõul et al. reacted lignin isolated by organic acid with 5-methylresorcinol-formaldehyde to create aerogel and according to the data, formacell lignin had good reactivity to create a high surface area of aerogel [68]. According to Talabi et al. lignin with rich hydroxyl carbon, low molecular weight, and less in the methoxyl group was suitable for lignin-based-formaldehyde resin with a 73% graphitization level [69], and hence formacell lignin with higher KOH and ethanol concentrations are appropriate for this application. Meanwhile, the high molecular weight of lignin is preferred as a matrix in carbon fiber composites because it improves the mechanical performance of the fiber.

#### 4 Conclusions

A strong base, such as KOH, was used to successfully isolate lignin from oil palm empty fruit bunch (OPEFB) formacell BL. Some identified lignin peaks can be found in the FTIR spectra, with no significant difference between lignins isolated with KOH and ethanol. The addition of KOH solution at 12.5% and 15% concentrations is the more effective method for isolating lignin from formacell BL. At this condition, isolated lignins have pH values of 3.86 and 4.27, lignin yield of 2.78% and 14.95%, methoxyl content of 11.33% and 10.13%, and lignin equivalent weights of 476.25 and 427.03, respectively. The lignin produced by the isolation process using KOH and ethanol was characterized by the low methoxy content and a low molecular weight that created its higher reactivity. According to these properties, lignin derived from formacell is suitable for developing green, bio-based additives in biocomposite applications such as wood adhesives from non-isocyanate polyurethane, coatings, lignin-based-formaldehyde resins, formaldehyde scavengers, composite fillers, and other value-added industrial applications.

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**JRM-27579-online notice**

2 messages

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Wed, Feb 1, 2023 at 7:48 AM

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Because of the newly released policy about funding statement, we would like you to confirm that whether this acknowledgement contains the funding number.

based-formaldehyde resins, formaldehyde scavengers, composite fillers, and other value-added industrial applications.

**Acknowledgement:** Authors acknowledge the Ministry of Education and Culture of the Republic of Indonesia for the financial support through the Basic Research Fund for the 2017/2018 Fiscal Year. The authors also acknowledge Advanced Characterization Laboratories Cibinong—Integrated Laboratory of Bioproduct, National Research, and Innovation Agency through E-Layanan Sains, Badan Riset dan Inovasi Nasional for the facilities, scientific and technical support form. This work was also supported by the project “Development, Properties, and Application of Eco-Friendly Wood-Based Composites”, No. HHC-B-1145/04.2021, carried out at the University of Forestry, Sofia, Bulgaria. The authors would like to acknowledge the Fundamental Research Grant Scheme (FRGS 2018-1), Reference code: FRGS/1/2018/WAB07/UPM/1 provided by the Ministry of Higher Education, Malaysia.

**Funding Statement:** The authors received no specific funding for this study.

**Conflicts of Interest:** The authors declare that they have no conflicts of interest to report regarding the present study.

Look forward to your kind reply.

Best regards,

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*International and Public Relations Coordinator*

*University of Forestry, Sofia, Bulgaria*

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Petar

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Dear Gabriel,

Many thanks for this information and your kind assistance during the processing of our paper!

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ARTICLE

## Characterization of Formacell Lignin Derived from Black Liquor as a Potential Green Additive for Advanced Biocomposites

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### ABSTRACT

Black liquor is obtained as a by-product of the pulping process, which is used to convert biomass into pulp by removing lignin, hemicelluloses and other extractives from wood to free cellulose fibers. Lignin represents a major constituent in black liquor, with quantities varying from 20% to 30%, of which a very low share is used for manufacturing value-added products, while the rest is mainly burned for energy purposes, thus underestimating its great potential as a raw material. Therefore, it is essential to establish new isolation and extraction methods to increase lignin valorization in the development of bio-based chemicals. The aim of this research work was to determine the effect of KOH or ethanol concentration as an isolation agent on lignin yields and the chemical characteristics of lignin isolated from formacell black liquor of oil palm empty fruit bunch (OPEFB). Isolation of lignin was carried out using KOH with various concentrations ranging from 5% to 15% (w/v). Ethanol was also used to precipitate lignin from black liquor at concentrations varying from 5% to 30% (v/v). The results obtained showed that the addition of KOH solution at 12.5% and 15% concentrations resulted in better lignin yield and chemical properties of lignin, i.e., pH values of 3.86 and 4.27, lignin yield of 12.78% and 14.95%, methoxy content of 11.33% and 10.13%, and lignin equivalent weights of 476.25 and 427.03, respectively. Due to its phenolic structure and rich functional groups that are favorable for modifications, lignin has the potential to be used as a green additive in the development of advanced biocomposite products in various applications to replace current fossil fuel-based material, ranging from fillers, fire retardants, formaldehyde scavengers, carbon fibers, aerogels, and wood adhesives.



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**KEYWORDS**

Formacell black liquor; lignin properties; KOH; ethanol; oil palm empty fruit bunch; advanced biocomposite

**1 Introduction**

Global challenges such as food security and environmental threats can be treated by applying the circular bioeconomy principles, including sustainable conversion of biomass components into bio-based products as green alternatives to their petroleum-based counterparts, thus closing the material resource loops [1]. Black liquor (BL) is liquid waste left over from cooking pulp, aimed at removing lignin, hemicelluloses, and other extractable constituents from wood in order to free the cellulose fibers. Lignin is the main organic substance in BL, reaching 45% dry weight [2]. About 150 billion tons of BL are released from the pulp and paper industry, where every 1 ton of pulp production will produce 7 tons of BL [3]. Considering the increased production of bioethanol, this availability is projected to reach 225 million tons annually in 2030 [4–6]. However, only 2%–5% of BL has been valorized into biomaterial [7], and the rest for energy purposes [8–10]. Hence, it is important to develop new techniques aimed at increasing the valorization of lignin as a renewable feedstock in various value-added industrial applications. Lignin is a complex polyphenol compound with a complex three-dimensional chemical structure that is difficult to decompose naturally, so it has the potential to cause water pollution if discharged into the environment [11]. Lignin has a highly aromatic structure that is stable to heat and has high carbon content. In addition, lignin contains various functional groups, e.g., aliphatic, phenolic, methoxyl, and carbonyl hydroxyl groups, allowing its modification. Thus, it can be used in many functional applications such as biomass-based fuels, adhesives, flame retardants, dispersants, and surfactant formulations, as antioxidants in plastics and rubbers, dyes, synthetic floors, thermosets, paints, food packaging, filler in adhesives, seed coatings, automotive devices, 3D printing, and fuels for highway maintenance [12–17]. However, the utilization of lignin is still limited on an industrial scale due to the inhomogeneity of structure.

A lignin component is a phenylpropane unit with several different methoxy groups [18]. Chemical structures of lignin are identified by the presence of polypropene units such as p-hydroxyphenyl (or p-coumaryl alcohol), guaiacyl (or coniferyl alcohol), and syringyl (or sinapyl alcohol), and their percentage vary depending on the botanical origin. Polypropene units can be chemically bonded in different bonding patterns where the  $\beta$ -O-4 aryl glycerol ether bond is the primary linkage [19]. However, the technical lignin's structure differs from the native lignin and depends on the pulping method used. Besides, the source of raw materials and isolation method, including the type of chemical used and temperature, play critical roles in the physicochemical properties of lignin [20].

Lignin can be extracted in powder form from BL with proper chemical treatment and screening process [21]. Precipitation of lignin in the BL occurs due to the condensation reaction on the lignin constituent units, which were initially soluble and will be polymerized and form large molecules [22]. Base, acid, and organic solvents are common solutions to isolate lignin from BL. The process of lignin separation using organic solvents is known as the alcell or organosolv process [23]. This method is popular for breaking down lignin fractions [24]. The benefits of this method include obtaining lignin with a low molecular weight that is free of sulfur, and its application can be improved through fractionation or chemical modification [25], but organosolv fractionation is laborious work [26]; hence, acid and base deposition methods are more feasible. However, this method depends on the pH of the liquor, residence time, and temperature [22]. Some acids such as H<sub>2</sub>SO<sub>4</sub>, phosphoric acid (H<sub>3</sub>PO<sub>4</sub>), or HCl have been reported in isolating lignin from base BL, such as from the kraft process [27]. Meanwhile, lignin from formacell BL, BL derived from acetic acid, or formic acid as cooking liquid can be released by different alkalis, especially KOH,



Ca(OH)<sub>2</sub>, and NaOH [20]. KOH, a strong base, is stronger than NaOH, and its use is expected to result in higher lignin yield.

Based on Miller et al. [28], a strong base (e.g., NaOH and KOH) provides a higher result in lignin yield than a weak base, and it would be a promising technique for depolymerizing lignin. The concentration of base is important to measure because it will influence selectivity, chemical-physical properties, and lignin yield [20,29]. Recently, Hidayati et al. evaluated the effect of NaOH concentration on lignin properties [20] while the disadvantage of NaOH was monoaromatic re-condensation led to the higher molecular weight of lignin [30]. Consequently, an alternative base such as KOH and ethanol is needed to overcome this problem. To date, no one reported lignin isolation from formacell BL using different concentrations of KOH and ethanol. Therefore, this study aimed to determine the effect of KOH and ethanol concentrations on the yield and chemical characteristics of lignin isolated from formacell BL of oil palm empty fruit bunch (OPEFB).

## 2 Material and Methods

### 2.1 Materials

Black liquor used in this research is a by-product of the formacell pulping of OPEFB, as reported by Hidayati et al. [31]. The pulping conditions are presented in detail in the next section. OPEFB was obtained from PTPN Business Unit VII Central Lampung Bekri, Indonesia. Meanwhile, KOH, NaCl, NaOH, HCl, and ethanol were supplied by Merck (Darmstadt, Germany).

### 2.2 Pulping Process

The formacell pulping was conducted in the autoclave at a liquor-to-particle ratio of 15:1 for 1 h at 130°C. This ratio of liquor to OPEFB particle ratio was used based on our initial experimental trials in the laboratory, considering the volumetric of OPEFB as a typical example of non-woody biomass. In this ratio, the OPEFB particles can be immersed completely in the chemical liquor. The ratio solvent of acetic acid and formic acid was 85:15 with the addition of HCl of 0.5% as the catalyst. The cooking liquor was collected after filtration and washing the completed softened OPEFB with fresh water at room temperature. This formacell BL was used for the next step.

### 2.3 Lignin Isolation

The formacell BL obtained from the pulping process of 100 mL contained a total solid content of around 25.10%. There are two methods for lignin isolation from formacell BL of OPEFB. The first one, i.e., the isolation of lignin from BL was conducted using KOH with a concentration of 2.5%; 5%; 7.5%; 10%; 12.5%; and 15% (w/v). The second isolation technique used ethanol at concentrations of 5%, 10%, 15%, 20%, 25% and 30% (v/v). As much as 100 mL of the KOH or ethanol solution was added into 100 mL BL, then stirred and measured the pH of the liquor was. The solution was allowed to stand for 10 h, then centrifugated for 20 min at 2500 rpm, and then separated using filter paper. The precipitated lignin was then oven-dried at 50°C–60°C for 24 h. Dried lignin was crushed manually to produce fine lignin powder (Fig. 1). The experiment was conducted in triplicate.

The data were calculated and presented in average and standard deviation tables and graphs. Observations made were pH value, the yield of lignin, lignin methoxyl content, the equivalent weight of lignin, analysis of lignin with Fourier Transform Infra-Red spectroscopy (FTIR) spectrophotometer (Cary 630 FTIR, Agilent, Australia), and lignin morphology using a scanning electron microscope (SEM) (JEOL JSM 6510 LA, Japan).

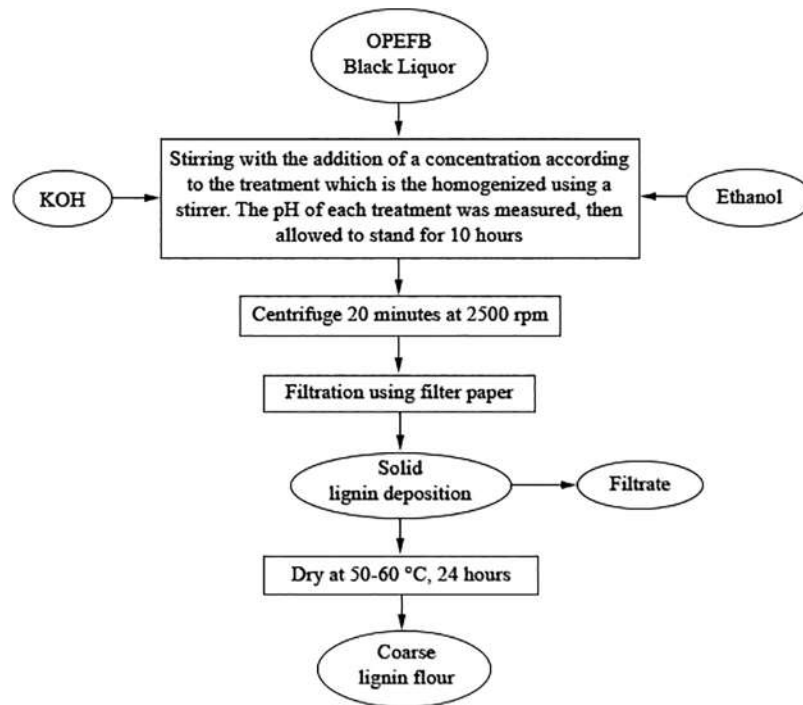


Figure 1: Flowchart of lignin isolation process using KOH/Ethanol

#### 2.4 Lignin Yield

Lignin yield was calculated based on the method according to Sluiter et al. [32], as presented in Eq. (1).

$$\text{Lignin Yield } \delta\% \text{ p } \frac{a}{b} \times 100\% \quad (1)$$

Notation:

a = weight of isolated lignin;

b = weight of lignin in black liquor.

#### 2.5 Methoxyl Content of Lignin

The methoxyl content of lignin was determined by using the ASTM 15120-81 method [33]. As much as 0.5 g of lignin was added to 5 mL of ethanol, following addition to 100 mL of distilled water containing 1 g of NaCl, and made in the form of suspension. Neutralization was performed using 0.1 N NaOH, given 6 drops of phenolphthalein (pp) indicator, and then 25 mL of 0.25 N NaOH was added and homogenized in a closed state for 30 min at room temperature. After that, 25 mL of 0.25 N HCl was added and titrated with 0.1 N NaOH until the end of the lasting color change (at least 30 s). The methoxyl content of lignin was calculated according to Eq. (2) as follows:

$$\text{Methoxyl } \delta\% \text{ p } \frac{\text{ml NaOH} \times \text{N NaOH} \times 3;1}{\text{Berat sampel } \delta\text{gram}} \times 100\% \quad (2)$$

#### 2.6 Lignin Equivalent Weight

Isolated lignin equivalent weight was calculated using the method of Brauns et al. [34]. 0.5 g lignin was put into 250 mL Erlenmeyer and moistened with 5 mL ethanol. The mixture is spiked with 1 g of NaCl which is then added with 100 mL of distilled water and 6 drops of phenolphthalein indicator. The solution was then titrated with 0.1 N NaOH until pH 7.5. The equivalent weight of isolated lignin was calculated by using Eq. (3).

$$\text{Equivalent Weight} = \frac{1000 \times \text{gram sample}}{\delta mLN \cdot NaOH} \quad (3)$$

### 2.7 FT-IR Analysis of Isolated Lignin

As much as 1 mg isolated lignin was added with 150 mg KBr, pelletized, and then the samples were analyzed by FT-IR spectrophotometer (Cary 630 FTIR Agilent). The analysis was set at a wavenumber of 4000 to 400  $\text{cm}^{-1}$  (wavelength of 2.5–25  $\mu\text{m}$ ).

### 2.8 SEM Analysis

Morphology of isolated lignin was carried out using Scanning Electron Microscope (SEM) (JEOL JSM 6510 LA) with 1000  $\times$  magnification.

## 3 Results and Discussion

### 3.1 pH of the Black Liquor

The pH of BL from formacell pulping OPEFB is  $0.59 \pm 0.01$ , indicating that the liquor is acidic; thus, base or ethanol can be used to precipitate lignin from BL. To speed up the reaction, solvents such as acetic acid and formic acid are used in the formacell pulping process, along with HCl as a catalyst [31]. This process causes the pH of the formacell BL to become very acidic. Zhuang et al. [35] stated that formic acid and acetic acid could delignify lignin because of their acidic nature, so they can degrade lignin well. In another study, a combination of formic acid, acetic acid, and water achieved more than 50% lignin depolymerization in biomass [36]. The pH of the BL will be affected by the addition of KOH solution. According to the research, the pH value obtained from formacell pulping added with KOH solution ranged from  $2.43 \pm 0.07$  to  $4.27 \pm 0.35$  (Table 1), while the addition of ethanol concentrations can slightly increase the pH value from  $1.0 \pm 0.01$  to  $1.29 \pm 0.03$ . According to the findings, KOH has a greater effect on increasing pH than ethanol due to the strong base property of KOH.

Table 1: Effect of KOH and ethanol concentrations on pH, yield, methoxyl content, and an equivalent weight of isolated lignin

Treatment	pH	Yield (%)	Lignin methoxyl (%)	Equivalent weight
KOH concentration (%)				
2.5	$2.43 \pm 0.07$	$3.57 \pm 0.38$	$13.06 \pm 0.9$	$1372.94 \pm 26.73$
5.0	$2.94 \pm 0.06$	$4.85 \pm 1.12$	$12.94 \pm 1.31$	$655.73 \pm 45.16$
7.5	$3.21 \pm 0.1$	$8.63 \pm 1.41$	$12.81 \pm 0.84$	$528.74 \pm 54.44$
10	$3.61 \pm 0.15$	$11.20 \pm 2.69$	$12.36 \pm 0.9$	$510.33 \pm 49.05$
12.5	$3.86 \pm 0.15$	$12.78 \pm 0.78$	$11.33 \pm 0.4$	$476.25 \pm 34.61$
15	$4.27 \pm 0.35$	$14.95 \pm 1.10$	$10.13 \pm 1.42$	$427.03 \pm 44.20$
Ethanol concentration (%)				
5	$1.00 \pm 0.01$	$1.95 \pm 0.18$	$17.03 \pm 0.42$	$449.88 \pm 48.47$
10	$1.08 \pm 0.06$	$2.27 \pm 0.317$	$16.45 \pm 1.44$	$624.67 \pm 59.2$
15	$1.15 \pm 0.07$	$1.69 \pm 0.091$	$15.05 \pm 1.03$	$767.97 \pm 56.6$
20	$1.20 \pm 0.047$	$1.77 \pm 0.207$	$14.47 \pm 1.17$	$896.95 \pm 64.15$
25	$1.22 \pm 0.056$	$1.44 \pm 0.174$	$13.14 \pm 1.78$	$1521.16 \pm 72.10$
30	$1.29 \pm 0.03$	$1.08 \pm 0.179$	$11.99 \pm 1.20$	$2123.02 \pm 70.72$

The pH steadily increased as an up-surging concentration of KOH, where the lowest pH,  $2.43 \pm 0.07$ , was obtained from 2.5% KOH, and the highest was a pH of  $4.27 \pm 0.35$  from KOH 15%. Increasing the concentration of KOH solution causes more  $\text{OH}^-$  ions in the BL so that the pH of the solution becomes more alkaline. It can also be explained that KOH is a strong base. The stronger the base, the more OH ions are released, increasing the pH of the solution and making it more alkaline. Ethanol has a higher pKa than KOH, indicating a weaker acid. Unlike KOH, increasing the ethanol concentration slightly increased the pH, with the lowest being 1 and the highest being 1.29 after adding 5% and 30%, as shown in Table 1.

### 3.2 Lignin Yield

The lignin yield from adding KOH solution at various concentrations in isolation of BL ranged from  $3.57 \pm 0.38$  to  $14.95 \pm 1.10$  (Table 1). In comparison, ethanol isolation resulted in lower lignin yields of about  $0.51 \pm 0.00$  to  $1.06 \pm 0.00$ . The highest lignin yield was produced at a concentration of 15% KOH solution ( $14.95\% \pm 1.10$ ). Increasing the concentration of KOH solution caused the lignin yield to increase. It can be affected by the increasing concentration of an alkaline solution (KOH) that facilitates easier breaking of lignin bonds with other compounds, and a condensation reaction occurs in the lignin constituent units [37]. It is also supported by Sundin [38] who stated that lignin deposition from BL due to the protonation of phenol groups on lignin molecules caused by the addition of  $\text{OH}^-$  ions from KOH. It reduces the electrostatic force between lignin molecules, resulting in the deposition of lignin and reduced solubility. The more  $\text{OH}^-$  ions, the more lignin deposits will form. The deposit lignin increase occurred because of an increase in ionic strength and protonation. The protonation of the phenolic group in lignin leads the lignin nucleus to form aggregates when the pKa value of lignin is reached [39].

The lignin yield with KOH liquor treatment is higher than that of NaOH, as reported by Hidayati et al. [20]. Lignin was isolated from formacell BL of OPEFB by using NaOH, producing lignin yields ranging from 1.48% to 5.67%. It might be caused by the stronger base of KOH than NaOH. As seen in the periodic system, the metal  $\text{Na}^+$  and  $\text{K}^+$  are included in Group 1A. This is also related to the lower nature of alkali metal bases; the stronger, the lower the metal, the more easily reduced. Besides pH, temperature and ionic strength also affect lignin solubility. The molecular weight distribution in lignins is related to yield [40]. Both molecular weight and the ratio of phenols to aromatic units contribute to the solubility of lignin [40]. The changes in lignin yield in isolation by adding ethanol concentration are very low. The very low electronegativity of ethanol can suggest the presence of carbon compounds that cannot precipitate lignin properly. In the absence of sulfide, delignification was slower in the Alcell process.

As opposed to KOH precipitation, increasing ethanol concentrations leads to almost 0% lignin recovery. This result was in agreement with the precipitation of lignin from *Miscanthus x giganteus*, where after the addition of 75% of ethanol, there was no lignin precipitated [41]. In the low concentration of ethanol, lignin precipitation is carried out by diluting liquor with water, and the solubility of lignin decreases, resulting in more lignin being recovered. In other words, when the water content in the ethanol is limited, most of the lignin is soluble in the system, and hence the aggregate is not formed.

### 3.3 Methoxyl Content in Lignin

Methoxyl is one of the chemical groups in lignin for identifying one of the characteristics of lignin. The methoxyl group in each type of lignin has different content because of the different structures of lignin types. Determining methoxyl contents gives information about the average C9 units in lignin, and eventually, the unsaturated side chain and average oxygen content can be calculated [42]. The methoxyl content in KOH lignin ranged from  $10.13\% \pm 1.92$  to  $13.06\% \pm 0.9$ , whereas the use of ethanol concentrations results in methoxyl contents between  $11.99 \pm 0.02$  to  $17.03 \pm 0.42$  (Table 1). The highest methoxyl content in lignin was acquired from isolated lignin by adding a 2.5% KOH solution. Increasing the concentration of

KOH and ethanol solution leads to a decrease in the methoxyl content of isolated lignins. This may be due to the use of KOH as a strong base as a precipitating solution, which allows some methoxyl groups to degrade and transform into other compounds. This decrease in methoxyl content can be influenced by the disruption of structural stability in lignin caused by the addition of KOH. Furthermore, according to the pathway proposed by Yin et al. the removal of the methoxy group in lignin created a higher hydroxyl group of lignin by KOH solution. The presence of potassium in lignin isolation decreased the methoxyl content due to cleavage  $C\alpha-C\beta$  through  $C\beta-O$  bond. This cleavage leads to the removal of side chains such as methoxyl. The mechanism of this reaction has been proved by Yin et al. [43].

The various methoxyl content in lignin depends on the source of lignin and the delignification process used. Generally, high methoxyl content will inhibit lignin reactivity during use in the resin field. Lignin has phenolic hydroxyl groups that are typically linked to nearby phenyl propane units, allowing lignin to connect with formaldehyde in a way analogous to phenol and formaldehyde [44]. Molecular weight and lignin purity are important factors during the production of biocarbon fibers [44,45].

In the case of lignin application as an adhesive raw material, the low methoxyl content is more beneficial because it will increase the reactivity of aromatic nuclei in lignin [46]. It will facilitate the reaction of methylation or hydroxymethylation with adhesive-forming reactants such as NaOH and formaldehyde, hinting at the ease of gel formation. Recently, Gendron et al. compared four types of lignin for green adhesive, where the lowest methoxyl content of lignin had the highest water solubility and shear resistance as an adhesive [47].

The lignin standard of Indulin AT has a methoxyl content of around 13.5%–14.5% [48], so the methoxyl contents in isolated lignin in this study are still lower. Meanwhile, compared to methoxyl content by Hidayati et al. [20] with a value of 14.61%–20.77% by using NaOH as precipitating solution, the results of this study are also lower. These results are probably influenced by the use of KOH, which is classified as a strong base with a higher reactivity than NaOH, as seen from the periodic system. The influence of harsh chemicals and temperature during isolation causes the structure of lignin to undergo many changes, including the methoxyl group. The methoxyl group is degraded and transformed into other degradation compounds such as aromatic hydrocarbon and phenolic types, resulting in lower methoxyl content [49].

### 3.4 The Equivalent Weight of Lignin

The determination of the equivalent weight of lignin is intended to determine the molecular weight of lignin to identify lignin degradation and condensation reactions. The molecular weight of lignin is an important property that influences biomass recalcitrance and lignin value. Determination of the molecular weight of lignin in the original biomass depends on the source of the raw material used, chemicals used for isolation, and purification methods [50,51]. Based on the results, the equivalent weight of lignin from the KOH solution ranged from  $427.03 \pm 74.20$  to  $1372.94 \pm 269.73$ , whereas the addition of ethanol concentration resulted in molecular weights ranging from  $449.88 \pm 1.9$  to  $2123.03 \pm 27.5$  (Table 1).

Increasing the concentration of KOH solution resulted in a decrease in lignin equivalent weight, so the lowest value at 15% KOH solution concentration was  $427.03 \pm 74.20$ . This might be attributed to the increasing addition of a KOH solution as a strong base will degrade a portion of lignin into a derivative compound with shorter chains. It can degrade lignin resulting in a low equivalent weight. According to Patil et al., lignin depolymerization has two routes: harsh and moderate, resulting in different lignin structures [52]. The average molecular weight of lignin decreases with increasing precipitation of lignin yield by KOH. It was shown that increasing the amount of lignin with lower molecular weight deposited a high yield of lignin. Lignin is degraded into smaller fragments so that there are more phenolic groups with lower molecular weights [53]. Increasing salt concentration can lower the product's molecular weight [54,55].

According to Gellerstedt [56], the termination of methyl aryl ether bonds from the aromatic ring of lignin resulted in decreased methoxyl content and low molecular weight of lignin due to the lignin degradation process. Based on several previous studies, lignin molecular weight values were obtained, namely 2500–14,000 [57], and 1327.64–1787.23 [20]. In contrast, the equivalent weight of Indulin AT reached 3357–3366 [58]. This shows that the equivalent weight value of lignin varies greatly.

Lignin that has a high molecular weight can be used as a matrix in polyolefin composites, because a higher molecular mass of lignin has a better affinity with the matrix [59], while lignin with a lower molecular weight can be used for the development of phenol-formaldehyde resins, antioxidants, adhesives, and paints due to their higher reactivity than high molecular weight lignin [59].

Differences in elemental composition, functional group types, proportions, and molecular weight in lignin molecules provide opportunities to use lignin in a variety of value-added applications. Some factors that influence the molecular weight of lignin are the diversity of lignin isolation procedures, macromolecular degradation during isolation, the effect of condensation mainly on acidic conditions, the apparent polydispersity of dissolved lignin, inadequate determination methods used to characterize the isolated lignin, and uncertainties in the properties of lignin. Because lignin is heterogeneous and inconstant, characterizing native lignin is also difficult [60].

The molecular weight of lignin is very important in the development of such polymeric products; similarly, low-molecular-weight lignin isolated from wheat straw by acetic acid pulping is an ideal feedstock for adhesive manufacturing [61]. Doherty et al. [62] stated that lignin from the soda process of wheat plants ranges from 1700 with a methoxyl content of 16. The organosolv pulping process at bagasse produces a molecular weight of around 2000 and a methoxyl content of 15.1. Lignin produced in the isolation process using alcohol or alcell process has a low molecular weight ( $M_w < 900$ ) with low polydispersity, no sulfur, and low ash content, although the value depends on the analytical method. There is also a molecular weight of  $2580 \text{ g mol}^{-1}$  with a polydispersity of 4.3. Sameni et al. compared four types of lignin from different isolation methods, where the highest  $M_w$  (13488) was obtained from the steam explosion process with a methoxyl content of 0.69. Meanwhile, with the same methoxyl content, the lowest  $M_w$  (2565) was derived from the kraft process [57]. Yun et al. reported that organosolv fractionation from native lignin decreased its molecular weight from 5070 to 1810 [23].

### 3.5 Lignin Analysis with FT-IR Spectrophotometer

FTIR was performed to analyze differences in the functional groups of lignin in the sample (Figs. 2 and 3). FTIR spectra analysis showed that the peak in the aromatic ring vibrations decreased with the absorption band at  $1446 \text{ cm}^{-1}$  (a) and  $1408 \text{ cm}^{-1}$  (b), especially in the treatment using the highest concentration of KOH (Fig. 2) and ethanol (Fig. 3). There are similarities in the wavelength of  $3500$  to  $3109 \text{ cm}^{-1}$  which refer to the presence of hydrogen bonds in the hydroxyl group (alcohol and phenolic). A wavelength absorption of  $1587$  and  $1513 \text{ cm}^{-1}$  indicates the aromatic lignin skeletal vibration [60]. Wavenumbers at  $1460$  to  $1420 \text{ cm}^{-1}$  are associated with stretching wavelengths of CH (methyl and methylene) and CH deformation with aromatic ring stretching fields [63]. The peaks observed in the range of  $1220$  to  $1270 \text{ cm}^{-1}$  in all spectra may refer to the C-H deformation vibrations of the guaiacyl [64]. The bands at  $1300 \text{ cm}^{-1}$  (syringyl) and  $1200 \text{ cm}^{-1}$  (guaiacyl) indicate the presence of both syringyl and guaiacyl in lignin's chemical structure as the unique peaks of lignin precursor [65]. A similar peak was also found in kraft lignin isolated from *Acacia mangium* black liquor [27]. In general, peaks in Figs. 2 and 3 show that the treatment using KOH had a sharper peak than that of ethanol treatment. However, no difference in the peaks resulting from these two treatments was determined. Hidayati et al. [20] reported the experiment in isolated lignin from formacell BL of OPEFB using NaOH with the wave number of isolated lignin for guaiacyl lignin at around  $1273.02 \text{ cm}^{-1}$ .

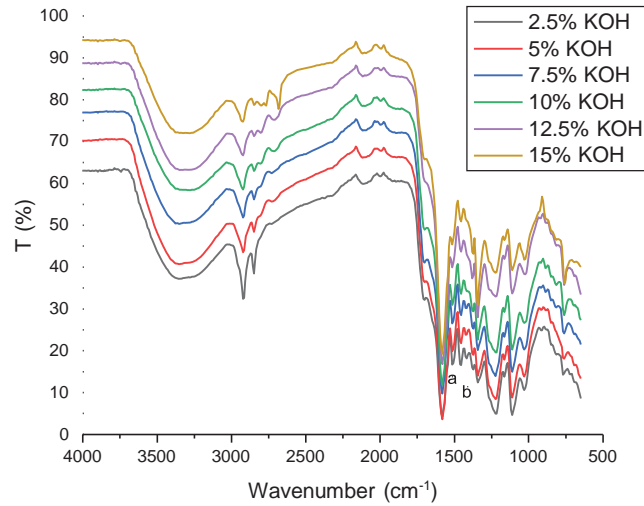


Figure 2: The FT-IR spectra of lignin using KOH isolation

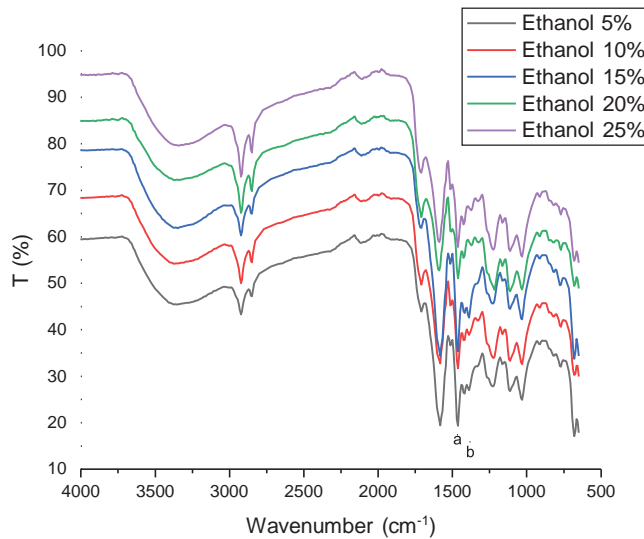


Figure 3: The FT-IR spectra of lignin using ethanol isolation

### 3.6 Morphological Observation

Scanning Electron Microscope (SEM) was used to observe the size and morphology of lignin. In this study, SEM images were taken from the lowest and the highest concentration of KOH and ethanol as representative lignin morphology. As seen in Fig. 4, increasing the concentration of KOH acid from 2.5% to 15% showed differences in lignin morphology. Lignin isolation using 15% KOH (Fig. 4b) produced a more compact formation and morphology compared to lignin produced by isolation using 2.5% KOH concentration (Fig. 4a). In stark contrast, in treatment using ethanol appears that treatment with a 5% ethanol concentration resulted in a more condensed form and morphology than those using a 30% concentration. This result was in accordance with the findings reported by Solihat et al. [27] and Hamzah et al. [41], where increasing ethanol concentration created more rupture and amorphous lignin surface.

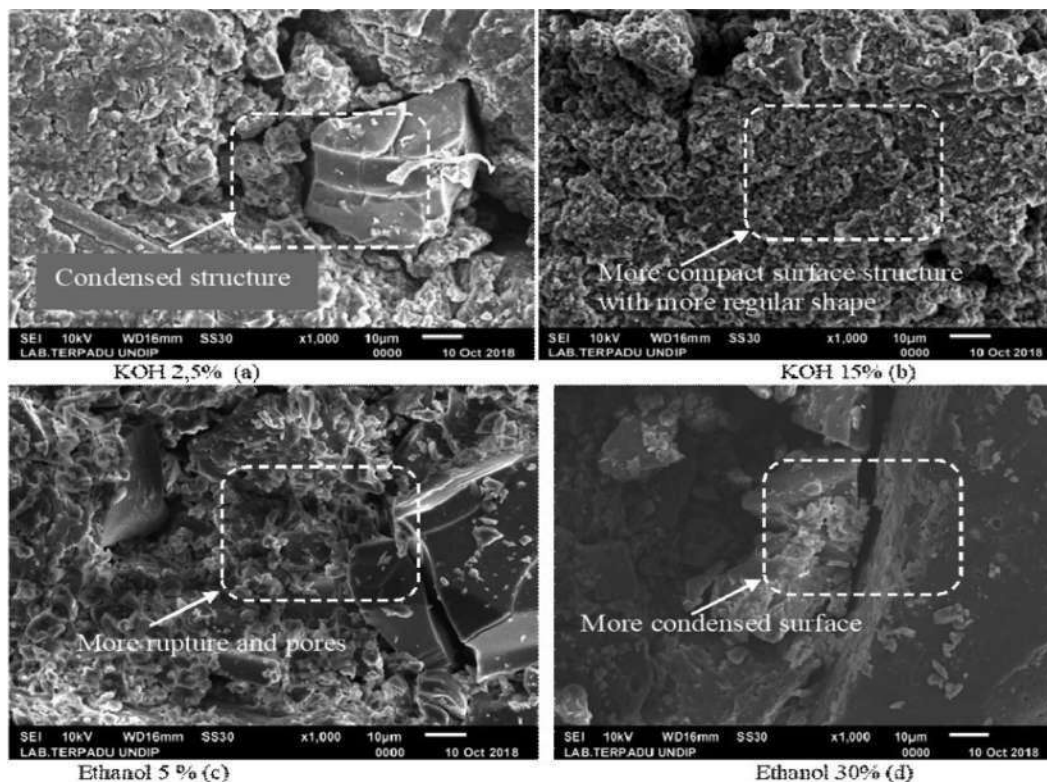


Figure 4: Morphological images of isolated lignin (a) KOH 2.5%, (b) KOH 15%, (c) ethanol 5%, (d) ethanol 30% with 1000 × magnification

### 3.7 Prospective Application of Formacell Lignin as Advanced Biocomposite Products

The lignin molecule contains a variety of active functional groups, including aliphatic hydroxyl (Al-OH), phenolic hydroxyl (Ph-OH), carboxyl (-COOH), carbonyl (-C=O), and methoxy groups (-OCH<sub>3</sub>), which determine its properties, chemistry, and reactivity of lignin. Lignin's chemical properties enable it and its derivatives to be used as high-value materials. The lignin molecule can be used in a variety of value-added applications due to differences in molecular weight, elemental composition, and the types and proportions of functional groups. Currently, Saražin et al. investigated the potency of organosolv lignin-based non-isocyanate polyurethane for wood adhesive and the result demonstrated satisfactory mechanical properties [66] and its curing kinetics for interior furniture showed that it was more suitable than urea-formaldehyde (UF) adhesive [67]. Sulfur-free lignin is produced by isolating lignin from the formacell process. Most value-added applications prefer lignin with a lower percentage of sulfur and ash. For example, sulfur-free lignin is preferred for use in aerogel composites. Jõul et al. reacted lignin isolated by organic acid with 5-methylresorcinol-formaldehyde to create aerogel and according to the data, formacell lignin had good reactivity to create a high surface area of aerogel [68]. According to Talabi et al. lignin with rich hydroxyl carbon, low molecular weight, and less in the methoxyl group was suitable for lignin-based-formaldehyde resin with a 73% graphitization level [69], and hence formacell lignin with higher KOH and ethanol concentrations are appropriate for this application. Meanwhile, the high molecular weight of lignin is preferred as a matrix in carbon fiber composites because it improves the mechanical performance of the fiber.



#### 4 Conclusions

A strong base, such as KOH, was used to successfully isolate lignin from oil palm empty fruit bunch (OPEFB) formacell BL. Some identified lignin peaks can be found in the FTIR spectra, with no significant difference between lignins isolated with KOH and ethanol. The addition of KOH solution at 12.5% and 15% concentrations is the more effective method for isolating lignin from formacell BL. At this condition, isolated lignins have pH values of 3.86 and 4.27, lignin yield of 2.78% and 14.95%, methoxyl content of 11.33% and 10.13%, and lignin equivalent weights of 476.25 and 427.03, respectively. The lignin produced by the isolation process using KOH and ethanol was characterized by the low methoxy content and a low molecular weight that created its higher reactivity. According to these properties, lignin derived from formacell is suitable for developing green, bio-based additives in biocomposite applications such as wood adhesives from non-isocyanate polyurethane, coatings, lignin-based-formaldehyde resins, formaldehyde scavengers, composite fillers, and other value-added industrial applications.

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