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Quartile 2, SJR 0,38

Sri Hidayati

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2023

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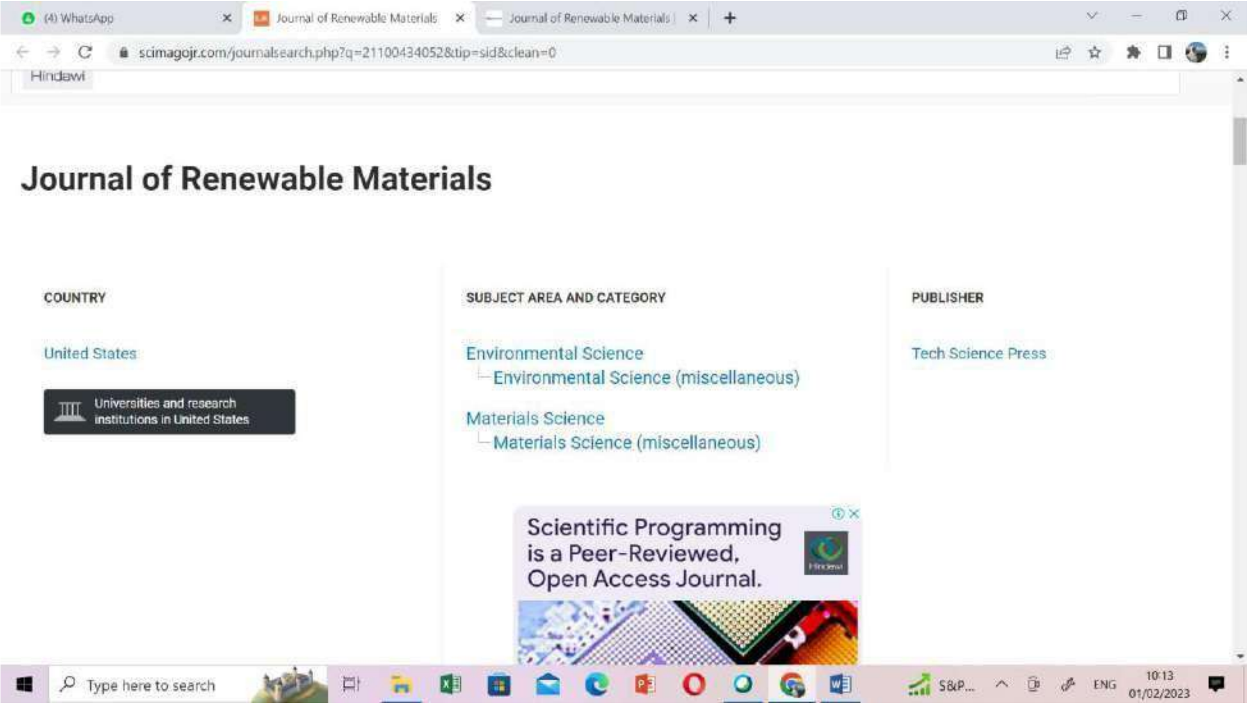

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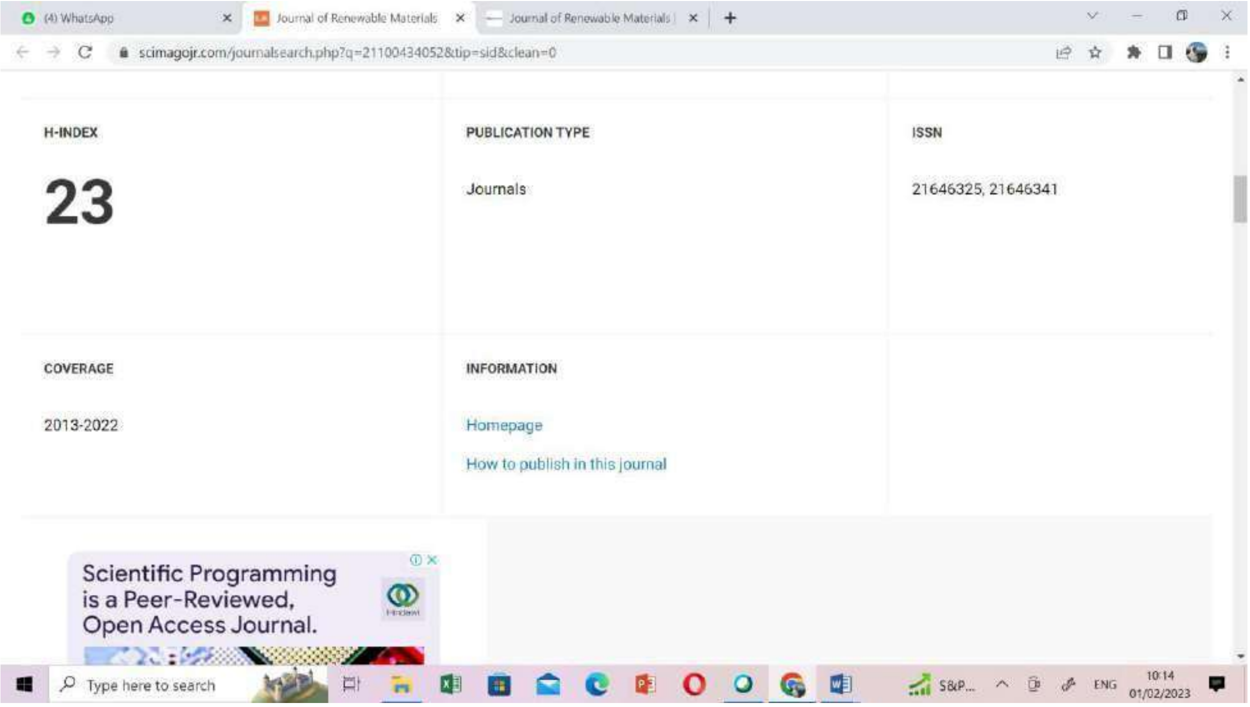

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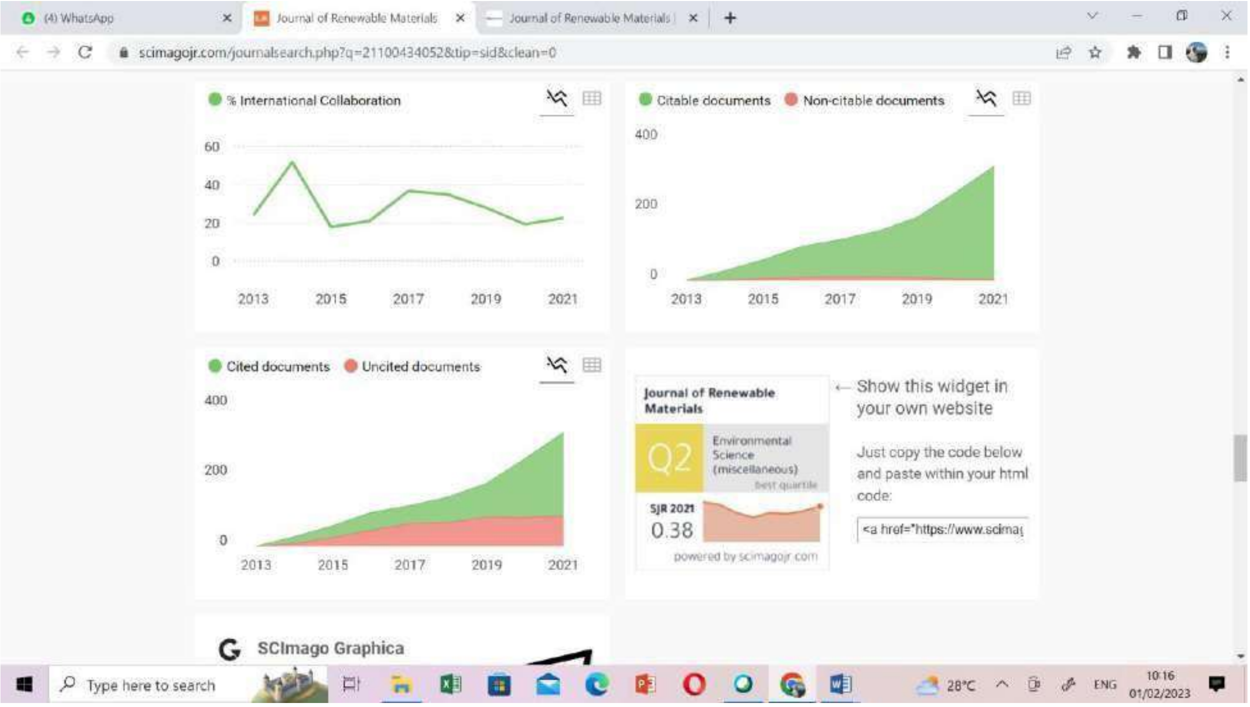

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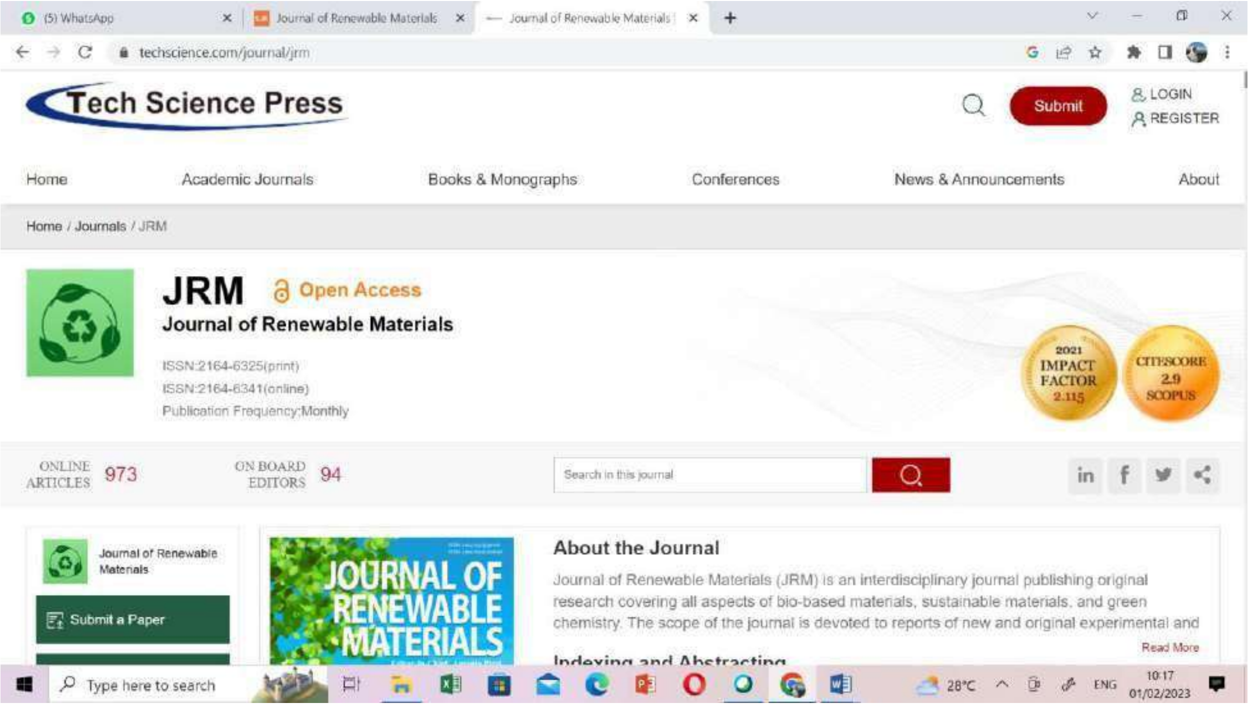

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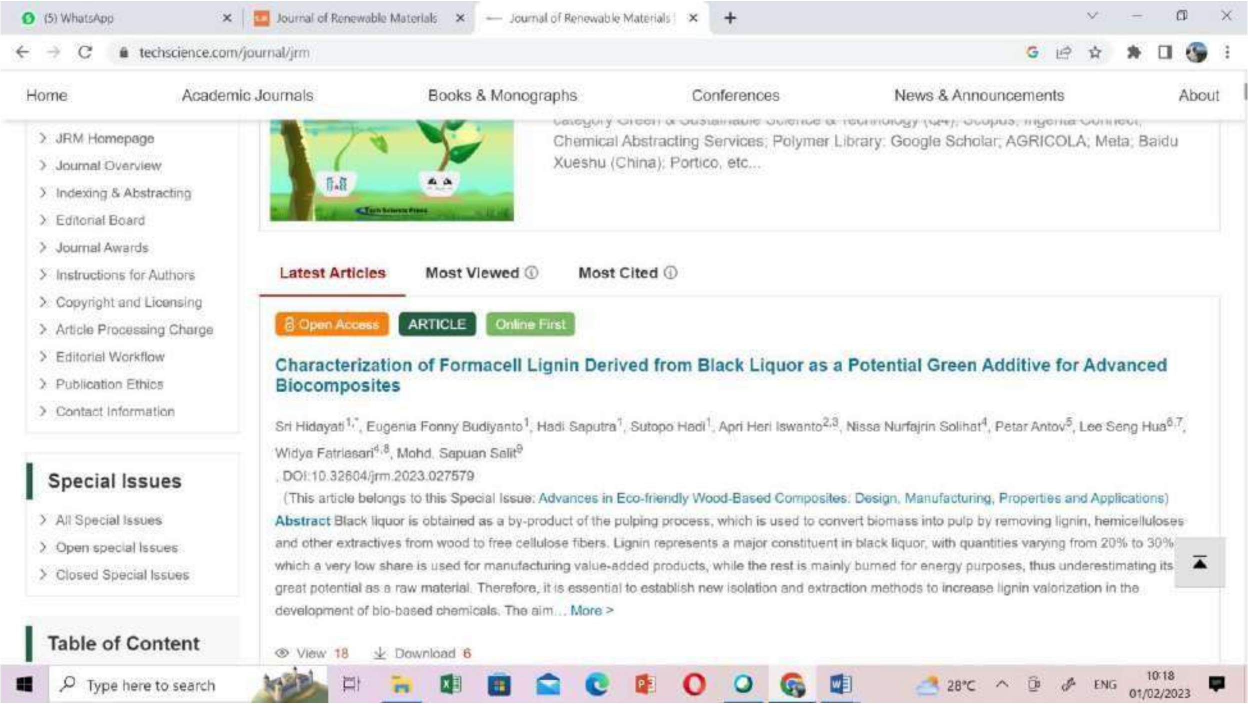

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Characterization of Formacell Lignin Derived from Black Liquor as a Potential Green Additive for Advanced Biocomposites

Sri Hidayati[1,*], Eugenia Fonny Budiyanto[1], Hadi Saputra[1], Sutopo Hadi[1], Apri Heri Iswanto[2,3], Nissa Nurfajrin Solihat[4], Petar Antov[5], Lee Seng Hua[6,7], Widya Fatriesari[4,8], Mohd. Sapuan Salit[9]

, DOI:10.32604/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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8.	**Proof Submitted**	**18 Januari 2023**
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10.	**Publish**	**10 April 2023**

Gmail

sri hidayati <srihidayati.unila@gmail.com>

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1 message

JRM Editorial <noreply@tspsubmission.com> Fri, Nov 4, 2022 at 1:18 PM
Reply-To: JRM Editorial <jrm@techscience.com>
To: Sri Hidayati <srihidayati.unila@gmail.com>

Sri Hidayati

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sri hidayati <srihidayati.unila@gmail.com>

[jrm] ID:27579 Submission Acknowledgement

1 message

JRM Editorial <noreply@tspsubmission.com> Fri, Nov 4, 2022 at 4:24 PM
To: Sri Hidayati <srihidayati.unila@gmail.com>

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:

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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 <srihidayati.unila@gmail.com>

[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 Fonny 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 Nurfajrin 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 Fonny Budiyanto, Hadi Saputra, Sutopo Hadi, Dr. Apri Heri Iswanto, Mrs Nissa Nurfajrin 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 α-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 ºC] -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

_ _

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

JRM-27579-additional review comments

1 message

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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

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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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Response to editors and Reviewers WFNN_PA_Lee (2).docx
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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 inthe 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 Cα—Cβ through Cβ—O bond. This cleavage leads to the removal of side chains suchas 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 α-O-4 cleavage, which is not true at all.

Author's response:

Thank you for the suggestion. The information about lignin depolymerization involving α-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 ºC] -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

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ARTICLE

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

Sri Hidayati[1*], Eugenia Fonny Budiyanto[1], Hadi Saputra[1], Sutopo Hadi[1], Apri Heri Iswanto[2,3], Nissa Nurfajrin Solihat[4], Petar Antov[5], Lee Seng Hua[6,7], Widya Fatriasari[4,8], Mohd. Sapuan Salit[9]

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*Corresponding Author: srihidayati.unila@gmail.com

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 itsphenolic 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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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]. Taking into account 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. Polypropane units can be chemically bonded in different bonding patterns where the β-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_2SO_4, phosphoric acid (H_3PO_4), 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, $Ca(OH)_2$, 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 black liquor 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 ºC. The ratio of liquor to OPEFB particle ratio of 15:1 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 hours, then centrifugated for 20 minutes at 2500 rpm, and then separated using filter paper. The precipitated lignin was then oven-dried at 50-60 ˚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).

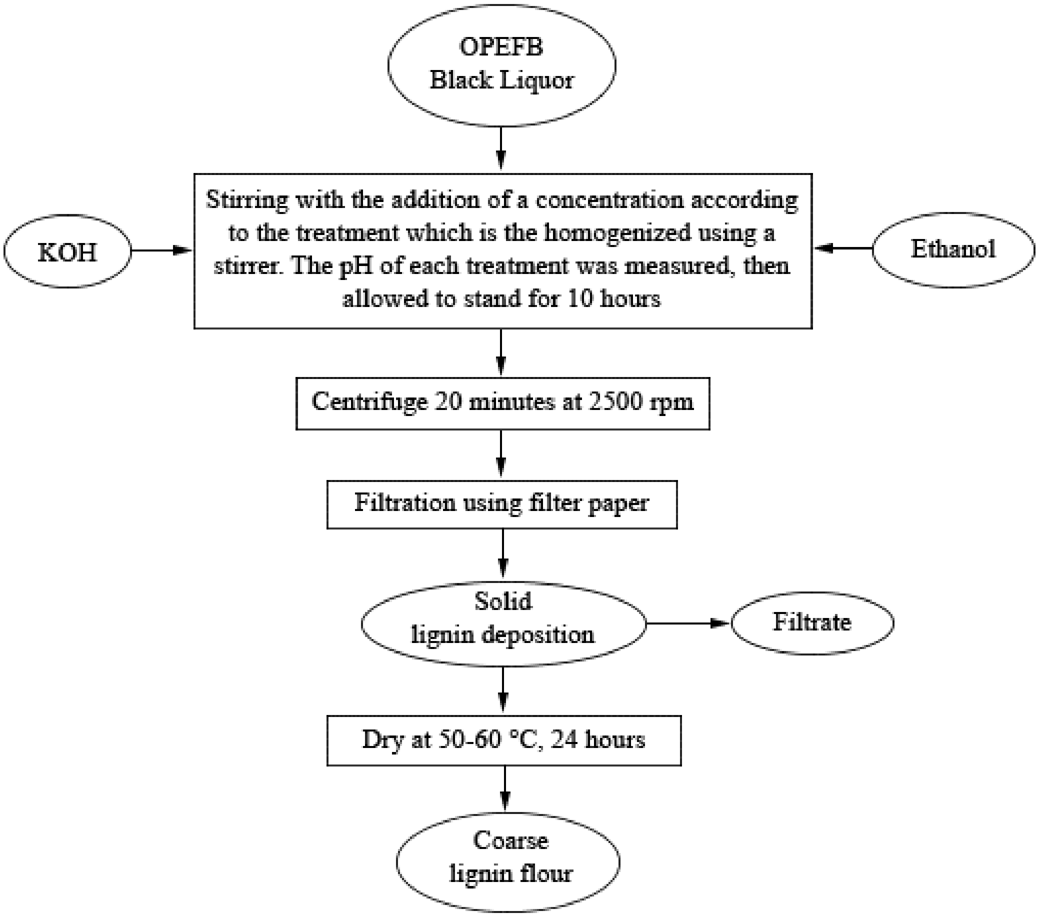


Figure 1: Flowchart of lignin isolation process using KOH/Ethanol.

2.4 Lignin Yield

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

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

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, then 25 mL of 0.25 N NaOH was added and homogenized in a closed state for 30 minutes 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 seconds). The methoxyl content of lignin was calculated according to Equation 2 as follows.

$$\text{Methoxyl } (\%) = \frac{ml\ NaOH\ x\ N\ NaOH\ x\ 3{,}1}{Berat\ sampel\ (gram)} x 100\% \qquad (2)$$

2.6 Lignin Equivalent Weight

Isolated lignin equivalent weight was calculated using the method of Santoso [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 Equation 3.

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

2.7 FT-IR analysis of isolated lignin

As much as 1 mg isolated lignins were 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 cm^{-1} to 400 cm^{-1} (wavelength of 2.5–25 πm).

2.7 SEM analysis

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

3 Results and Discussion

3.1 pH of the liquor

The pH of black liquor from formacell pulping OPEFB is 0.59 ± 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 black liquor 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 ± 0.07 to 4.27 ± 0.35 (Table 1), while the addition of ethanol concentrations can slightly increase the pH value from 1.0 ± 0.01 to 1.29 ± 0.03. According to the findings, KOH has a greater effect on increasing pH than ethanol due to the strong base property of KOH.

The pH steadily increased as an upsurging concentration of KOH, where the lowest pH, 2.43 ± 0.07, was obtained from 2.5% KOH, and the highest was a pH of 4.27 ± 0.35 from KOH 15%. Increasing the concentration of KOH solution causes more OH^- ions in the black liquor 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 ion 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.

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±0.07	3.57±0.38	13.06±0.9	1372.94±26.73
5.0	2.94±006	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

3.2 Lignin yield

The lignin yield from adding KOH solution at various concentrations in isolation of BL ranged from 3.57 ± 0.38 to 14.95 ± 1.10 (Table 1). In comparison, ethanol isolation resulted in lower lignin yields of about 0.51 ± 0.00 to 1.06 ± 0.00. The highest lignin yield was produced at a concentration of 15% KOH solution (14.95% ± 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's [38] who stated that lignin deposition from BL due to the protonation of phenol groups on lignin molecules caused by the addition of OH^- ions from KOH. It reduces the electrostatic force between lignin molecules, resulting in the deposition of lignin (reduced solubility). The more 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 black liquor 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 Na^+ and 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 it is due to 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% ± 1.92 to 12.94% ± 0.90, whereas the use of ethanol concentrations results in methoxyl contents between 11.99 ± 0.02 to 17.03 ± 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 Cα—Cβ through Cβ—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. [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 ± 74.20 to 1372.94 ± 269.73, whereas the addition of ethanol concentration resulted in molecular weights ranging from 449.88 ± 1.9 to 2123.03 ± 27.5 (Table 1).

Increasing the concentration of KOH solution resulted in a decrease in lignin equivalent weight so that the lowest value at 15% KOH solution concentration was 427.03 ± 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., there are two routes for lignin depolymerization: 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]. The product's molecular weight can be lowered by increasing salt concentration [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 (Mw <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 g mol^{-1} with a polydispersity of 4.3. Sameni et al. compared four types of lignin from different isolation methods, where the highest Mw (13488) was obtained from the steam explosion process with a methoxyl content of 0.69. Meanwhile, with the same methoxyl content, the lowest Mw (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].

3.6 Lignin Analysis with FT-IR Spectrophotometer

FTIR was performed to analyze differences in the functional groups of lignin in the sample (Fig. 2 and 3). FTIR spectra analysis showed that the peak in the aromatic ring vibrations decreased with the absorption band at 1446 cm^{-1} (a) and 1408 cm^{-1} (b), especially in the treatment using the highest concentration of KOH (Figure 2) and ethanol (Figure 3). There are similarities in the wavelength of 3500 cm^{-1} to 31090 cm^{-1} which refer to the presence of hydrogen bonds in the hydroxyl group (alcohol and phenolic). A wavelength absorption of 1587 cm^{-1} and 1513 cm^{-1} indicates the aromatic lignin skeletal vibration [60]. Wavenumbers at 1460 cm^{-1} to 1420 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 cm^{-1} to 1270 cm^{-1} in all spectra may refer to the C-H deformation vibrations of the guaiacyl [64]. The bands at 1300 cm^{-1} (syringyl) and 1200 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 Fig. 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 black liquor of OPEFB using NaOH with the wave number of isolated lignin for guaiacyl lignin at around 1273.02 cm^{-1}.

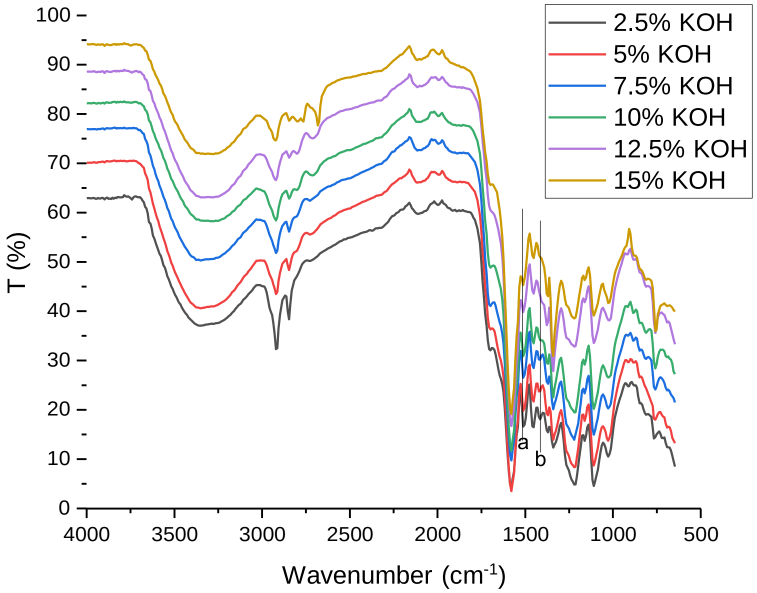


Figure 2: The FT-IR spectra of lignin using KOH isolation

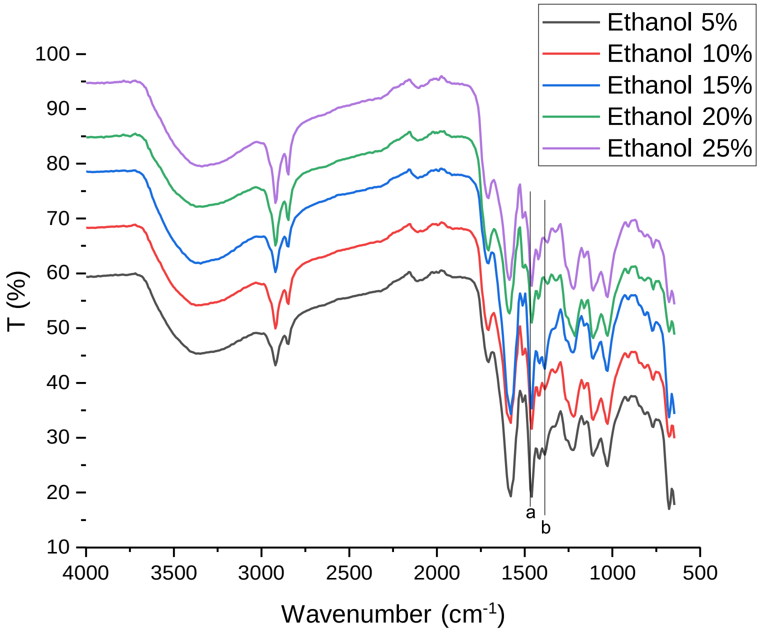
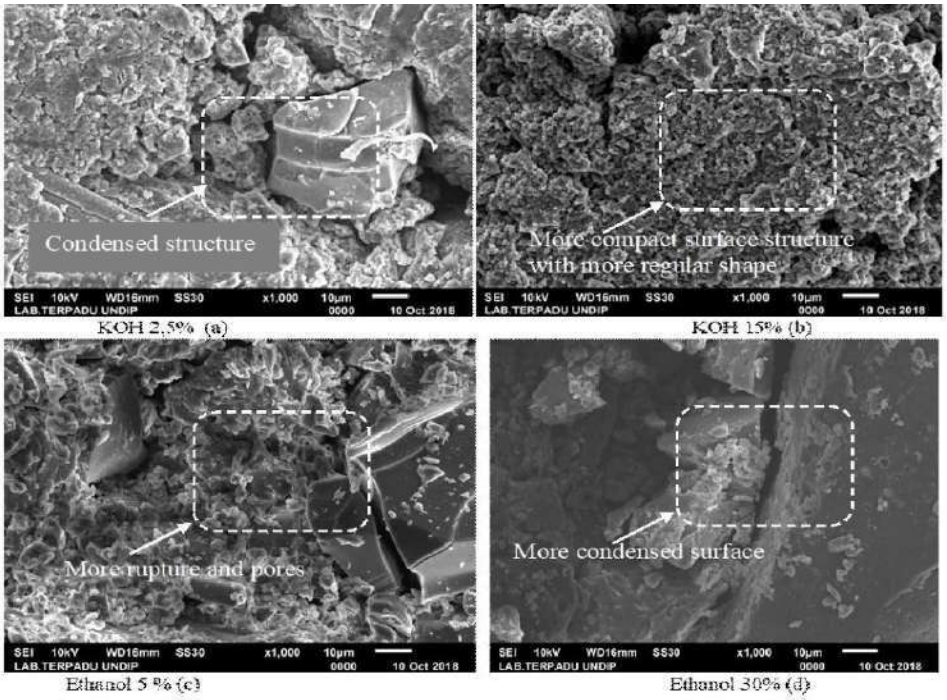


Figure 3: The FT-IR spectra of lignin using ethanol isolation

3.7 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.



KOH 2.5% (a) KOH 15% (b)

Ethanol 5 % (c) Ethanol 30% (d)

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

3.8 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_3), 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 formacell BL (OPEFB). 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 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, 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 itsphenolic 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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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]. Taking into account 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. Polypropane units can be chemically bonded in different bonding patterns where the β-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_2SO_4, phosphoric acid (H_3PO_4), 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, $Ca(OH)_2$, 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 black liquor 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 details 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 ºC. The ratio of liquor to OPEFB particle ratio of 15:1 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 hours, then centrifugated for 20 minutes at 2500 rpm, and then separated using filter paper. The precipitated lignin was then oven-dried at 50-60 ˚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).

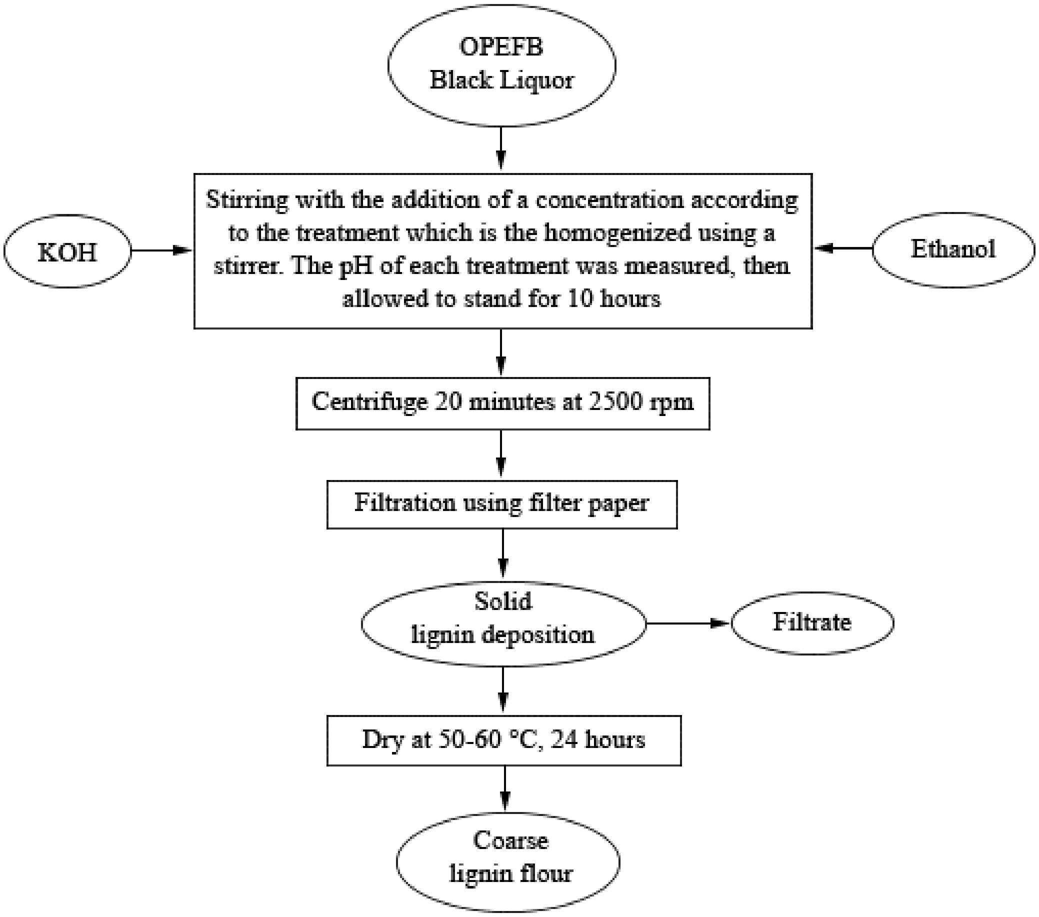


Figure 1: Flowchart of lignin isolation process using KOH/Ethanol.

2.4 Lignin Yield

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

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

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, then 25 mL of 0.25 N NaOH was added and homogenized in a closed state for 30 minutes 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 seconds). The methoxyl content of lignin was calculated according to Equation 2 as follows.

$$\text{Methoxyl (\%)} = \frac{ml\ Na0H\ x\ N\ Na0H\ x\ 3{,}1}{Berat\ sampel\ (gram)} x 100\% \qquad (2)$$

2.6 Lignin Equivalent Weight

Isolated lignin equivalent weight was calculated using the method of Santoso [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 Equation 3.

$$\text{Equivalent Weight} = \frac{1000 x gram\ sample}{(mLN)Na0H} \qquad (3)$$

2.7 FT-IR analysis of isolated lignin

As much as 1 mg isolated lignins were 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 cm^{-1} to 400 cm^{-1} (wavelength of 2.5–25 πm).

2.7 SEM analysis

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

3 Results and Discussion

3.1 pH of liquor

The pH of black liquor from formacell pulping OPEFB is 0.59 ± 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 black liquor 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 ± 0.07 to 4.27 ± 0.35 (Table 1), while the addition of ethanol concentrations can slightly increase the pH value from 1.0 ± 0.01 to 1.29 ± 0.03. According to the findings, KOH has a greater effect on increasing pH than ethanol due to the strong base property of KOH.

The pH steadily increased as an upsurging concentration of KOH, where the lowest pH, 2.43 ± 0.07, was obtained from 2.5% KOH, and the highest was a pH of 4.27 ± 0.35 from KOH 15%. Increasing the concentration of KOH solution causes more OH^- ions in the black liquor 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 ion 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.

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±0.07	3.57±0.38	13.06±0.9	1372.94±26.73
5.0	2.94±006	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

3.2 Lignin yield

The lignin yield from adding KOH solution at various concentrations in isolation of BL ranged from 3.57 ± 0.38 to 14.95 ± 1.10 (Table 1). In comparison, ethanol isolation resulted in lower lignin yields of about 0.51 ± 0.00 to 1.06 ± 0.00. The highest lignin yield was produced at a concentration of 15% KOH solution (14.95% ± 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's [38] who stated that lignin deposition from BL due to the protonation of phenol groups on lignin molecules caused by the addition of OH^- ions from KOH. It reduces the electrostatic force between lignin molecules, resulting in the deposition of lignin (reduced solubility). The more 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 black liquor 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 Na^+ and 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 it is due to 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% ± 1.92 to 12.94% ± 0.90, whereas the use of ethanol concentrations results in methoxyl contents between 11.99 ± 0.02 to 17.03 ± 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 Cα—Cβ through Cβ—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. [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 ± 74.20 to 1372.94 ± 269.73, whereas the addition of ethanol concentration resulted in molecular weights ranging from 449.88 ± 1.9 to 2123.03 ± 27.5 (Table 1).

Increasing the concentration of KOH solution resulted in a decrease in lignin equivalent weight so that the lowest value at 15% KOH solution concentration was 427.03 ± 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., there are two routes for lignin depolymerization: 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]. The product's molecular weight can be lowered by increasing salt concentration [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 (Mw <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 g mol^{-1} with a polydispersity of 4.3. Sameni et al. compared four types of lignin from different isolation methods, where the highest Mw (13488) was obtained from the steam explosion process with a methoxyl content of 0.69. Meanwhile, with the same methoxyl content, the lowest Mw (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].

3.6 Lignin Analysis with FT-IR Spectrophotometer

FTIR was performed to analyze differences in the functional groups of lignin in the sample (Fig. 2 and 3). FTIR spectra analysis showed that the peak in the aromatic ring vibrations decreased with the absorption band at 1446 cm^{-1} (a) and 1408 cm^{-1} (b), especially in the treatment using the highest concentration of KOH (Figure 2) and ethanol (Figure 3). There are similarities in the wavelength of 3500 cm^{-1} to 31090 cm^{-1} which refer to the presence of hydrogen bonds in the hydroxyl group (alcohol and phenolic). A wavelength absorption of 1587 cm^{-1} and 1513 cm^{-1} indicates the aromatic lignin skeletal vibration [60]. Wavenumbers at 1460 cm^{-1} to 1420 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 cm^{-1} to 1270 cm^{-1} in all spectra may refer to the C-H deformation vibrations of the guaiacyl [64]. The bands at 1300 cm^{-1} (syringyl) and 1200 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 Fig. 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 black liquor of OPEFB using NaOH with the wave number of isolated lignin for guaiacyl lignin at around 1273.02 cm^{-1}.

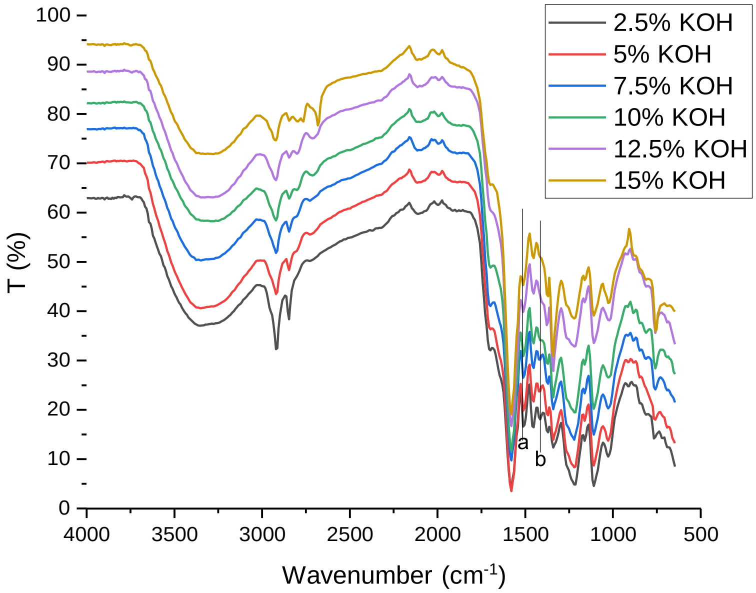


Figure 2: The FT-IR spectra of lignin using KOH isolation

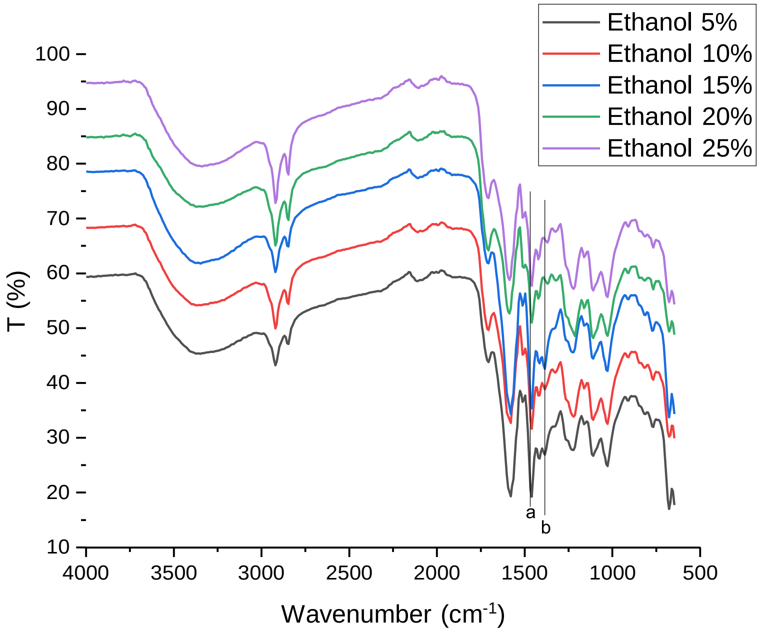
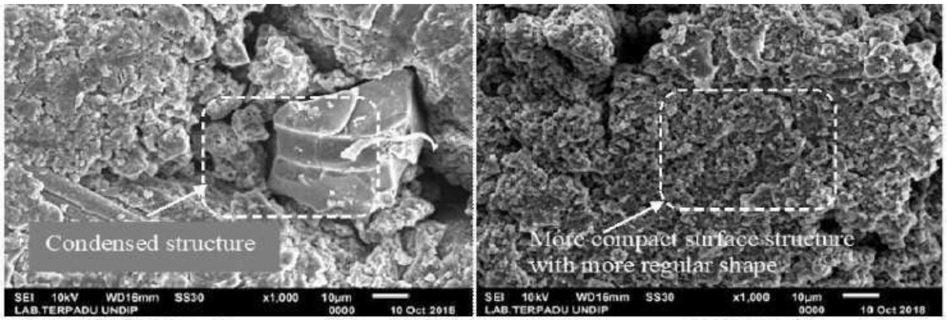


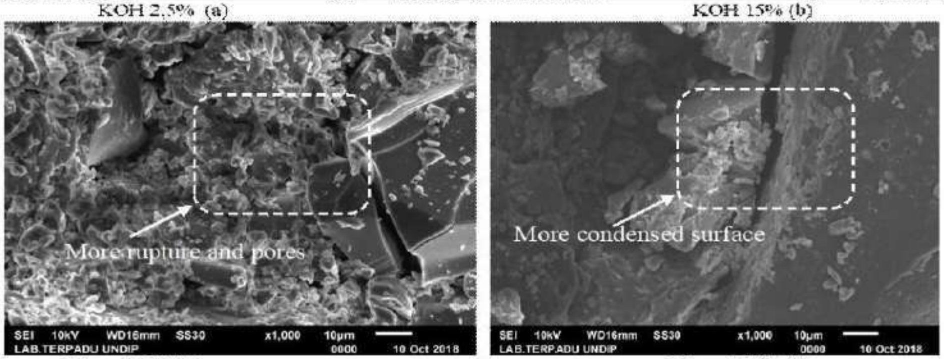
Figure 3: The FT-IR spectra of lignin using ethanol isolation

3.7 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.



KOH 2.5% (a) KOH 15% (b)



Ethanol 5 % (c) Ethanol 30% (d)

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

3.8 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_3), 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 formacell BL (OPEFB). 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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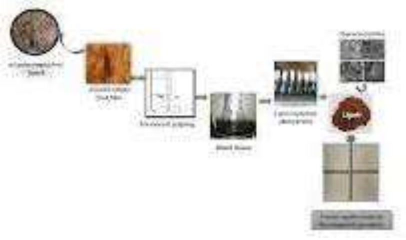

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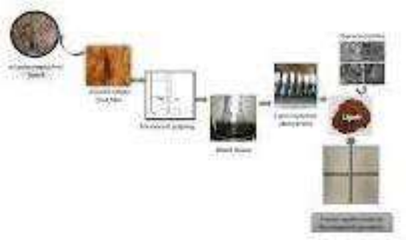

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ARTICLE

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, 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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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]. Taking into account 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. Polypropane units can be chemically bonded in different bonding patterns where the β-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_2SO_4, phosphoric acid (H_3PO_4), 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, $Ca(OH)_2$, 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 ºC. 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 hours, then centrifugated for 20 minutes at 2500 rpm, and then separated using filter paper. The precipitated lignin was then oven-dried at 50-60 ˚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).

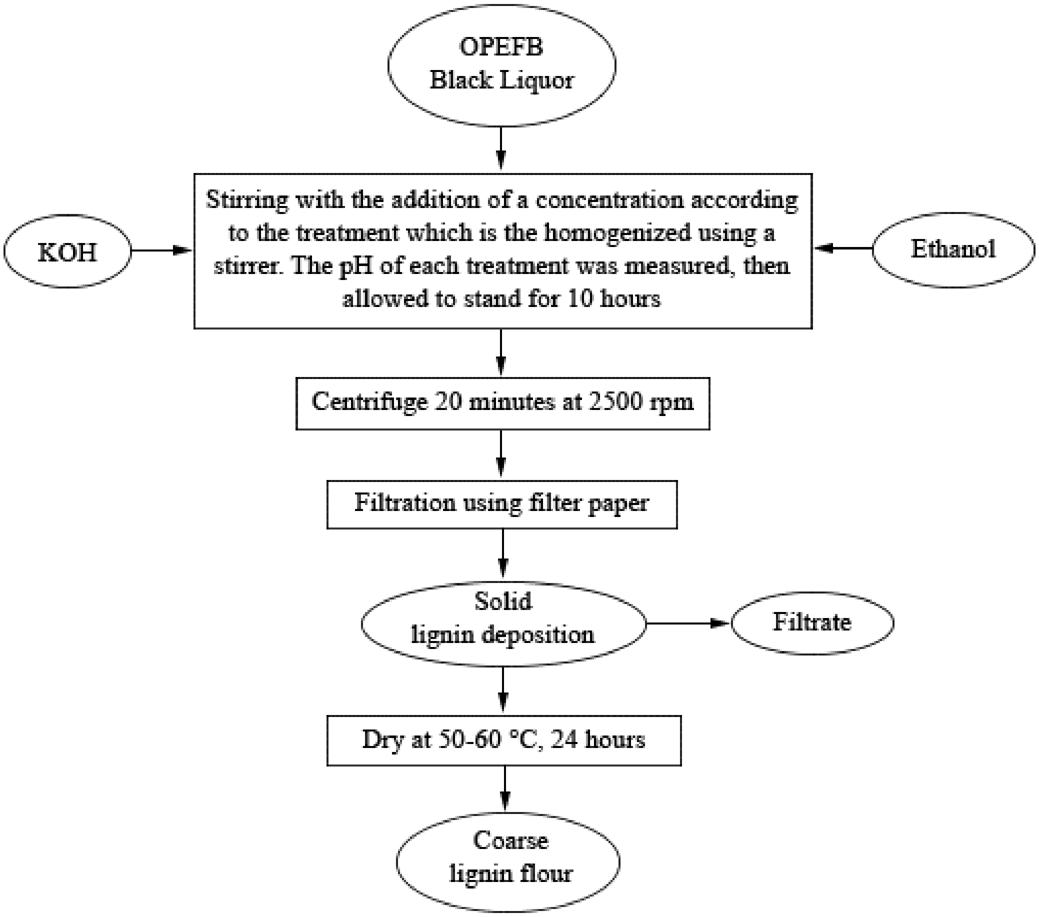


Figure 1: Flowchart of lignin isolation process using KOH/Ethanol.

2.4 Lignin Yield

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

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

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 minutes 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 seconds). The methoxyl content of lignin was calculated according to Equation 2 as follows.

$$\text{Methoxyl (\%)} = \frac{ml\ Na0H\ x\ N\ Na0H\ x\ 3{,}1}{Berat\ sampel\ (gram)} x100\% \qquad (2)$$

2.6 Lignin Equivalent Weight

Isolated lignin equivalent weight was calculated using the method of Santoso [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 Equation 3.

$$\text{Equivalent Weight} = \frac{1000xgram\ sample}{(mLN)Na0H} \qquad (3)$$

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 cm^{-1} to 400 cm^{-1} (wavelength of 2.5–25 πm).

2.7 SEM analysis

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

3 Results and Discussion

3.1 pH of the black liquor

The pH of BL from formacell pulping OPEFB is 0.59 ± 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 ± 0.07 to 4.27 ± 0.35 (Table 1), while the addition of ethanol concentrations can slightly increase the pH value from 1.0 ± 0.01 to 1.29 ± 0.03. According to the findings, KOH has a greater effect on increasing pH than ethanol due to the strong base property of KOH.

The pH steadily increased as an up-surging concentration of KOH, where the lowest pH, 2.43 ± 0.07, was obtained from 2.5% KOH, and the highest was a pH of 4.27 ± 0.35 from KOH 15%. Increasing the concentration of KOH solution causes more 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.

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±0.07	3.57±0.38	13.06±0.9	1372.94±26.73
5.0	2.94±006	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

3.2 Lignin yield

The lignin yield from adding KOH solution at various concentrations in isolation of BL ranged from 3.57 ± 0.38 to 14.95 ± 1.10 (Table 1). In comparison, ethanol isolation resulted in lower lignin yields of about 0.51 ± 0.00 to 1.06 ± 0.00. The highest lignin yield was produced at a concentration of 15% KOH solution (14.95% ± 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 OH^- ions from KOH. It reduces the electrostatic force between lignin molecules, resulting in the deposition of lignin and reduced solubility. The more 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 Na^+ and 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% ± 1.92 to 12.94% ± 0.90, whereas the use of ethanol concentrations results in methoxyl contents between 11.99 ± 0.02 to 17.03 ± 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 Cα—Cβ through Cβ—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 ± 74.20 to 1372.94 ± 269.73, whereas the addition of ethanol concentration resulted in molecular weights ranging from 449.88 ± 1.9 to 2123.03 ± 27.5 (Table 1).

Increasing the concentration of KOH solution resulted in a decrease in lignin equivalent weight so that the lowest value at 15% KOH solution concentration was 427.03 ± 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., there are two routes for lignin depolymerization: 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]. The product's molecular weight can be lowered by increasing salt concentration [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 (Mw <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 g mol^{-1} with a polydispersity of 4.3. Sameni et al. compared four types of lignin from different isolation methods, where the highest Mw (13488) was obtained from the steam explosion process with a methoxyl content of 0.69. Meanwhile, with the same methoxyl content, the lowest Mw (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].

3.6 Lignin Analysis with FT-IR Spectrophotometer

FTIR was performed to analyze differences in the functional groups of lignin in the sample (Fig. 2 and 3). FTIR spectra analysis showed that the peak in the aromatic ring vibrations decreased with the absorption band at 1446 cm^{-1} (a) and 1408 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 cm^{-1} to 31090 cm^{-1} which refer to the presence of hydrogen bonds in the hydroxyl group (alcohol and phenolic). A wavelength absorption of 1587 cm^{-1} and 1513 cm^{-1} indicates the aromatic lignin skeletal vibration [60]. Wavenumbers at 1460 cm^{-1} to 1420 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 cm^{-1} to 1270 cm^{-1} in all spectra may refer to the C-H deformation vibrations of the guaiacyl [64]. The bands at 1300 cm^{-1} (syringyl) and 1200 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 Fig. 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 cm^{-1}.

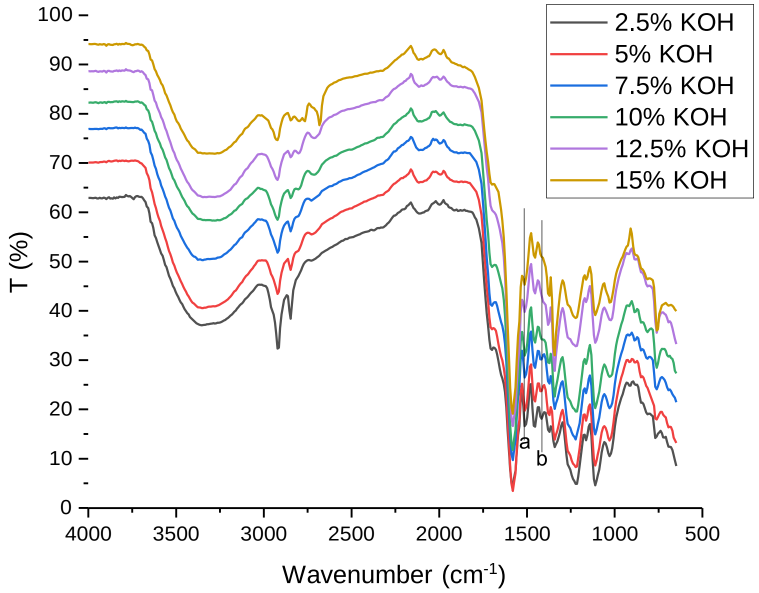


Figure 2: The FT-IR spectra of lignin using KOH isolation

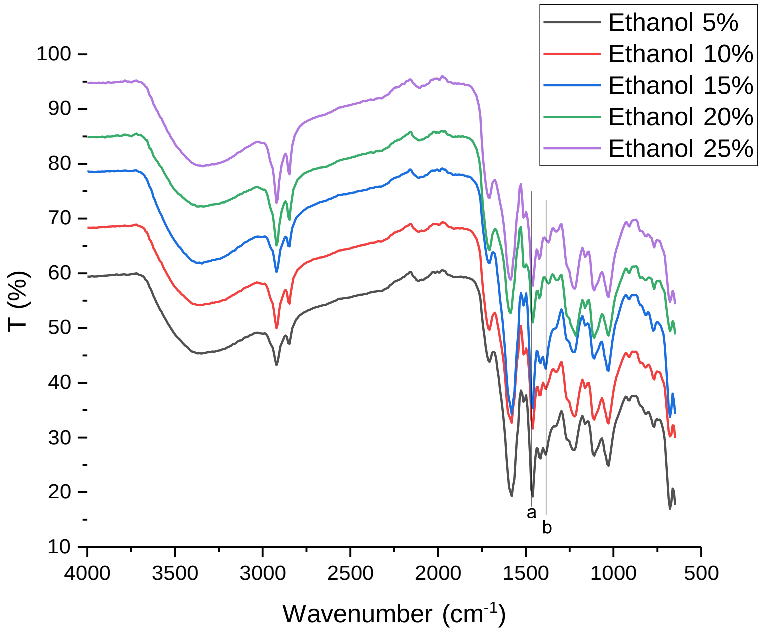
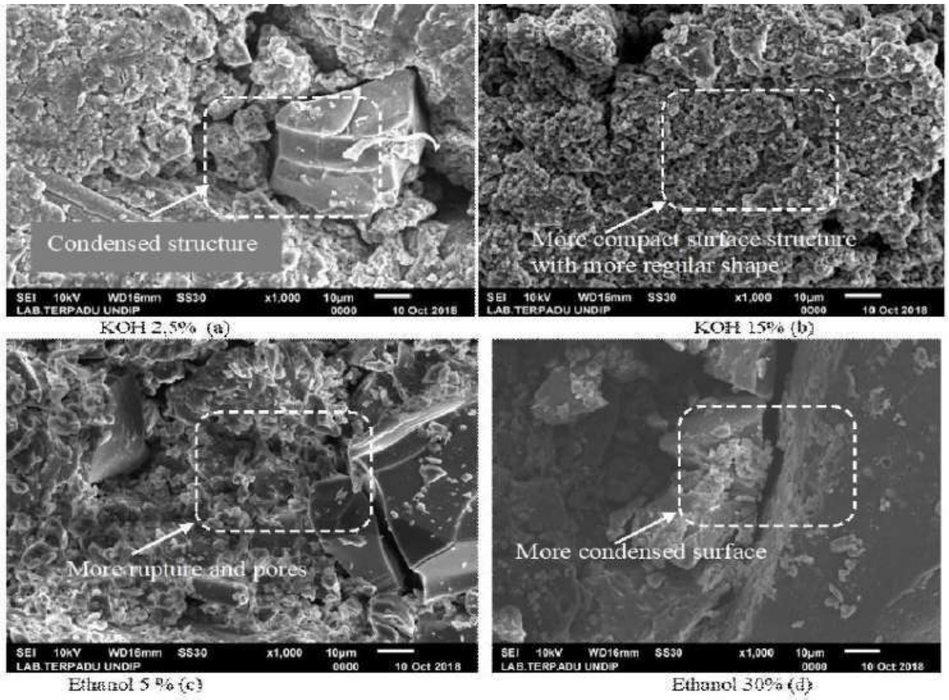


Figure 3: The FT-IR spectra of lignin using ethanol isolation

3.7 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.



KOH 2.5% (a) KOH 15% (b)

Ethanol 5 % (c) Ethanol 30% (d)

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

3.8 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_3), 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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5 messages

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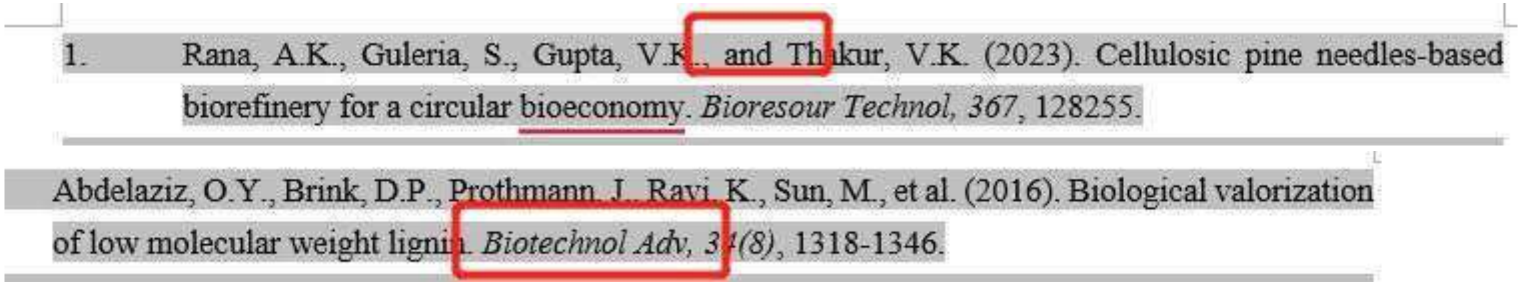
-In the reference part, the word"and" between the authors' names are unnecessary. Please delete them. Secondly, the full name of the title of journals should be provided. For the detailed format in the reference part please refer tothe JRM-template, which is attached. Please amend all the same problems in the references;



1. Rana, A.K., Guleria, S., Gupta, V.K., and Thakur, V.K. (2023). Cellulosic pine needles-based biorefinery for a circular bioeconomy. *Bioresour Technol, 367*, 128255.

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.

We look forward to your reply within 2-3 working days.

Thanks for your hard work.

Best regards,
Gabriel Cao

Journal of Renewable Materials

2590 Windmill Ln #308, Henderson, NV 89074, USA
Tel: +1 702 673 0457
Fax: +1 844 635 2598
Office Hours: 9:00-17:00 (UTC -8:00)
Email: jrm@techscience.com

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183K

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sri hidayati <srihidayati.unila@gmail.com> Sun, Dec 25, 2022 at 5:50 AM
To: "gabriel.cao@techscience.com" <gabriel.cao@techscience.com>

Dear: JRM Journal Editor

Thank you very much for accepting our paper. We hereby send the results of improvements from our paper, especially regarding errors in writing in the bibliography and we have adjusted them to the journal template.

Greetings,

Sri Hidayati
[Quoted text hidden]

27579-Manuscript-SHWF24122022 final.docx
1050K

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gabriel.cao@techscience.com <gabriel.cao@techscience.com> Mon, Dec 26, 2022 at 4:02 PM
To: "srihidayati.unila" <srihidayati.unila@gmail.com>

Dear Sri hudayati,

Sincerely thanks for your prompt reply.

We will further check your manuscript ASAP.

Happy holidays!

Best regards,
Gabriel Cao

Journal of Renewable Materials
P.O. Box 308
2590 Windmill Ln, Henderson, NV 89074
U.S.A.
Tel: +1 702 673 0457
Website: www.techscience.com
Email: jrm@techscience.com

[Quoted text hidden]

---

sri hidayati <srihidayati.unila@gmail.com> Thu, Dec 29, 2022 at 7:21 AM
To: "gabriel.cao@techscience.com" <gabriel.cao@techscience.com>

Thank you very much.
[Quoted text hidden]

Petar Antov <p.antov@ltu.bg> Thu, Jan 5, 2023 at 9:58 PM
To: "gabriel.cao@techscience.com" <gabriel.cao@techscience.com>, "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>, leesenghua <leesenghua@hotmail.com>, widy003 <widy003@brin.go.id>, sapuan <sapuan@upm.edu.my>

Dear Gabriel Cao,

Hope you are doing well. Could you please provide information on the current status of our manuscript processing? We answered the requests in your last email and sent the revised version.

Thank you for your time and consideration!

Best regards,

Petar

Prof. Petar Antov, PhD
International and Public Relations Coordinator
University of Forestry, Sofia, Bulgaria
e-mail: p.antov@ltu.bg
website: www.ltu.bg

From: gabriel.cao@techscience.com <gabriel.cao@techscience.com>
Sent: Friday, December 23, 2022 09:05
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>; Petar Antov <p.antov@ltu.bg>; leesenghua <leesenghua@hotmail.com>; widy003 <widy003@brin.go.id>; sapuan <sapuan@upm.edu.my>
Subject: JRM-27579-format comments

[Quoted text hidden]

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

[TSP_JRM_27579] - Proof submitted for your review

4 messages

---

pm@transforma.in <pm@transforma.in> Wed, Jan 18, 2023 at 8:20 PM
To: srihidayati.unila@gmail.com
Cc: typesetting@techscience.com

Dear Dr. Sri Hidayati,

Thank you for your excellent contribution to the ***Journal of Renewable Materials***

We are pleased to inform you that the proof of your article is ready and can be accessed via the link below. We request that you carefully check and mark your corrections, if any, either via the offline (using PDF annotation) or online method.

Note: If you opt to annotate your article via the offline mode, you will need Adobe Reader installed (free version) on your system. You can download the reader through this link. If you opt for the online mode, we recommend using a Firefox or Chrome browser for better compatibility (not Safari).

To ensure timely publication of your proof, please return your corrections within 48 hours.

Information	Details
Article ID	TSP_JRM_27579
Title	Characterization of Formacell Lignin Derived from Black Liquor as a Potential Green Additive for Advanced Biocomposites
Author Name	Sri Hidayati
Link	http://xpertproof.transforma.in/xpertproofing/Transforma_XPro/xpertproof/fsp?fs=i3SF1wqDnxguOLXTl

Regards,
Tech Science Publications.

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---

sri hidayati <srihidayati.unila@gmail.com> Thu, Jan 19, 2023 at 5:22 AM
To: widy003@brin.go.id

[Quoted text hidden]

---

sri hidayati <srihidayati.unila@gmail.com> Thu, Jan 19, 2023 at 12:05 PM

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

[Quoted text hidden]

---

sri hidayati <srihidayati.unila@gmail.com> Thu, Jan 19, 2023 at 4:10 PM
To: "pm@transforma.in" <pm@transforma.in>

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

[jrm] Validate Your Account

1 message

JRM Editorial <noreply@tspsubmission.com> Fri, Nov 4, 2022 at 1:18 PM
Reply-To: JRM Editorial <jrm@techscience.com>
To: Sri Hidayati <srihidayati.unila@gmail.com>

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

Thank you,
JRM Editorial

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Tel: +1 702 673 0457
Fax: +1 844 635 2598
Office Hours: 9:00-17:00 (UTC -8:00)
Email: jrm@techscience.com

sri hidayati <srihidayati.unila@gmail.com>

[jrm] ID:27579 Submission Acknowledgement

1 message

JRM Editorial <noreply@tspsubmission.com> Fri, Nov 4, 2022 at 4:24 PM
To: Sri Hidayati <srihidayati.unila@gmail.com>

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
Tel: +1 702 673 0457
Fax: +1 844 635 2598
Office Hours: 9:00-17:00 (UTC -8:00)
Email: jrm@techscience.com

[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 Fonny 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 Nurfajrin 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 Fonny Budiyanto, Hadi Saputra, Sutopo Hadi, Dr. Apri Heri Iswanto, Mrs Nissa Nurfajrin 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 α-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% 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:

-"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 ºC] -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 <srihidayati.unila@gmail.com>

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
U.S.A.
Tel: +1 702 673 0457
Website: www.techscience.com
Email: jrm@techscience.com

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

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

Response to editors and Reviewers WFNN_PA_Lee (2).docx
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27579-Manuscript-NNSWF_PA_LSH 09122022 NNS.docx
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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 inthe 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 Cα—Cβ through Cβ—O bond. This cleavage leads to the removal of side chains suchas 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 α-O-4 cleavage, which is not true at all.

Author's response:

Thank you for the suggestion. The information about lignin depolymerization involving α-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 ºC] -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

Journal of Renewable Materials

Tech Science Press

DOI: XXXXX

ARTICLE

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

Sri Hidayati[1*], Eugenia Fonny Budiyanto[1], Hadi Saputra[1], Sutopo Hadi[1], Apri Heri Iswanto[2,3], Nissa Nurfajrin Solihat[4], Petar Antov[5], Lee Seng Hua[6,7], Widya Fatriasari[4,8], Mohd. Sapuan Salit[9]

1)Agricultural Product Technology Department, Faculty of Agriculture, The University of Lampung, Jl. Sumantri Brojonegoro No. 1 Bandar Lampung, Indonesia

2)Department of Forest Product, Faculty of Forestry, Universitas Sumatera Utara. Kampus USU Padang Bulan, Medan 20155, North Sumatra, Indonesia

3)JATI-Sumatran Forestry Analysis Study Center, Jl. Tridharma Ujung No.1, Kampus USU, Medan, North Sumatra, Indonesia

4)Research Center for Biomass and Bioproducts, National Research and Innovation Agency (BRIN), Jl Raya Bogor KM 46 Cibinong 16911, Indonesia

5)Faculty of Forest Industry, University of Forestry, 1797 Sofia, Bulgaria

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

7)Institute of Tropical Forestry and Forest Products, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

8)Research Collaboration Center for Marine Biomaterials, Jl. Ir. Sukarno, KM 21, Jatinangor, Sumedang, West Java 45363, Indonesia

9)Advanced engineering Materials and Composites Research Centre, Department of Mechanical and Manufacturing Engineering, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

*Corresponding Author: srihidayati.unila@gmail.com

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 itsphenolic 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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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]. Taking into account 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. Polypropane units can be chemically bonded in different bonding patterns where the β-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_2SO_4, phosphoric acid (H_3PO_4), 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, $Ca(OH)_2$, 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 black liquor 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 ºC. The ratio of liquor to OPEFB particle ratio of 15:1 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 hours, then centrifugated for 20 minutes at 2500 rpm, and then separated using filter paper. The precipitated lignin was then oven-dried at 50-60 ˚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).

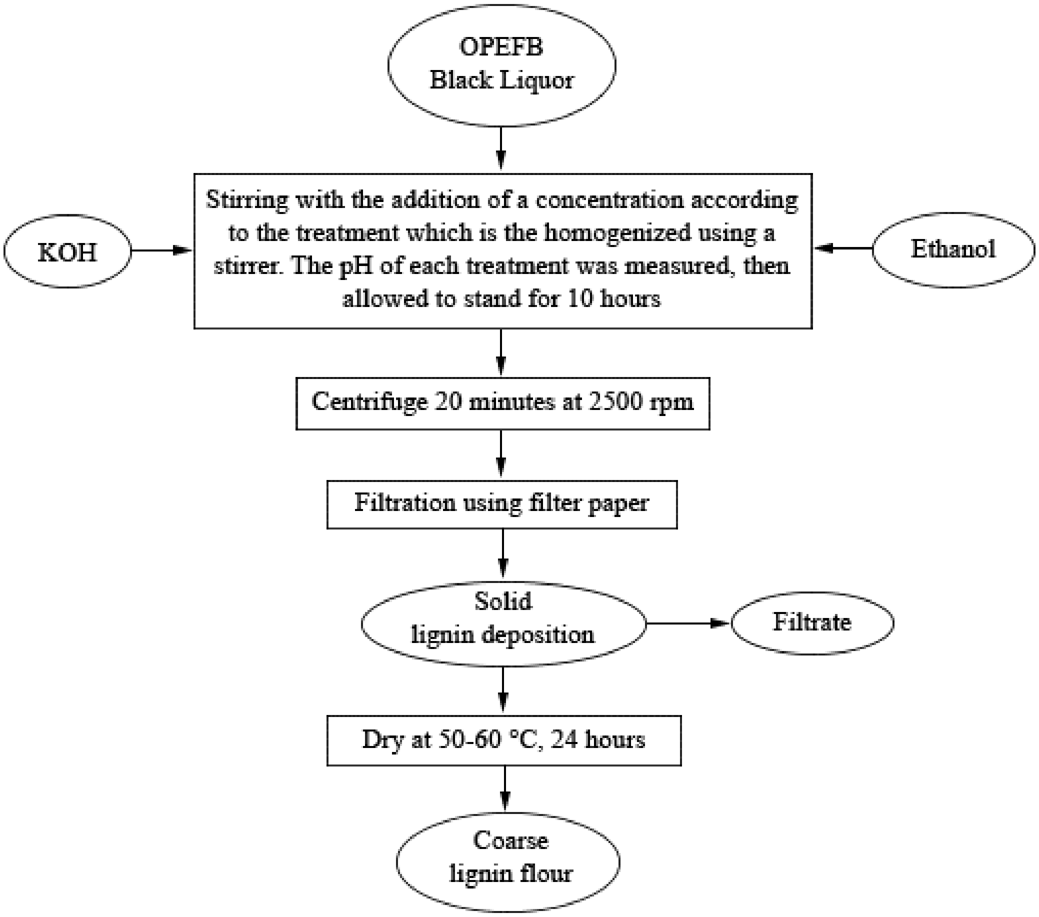


Figure 1: Flowchart of lignin isolation process using KOH/Ethanol.

2.4 Lignin Yield

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

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

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, then 25 mL of 0.25 N NaOH was added and homogenized in a closed state for 30 minutes 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 seconds). The methoxyl content of lignin was calculated according to Equation 2 as follows.

$$\text{Methoxyl}\ (\%) = \frac{ml\ Na0H\ x\ N\ Na0H\ x\ 3{,}1}{Berat\ sampel\ (gram)} x 100\% \qquad (2)$$

2.6 Lignin Equivalent Weight

Isolated lignin equivalent weight was calculated using the method of Santoso [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 Equation 3.

$$\text{Equivalent Weight} = \frac{1000 x gram\ sample}{(mLN)Na0H} \qquad (3)$$

2.7 FT-IR analysis of isolated lignin

As much as 1 mg isolated lignins were 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 cm^{-1} to 400 cm^{-1} (wavelength of 2.5–25 πm).

2.7 SEM analysis

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

3 Results and Discussion

3.1 pH of the liquor

The pH of black liquor from formacell pulping OPEFB is 0.59 ± 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 black liquor 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 ± 0.07 to 4.27 ± 0.35 (Table 1), while the addition of ethanol concentrations can slightly increase the pH value from 1.0 ± 0.01 to 1.29 ± 0.03. According to the findings, KOH has a greater effect on increasing pH than ethanol due to the strong base property of KOH.

The pH steadily increased as an upsurging concentration of KOH, where the lowest pH, 2.43 ± 0.07, was obtained from 2.5% KOH, and the highest was a pH of 4.27 ± 0.35 from KOH 15%. Increasing the concentration of KOH solution causes more OH^- ions in the black liquor 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 ion 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.

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±0.07	3.57±0.38	13.06±0.9	1372.94±26.73
5.0	2.94±006	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

3.2 Lignin yield

The lignin yield from adding KOH solution at various concentrations in isolation of BL ranged from 3.57 ± 0.38 to 14.95 ± 1.10 (Table 1). In comparison, ethanol isolation resulted in lower lignin yields of about 0.51 ± 0.00 to 1.06 ± 0.00. The highest lignin yield was produced at a concentration of 15% KOH solution (14.95% ± 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's [38] who stated that lignin deposition from BL due to the protonation of phenol groups on lignin molecules caused by the addition of OH^- ions from KOH. It reduces the electrostatic force between lignin molecules, resulting in the deposition of lignin (reduced solubility). The more 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 black liquor 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 Na^+ and 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 it is due to 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% ± 1.92 to 12.94% ± 0.90, whereas the use of ethanol concentrations results in methoxyl contents between 11.99 ± 0.02 to 17.03 ± 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 Cα—Cβ through Cβ—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. [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 ± 74.20 to 1372.94 ± 269.73, whereas the addition of ethanol concentration resulted in molecular weights ranging from 449.88 ± 1.9 to 2123.03 ± 27.5 (Table 1).

Increasing the concentration of KOH solution resulted in a decrease in lignin equivalent weight so that the lowest value at 15% KOH solution concentration was 427.03 ± 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., there are two routes for lignin depolymerization: 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]. The product's molecular weight can be lowered by increasing salt concentration [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 (Mw <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 g mol^{-1} with a polydispersity of 4.3. Sameni et al. compared four types of lignin from different isolation methods, where the highest Mw (13488) was obtained from the steam explosion process with a methoxyl content of 0.69. Meanwhile, with the same methoxyl content, the lowest Mw (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].

3.6 Lignin Analysis with FT-IR Spectrophotometer

FTIR was performed to analyze differences in the functional groups of lignin in the sample (Fig. 2 and 3). FTIR spectra analysis showed that the peak in the aromatic ring vibrations decreased with the absorption band at 1446 cm^{-1} (a) and 1408 cm^{-1} (b), especially in the treatment using the highest concentration of KOH (Figure 2) and ethanol (Figure 3). There are similarities in the wavelength of 3500 cm^{-1} to 31090 cm^{-1} which refer to the presence of hydrogen bonds in the hydroxyl group (alcohol and phenolic). A wavelength absorption of 1587 cm^{-1} and 1513 cm^{-1} indicates the aromatic lignin skeletal vibration [60]. Wavenumbers at 1460 cm^{-1} to 1420 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 cm^{-1} to 1270 cm^{-1} in all spectra may refer to the C-H deformation vibrations of the guaiacyl [64]. The bands at 1300 cm^{-1} (syringyl) and 1200 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 Fig. 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 black liquor of OPEFB using NaOH with the wave number of isolated lignin for guaiacyl lignin at around 1273.02 cm^{-1}.

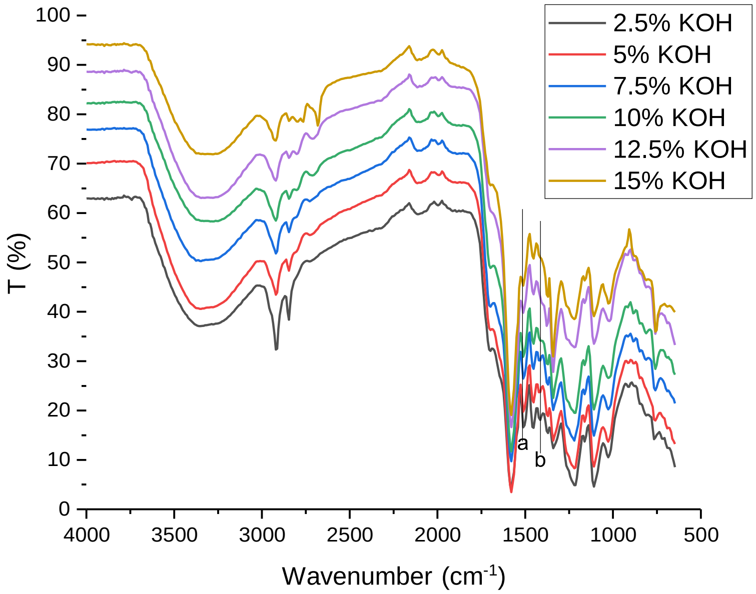


Figure 2: The FT-IR spectra of lignin using KOH isolation

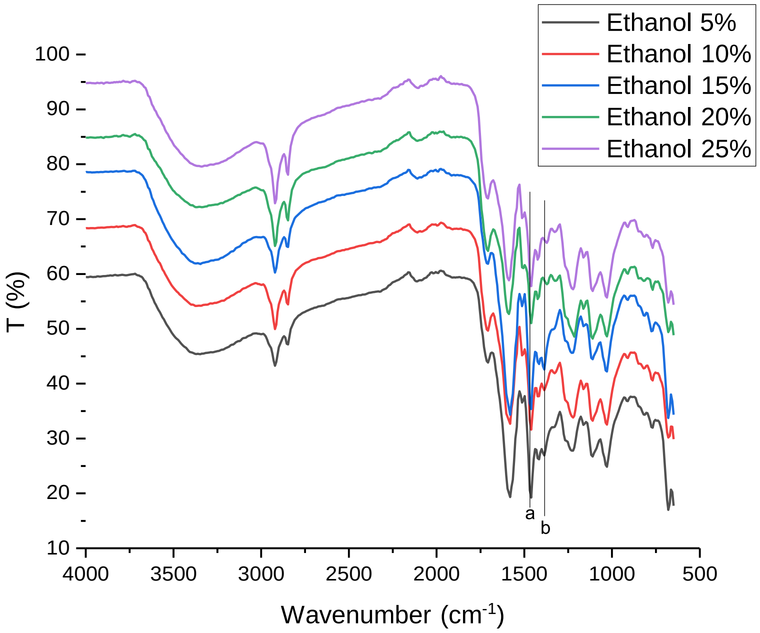
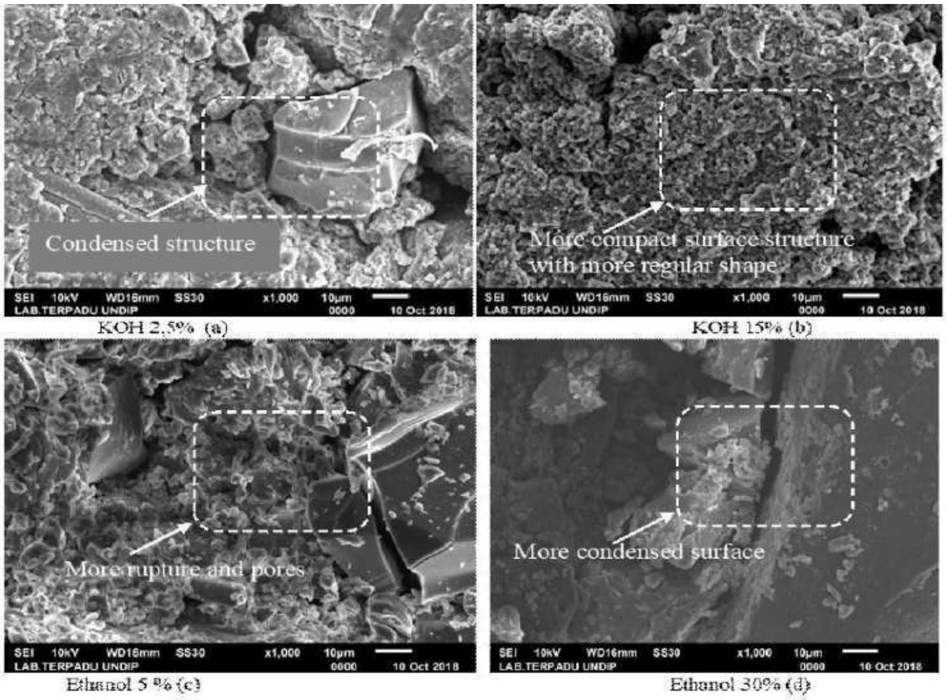


Figure 3: The FT-IR spectra of lignin using ethanol isolation

3.7 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.



KOH 2.5% (a)

KOH 15% (b)

Ethanol 5 % (c)

Ethanol 30% (d)

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

3.8 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_3), 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 formacell BL (OPEFB). 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 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, 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 itsphenolic 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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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]. Taking into account 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. Polypropane units can be chemically bonded in different bonding patterns where the β-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_2SO_4, phosphoric acid (H_3PO_4), 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, $Ca(OH)_2$, 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 black liquor 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 details 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 ºC. The ratio of liquor to OPEFB particle ratio of 15:1 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 hours, then centrifugated for 20 minutes at 2500 rpm, and then separated using filter paper. The precipitated lignin was then oven-dried at 50-60 ˚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).

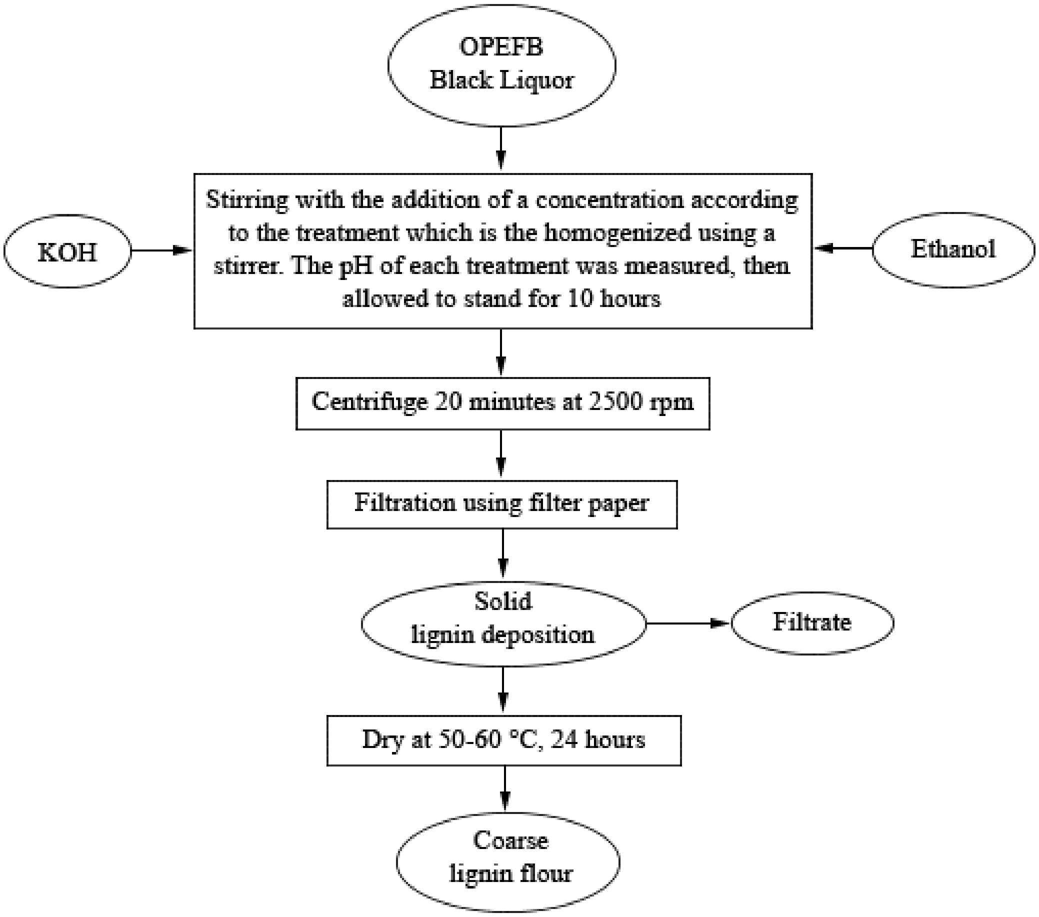

Figure 1: Flowchart of lignin isolation process using KOH/Ethanol.

2.4 Lignin Yield

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

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

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, then 25 mL of 0.25 N NaOH was added and homogenized in a closed state for 30 minutes 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 seconds). The methoxyl content of lignin was calculated according to Equation 2 as follows.

$$\text{Methoxyl (\%)} = \frac{ml\ Na0H\ x\ N\ Na0H\ x\ 3{,}1}{Berat\ sampel\ (gram)} x100\% \qquad (2)$$

2.6 Lignin Equivalent Weight

Isolated lignin equivalent weight was calculated using the method of Santoso [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 Equation 3.

$$\text{Equivalent Weight} = \frac{1000xgram\ sample}{(mLN)Na0H} \qquad (3)$$

2.7 FT-IR analysis of isolated lignin

As much as 1 mg isolated lignins were 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 cm^{-1} to 400 cm^{-1} (wavelength of 2.5–25 πm).

2.7 SEM analysis

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

3 Results and Discussion

3.1 pH of liquor

The pH of black liquor from formacell pulping OPEFB is 0.59 ± 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 black liquor 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 ± 0.07 to 4.27 ± 0.35 (Table 1), while the addition of ethanol concentrations can slightly increase the pH value from 1.0 ± 0.01 to 1.29 ± 0.03. According to the findings, KOH has a greater effect on increasing pH than ethanol due to the strong base property of KOH.

The pH steadily increased as an upsurging concentration of KOH, where the lowest pH, 2.43 ± 0.07, was obtained from 2.5% KOH, and the highest was a pH of 4.27 ± 0.35 from KOH 15%. Increasing the concentration of KOH solution causes more OH^- ions in the black liquor 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 ion 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.

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±0.07	3.57±0.38	13.06±0.9	1372.94±26.73
5.0	2.94±006	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

3.2 Lignin yield

The lignin yield from adding KOH solution at various concentrations in isolation of BL ranged from 3.57 ± 0.38 to 14.95 ± 1.10 (Table 1). In comparison, ethanol isolation resulted in lower lignin yields of about 0.51 ± 0.00 to 1.06 ± 0.00. The highest lignin yield was produced at a concentration of 15% KOH solution (14.95% ± 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's [38] who stated that lignin deposition from BL due to the protonation of phenol groups on lignin molecules caused by the addition of OH^- ions from KOH. It reduces the electrostatic force between lignin molecules, resulting in the deposition of lignin (reduced solubility). The more 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 black liquor 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 Na^+ and 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 it is due to 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% ± 1.92 to 12.94% ± 0.90, whereas the use of ethanol concentrations results in methoxyl contents between 11.99 ± 0.02 to 17.03 ± 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 Cα—Cβ through Cβ—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. [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 ± 74.20 to 1372.94 ± 269.73, whereas the addition of ethanol concentration resulted in molecular weights ranging from 449.88 ± 1.9 to 2123.03 ± 27.5 (Table 1).

Increasing the concentration of KOH solution resulted in a decrease in lignin equivalent weight so that the lowest value at 15% KOH solution concentration was 427.03 ± 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., there are two routes for lignin depolymerization: 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]. The product's molecular weight can be lowered by increasing salt concentration [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 (Mw <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 g mol^{-1} with a polydispersity of 4.3. Sameni et al. compared four types of lignin from different isolation methods, where the highest Mw (13488) was obtained from the steam explosion process with a methoxyl content of 0.69. Meanwhile, with the same methoxyl content, the lowest Mw (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].

3.6 Lignin Analysis with FT-IR Spectrophotometer

FTIR was performed to analyze differences in the functional groups of lignin in the sample (Fig. 2 and 3). FTIR spectra analysis showed that the peak in the aromatic ring vibrations decreased with the absorption band at 1446 cm^{-1} (a) and 1408 cm^{-1} (b), especially in the treatment using the highest concentration of KOH (Figure 2) and ethanol (Figure 3). There are similarities in the wavelength of 3500 cm^{-1} to 31090 cm^{-1} which refer to the presence of hydrogen bonds in the hydroxyl group (alcohol and phenolic). A wavelength absorption of 1587 cm^{-1} and 1513 cm^{-1} indicates the aromatic lignin skeletal vibration [60]. Wavenumbers at 1460 cm^{-1} to 1420 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 cm^{-1} to 1270 cm^{-1} in all spectra may refer to the C-H deformation vibrations of the guaiacyl [64]. The bands at 1300 cm^{-1} (syringyl) and 1200 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 Fig. 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 black liquor of OPEFB using NaOH with the wave number of isolated lignin for guaiacyl lignin at around 1273.02 cm^{-1}.

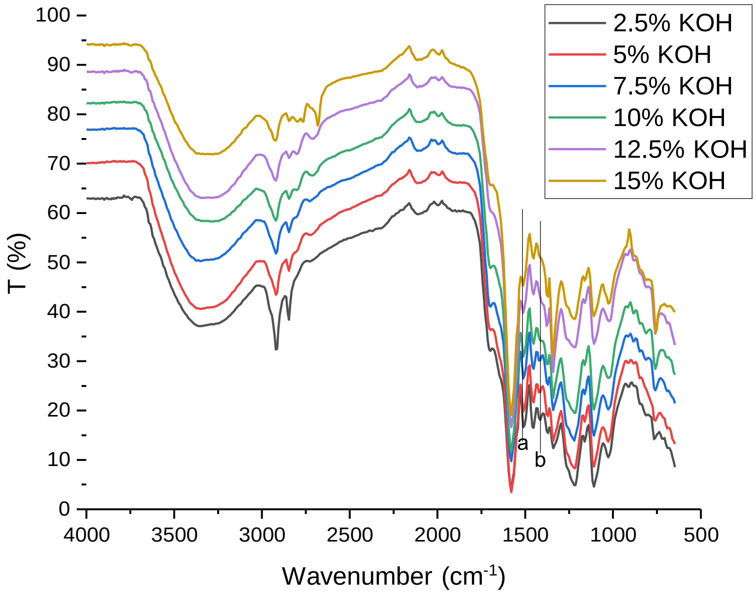

Figure 2: The FT-IR spectra of lignin using KOH isolation

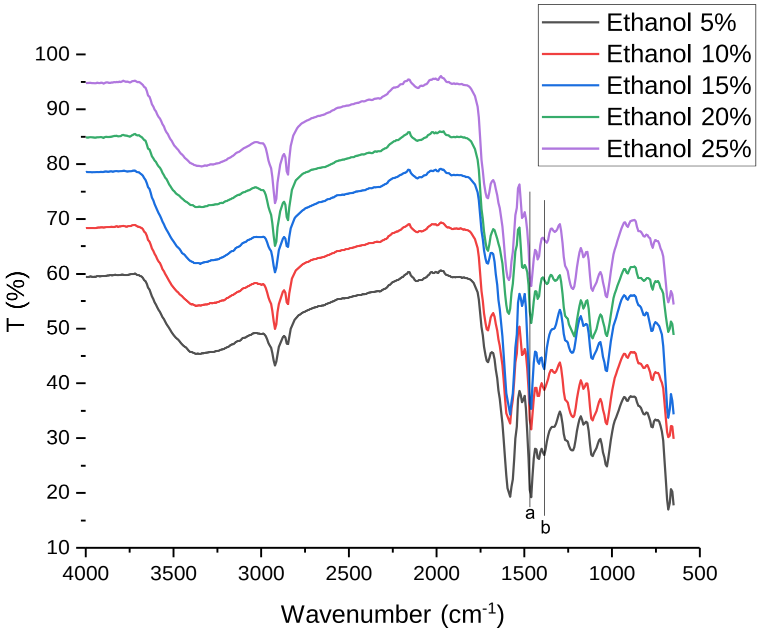

Figure 3: The FT-IR spectra of lignin using ethanol isolation

3.7 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.

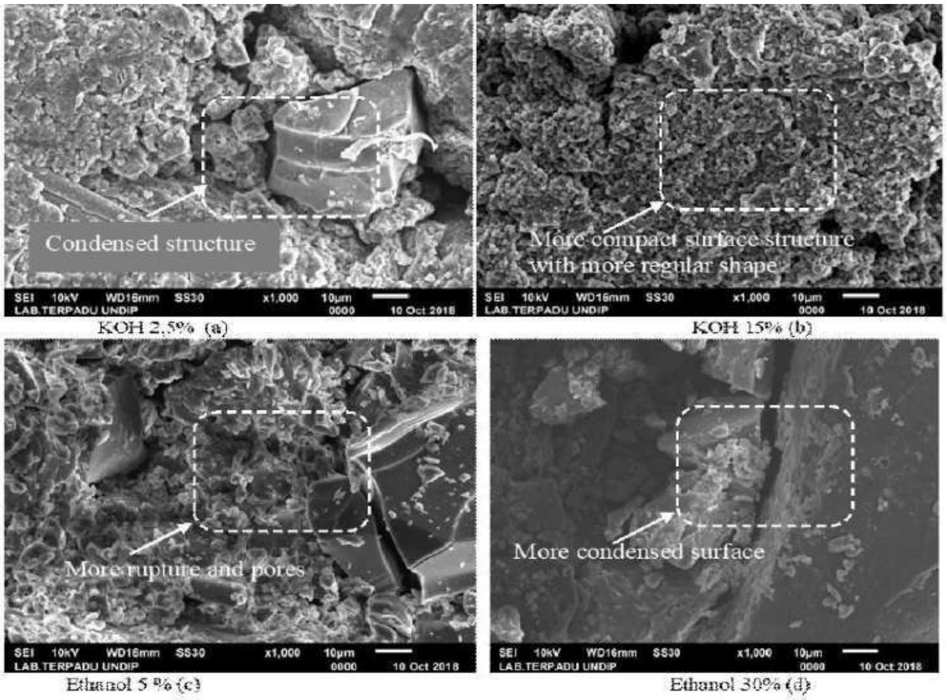

Figure 4: Morphological images of isolated lignin (a) KOH 2.5%, (b) KOH 15%, (c) ethanol 5%, (d) ethanol 30% with 1000 x magnification

3.8 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_3), 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 formacell BL (OPEFB). 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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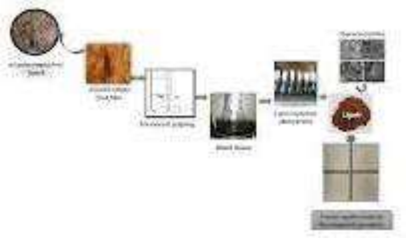

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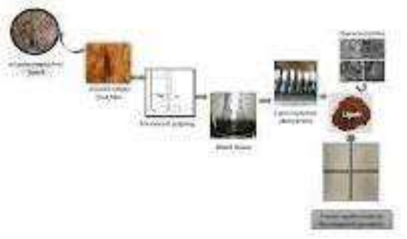

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ARTICLE

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, 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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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]. Taking into account 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. Polypropane units can be chemically bonded in different bonding patterns where the β-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_2SO_4, phosphoric acid (H_3PO_4), 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, $Ca(OH)_2$, 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 ºC. 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 hours, then centrifugated for 20 minutes at 2500 rpm, and then separated using filter paper. The precipitated lignin was then oven-dried at 50-60 ˚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).

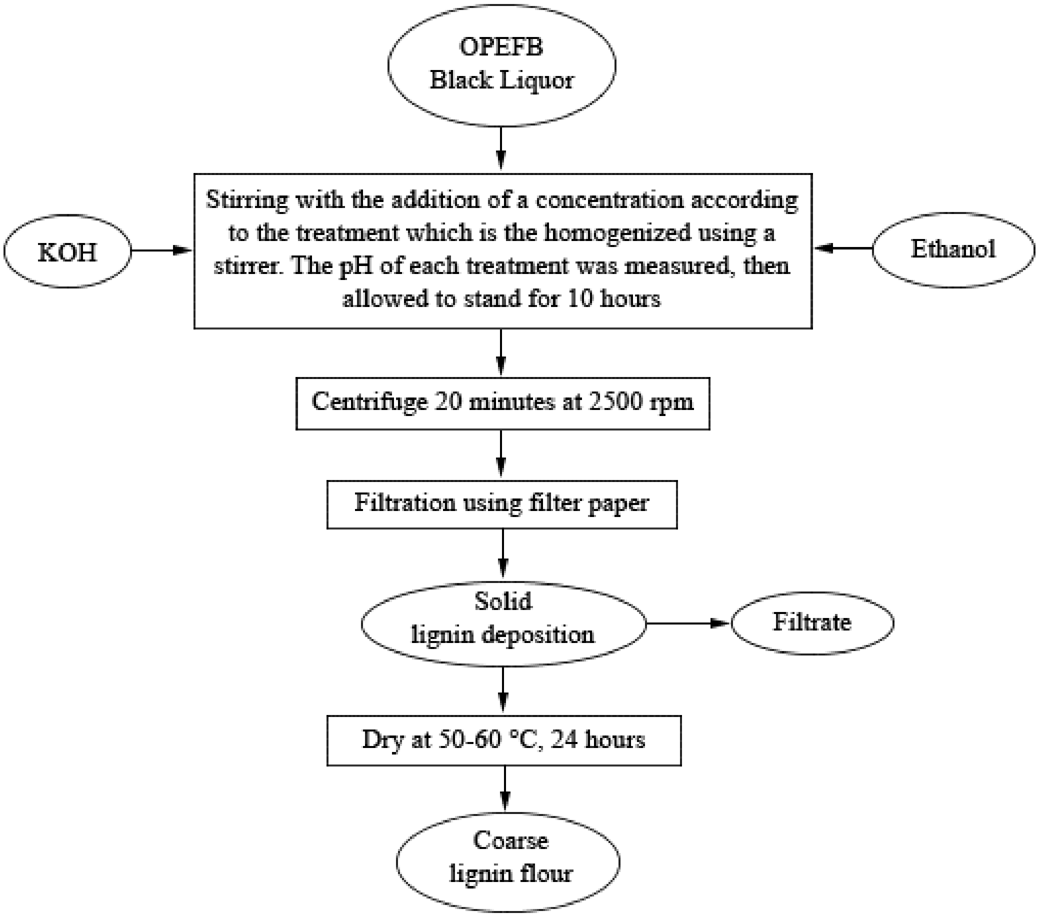

Figure 1: Flowchart of lignin isolation process using KOH/Ethanol.

2.4 Lignin Yield

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

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

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 minutes 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 seconds). The methoxyl content of lignin was calculated according to Equation 2 as follows.

$$\text{Methoxyl } (\%) = \frac{ml\ NaOH\ x\ N\ NaOH\ x\ 3{,}1}{Berat\ sampel\ (gram)} x 100\% \qquad (2)$$

2.6 Lignin Equivalent Weight

Isolated lignin equivalent weight was calculated using the method of Santoso [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 Equation 3.

$$\text{Equivalent Weight} = \frac{1000xgram\ sample}{(mLN)NaOH} \qquad (3)$$

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 cm^{-1} to 400 cm^{-1} (wavelength of 2.5–25 πm).

2.7 SEM analysis

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

3 Results and Discussion

3.1 pH of the black liquor

The pH of BL from formacell pulping OPEFB is 0.59 ± 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 ± 0.07 to 4.27 ± 0.35 (Table 1), while the addition of ethanol concentrations can slightly increase the pH value from 1.0 ± 0.01 to 1.29 ± 0.03. According to the findings, KOH has a greater effect on increasing pH than ethanol due to the strong base property of KOH.

The pH steadily increased as an up-surging concentration of KOH, where the lowest pH, 2.43 ± 0.07, was obtained from 2.5% KOH, and the highest was a pH of 4.27 ± 0.35 from KOH 15%. Increasing the concentration of KOH solution causes more 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.

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±0.07	3.57±0.38	13.06±0.9	1372.94±26.73
5.0	2.94±006	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

3.2 Lignin yield

The lignin yield from adding KOH solution at various concentrations in isolation of BL ranged from 3.57 ± 0.38 to 14.95 ± 1.10 (Table 1). In comparison, ethanol isolation resulted in lower lignin yields of about 0.51 ± 0.00 to 1.06 ± 0.00. The highest lignin yield was produced at a concentration of 15% KOH solution (14.95% ± 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 OH^- ions from KOH. It reduces the electrostatic force between lignin molecules, resulting in the deposition of lignin and reduced solubility. The more 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 Na^+ and 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% ± 1.92 to 12.94% ± 0.90, whereas the use of ethanol concentrations results in methoxyl contents between 11.99 ± 0.02 to 17.03 ± 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 Cα—Cβ through Cβ—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 ± 74.20 to 1372.94 ± 269.73, whereas the addition of ethanol concentration resulted in molecular weights ranging from 449.88 ± 1.9 to 2123.03 ± 27.5 (Table 1).

Increasing the concentration of KOH solution resulted in a decrease in lignin equivalent weight so that the lowest value at 15% KOH solution concentration was 427.03 ± 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., there are two routes for lignin depolymerization: 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]. The product's molecular weight can be lowered by increasing salt concentration [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 (Mw <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 g mol^{-1} with a polydispersity of 4.3. Sameni et al. compared four types of lignin from different isolation methods, where the highest Mw (13488) was obtained from the steam explosion process with a methoxyl content of 0.69. Meanwhile, with the same methoxyl content, the lowest Mw (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].

3.6 Lignin Analysis with FT-IR Spectrophotometer

FTIR was performed to analyze differences in the functional groups of lignin in the sample (Fig. 2 and 3). FTIR spectra analysis showed that the peak in the aromatic ring vibrations decreased with the absorption band at 1446 cm^{-1} (a) and 1408 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 cm^{-1} to 31090 cm^{-1} which refer to the presence of hydrogen bonds in the hydroxyl group (alcohol and phenolic). A wavelength absorption of 1587 cm^{-1} and 1513 cm^{-1} indicates the aromatic lignin skeletal vibration [60]. Wavenumbers at 1460 cm^{-1} to 1420 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 cm^{-1} to 1270 cm^{-1} in all spectra may refer to the C-H deformation vibrations of the guaiacyl [64]. The bands at 1300 cm^{-1} (syringyl) and 1200 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 Fig. 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 cm^{-1}.

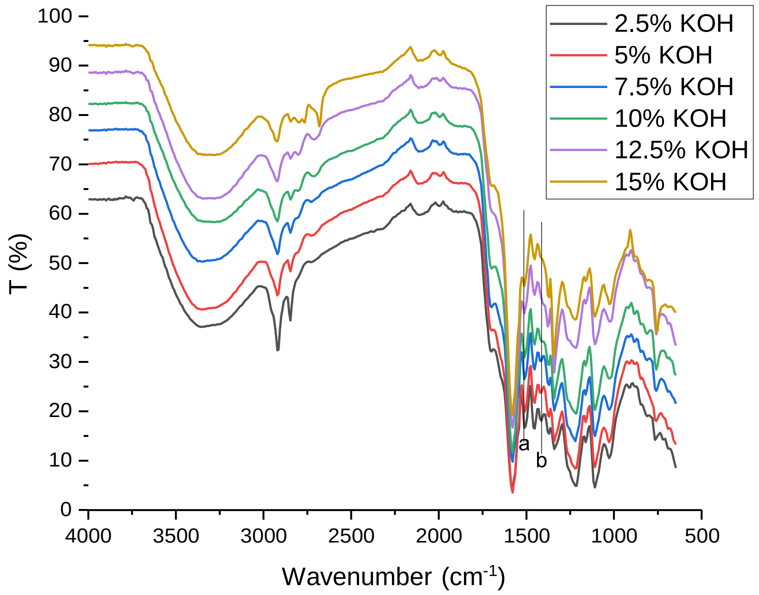

Figure 2: The FT-IR spectra of lignin using KOH isolation

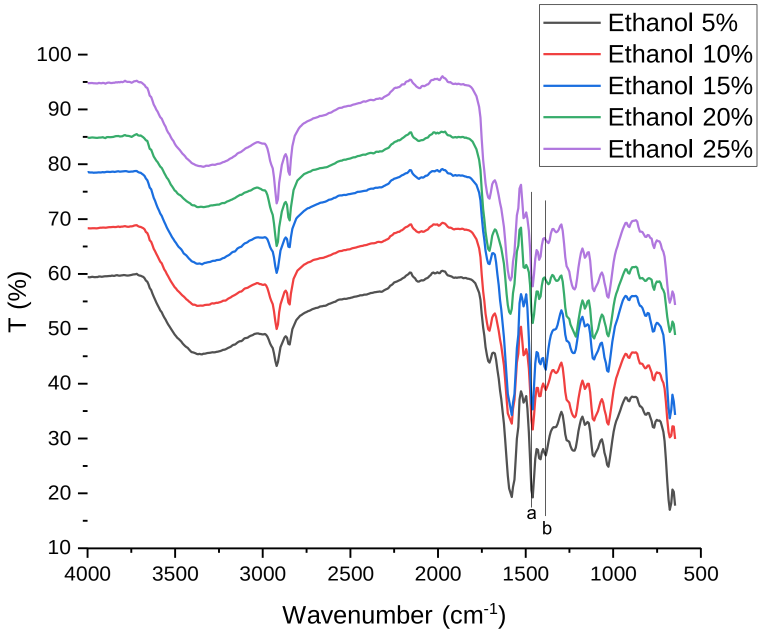

Figure 3: The FT-IR spectra of lignin using ethanol isolation

3.7 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.

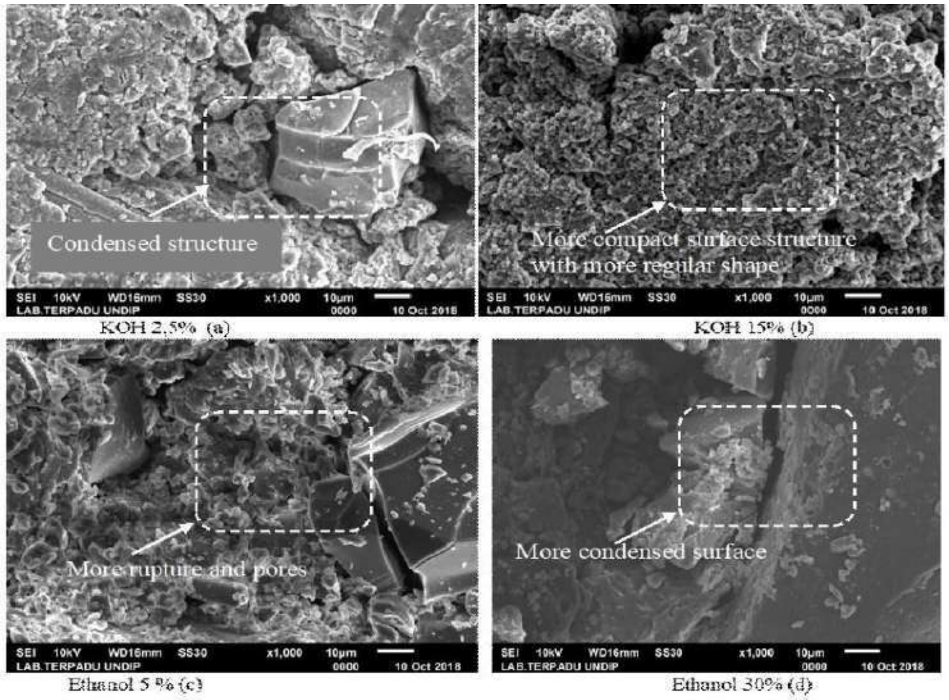

Figure 4: Morphological images of isolated lignin (a) KOH 2.5%, (b) KOH 15%, (c) ethanol 5%, (d) ethanol 30% with 1000 x magnification

3.8 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_3), 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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5 messages

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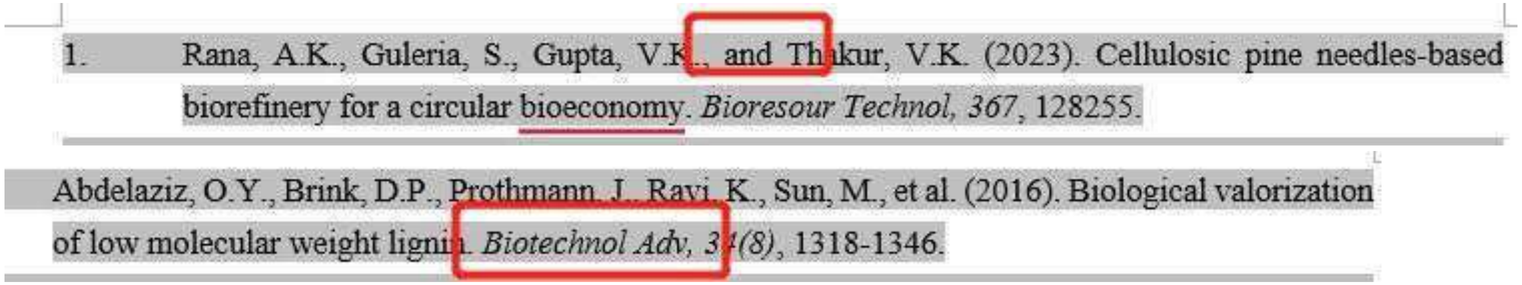

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Thanks for your hard work.

Best regards,
Gabriel Cao

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sri hidayati <srihidayati.unila@gmail.com> Sun, Dec 25, 2022 at 5:50 AM
To: "gabriel.cao@techscience.com" <gabriel.cao@techscience.com>

Dear: JRM Journal Editor

Thank you very much for accepting our paper. We hereby send the results of improvements from our paper, especially regarding errors in writing in the bibliography and we have adjusted them to the journal template.

Greetings,

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Dear Sri hudayati,

Sincerely thanks for your prompt reply.

We will further check your manuscript ASAP.

Happy holidays!

Best regards,
Gabriel Cao

Journal of Renewable Materials
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Dear Gabriel Cao,

Hope you are doing well. Could you please provide information on the current status of our manuscript processing? We answered the requests in your last email and sent the revised version.

Thank you for your time and consideration!

Best regards,

Petar

Prof. Petar Antov, PhD
International and Public Relations Coordinator
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From: gabriel.cao@techscience.com <gabriel.cao@techscience.com>
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4 messages

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pm@transforma.in <pm@transforma.in> Wed, Jan 18, 2023 at 8:20 PM
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Dear: JRM editorial board

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

Greetings

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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%, meth- oxyl 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. Polypropane units can be chemically bonded in different bonding patterns where the β-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_2SO_4, phosphoric acid (H_3PO_4), 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,

$Ca(OH)_2$, 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).

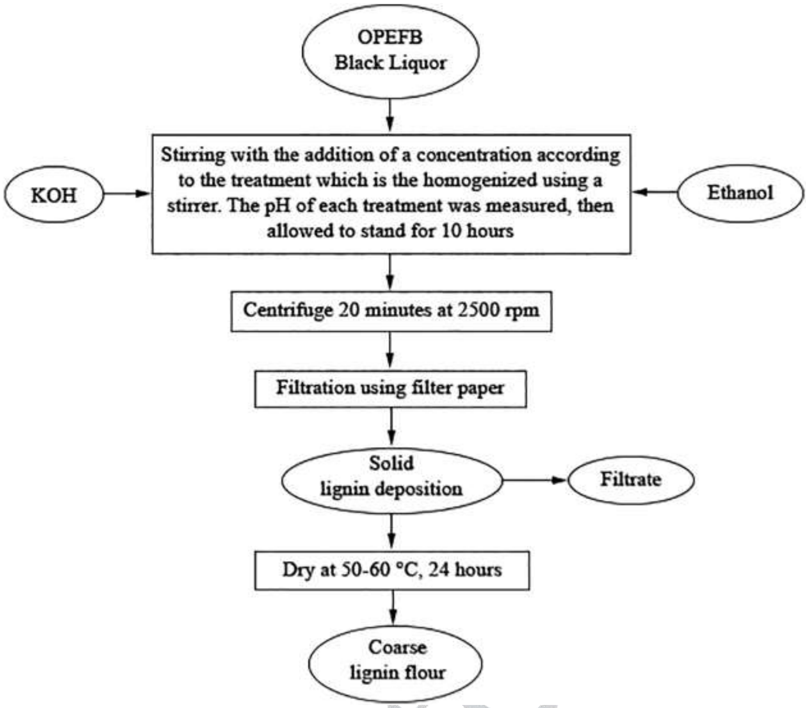

Figure 1: Flowchart of lignin isolation process using KOH/Ethanol

2.4 *Lignin Yield*

Lignin yield was calculated based on the method according to Sluiter et al. [32], as presented in Eq. (1). [Q1]

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

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.

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

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).

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

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 cm^{-1} (wavelength of 2.5–25 μm).

2.8 *SEM Analysis*

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

3 Results and Discussion

3.1 *pH of the Black Liquor*

The pH of BL from formacell pulping OPEFB is 0.59 ± 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 ± 0.07 to 4.27 ± 0.35 (Table 1), while the addition of ethanol concentrations can slightly increase the pH value from 1.0 ± 0.01 to 1.29 ± 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 ± 0.07	3.57 ± 0.38	13.06 ± 0.9	1372.94 ± 26.73
5.0	2.94 ± 006	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

The pH steadily increased as an up-surging concentration of KOH, where the lowest pH, 2.43 ± 0.07, was obtained from 2.5% KOH, and the highest was a pH of 4.27 ± 0.35 from KOH 15%. Increasing the concentration of KOH solution causes more 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 ± 0.38 to 14.95 ± 1.10 (Table 1). In comparison, ethanol isolation resulted in lower lignin yields of about 0.51 ± 0.00 to 1.06 ± 0.00. The highest lignin yield was produced at a concentration of 15% KOH solution (14.95% ± 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 OH^- ions from KOH. It reduces the electrostatic force between lignin molecules, resulting in the deposition of lignin and reduced solubility. The more 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 Na^+ and 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% ± 1.92 to 12.94% ± 0.90, whereas the use of ethanol concentrations results in methoxyl contents between 11.99 ± 0.02 to 17.03 ± 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 Cα—Cβ through Cβ—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 ± 74.20 to 1372.94 ± 269.73, whereas the addition of ethanol concentration resulted in molecular weights ranging from 449.88 ± 1.9 to 2123.03 ± 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 ± 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 (Mw < 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 g mol^{-1} with a polydispersity of 4.3. Sameni et al. compared four types of lignin from different isolation methods, where the highest Mw (13488) was obtained from the steam explosion process with a methoxyl content of 0.69. Meanwhile, with the same methoxyl content, the lowest Mw (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 cm^{-1} (a) and 1408 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 cm^{-1} which refer to the presence of hydrogen bonds in the hydroxyl group (alcohol and phenolic). A wavelength absorption of 1587 and 1513 cm^{-1} indicates the aromatic lignin skeletal vibration [60]. Wavenumbers at 1460 to 1420 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 cm^{-1} in all spectra may refer to the C-H deformation vibrations of the guaiacyl [64]. The bands at 1300 cm^{-1} (syringyl) and 1200 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 cm^{-1}.

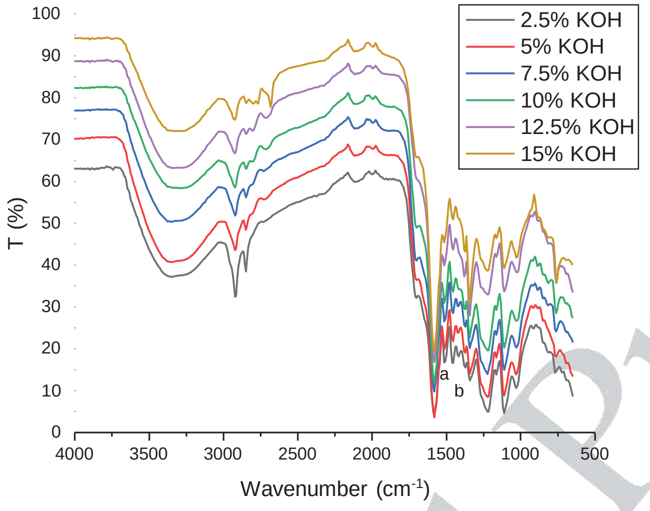

Figure 2: The FT-IR spectra of lignin using KOH isolation

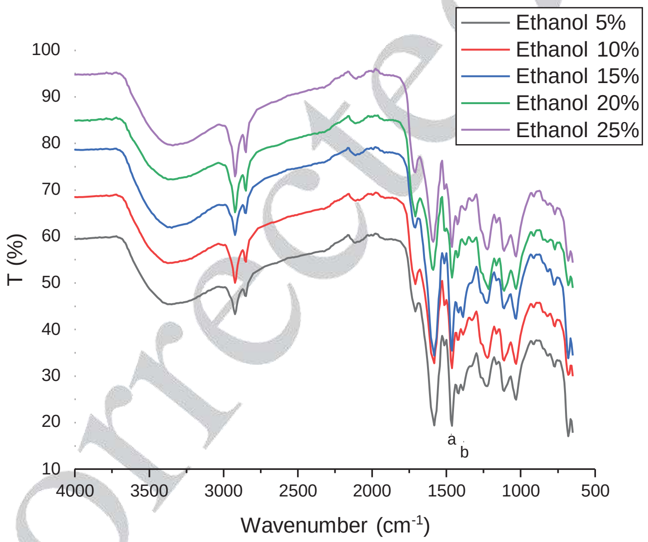

Figure 3: The FT-IR spectra of lignin using ethanol isolation

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.

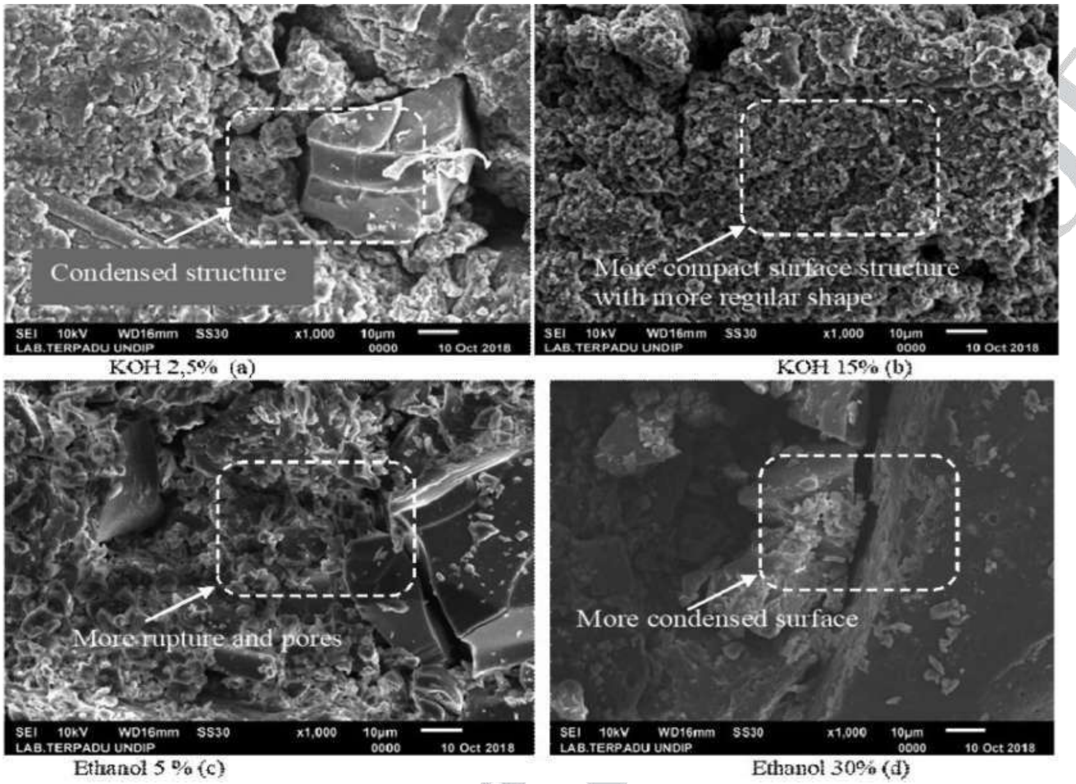

Figure 4: Morphological images of isolated lignin (a) KOH 2.5%, (b) KOH 15%, (c) ethanol 5%, (d) ethanol 30% with 1000 × magnification

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 ($-OCH_3$), 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%, meth- oxyl content of 11.33% and 10.13%, and lignin equivalent weights of 476.25 and 427.03, respectively. Due to itsphenolic 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. Polypropane units can be chemically bonded in different bonding patterns where the β-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_2SO_4, phosphoric acid (H_3PO_4), 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,

$Ca(OH)_2$, 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).

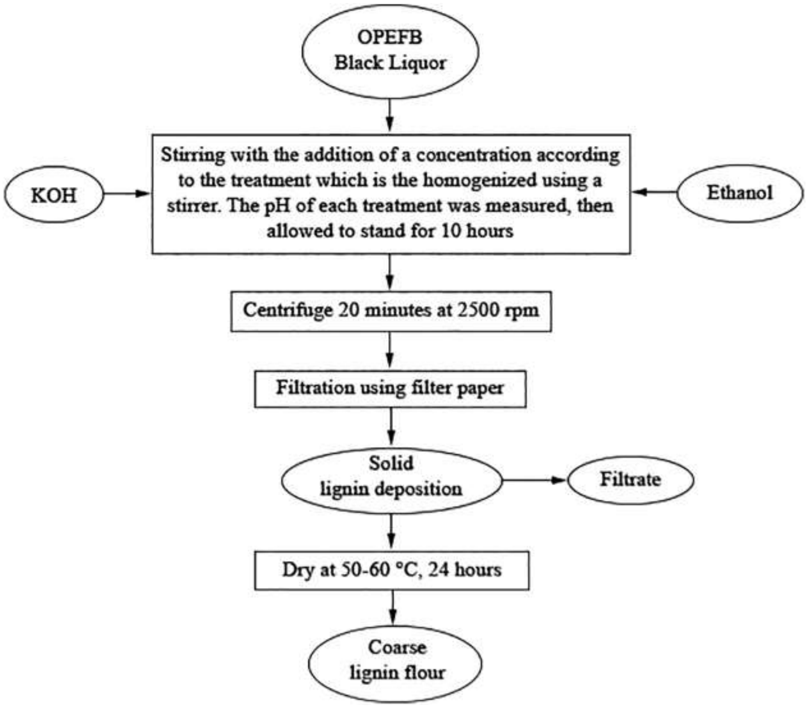

Figure 1: Flowchart of lignin isolation process using KOH/Ethanol

2.4 Lignin Yield

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

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

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.

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

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).

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

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 cm^{-1} (wavelength of 2.5–25 μm).

2.8 *SEM Analysis*

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

3 Results and Discussion

3.1 *pH of the Black Liquor*

The pH of BL from formacell pulping OPEFB is 0.59 ± 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 ± 0.07 to 4.27 ± 0.35 (Table 1), while the addition of ethanol concentrations can slightly increase the pH value from 1.0 ± 0.01 to 1.29 ± 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 ± 0.07	3.57 ± 0.38	13.06 ± 0.9	1372.94 ± 26.73
5.0	2.94 ± 006	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

The pH steadily increased as an up-surging concentration of KOH, where the lowest pH, 2.43 ± 0.07, was obtained from 2.5% KOH, and the highest was a pH of 4.27 ± 0.35 from KOH 15%. Increasing the concentration of KOH solution causes more 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 ± 0.38 to 14.95 ± 1.10 (Table 1). In comparison, ethanol isolation resulted in lower lignin yields of about 0.51 ± 0.00 to 1.06 ± 0.00. The highest lignin yield was produced at a concentration of 15% KOH solution (14.95% ± 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 OH^- ions from KOH. It reduces the electrostatic force between lignin molecules, resulting in the deposition of lignin and reduced solubility. The more 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 Na^+ and 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% ± 1.92 to 12.94% ± 0.90, whereas the use of ethanol concentrations results in methoxyl contents between 11.99 ± 0.02 to 17.03 ± 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 Cα—Cβ through Cβ—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 ± 74.20 to 1372.94 ± 269.73, whereas the addition of ethanol concentration resulted in molecular weights ranging from 449.88 ± 1.9 to 2123.03 ± 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 ± 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 (Mw < 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 g mol^{-1} with a polydispersity of 4.3. Sameni et al. compared four types of lignin from different isolation methods, where the highest Mw (13488) was obtained from the steam explosion process with a methoxyl content of 0.69. Meanwhile, with the same methoxyl content, the lowest Mw (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 cm^{-1} (a) and 1408 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 cm^{-1} which refer to the presence of hydrogen bonds in the hydroxyl group (alcohol and phenolic). A wavelength absorption of 1587 and 1513 cm^{-1} indicates the aromatic lignin skeletal vibration [60]. Wavenumbers at 1460 to 1420 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 cm^{-1} in all spectra may refer to the C-H deformation vibrations of the guaiacyl [64]. The bands at 1300 cm^{-1} (syringyl) and 1200 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 cm^{-1}.

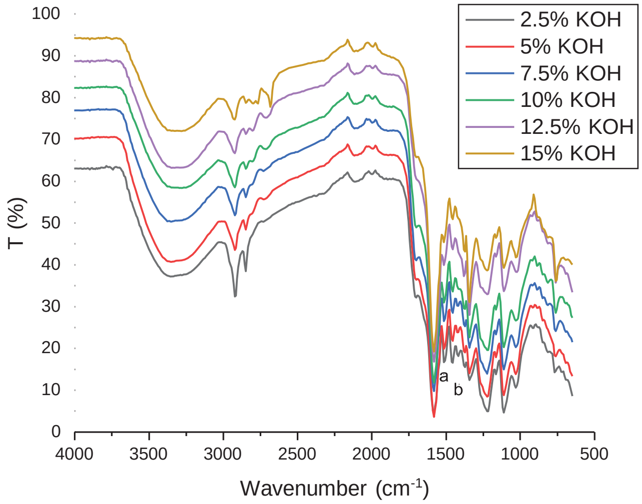

Figure 2: The FT-IR spectra of lignin using KOH isolation

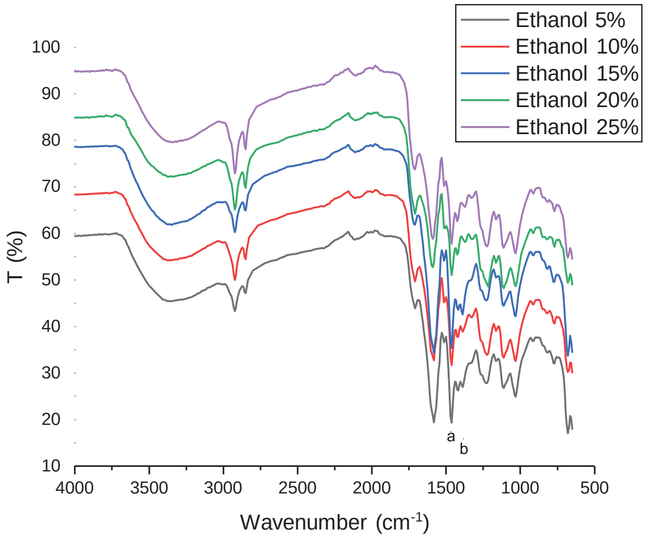

Figure 3: The FT-IR spectra of lignin using ethanol isolation

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.

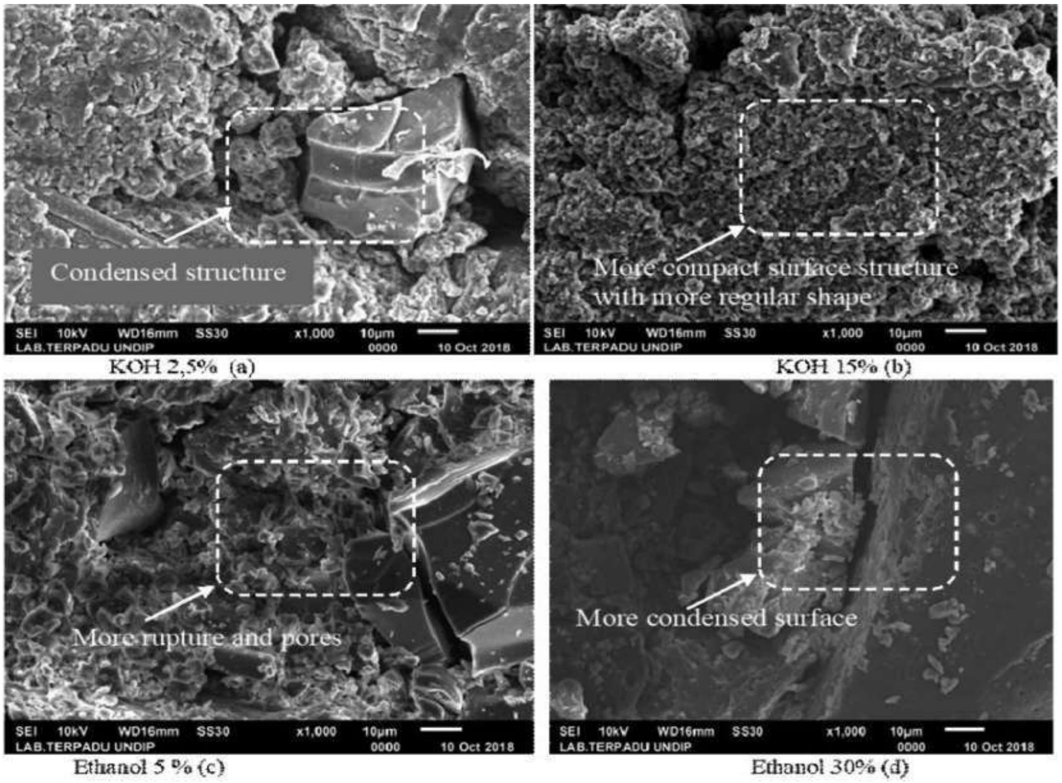

Figure 4: Morphological images of isolated lignin (a) KOH 2.5%, (b) KOH 15%, (c) ethanol 5%, (d) ethanol 30% with 1000 × magnification

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 ($-OCH_3$), 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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Conflicts of Interest: The authors declare that they have no conflicts of interest to report regarding the present study.

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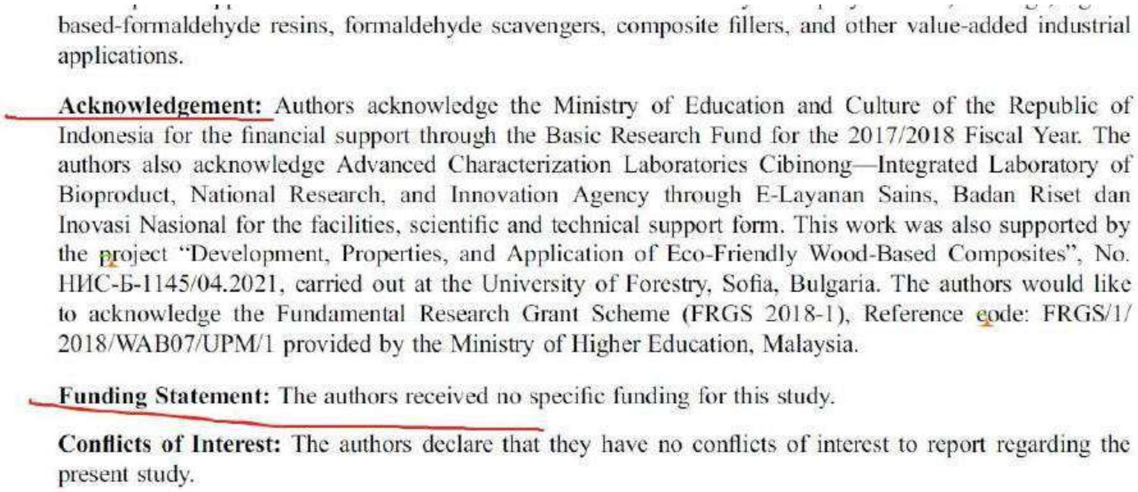

based-formaldehyde resins, formaldehyde scavengers, composite fillers, and other value-added industrial applications.

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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%, meth- oxyl 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

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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. Polypropane units can be chemically bonded in different bonding patterns where the β-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_2SO_4, phosphoric acid (H_3PO_4), 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,

$Ca(OH)_2$, 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).

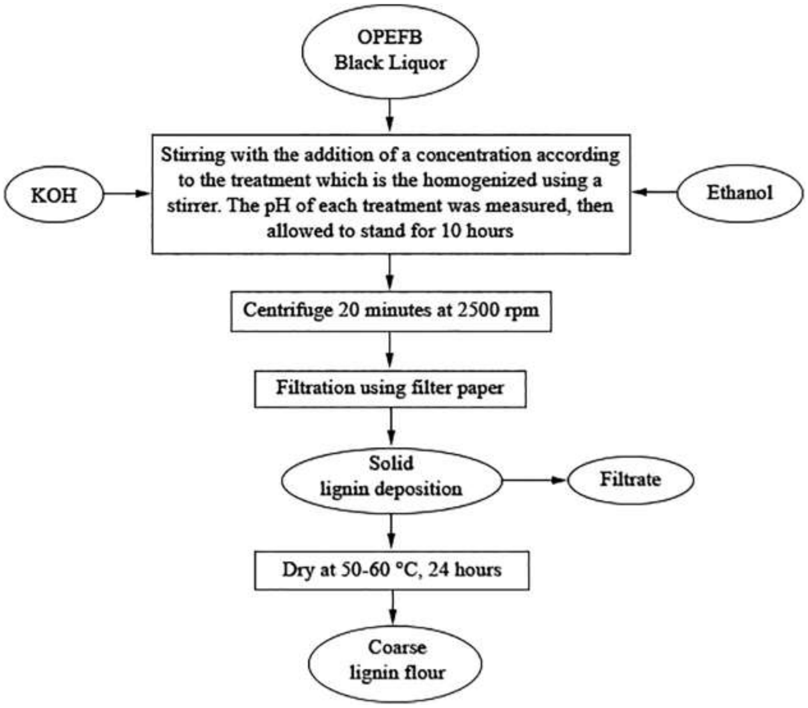


Figure 1: Flowchart of lignin isolation process using KOH/Ethanol

2.4 *Lignin Yield*

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

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

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:

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

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).

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

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 cm^{-1} (wavelength of 2.5–25 μm).

2.8 *SEM Analysis*

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

3 Results and Discussion

3.1 *pH of the Black Liquor*

The pH of BL from formacell pulping OPEFB is 0.59 ± 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 ± 0.07 to 4.27 ± 0.35 (Table 1), while the addition of ethanol concentrations can slightly increase the pH value from 1.0 ± 0.01 to 1.29 ± 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 ± 0.07	3.57 ± 0.38	13.06 ± 0.9	1372.94 ± 26.73
5.0	2.94 ± 006	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

The pH steadily increased as an up-surging concentration of KOH, where the lowest pH, 2.43 ± 0.07, was obtained from 2.5% KOH, and the highest was a pH of 4.27 ± 0.35 from KOH 15%. Increasing the concentration of KOH solution causes more 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 ± 0.38 to 14.95 ± 1.10 (Table 1). In comparison, ethanol isolation resulted in lower lignin yields of about 0.51 ± 0.00 to 1.06 ± 0.00. The highest lignin yield was produced at a concentration of 15% KOH solution (14.95% ± 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 OH^- ions from KOH. It reduces the electrostatic force between lignin molecules, resulting in the deposition of lignin and reduced solubility. The more 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 Na^+ and 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% ± 1.92 to 13.06% ± 0.9, whereas the use of ethanol concentrations results in methoxyl contents between 11.99 ± 0.02 to 17.03 ± 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 Cα—Cβ through Cβ—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 ± 74.20 to 1372.94 ± 269.73, whereas the addition of ethanol concentration resulted in molecular weights ranging from 449.88 ± 1.9 to 2123.03 ± 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 ± 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 (Mw < 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 g mol^{-1} with a polydispersity of 4.3. Sameni et al. compared four types of lignin from different isolation methods, where the highest Mw (13488) was obtained from the steam explosion process with a methoxyl content of 0.69. Meanwhile, with the same methoxyl content, the lowest Mw (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 cm^{-1} (a) and 1408 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 cm^{-1} which refer to the presence of hydrogen bonds in the hydroxyl group (alcohol and phenolic). A wavelength absorption of 1587 and 1513 cm^{-1} indicates the aromatic lignin skeletal vibration [60]. Wavenumbers at 1460 to 1420 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 to1270 cm^{-1} in all spectra may refer to the C-H deformation vibrations of the guaiacyl [64]. The bands at 1300 cm^{-1} (syringyl) and 1200 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 cm^{-1}.

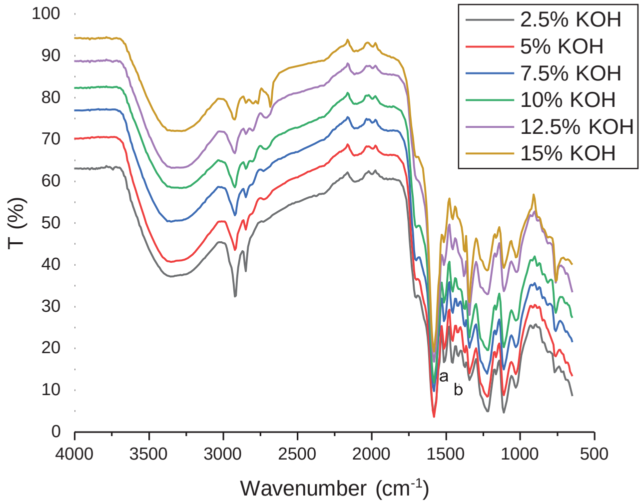


Figure 2: The FT-IR spectra of lignin using KOH isolation

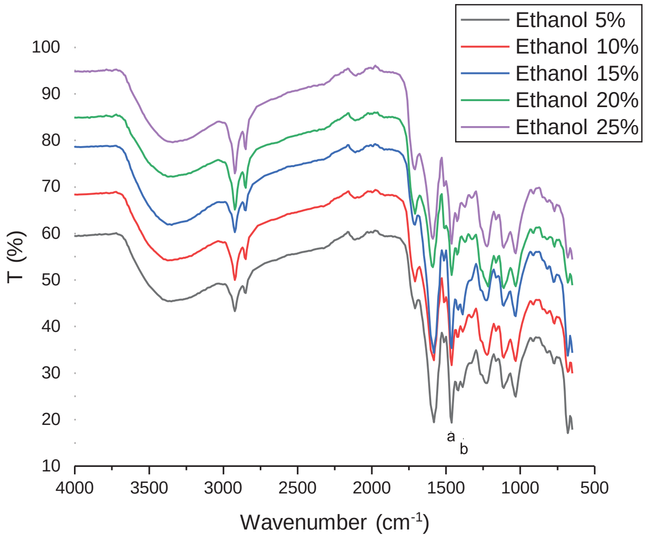
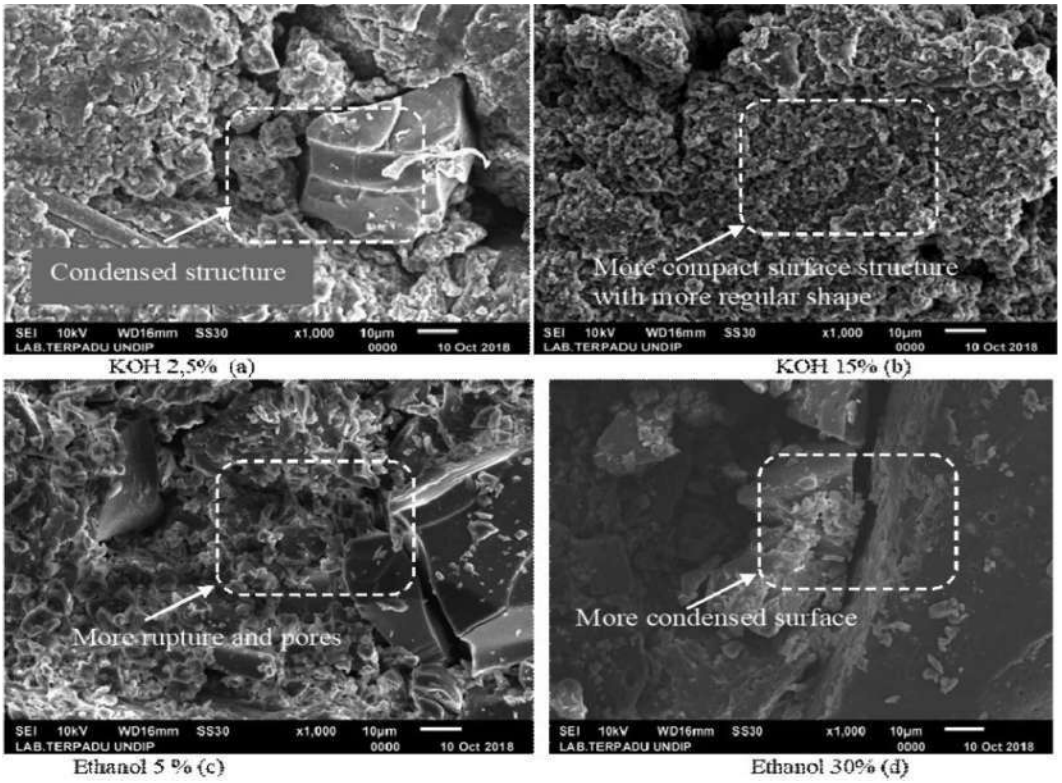


Figure 3: The FT-IR spectra of lignin using ethanol isolation

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.



KOH 2,5% (a) KOH 15% (b)

Ethanol 5 % (c) Ethanol 30% (d)

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 ($-OCH_3$), 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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