EFFECT OF CATALYSTS ON THE YIELD AND PROPERTIES OF LIGNIN FROM MICROWAVE-ASSISTED ACETOSOLV EXTRACTION OF OIL PALM EMPTY FRUIT BUNCH FIBRES

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ABSTRACT
Acetosolv is an enhancement organosolv technique utilising acetic acid as solvent and produces high purity of lignin. However, the limitation of this technique in the conventional heating method is the high energy consumption during a long reaction time. Therefore, the employment of microwave is used to overcome this limitation with the expectation of a lower power consumption and short reaction time. In this study, three types of catalysts, sulphuric acid (H$_2$SO$_4$), aluminium chloride (AlCl$_3$), and chromium nitrate [Cr(NO$_3$)$_3$] were used to investigate the lignin extraction performance and its properties from microwave-assisted (MWA) acetosolv treatment of oil palm empty fruit bunches (EFB). The highest yields of lignin (76.98%) were obtained using an aqueous solution of acetic acid combined with 3.0% of H$_2$SO$_4$ under 110°C for 30 min. Meanwhile, AlCl$_3$ performed almost similar to H$_2$SO$_4$, providing lignin yield of 71.57% at the highest temperature of 110°C. The usage of microwave-assisted technique also produces a high yield and high purity of lignin. It is also proven that AlCl$_3$ can be a substitute to Bronsted acid for lignin extraction. However, Cr(NO$_3$)$_3$ was found not suitable for the lignin’s extraction despite having a high potential for cellulose extraction.

Keywords: lignocellulose, microwave-assisted, extraction lignin.

Received: 22 March 2020; Accepted: 16 June 2020; Published online: 5 October 2020.

INTRODUCTION
In recent years, concerns over the continuous depletion of fossil resources as well as an increment in ecological awareness have drawn a remarkable interest to reduce the dependence on fossil resources as raw materials. Countless research have been conducted to overcome these issues and lignocellulosic biomass has been considered as the best candidate to replace or provide alternative to petroleum-based materials (Amran et al., 2017). This reason is not only for its sustainability but the content of cellulose, lignin and hemicellulose in the biomass provide various functionalities and structures that can be tailored into desired applications. By utilising lignocellulosic biomass, the issues related to petroleum depletion can be prevented as this biomass can be obtained in large quantity at low economical and energy cost (Chen and Lee, 2018). Furthermore, this waste can also be converted into a high-value product, simultaneously solving the waste management problem (Roslan et al., 2014).
In general, the oil palm empty fruit bunches (EFB) is an organic substrate derived from harvested or processed oil palm fruit bunches (Kheong et al., 2010). These organic substrate is also difficult to degrade biologically (David et al., 2019). In Malaysia, EFB are the colossal solid waste from the oil palm industry and regarded as the most important lignocellulosic biomass for production of chemical and fuels (Coral et al., 2018). The oil palm planted area in 2019 reached 3.90 million hectares, and the production of crude palm oil in the same year was 19.86 million tonnes (MPOB, 2020). The amount of unutilised EFB sent back to landfill is around 40% (Reeb et al., 2014). There were several reports regarding to the utilisation of the EFB as raw materials for the generation of high value-added products, such as production of cellulose (Aditiawati et al., 2019; Owi et al., 2016), adhesives (Rohimi et al., 2020), activated carbon (Choi et al., 2018; Zaini and Ali, 2018) and composites (Amir et al., 2018). In this study, the effective valorisation of lignin will be the focus on the pursuit of more sustainable and competitive biorefineries.

Basically, oil palm EFB fibre consists about 42%-63% cellulose, 21.9%-33% hemicellulose and 10%-36.6% lignin (Omar et al., 2011). Lignin is the second most abundant terrestrial organic polymer on earth after cellulose (Fan et al., 2015). Basically, it consists of three types of monolignols, which are p-coumaryl, coniferyl, and syringyl alcohol. It generally has an irregular structure with a highly condensed cross-linked polymer network (Constant et al., 2015). The composition and properties of lignin are influenced by solvent, extraction technique, catalyst, and the nature of the raw material. However, it is regrettable to notice that only a small portion is currently used for value-added product (Sameni et al., 2017).

As a by-product of the pulp and paper industry, lignin is typically extracted by utilising acid or alkali medium to increase the rate of delignification. The raw material is usually heated at elevated temperatures under high pressure by using high-pressure reactors or autoclaves. This method is not favourable since it consumes high energy due to the long reaction time, resulting from conductive heating for several hours (Avelino et al., 2018). Therefore, in this study, microwave-assisted (MWA) extraction as the heating method will be introduced to promote the delignification process. Compared to the traditional oven or oil bath convection heating, microwave irradiation utilises the dipole rotation and ionic conduction to heat, and the heating process will occur directly to the targeted sample (Fatrasiari et al., 2017; Kappe, 2004; Pricel and Lopez-Sanchez, 2018). This technique can be used as a sustainable methodology for lignin extraction since it operates on low energy consumption due to reduced reaction time and simultaneously increases the efficiency and quality of the product.

In MWA technique, polar compounds must be used in order to absorb the radiation. Therefore, acetosolv technique will be employed as the method of lignin extraction. In addition, acetosolv technique was also chosen as it produces high purity of lignin compared to sulphite and Kraft processes. Sulphite and Kraft will limit the lignin suitability as a resource for future processing and disturb any application that requires ‘clean’ lignin (Sammons et al., 2013). In this technique, acetic acid was used as a solvent to collapse the plant tissue and promote the lignin degradation from lignocellulosic biomass with the assistance of temperature and acid catalyst (Hernández-Hernández et al., 2016). It can be used to delignify biomass and to remove most of the hemicellulose. Moreover, the lignin extracted from this process also shows excellent properties such as low molecular weight and solubility in organic solvents (Schwiderski et al., 2014). Commonly, aqueous solutions of acetic acid and ethanol combined with low concentrations of Bronsted acids as a catalyst are used to separate lignin and carbohydrates. In general, Bronsted acid is the proton donor substance that donates proton in acid-base reactions such as H₂SO₄ and HCl. However, the concentrated H₂SO₄ has a drawback, of which expensive materials are needed to fabricate the reaction vessel for anti-corrosion purposes. Therefore, the application of Lewis acid; molecules with incomplete octet of electrons that can accept electrons, in the extraction of lignin as substitute to Bronsted acids will be the main objective in this study (Abdullah et al., 2012).

Therefore, this study is aimed to evaluate the physico-chemical properties of acetosolv lignin (AL) extracted from EFB fibres via MWA acetosolv technique using different Lewis acid catalyst [AlCl₃, and Cr(NO₃)₇] and compared with commonly used Bronsted acids (H₂SO₄). The reaction time was fixed at 30 min to avoid incomplete reaction from occurring below that reaction time.

**MATERIALS AND METHOD**

**Materials**

EFB were provided by Szetech Engineering Sdn Bhd. The following chemicals were used in the study: sulphuric acid (H₂SO₄, 95%-98%, R&M Chemicals), aluminium chloride (AlCl₃, 98%, Sigma-Aldrich), chromium nitrate Cr(NO₃)₃, 98%, Sigma-Aldrich and glacial acetic acid.

**MWA Acetosolv Reaction for Lignin Extraction**

The MWA acetosolv was conducted in a 1L reaction flask equipped with a reflux system. Several temperatures were studied during the MWA
which are 90°C, 100°C and 110°C at a fixed 30 min reaction time in the presence of 3% catalyst; H\textsubscript{2}SO\textsubscript{4}, AlCl\textsubscript{3}, and Cr(NO\textsubscript{3})\textsubscript{3}. In these experiments, the EFB to solvent ratio was fixed at 1:10, and the reaction took place in a four-neck flat bottom reaction flask containing the acetosolv solution [acetic acid: water solution (9:1, v:v)] with the presence of catalysts. After the reaction completed, black liquor was obtained and filtered for separation of residue before being precipitated using deionised water. Finally, the lignin was vacuum filtered, washed with deionised water several times until reaching neutral and dried in an oven for 12 hr.

**Lignin Extraction Yield and Purity**

Lignin yield was calculated according to Equation (1):

\[ \text{\textit{n}} = \frac{\text{mMWAL}}{\text{mLig}} \quad \text{Equation (1)} \]

where \( \text{\textit{n}} \) is the lignin yield (%); mMWAL is the mass of lignin extracted in the MWAL process (g) while mLig is the mass of lignin gained from overall biomass (g) as determined by TAPPI standards (Hames et al., 2008). The purity of lignin was carried out using the National Renewable Energy Laboratory (NREL) standard biomass analytical procedure with three replication.

**Characterisation of Lignin**

**Scanning electron microscope (SEM).** The surface morphology of the raw EFB and residues, the samples were placed on specimen stub, followed by binding with double-sided carbon tape before being observed using FEI Quanta450 SEM with 1000X image magnification.

**Fourier transform infrared spectroscopy (FT-IR).** FT-IR was performed in a Perkin Elmer Spectrum One under KBr disc technique. Spectra were acquired between 4000 and 500 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\). Proton nuclear magnetic resonance (\(^1\)H NMR) was used to support the structural analysis, which was recorded on 500 MHz, Bruker NMR spectrometry. The solvent used was deuterated dimethylsulfoxide, DMSO-d6 and the solvent chemical shift was set and calibrated at 2.5 ppm.

**Thermogravimetric (TGA) analysis.** TGA analysis was performed in a TGA Q500 from the TA instrument. The 15 mg of the sample was heated from 30°C-700°C under a nitrogen atmosphere of 40 ml min\(^{-1}\) at a scanning rate of 10°C min\(^{-1}\).

**RESULT AND DISCUSSION**

**Effect of Reaction Temperature and Catalyst on Yield of Crude and Purified Lignin Gained via MWA Acetosolv Treatment**

Initially, two parameters were evaluated in this study; the reaction temperature and the catalyst [H\textsubscript{2}SO\textsubscript{4}, AlCl\textsubscript{3}, and Cr(NO\textsubscript{3})\textsubscript{3}], as shown in Figure 1. In acetosolv technique, acetic acid (CH\textsubscript{3}COOH) was used to produce H\textsubscript{3}O\textsuperscript{+} ions, which are responsible for the protonation of ether groups present in lignin; hence, affecting the yield of lignin. However, the ability of these CH\textsubscript{3}COOH to produce the H\textsubscript{3}O\textsuperscript{+} ions is low, and the presence of catalysts is vital for improving this behaviour. From Figure 1, the employment of Cr(NO\textsubscript{3})\textsubscript{3} was not able to extract any lignin. Meanwhile, AlCl\textsubscript{3} gave quite the same lignin yield as H\textsubscript{2}SO\textsubscript{4} at the highest temperature (100°C) used in this study. It is proven that the yield of lignin is affected by the nature of catalysts used. From a previous study (Avelino et al., 2018; Schwiderski et al., 2014), AlCl\textsubscript{3} showed quite a similar yield to Bronsted acids as it has similar acidic power despite the effect of higher cation hardness compared to other Lewis acids. This acidic power leads to more efficient coordination with the oxygen atoms present in the ether groups and making them more susceptible to hydrolysis. Therefore, these results support the fact that the acidic power also has a significant influence on yield, but not so much in the lignin purity, as shown in Figure 1. For Cr(NO\textsubscript{3})\textsubscript{3}, the only possible reason that can be explained to the absence of lignin is that Cr is adsorbed on the lignin fragment since lignin has a higher affinity for Cr(III) before the precipitation process being done. This high affinity eventually leads to the formation of water repellent lignin (Garcia-Reyes and Rangel-Mendez, 2009; Pandey et al., 1998; Wu et al., 2008).

The lignin yield based on reaction temperature was increased with the increased temperature. From Figure 1, it is shown that as temperature increased from 90°C-110°C, the lignin yield obtained had also increases from 43.07%-76.98%, with the highest purity of 94.15% for H\textsubscript{2}SO\textsubscript{4}. As for AlCl\textsubscript{3}, the yield increased from 28.81%-71.57%, with an increment of purity from 83.39%-92.89%. Basically, temperature plays a vital role in lignin extraction as it enhances the degradation of cell walls while the lignin and hemicellulose were decomposed and dissolved in the organic solvent (Amran et al., 2017; 2019). The higher yield obtained was also due to the extensive lignin depolymerisation which led to higher lignin solubilisation in the organic solvent, especially with the presence of microwave irradiation (Monteil-Rivera et al., 2012). Theoretically, microwave irradiation provides the homogeneity of temperature in the reactor compared with conventional heating and, consequently, facilitated the cleavage of the
C–C bond which led to the higher yield of lignin extracted from EFB.

### Morphological Observation of Oil Palm EFB Fibres Before and After MWA Acetosolv

The morphology of the EFB fibre and EFB residue are shown in Figure 2. In general, the SEM results showed that the EFB fibre’s morphology is made up of distinct cell wall layers. For the EFB residues, the acetosolv technique has changed the morphology of EFB fibres due to the removal of lignin. At the lowest temperature (90°C), it can be seen that the morphology of the fibre undergoes a little change as the acetosolv technique had roughened the structure of cell wall surface of the fibre which disrupted the lignin’s structure (Tajuddin et al., 2019; Yaakob et al., 2020). This generally occurred to all the catalysts used in this study. At medium temperature (100°C), the cell wall is continuously removed from the structure of the fibres for all the residues. At the highest temperature (110°C), all the residues have a different morphology based on the catalyst used. For the H$_2$SO$_4$ catalyst, it was clearly observed that the cell wall of the fibres was completely removed and exposed to the defibrated inner microfibrils, as shown in Figure 2d. Compared to H$_2$SO$_4$, Figure 2g showed the appearance of spherical droplets on the surface at the highest temperature (110°C) for AlCl$_3$ residues. The presence of this spherical droplet can be explained due to the derivation of dehydrated carbohydrates and resulting in the formation of lignin-like materials (Shen et al., 2016). From Figure 2j, it is noticed that the separation of fibres bundles into individual fibres had taken place in Cr(NO$_3$)$_3$ residue. The formation of these individual fibres can be explained by the mechanism of the dissociation of Cr$^{3+}$ ions into a coordination complex structure with water molecules (H$_2$O) at the initial hydrolysis stage. This finding also proves the successive hydrolysis treatment initiated by the Cr(NO$_3$)$_3$ in the dissolution of the less-ordered defective crystalline regions (Chen et al., 2017).

### Determination of Chemical Structural Using FT-IR

Basically, the structural properties of lignin are affected by the raw material origin, the environmental conditions, and the method to extract the lignin itself. Figure 3 presented the FT-IR spectra that were used to investigate the functional group of the acetosolv lignin at various temperatures with different catalysts. In general, the spectra showed that there are no significant differences in terms of functional groups, and the spectra can be explained by dividing into two regions; the backbone region and the lignin-carbohydrates complexes regions.
In the backbone region, the functional groups related to lignin aromatic ring skeleton usually occur at the band around 1600 and 1500 cm\(^{-1}\) (Watkins et al., 2015). In this study, these bands were observed at 1594 cm\(^{-1}\) and 1513 cm\(^{-1}\) by the presence of C=C stretching of the aromatic ring skeleton, 1463 cm\(^{-1}\) for the C-H deformations, and aromatic skeletal vibrations coupled with C-H in-plane deformation at 1425 cm\(^{-1}\). As the lignin is not 100% pure, the presence of the lignin-carbohydrate complexes can be seen by the signals observed at 1714, 1269, 1165 and 1125 cm\(^{-1}\) which represent the existence of C=O stretching that is generally attributed to lignin-carbohydrate complexes (LCC) (Avelino et al., 2018).

In general, there is no significant damage occurring on the lignin during the acetosolv process since the basic aromatic lignin is present as in Figure 3. The presence of syringyl unit can be seen at band 1329 and 1125 cm\(^{-1}\), while at band 1513 and 1269 cm\(^{-1}\) showed the existence of guaiacyl units in the lignin and the band at 851 cm\(^{-1}\) was assigned to C-H out-of-plane in positions 2, 5 and 6 of guaiacyl units.

\(^{1}\)HNMR Analysis

Figure 4 presents the \(^{1}\)HNMR spectra of MWA acetosolv lignin with the presence of a different acid catalyst at various temperatures. The sharp peak shown at the range of 2.33-2.51 ppm is the solvent used; DMSO-d6 to solubilise lignin for the sample preparation phase. The presence of aliphatic moiety is shown at the signals between 0.8 and 1.5 ppm (Li et al., 2018). The methoxyl proton can be observed by the presence of a signal between 3.1 and 4.0 ppm. The complex signals at 3.0-4.5 also confirmed the presence of free polysaccharide moieties in the lignin (Abdelkafi et al., 2011). At 3.20 ppm, it can be seen that the signal of -CH\(_2\) linkages in the hydroxymethyl chain of the lignin was strong in all lignin except for HL100 and HL110. The possible explanation for this occurrence is due to the catalyst efficiency used at high temperature. Above 100°C, the hydrolysis reaction which occurred with the presence of H\(_2\)SO\(_4\) are capable of breaking the lignin cellulose complex (LCC) bond effectively without leaving the CH\(_2\)

![Figure 2. Scanning electron microscopy (SEM) image of a) native empty fruit bunches (EFB) and residues after microwave-assisted (MWA) acetosolv in the presence of b) at 90°C, c) H\(_2\)SO\(_4\) at 100°C, d) H\(_2\)SO\(_4\) at 110°C, e) AlCl\(_3\) at 90°C, f) AlCl\(_3\) at 100°C, g) AlCl\(_3\) at 110°C, h) Cr(NO\(_3\))\(_3\) at 90°C, i) Cr(NO\(_3\))\(_3\) at 100°C and j) Cr(NO\(_3\))\(_3\) at 110°C.](image-url)
Figure 3. Fourier transform infrared (FT-IR) spectra for microwave-assisted (MWA) acetosolv lignin in the presence of H$_2$SO$_4$ at 90°C (HL90), 100°C (HL100) and 110°C (HL110) and AlCl$_3$ at 90°C (AIL90), 100°C (AIL100) and 110°C (AIL110).

Figure 4. Proton nuclear magnetic resonance (¹H NMR) of microwave-assisted (MWA) acetosolv lignins.
linkage on the lignin structure. The $\beta$-O-4 structures in the lignin are shown between 5.9-6.6 ppm and the active proton at C5 position was also observed at signal around 6.96 ppm (Li et al., 2018; Hussin et al., 2013; Rashid et al., 2018). The presence of signals between 6.0 and 8.9 ppm indicates the presence of aromatic protons in the lignin’s unit (Rashid et al., 2018).

Thermal Decomposition of Acetosolv Lignin

The decomposition of lignin in this work was investigated using TGA under nitrogen flow, and the percentage of lignin weight loss in relation to temperature was revealed by the TGA curves, as shown in Figure 5. From this result, it is shown that the decomposition stages of lignin can be divided into three stages from 30°C-800°C. The first stage started below 100°C, where the evaporation of water, carbon dioxide, and carbon monoxide occurred. The second decomposition stage referred to the remaining lignin-carbohydrate complex (LCC) and hemicellulose at the range of 200°C-350°C (Hashim et al., 2016; Watkin et al., 2015). The final stage occurred at a temperature above 400°C due to the cleavage of the monomeric unit bond lead to the degradation of volatile products such as phenolic and alcohol derived from lignin. Therefore, in general, the wide range of the lignin decomposition is a result of the various branching of the lignin molecular structure. In terms of catalyst effect on the thermal stability of the lignin, the TGA curve proved the ability of the catalyst in removing the bonding in LCC as thermal stability is directly proportional to the purity of the lignin. Therefore, in this study, it is observed that the thermal stability for all lignin has no significant difference as the purity of the lignin in all parameter is quite similar.

CONCLUSION

High purity lignin was successfully obtained from oil palm EFB via MWA acetosolv process with a high yield of crude lignin. It is shown that the yield of lignin obtained via utilisation of Bronsted acid (76.98%) is slightly higher compared to utilisation of Lewis acid (71.57%) and it is noted that chromium (III) nitrate is not suitable for extraction of lignin but has a high potential for production of cellulose. The extraction process with different acid catalysts produced lignin with similar structural and thermal properties. Moreover, the extraction of lignin can be done using a simple and time-saving method, as presented by the MWA acetosolv process.

ACKNOWLEDGEMENT

The authors gratefully acknowledge and thank Universiti Malaysia Pahang for financial support via internal grant RDU190330. The authors would also like to acknowledge the Postgraduate Research Grant Scheme (PGRS1903195) and the Faculty of Industrial Sciences and Technology for the support given via its Master Research Scheme (MRS) in this work.

Figure 5. Thermogravimetric analysis (TGA) curves of lignins gained for different acid catalyst and at different temperatures.
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