# 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 ($H_2SO_4$), aluminium choride ($AlCl_3$), 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 $H_2SO_4$ under 110°C for 30 min. Meanwhile, $AlCl_3$ performed almost similar to $H_2SO_4$, 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.*

## 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).

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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 5.90 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 synapyl 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 (Fatriasari *et al.*, 2017; Kappe, 2004; Priecel 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 $H_2SO_4$ and HCl. However, the concentrated $H_2SO_4$ 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 [$AlCl_3$ and $Cr(NO_3)_3$] and compared with commonly used Bronsted acids ($H_2SO_4$). 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 ($H_2SO_4$, 95%-98%, R&M Chemicals), aluminium chloride ($AlCl_3$, 98%, Sigma-Aldrich), chromium nitrate $Cr(NO_3)_3$, 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; $H_2SO_4$, $AlCl_3$ and $Cr(NO_3)_3$. 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):

$$ń = \frac{mMWAL}{mLig}$$

Equation (1)

where ń 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 [$H_2SO_4$, $AlCl_3$ and $Cr(NO_3)_3$], as shown in *Figure 1*. In acetosolv technique, acetic acid ($CH_3COOH$) was used to produce $H_3O^+$ ions, which are responsible for the protonation of ether groups present in lignin; hence, affecting the yield of lignin. However, the ability of these $CH_3COOH$ to produce the $H_3O^+$ ions is low, and the presence of catalysts is vital for improving this behaviour. From *Figure 1*, the employment of $Cr(NO_3)_3$ was not able to extract any lignin. Meanwhile, $AlCl_3$ gave quite the same lignin yield as $H_2SO_4$ 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), $AlCl_3$ 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 $Cr(NO_3)_3$, 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 $H_2SO_4$. As for $AlCl_3$, 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
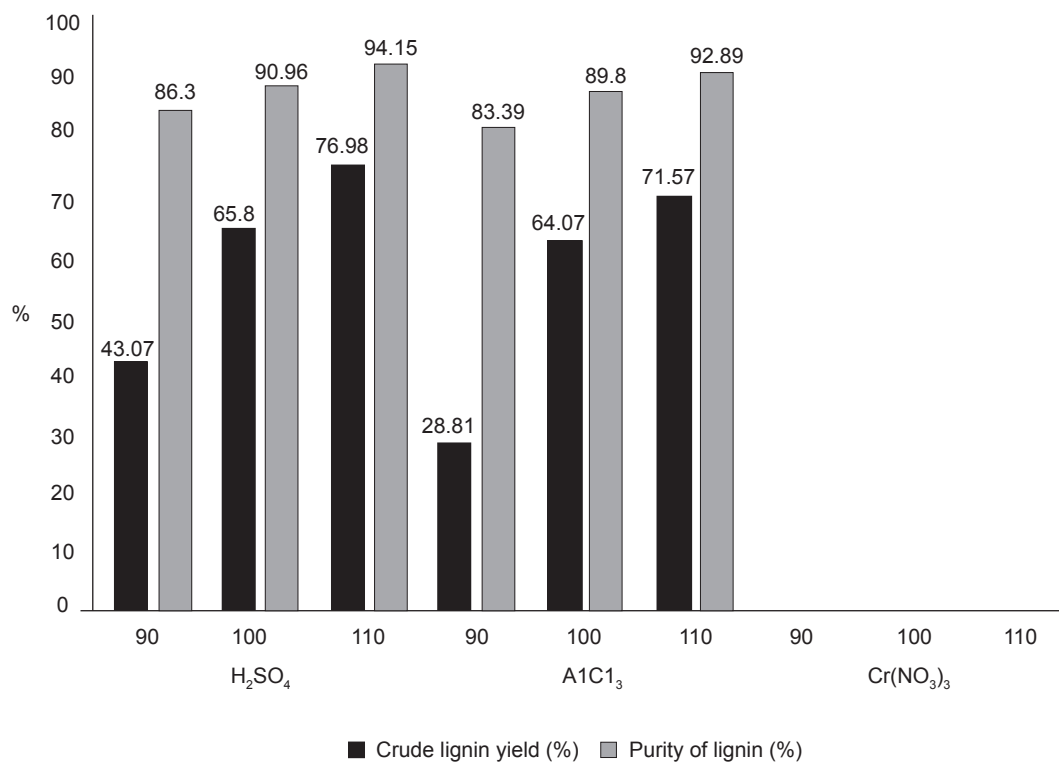
Figure 1. The percentage of crude lignin and purity of lignin by sulphuric acid ($H_2SO_4$), aluminium chloride ($AlCl_3$) and chromium (III) nitrate [$Cr(NO_3)_3$].

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 $H_2SO_4$ 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 $H_2SO_4$, *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 ($H_2O$) 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.

**¹HNMR Analysis**

*Figure 4* presents the ¹HNMR 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$_2$
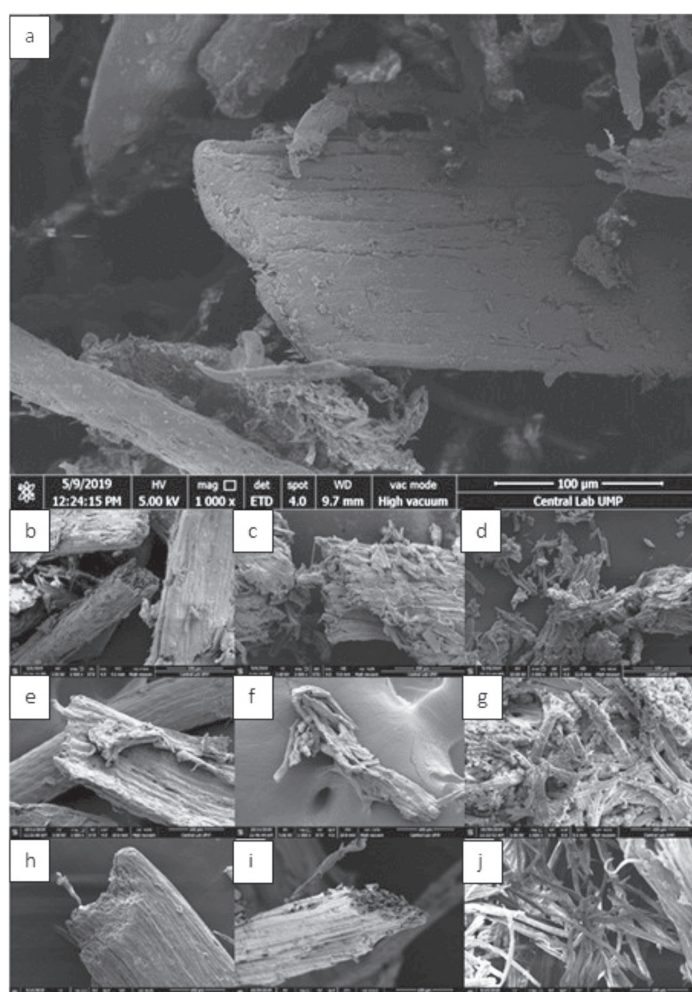


*Figure 2. Scanning electron microscopy (SEM) image of a) native empty fruit bunches (EFB) and residues after microwave-assisted (MWA) acetosolv in the presence of b) at 90°C, c) H₂SO₄ at 100°C, d) H₂SO₄ at 110°C, e) AlCl₃ at 90°C, f) AlCl₃ at 100°C, g) AlCl₃ at 110°C, h) Cr(NO₃)₃ at 90°C, i) Cr(NO₃)₃ at 100°C and j) Cr(NO₃)₃ at 110°C.*
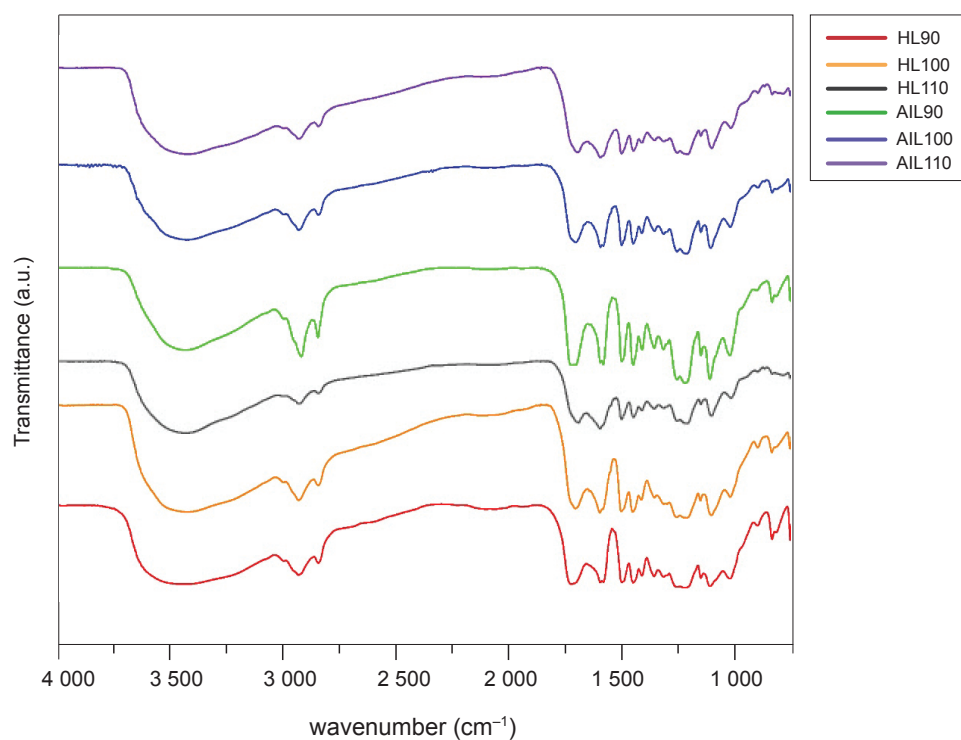
*Figure 3. Fourier transform infrared (FT-IR) spectra for microwave-assisted (MWA) acetosolv lignin in the presence of $H_2SO_4$ at 90°C (HL90), 100°C (HL100) and 110°C (HL110) and $AlCl_3$ at 90°C (AIL90), 100°C (AIL100) and 110°C (AIL110).*
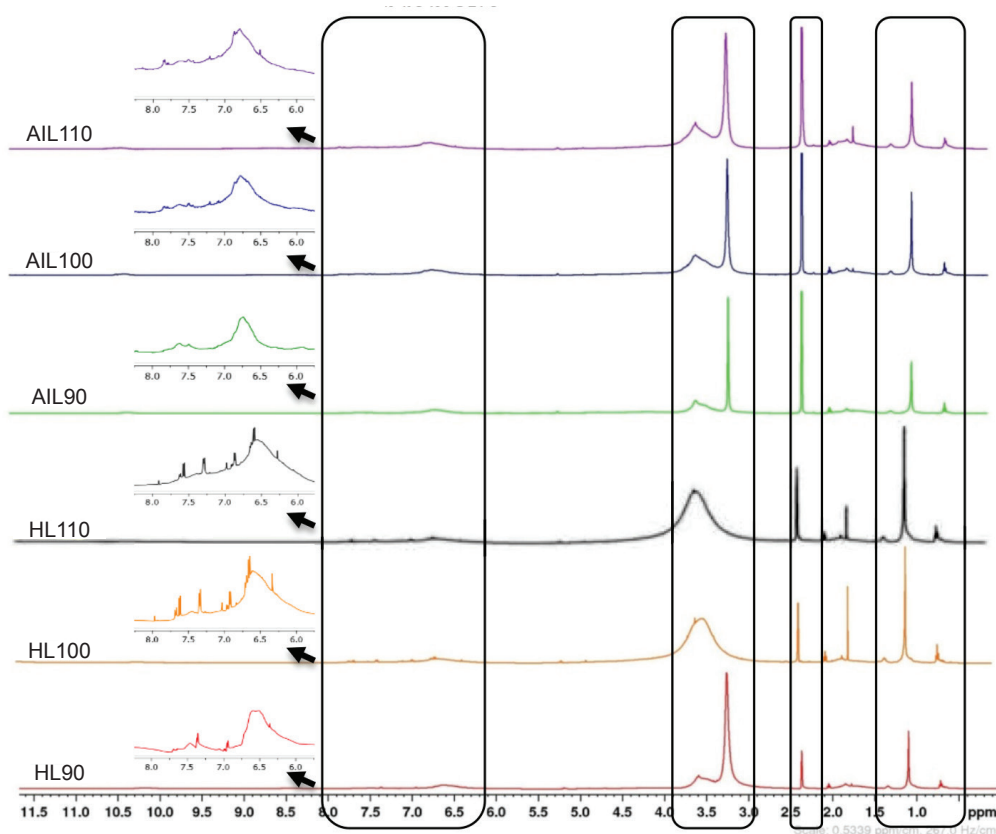


*Figure 4. Proton nuclear magnetic resonance ($^1$HNMR) of microwave-assisted (MWA) acetosolv lignins.*

linkage on the lignin structure. The β-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.
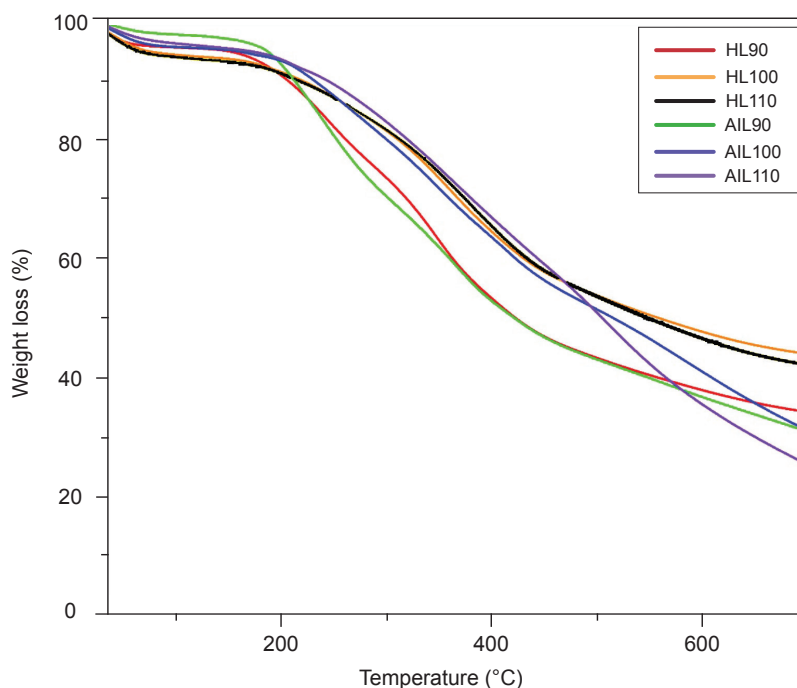
### ACKNOWLEDGEMENT

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

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