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REVIEW ARTICLE

A review on cellulose nanocrystals production and characterization methods from *Elaeis guineensis* empty fruit bunches

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Abstract Cellulose nanocrystals with various functionalities have received significant interest in recent years due to their wide applications. *Elaeis guineensis* empty fruit bunches (EFB) have been explored by researchers as one of the potential sources for cellulose nanocrystals extraction in recent years. However, cellulose nanocrystals extraction methods using EFB as raw materials are yet to be evaluated based on technical, economic and environmental aspects. Thus, this study aims to assess the effect of EFB pretreatment methods, cellulose nanocrystals isolation methods, with or without any post-treatment, towards the final properties of cellulose nanocrystals. Characterization methods suitable for evaluating the properties of cellulose nanocrystals extracted from EFB are suggested and supported with data from other similar studies. In brief, sulphuric acid hydrolysis exhibits a more significant advantage in cellulose nanocrystals conversion yield and stable suspension than other treatments when empty fruit bunch fibres are used as the cellulose source. By evaluating the benefits or limitations of extraction and characterization methods, future studies on the cellulose nanocrystals extraction from EFB could be further enhanced to prepare a more efficient cellulose nanocrystals extraction from EFB at a commercial scale.

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Contents

1. Introduction

Cellulose is a linear chain of anhydroglucose monomer units connected through 1–4 β-linkages, having amorphous and crystalline regions. Different sources of cellulose will yield distinct structures, properties and sizes of cellulose. Cellulose nanocrystals production could be varied depending on the sources from which it is extracted, which provides researchers with a broad range of choices to study, such as types of cellulose sources, reaction parameters and processing methods (Razali et al., 2017).

Plants are the primary potential sources of cellulose as plants are relatively cheap and abundant. Intrinsic structural variation in sources of the lignocellulosic materials and the isolation methods used can affect the size, morphology, and crystallinity of the cellulose nanocrystals extracted. Chemical compositions of nanofibres from various non-woody lignocellulosic sources are listed in Table 1.

Cellulose nanocrystals could have diameters up to 20 nm and lengths up to a few hundred nanometers. Potential applications of cellulose nanocrystals, including reinforcement of nanocomposite (Miao and Hamad, 2019), drug carrier (Wijaya et al., 2017), immobilization of lipase for the lipolysis of triglycerides (Restiawaty et al., 2021), catalyst support (Eisa et al., 2018), cement plasticizer (Montes et al., 2020), paint (Dogan-Guner et al., 2021), coating (Bai et al., 2019), nanostructured adsorbent (Mahfoudhi and Boufi, 2017) and cosmetic (Awan et al., 2018).

Several choices of sustainable raw materials are suitable to be used to extract cellulose nanocrystals. In this study, empty fruit bunches (EFB) will be evaluated as a viable and sustainable source for cellulose nanocrystals extraction due to the production of a large amount of EFB from the oil extraction activities, which are having quite limited and low-value applications at the moment (Ng et al., 2020).

Cellulose nanocrystals produced from empty fruit bunches were previously modified with tannic acid and decylamine. The binding efficiency of cellulose nanocrystals towards curcumin was improved from around 10 % to 95–99% (Foo et al., 2019). Other applications of cellulose nanocrystals derived from empty fruit bunches including food packaging thin film composite (Lani et al., 2014) and super adsorbent for water remediation (Septevani et al., 2020). The improvement in binding efficiency shows the economic potential of cellulose nanocrystals in the pharmaceutical industry in the future.

Table 1 Chemical composition of nanofibres from various non-woody lignocellulosic sources.

Materials	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Extractive (%)	References
Kenaf (stem)	63.5 ± 0.5	17.6 ± 1.4	12.7 ± 1.5	4 ± 1	(Jonoobi et al., 2015)
Wheat straw	43.2 ± 0.15	34.1 ± 1.2	22.0 ± 0.1	–	(Alemdar and Sain, 2008)
Soy hulls	56.4 ± 0.92	12.5 ± 0.72	18.0 ± 2.5	–	(Alemdar and Sain, 2008)
Hemp	75.56	10.66	6.61	–	(Wang et al., 2007)
Flax	73.0 ± 7.0	13.0 ± 2.0	5.0 ± 1.0	–	(Bhatnagar and Sain, 2005)
Empty fruit bunch	40.0 ± 2.0	23.0 ± 2.0	21.0 ± 1.0	–	(Jonoobi et al., 2015)
Pineapple leaf	81.3 ± 2.4	12.3 ± 1.3	3.5 ± 0.6	–	(Cherian et al., 2010)
Bagasse	70.6	26.8	–	Ash 16.8 %	(Hassan et al., 2012)
Rice straw	61.9	22.5	–	Ash 16.8 %	(Hassan et al., 2012)
Bamboo	41.8 ± 1.9	22.9 ± 4.3	20.91 ± 2.4	23.2 ± 2.7	(Xie et al., 2016)
Jute (stem)	68.3	15.4	10.7	–	(Jonoobi et al., 2015)
Sugar beet pulp	22	32	2	–	(Jonoobi et al., 2015)
White cotton	97.7 ± 2.2	0.5 ± 0.4	0.4 ± 0.1	–	(Jonoobi et al., 2015)
Banana (pseudo stem)	69.9	19.6	5.7	–	(Abraham et al., 2011)

To isolate cellulose nanocrystals from the biomass, pretreatment and hydrolysis steps must be included, whether in a combined stage or separate stages. This review aims to evaluate several approaches that are currently available and feasible for cellulose nanocrystals isolation. Comparisons are made between a few commonly used methods in isolating cellulose nanocrystals from empty fruit bunches. Conversion yield, ease of processing, availability of raw materials required and characteristics of cellulose nanocrystals produced will be predominantly emphasised. Furthermore, suitable characterisation techniques to analyse the cellulose nanocrystals yielded from a particular method are discussed. Such characterisation results are essential to identify and evaluate cellulose nanocrystals based on their structural properties, morphologies, functional groups, crystallinity, shape and size distribution.

Table 2 Chemical composition of empty fruit bunch (Chang, 2014).

Properties	Values
Moisture (%)	2.40–14.28
Proximate analysis based on a dry basis (wt%)	
Volatile matter	70.03–83.86
Fixed carbon	8.97–18.30
Ash	1.30–13.65
Ultimate analysis based on the dry and ash-free basis (wt%)	
Carbon (C)	43.80–54.76
Hydrogen (H)	4.37–7.42
Oxygen (O)	38.29–47.76
Nitrogen (N)	0.25–1.21
Sulphur (S)	0.035–1.10
Chemical composition based on a dry basis (wt%)	
Cellulose	23.7–65.0
Hemicellulose	20.58–33.52
Lignin	14.1–30.45
Extractive	3.21–3.70

2. *Elaeis guineensis* empty fruit bunch (EFB)

Empty fruit bunches are solid residues estimated to account for one-fifth of the fresh fruit weight of *Elaeis guineensis* (Chang, 2014). Empty fruit bunch is approximately 3.5 kg in mass, has a thickness up to 130 mm, 300 mm in width and 300 mm in length (Chang, 2014). Due to the steam sterilisation process in oil processing and the natural way of maturation, empty fruit bunches usually encompass a considerable amount of moisture (Loh, 2017). Table 2 summarises some chemical compositions in dried empty fruit bunches. Table 3 discloses the composition of various types of celluloses in untreated and pre-treated empty fruit bunches from recent work (Ying et al., 2014). Table 3 shows that α-cellulose is dominant in empty fruit bunches (around 56% without any treatment), responsible for higher cellulose yield in cellulose nanocrystals extraction (Wanrosli et al., 2004). The α-cellulose content in empty fruit bunches is comparable with other non-woody lignocellulosic sources. Besides, empty fruit bunches are widely available in the palm oil industries with no significant economic value (Chiew and Shimada, 2013). Thus, the empty fruit bunch is a viable source for manufacturing cellulose nanocrystals and their derivatives.

The cellulose composition of *Elaeis guineensis* empty fruit bunches is highly affected by the method employed during

Table 3 Chemical composition of different types of cellulose in untreated and pretreated empty fruit bunch fibres (Ying et al., 2014).

	Untreated EFB fibres	Water pre-treated EFB fibres	Acid pre-treated EFB fibres	Alkaline pre-treated EFB fibres
Solid yield (wt%)	100	51.1	53.0	53.8
Holocellulose (wt%)	88.1 ± 1.0	67.8 ± 2.4	69.7 ± 0.3	87.9 ± 1.0
α-cellulose (wt%)	56.0 ± 0.5	72.6 ± 0.4	69.3 ± 0.6	57.1 ± 0.1
β-cellulose (wt%)	<0.1 ± 0.6	20.4 ± 0.3	25.7 ± 1.0	3.9 ± 0.2
γ-cellulose (wt%)	44.0 ± 0.2	7.0 ± 0.1	5.0 ± 0.4	39.0 ± 1.0

the pulping process, affecting the efficiency of the cellulose nanocrystals isolation process. Other research works have reported the application of soda pulping, which was followed by a chlorine-free bleaching sequence of oxygen, ozone and hydrogen peroxide (Leh et al., 2008), to produce *Elaeis guineensis* empty fruit bunch pulp with as high as 97% of α-cellulose by mass (Rosli et al., 2003). Thus, evaluating the cellulose nanocrystals isolation process should complement the discussion on some of the pretreatment processes conducted on the *Elaeis guineensis* empty fruit bunches.

3. Cellulose nanocrystal production methods

Cellulose nanocrystals isolation from lignocellulosic arrays of empty fruit bunches necessitates a series of processes. This series of processes can generally be divided into two stages: the first stage is the pretreatment and the second stage is the cellulose nanocrystals isolation (Choong et al., 2018). Chemical pretreatment is to eliminate extractives, lignin and hemicellulose content from the empty fruit bunch fibres. Various types of extractives exist in empty fruit bunch fibres, such as lignans, flavonoids, waxes and complex phenolics (Taflick et al., 2017). However, after the chemical pretreatment step, pretreatment is only half-completed. The bleaching process using chlorine dioxide, sodium percarbonate, or hydrogen peroxide is necessary to obtain the desired degree of whiteness and remove the remaining extractives. The bleaching process using sodium hypochlorite is usually not encouraged due to the formation of dioxins, a toxic organic compound (Taflick et al., 2017).

Subsequently, cellulose nanocrystals can be extracted by hydrolysis under controlled conditions. The most commonly used hydrolysis agent is mineral acid. As the amorphous region subsides in the remaining cellulose is relatively weak, it is susceptible to acid attack and destruction, leaving only cellulose with substantial crystalline segments (El Achaby et al., 2018). At the acid hydrolysis stage, cellulose nanocrystals extracted are needle-shaped nanoparticles with high surface area, aspect ratio and crystallinity (Taflick et al., 2017). Homogenisation will typically be required in the next step to uniformly disperse the cellulose nanocrystals that are contained in the suspension as tiny particles (which are having a high tendency to agglomerate). Finally, the cellulose nanocrystals suspension will be freeze-dried to obtain a bright-white solid sample.

3.1. Pretreatment of celluloses

The pretreatment process is suggested as the first stage of the cellulose nanocrystals extraction from various biomass sources. The pretreatment functions effectively to dissociate the natural recalcitrance besides altering the macroscopic and microscopic size, chemical composition and structure of the fibres (Harmsen et al., 2010). Pretreatment operation can significantly improve the downstream process efficiency for cellulose extraction. In this case, cellulose, hemicellulose and lignin are contained in the bulk empty fruit bunch fibres. Thus, the primary pretreatment is to segregate the desired cellulose from lignin and hemicellulose, which is aimed to improve the accessibility of the cellulose for further treatment.

Generally, pretreatment can be classified into few categories, which are physical (such as milling, ultra-sonication, and mechanical extrusion), biological, chemical and multiple or combined pretreatments such as ammonia fibre freeze explosion (AFEX), CO_2 explosion pretreatment, sulphite pretreatment and steam explosion to overcome the recalcitrance of lignocellulose (Harmsen et al., 2010). Table 4 shows the comparisons between the pretreatment methods that have been employed by other researchers in treating the biomass from various sources.

Theoretically, most of the pretreatment methods can be used, with or without modification, to treat the biomass from different sources. However, only some of the pretreatment methods have been explored in treating the empty fruit bunch fibres. Some of the standard pretreatment methods that have been employed in previous studies in treating the empty fruit bunches will be discussed in the following sections. The discussion will be supported with some of the findings from the respective works for a better evaluation.

3.1.1. Alkaline pretreatment of empty fruit bunches

Chemical pretreatment can be conducted by utilizing alkaline or acidic agent, or a combination of them, at moderate conditions. Alkali pretreatment method is a more prominent method as it appears to be a simple yet effective method for converting lignocellulosic biomass (Kim et al., 2016). The liquid agent of pretreatment, NaOH, should be transported uniformly into the pores of lignocellulose. The transportation mechanisms of the pretreatment agent can be classified into two. First, it involves liquid agent penetration into the capillaries. Second, it involves the diffusion of the liquid agent via cell walls, pit membranes and interfaces (Harmsen et al., 2010). Penetration refers to the flow of liquid agents into the air-filled pores of the lignocellulose, which is assisted by hydrostatic pressure.

In contrast, diffusion can be defined as the diffusion of soluble substances and ions via the layer of water located in the cell wall, pit membrane structure, and interfaces affected by variation in concentration gradient (Sun and Cheng, 2002). In comparison, diffusion is a slow process. Initially, the sodium hydroxide solution must penetrate lignocelluloses. At this stage, penetration is the primary mechanism. New channels or pores will be created along with the initial reactions, such as lignin removal on the surface of lignocelluloses. New channels or pores created will further enhance the penetration of sodium hydroxide solution into the lignocellulose. Besides, the penetration of sodium hydroxide solution into the matrices of lignocellulose during the pretreatment can be amplified by the swelling of lignocellulose (Xu et al., 2016). After the complete penetration of sodium hydroxide solution into the pores of lignocellulose biomass, the diffusion process will occur. In the diffusion process, molecular diffusion replaces the reactants after they are consumed in chemical reactions with lignocelluloses. The transfer of sodium hydroxide solution and dissolved substances from lignocelluloses will occur via diffusion. Therefore, the degradation reactions of lignocellulose can be considered as a diffusion-controlled mechanism.

The chemical reactions between the alkaline solution and lignocelluloses mainly involve cellulose, hemicellulose and lignin. Reactions with lignin lead to the dissolution and degradation of lignin. Alkali pretreatment can efficiently break the ester bonds by cross-linking xylan and lignin via solvation and saponification (Liu et al., 2018). Typical lignocellulose degradation of lignin is the fracture of the phenol-type α-aryl

Table 4 Different pretreatment method for cellulose nanocrystals extraction.

Pretreatment method	Method	Advantage	Disadvantage
Biological pretreatment/ enzymatic de-lignification (Vasco-Correa et al., 2016)	An undesired lignocellulosic component such as lignin can be degraded by a group of oxidoreductases. This system includes peroxidases and laccases that have high redox potential to oxidise the structural polymer of lignin directly or by utilising low-molecular-weight organic compounds to diffuse into the pores of the plant cell wall and attack the lignin structure	Environmentally friendly approach. Low-cost requirement. No toxic chemicals required. The less energy-intensive process can be carried out under mild reaction conditions	Slow process. Some components such as (hemicelluloses and cellulose) of biomass might be degraded either by foreign microbes or by the same microorganisms
Chemical pretreatment (Foo et al., 2019; Singh et al., 2015; Zianor Azrina et al., 2017)	Utilises mild alkaline or mild acid agent to remove lignin and a part of the hemicellulose and decrease the polymerization degree of the plant cell in the biomass.	Remove acetyl and lignin at moderate pressure and temperature. Increasing the cellulose crystallinity index (CI) value.	Less cost-effective Inappropriate for environmentally benign bioconversion. High chemical waste generation and disposal
Physical pretreatment:			
Hydrothermal pretreatment (Pangsang et al., 2019)	It is performed at temperatures from 150 to 200 °C at a high pressure of around 30 bars and reaction times about 5 to 25 min to eliminate most hemicellulose and convert partial lignin fractions into the liquid phase.	Environmental friendly, A cost-effective process as no recovery of solvent is required	It is a high energy consumption process due to the high pressure and temperature condition
Ionic liquid pretreatment (Elgharbawy et al., 2016)	Pretreatment of biomass with [bmimHSO_4](1-butyl-3-methylimidazolium hydrogen sulphate) is performed in moderate conditions at around 80 °C for 1 h	High solvating power, Biomass extracted with excellent chemical, and thermal stability.	The solvent used is relatively expensive
Sono-assisted (Ultrasonic) organosolv/ H_2O_2 pretreatment; (Ofori-Boateng and Lee, 2014)	It utilises ultrasound with organosolv/ liquid peroxide pretreatment to pre-treat biomass at lower temperatures and shorter time for cellulose recovery. It is normally mixed with 2% aqueous NaOH and 80% ethanol (1:3 v/v) in a 500 ml capacity Erlenmeyer flask and placed in the ultrasonic cleaning bath at 60C for 60 min.	Optimise the material and energy inputs Improve energy utilisation by reducing process time and operating temperature	Does not significantly improve the yield of cellulose.
Physico-chemical pretreatments (Steam explosion) [34]	Injecting high-pressure saturated steam in a reactor at temperatures typically between 160 and 260 °C (0.69e4.83 MPa) and kept for a short period from few seconds to minutes This pretreatment process ensures lignocellulosic structural component of biomass to break down by the action of shearing force, saturated steam heating and formation of organic acids during the process	Enhanced pretreatment effectiveness in reducing hemicellulose and lignin content.	It might induce excessive degradation of the cellulose, which can affect cellulose's chemical and physical properties and the release of inhibitors.

ethers, the cleavage of the phenol-type β-aryl ethers and the fracture of the non-phenol-type β-aryl ethers. In contrast, the decomposition of amorphous cellulose and hemicellulose are represented by cellulose peeling reaction, alkaline hydrolysis of cellulose and the sulphide fracture of the phenol-type β-aryl ethers (Xu et al., 2016).

Alkaline pretreatment of empty fruit bunch pulp has been conducted using 4% of sodium hydroxide at 80 °C for 2 h (Zianor Azrina et al., 2017). According to their study, lignin content from the raw empty fruit bunches were successfully reduced from 25.33% to 1.05% through a combination of hot water and alkaline treatment, which were mainly targeted to dissolve the lignin and hemicellulose from the empty fruit bunches before the cellulose nanocrystals isolation stage.

3.1.2. Combination of sodium chlorite and alkaline pretreatment of empty fruit bunches

One of the recent works has utilized sodium chlorite solution made of an equal volume of 2 w/v% of $NaClO_2$ and acetate buffer, at a defined pH, to remove the lignin from the ground empty fruit bunches (Foo et al., 2019). The de-lignification process was conducted at a moderate temperature of 80 °C for a duration of 2 h. The alkaline pretreatment process has to be coupled with the treatment by 4 w/v% NaOH, at a mod-

erate temperature of 80 °C under a continuous stirring of 2 h, to degrade hemicellulose in empty fruit bunches. According to the work, the acidic chlorite solution has been successfully used to cleave the ether bond between the lignin and cellulose, evidenced by the disappearance of aromatic skeletal vibration in the lignin at the wavelengths 1,505 cm^{-1} and 1,592 cm^{-1} through Fourier-transform infrared spectroscopy analysis. Due to residual chemicals on the surfaces of fibres, the alkaline pretreatment method requires extensive cleaning using clean water before the pulp can be collected through the physical filtration method.

Such a moderate operating condition has dramatically benefited the application of chemical pretreatment in preparing the pulp for cellulose nanocrystals extraction. From the economic point of view, the alkaline pretreatment process will require lower equipment costing and energy consumption due to the lower temperature and pressure requirement when compared to the hydrothermal method (Rani et al., 2021). However, the chemical pretreatment process may require additional water washing steps to remove residual chemicals on the fibre surfaces (Wibowo et al., 2018). In the long term, the combination of sodium chlorite and alkaline pretreatment of empty fruit bunches remains an economical way of treating the pulp owing to the low requirement for operating temperature and pressure.

3.1.3. Combination of soda-anthraquinone and acidic pretreatment of empty fruit bunches

Another similar work has conducted pre-hydrolysis of empty fruit bunches using water, followed by soda-anthraquinone pulping (Rohaizu and Wanrosli, 2017). Researchers have used hydrochloric acid of 2.5 M in hydrolysing the bleached pulp to produce microcrystalline cellulose before the cellulose nanocrystals extraction using sono-assisted 2,2,6,6-tetramethyl piperidine-1-oxy-mediated oxidation, followed by sonication treatment at a low ultrasonic frequency of 40 kHz. The yield of cellulose nanocrystals was increased from 67 to 93% in the presence of the sono-assisted oxidation process, which could be reasoned with the production of acoustic cavitation that enhanced the chemical reaction rates. It was postulated that the mechanical forces produced during the sono-assisted treatment could be used to break the inter-fibrillar hydrogen bonds between the cellulose molecules (around 19 to 21 kJ/mol), in comparison to the O-H covalent bond (492 kJ/mol), in releasing the cellulose crystallites.

3.1.4. Deep eutectic solvent pretreatment of empty fruit bunches

Similarly, chemical pretreatment of empty fruit bunches has been explored using deep eutectic solvent (Gan et al., 2020), which could be more environmentally friendly compared to other chemical pretreatments. During the hydrolysis of cellulosic materials, deep eutectic solvent forms hydrogen bonds with hemicellulose and lignin through proton exchange, which can improve the solvation ability of the solvent. Deep eutectic solvent has several advantages compared to other chemicals during the hydrolysis of cellulosic materials, such as the ease of preparing the solvent at moderate pressure and temperature, low cost, and environmental friendly (Vanda et al., 2018).

Unlike the pretreatment method using acid or alkaline solution, the alkaline deep eutectic solvent was prepared by mixing potassium carbonate and glycerol at a mole ratio of 1:7 at 80 °C and stirred for 2 h to obtain a homogeneous mixture (Gan et al., 2020). Empty fruit bunches were then added into the deep eutectic solvent at 80 °C for 2 h prior to the bleaching process using equal parts of acetate buffer (prepared by dissolving 40 g of NaOH into a mixture of 75 ml glacial acetic acid and 925 ml distilled water), distilled water, and 1.7 wt% chlorite solution. The whole process of deep eutectic solvent treatment and leaching process was repeated three times to remove impurities. The hemicellulose and lignin content in raw empty fruit bunch fibres (31.9% and 25.9%, respectively) have been successfully reduced as observed in the unbleached deep eutectic solvent-treated fibres (16.5% and 9.4%, respectively) and bleached deep eutectic solvent-treated fibres (9.4% and 1%, respectively). The bleached deep eutectic solvent-treated fibres were then hydrolysed using sulphuric acid to isolate the cellulose nanocrystals from the empty fruit bunches.

3.1.5. Hydrothermal pretreatment of empty fruit bunches

Hydrothermal pretreatment is the refinement of lignocellulosic biomass with the aids of hot water under high pressure, such as a steam explosion. Hydrothermal water and hot compressed water are equivalent terms defined as water under elevated pressure and temperature. Under elevated pressure and temperature, hydrogen bonds in water are weakened and dissociate to form aggregates of concentrated molecules. The formation of concentrated molecules can induce changes in physicochemical characteristics of water and subsequently lead to the decomposition of lignocellulosic biomass structures, causing cellulose to be separated.

Hydrothermal pretreatment is working based on short-term heating in a hot, high-pressure saturated steam at a temperature of 180 to 210 °C for a few minutes (Kargarzadeh et al., 2017). It induces partial hydrolysis and expansion of the fibre cell walls. The hydrothermal pretreatment step, in the presence of compressed water, is completed with a sudden decompression. Decompression happens when the flash evaporation of water induces a great force and lead to the rupture of materials (Gao et al., 2016). Decompression effect results in a considerable breakdown of the plant material structure. In other words, the breaking down of the plant material structure will lead to the degradation of lignin, fibrillation of fibres and hydrolysis of hemicellulose. The dominant factors that can affect the reaction are the temperature of the medium and reaction time. The addition of certain chemicals, for instance, sodium hydroxide or sulphuric acid, can further promote hydrothermal efficiency (Kargarzadeh et al., 2017).

The purpose of hydrothermal pretreatment is to alter the structure of lignocellulosic biomass, especially on lignin and hemicellulose. Unlike cellulose, hemicellulose is heterogeneous, branched and amorphous polysaccharides, which is less stable than cellulose (Yu et al., 2013). During the hydrothermal pretreatment, the organic acid and acetyl group released from the hemicellulose side chain will catalyse the dissociation of long hemicellulose chains to become a shorter chain of oligomers (Patel et al., 2016). The disintegration of bonding between hemicellulose and lignin leads to the distortion of the hydrogen bond between the cellulose. Examples of well-known reactions for the degradation of hemicelluloses are the hydrolysis of hemicelluloses to sugars, followed by dehydration of hexoses and pentoses.

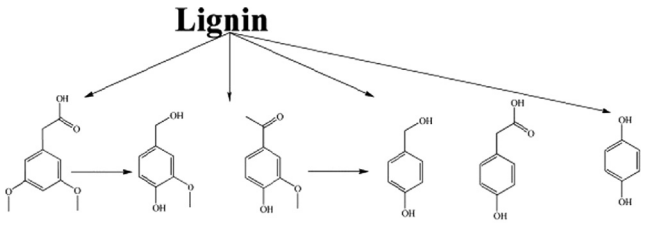

Fig. 1 Fragmentation of lignin structure during hydrothermal pretreatment. Adapted with permission from (Gao et al., 2016).

On the other hand, lignin appears as a complex amorphous structure (Gao et al., 2016). Simultaneously, the cellulose and hemicellulose are tightly connected to the lignin by covalent and hydrogen bonds. The depolymerization is signalled by cleavage of ester bonds and β-O-4 linkages during the hydrothermal pretreatment, whereas re-polymerization is represented by acid-catalysed condensation. Hydrothermal pretreatment can produce aromatic compounds with fewer side-chain (Gao et al., 2016). The fragmentation of lignin is shown in Fig. 1. However, it is virtually impossible to eliminate all the lignin during hydrothermal pretreatment because of the re-deposition of lignin on the biomass surface. Several works have evaluated the possibility of using hydrothermal pretreatment in treating the empty fruit bunches (Rani et al., 2021; Zulnazri et al., 2017). Researchers employed relatively low hydrothermal temperature at 110 to 120 °C in the presence of HCl in treating the empty fruit bunches (Zulnazri et al., 2017). Based on their observation, high hydrothermal temperature and long hydrothermal duration can reduce the final crystallinity of cellulose nanocrystals. The hydrothermal process has to be well controlled to prevent the hydrogen ion, from the acid solution, from reducing the quality of the cellulose nanocrystals.

3.1.6. H_2O_2 pretreatment of empty fruit bunches

Aqueous hydrogen peroxide has been used to delignify the pretreated empty fruit bunches. The Delignification step is often addressed as bleaching. Most of the lignin and hemicellulose will be solubilized, but the cellulose will remain in solid form. Another common suggestion to improve the selectivity of cellulose during pretreatment is to combine H_2O_2 pretreatment with ultrasound technology. Ultrasound provides physical augmentation via mass transfer, surface erosion and shear forces, as well as producing oxidizing radical chemical effects (Ofori-Boateng and Lee, 2014). Thus, it encourages the cleavage of linkages between the hemicellulose and lignin by degrading lignin compounds via hydroxyl attack of the phenolic ring (Ofori-Boateng and Lee, 2014).

3.1.7. Combination of alkaline and H_2O_2 pretreatment of empty fruit bunches

However, the production of microcrystalline cellulose before the isolation of cellulose nanocrystals as discussed above might increase the manufacturing cost, complexity, and time. Direct isolation of cellulose nanocrystals from *Elaeis guineensis* empty fruit bunch pulp could be preferable from the commercial perspective (Al-Dulaimi and Wanrosli, 2017).

Pretreatment has been conducted using water pre-hydrolysis and soda pulping of the *Elaeis guineensis* empty fruit bunch fibres before the totally chlorine-free bleaching sequence of oxygen (pulp consistency 10%, 100 psi, NaOH

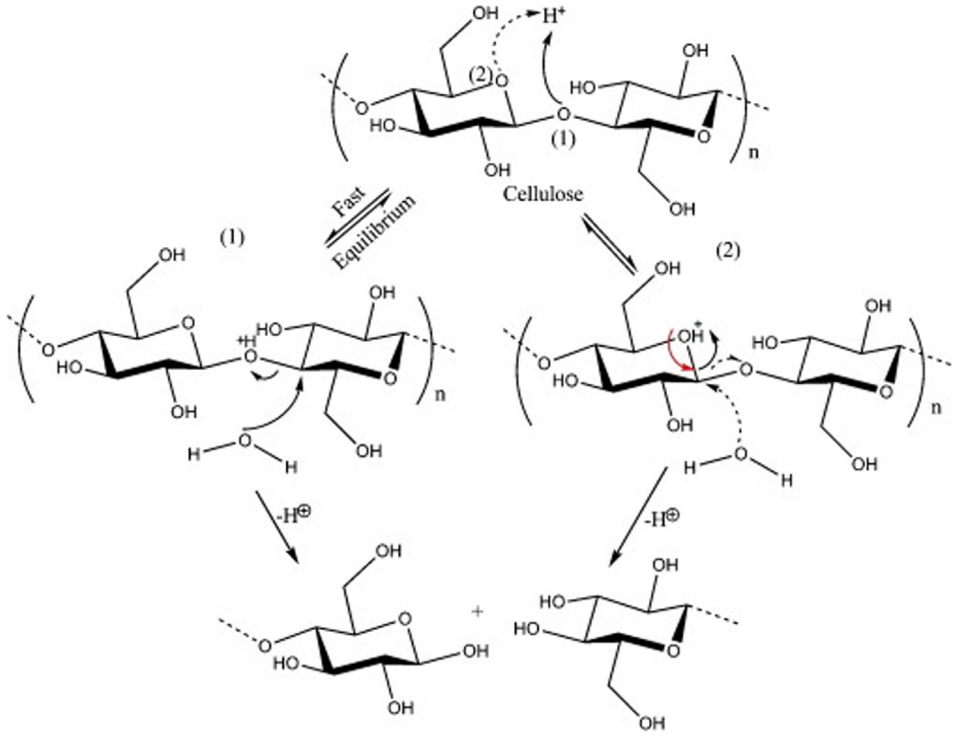

Fig. 2 Mechanism of cellulose chain acid hydrolysis. Adapted with permission from (Kargarzadeh et al., 2017).

2%, $MgSO_4$ 1%, 95 °C, 60 min), ozone (pulp consistency 20%, pH 1.5, 3 min), and peroxide (pulp consistency 15%, NaOH 2%, $MgSO_4$ 0.5%, H_2O_2 3%, 65 °C, 60 min) (Al-Dulaimi and Wanrosli, 2017). In general, totally chlorine-free bleaching method involves less harmful chemicals and mild operating conditions. It avoids the need for the formation of microcrystalline celluloses before the isolation of cellulose nanocrystals.

3.2. Cellulose nanocrystal extraction after pretreatment

Isolation of cellulose nanocrystals is the second stage in the production of cellulose nanocrystals from the fibre source. Isolation of cellulose nanocrystals usually involves acid hydrolysis at elevated temperatures, which is targeted to reduce polymerization by breaking down the accessible amorphous regions of the long glucose chains, liberating the crystalline materials from the fibre source (Qin et al., 2011). Other methods, including enzymatic hydrolysis and ionic liquid, can be used to isolate cellulose nanocrystals. Subsequently, the post-treatment of hydrolyzed celluloses, including sonication and purification, can be used to ensure the cellulose nanocrystals extracted are well-dispersed (Chieng et al., 2017).

In some of the research works, the effectiveness of chemical treatment could be enhanced by the presence of mechanical treatment during the isolation of cellulose nanocrystals from empty fruit bunches. For instance, cellulose nanocrystals with diameters from 5 to 40 nm and crystallinity values of 69 to 70% were successfully obtained from *Elaeis guineensis* empty fruit bunches through chemo-mechanical treatment (Jonoobi et al., 2011). However, mechanical or sonication treatment will not be considered one of the isolation methods in this study. Their roles are to assist the penetration of chemicals into the cellulose structures, which could further enhance the reactivity, thus the yield of cellulose nanocrystals (Pandi et al., 2021).

3.2.1. Sulphuric acid hydrolysis

Cellulose nanocrystals are commonly prepared by acid hydrolysis of a purified cellulose starting material such as cellulose microfibres (CMF). The acid is used to hydrolyse the amorphous region of the cellulose, in which the disordered regions of cellulose can be disintegrated by hydrolytic cleavage of the glycosidic bond. In contrast, the highly ordered cellulose fractions will remain unconverted as they are less susceptible to acid attacks (Cheng et al., 2017). Acid hydrolysis can produce a suspension of rod-like whiskers whose dimensions rely on cellulose origin and the pretreatment method (Dong et al., 2016). Typically, the length and diameter of cellulose nanocrystals are less than 1 μm and 100 nm, respectively, without agglomeration (Cheng et al., 2017).

Acid hydrolysis of purified cellulosic material is carried out using strong acids under controlled acid concentration, temperature and reaction time to produce a high yield of cellulose nanocrystals. When sulphuric acid is used as a hydrolysing agent, it reacts with the hydroxyl groups on the surface of nano-crystallites, which leads to the formation of sulphonic groups that are negatively charged (Kargarzadeh et al., 2017). The acid hydrolysis of amorphous regions of cellulose chains encompasses rapid protonation of glucosidic oxygen or cyclic oxygen. Subsequently, the addition of water will cause a slow splitting of the glucosidic bonds, as shown in Fig. 2 (Kargarzadeh et al., 2017). Sulphuric acid hydrolysis was previously conducted on *Elaeis guineensis* fibres, which produced cellulose nanofibers of 1 to 3.5 nm in width but 100 nm to 2 μm in length (Fahma et al., 2010). The crystallinity of the cellulose was around 51 to 59%, depending on the hydrolysis time.

Sulphuric acid hydrolysis can result in short-chain fragments while preserving the basic backbone structure. The hydrolysis of cellulose by sulphuric acid also involves partial esterification of the hydroxyl groups, as shown in Fig. 3. Esterification causes the attachment of negatively charged sulphate groups to the cellulose nanocrystals structure (Dong et al., 2016). Esterification induces the repulsion forces between cellulose layers that can prevent cellulose nanocrystals from forming aggregates. The attachment of negatively charged sulphate groups on the cellulose nanocrystals structure phenomenon is also known as anionic stabilisation (Cheng et al., 2017). Cellulose nanocrystals with high dispersion properties obtained through sulphuric acid hydrolysis can avoid surfactant and organic solvent employment in the subsequent handling process (Klemm et al., 2018).

Post-treatment of cellulose nanocrystals dispersion in a strong acid is commonly diluted with water and washed using successive centrifugations (Shaheen and Emam, 2018). The centrifugation speed could be as high as 10,000 rpm for 15 min (Foo et al., 2020), which aims to neutralise the suspension and discourage the formation of charges on the surface of cellulose nanocrystals to prevent aggregation. Agglomeration will enlarge the cellulose nanocrystals' size, thus reducing the dispersion and lowering the values as a composite reinforcing

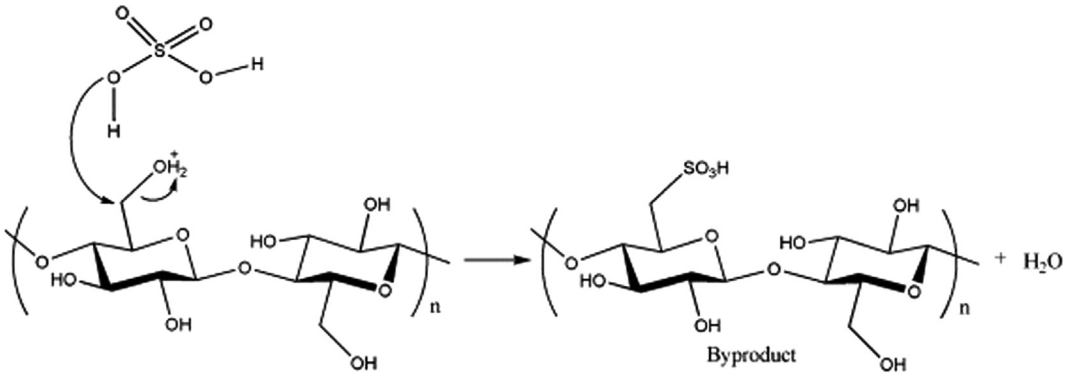

Fig. 3 Mechanism of cellulose nanocrystals esterification. Adapted with permission from (Kargarzadeh et al., 2017).

agent. Therefore, post-treatment is a critical step in acid hydrolysis.

Acid hydrolysis of freeze-dried fibres has previously been used to extract the cellulose nanocrystals from *Elaeis guineensis* empty fruit bunches using 58 wt% of H_2SO_4 at 45 °C for 45 min (Foo et al., 2019). Coldwater was employed to stop the acid hydrolysis of the fibres before centrifugation at 10,000 rpm for 15 min, which aimed to remove the residual acid in the cellulose nanocrystal samples (Foo et al., 2019). Dialysis, using a membrane with a molecular weight cut off around 12,000 to 14,000 Da, has been used to further purify the cellulose nanocrystal samples before dispersing the samples using sonication at 60% amplitude for 10 min. The cellulose nanocrystals obtained from the study was 13–30 nm width and 150–360 nm length.

A mild temperature at around 45 °C is typically employed for the acid hydrolysis of *Elaeis guineensis* empty fruit bunch fibres or pulp to control the reaction rate (Al-Dulaimi and Wanrosli, 2017). The reaction time between the acid and cellulose was suggested to be around 40 to 100 min because a high reaction duration can lead to reduced crystallinity (from 80.8% to 77.3%). In comparison, the width of the cellulose nanocrystals remained constant after the reaction duration is greater than 80 min (around 6.5 nm). In addition, sulphuric acid concentration and hydrolysis duration could produce cellulose nanocrystals with different characteristics, as previously reported. Insufficient hydrogen ions at low sulphuric acid (around 52%) may lead to an ineffective reaction with cellulose hydroxyls, leading to a low yield of cellulose nanocrystals. Conversely, a high concentration of sulphuric acid (around 62%) may lead to the complete dissolution of the cellulose, forming water-soluble oligomers. However, the yield of cellulose nanocrystals obtained under this mild condition was around 30 to 37%, depending on the duration of the acid hydrolysis.

Isolation of cellulose nanocrystals from empty fruit bunches also has been conducted through ultrasound-assisted acid hydrolysis (Zianor Azrina et al., 2017). According to the work, the treated empty fruit bunch pulp was hydrolysed using 64% (w/v) of H_2SO_4 solution in an ultrasound bath (37 kHz and a power capacity of 320 W) at 45 °C for a duration of 2 h. Similarly, centrifugation of the cellulose nanocrystals suspension was performed to remove the excess acid solution before washed with deionized water and dialyzed using a dialysis membrane having molecular weight cut-off value of 12,000 to 14,000 for 3 days. In addition, ultrasound bath also was used to disperse the dialyzed cellulose nanocrystals but for a duration of 30 min. Unlike other reported work (Foo et al., 2019), researchers have successfully obtained spherical shaped cellulose nanocrystals with an average diameter range of 30 to 40 nm through ultrasound-assisted acid hydrolysis (Zianor Azrina et al., 2017). The formation of small-sized cellulose nanocrystals shows that ultrasound-assisted acid hydrolysis can improve the mixing of the reactants, enhance the penetration of H2SO4 into the treated empty fruit bunch pulp, and, thus, elevate the hydrolysis reaction rate. Smaller and more homogeneous sizes of the cellulose nanocrystals obtained from the work could be attributed to the cavitation from the ultrasound process (Zianor Azrina et al., 2017), at the expense of higher operating and equipment costs from an economic perspective. In general, the application of H_2SO_4 in the production of cellulose nanocrystals is preferable because it can produce negatively charged surfaces with the formation of sulfate esters to produce a stable suspension (Gan et al., 2020; Tang et al., 2014). One of the recent works has suggested that the production of cellulose nanocrystals with smaller diameters, higher stability and better dispersion can be obtained using sulphuric acid hydrolysis compared to the cellulose nanocrystals obtained through formic acid hydrolysis (Liu et al., 2016).

The optimum conditions of acid hydrolysis using empty fruit bunches are seldom reported due to the different pretreatment approaches employed. In one of the recent works, researchers have proposed an optimum condition based on the Response Surface Methodology to conduct the acid hydrolysis of empty fruit bunches (Gan et al., 2020). The optimum condition has been suggested to be at an acid concentration of 60 wt%, a hydrolytic temperature of 46.1 °C, and a reaction duration of 58.5 min. The maximum yield of cellulose nanocrystals that can be obtained under this optimum condition was predicted to be 37.1%. However, the validity of the proposed model was not validated by any experimental data. In addition, the optimum condition to obtain the highest yield of cellulose nanocrystals is only valid using deep eutectic solvent as the pretreatment method and sulphuric acid hydrolysis as the cellulose nanocrystals isolation method.

Some disadvantages have associated with the sulphuric acid hydrolysis method. From a previous study, cellulose nanocrystals produced from sulphuric acid hydrolysis showed high thermal sensitivity, which could be explained by the presence of acidic moieties at the surfaces of cellulose nanocrystals (Lin and Dufresne, 2013). From the commercialization perspective, the acid hydrolysis method also may require high water consumption (due to the requirement for extensive cleaning), expensive equipment (to withstand the highly corrosive environment), as well as large production of waste materials (relatively low yield of the cellulose nanocrystals). The presence of sulfate groups in sulphuric acid, which acts as a catalyst in oxidative decomposition, may cause the degradation of cellulose during the hydrolysis process (Wang et al., 2017).

3.2.2. Hydrochloric acid hydrolysis

One of the initiatives to evaluate the effectiveness of hydrochloric acid in hydrolysing the empty fruit bunches was conducted by a group of researchers from Japan (Hastuti et al., 2018). In their study, the bleached empty fruit bunches, alkaline-treated bleached empty fruit bunches, and alkaline-treated bleached empty fruit bunches soaked in hot water at 60 °C, were suspended in 100 ml 3 M HCl at 80 °C and continuously stirred for 2 h. The yields of cellulose nanocrystals obtained from the bleached empty fruit bunches, alkaline-treated bleached empty fruit bunches, and alkaline-treated bleached empty fruit bunches soaked in hot water at 60 °C were 21, 18, and 19%, respectively, which is much lower than the isolation process using sulphuric acid as discussed above (which can easily achieve 30% and above based on the pretreatment and hydrolysis conditions). In the same study, the crystallinity values of the cellulose nanocrystals obtained were ranged from 53 to 65%, which is much lower than those conducted using sulphuric acid hydrolysis (which can easily achieve 70% and above based on the pretreatment and hydrolysis conditions). However, hydrochloric acid hydrolysis can be used to produce cellulose nanocrystals with higher thermal sta-

bility (maximum degradation temperature ranged from 346 to 358 °C) compared to those produced from sulphuric acid hydrolysis (maximum degradation temperature is around 200 °C) (Al-Dulaimi and Wanrosli, 2017), which could be highly beneficial to the fabrication of thermoplastic polyurethane composites.

3.2.3. Phosphotungstic acid hydrolysis

Another group of researchers also have introduced the application of solid acid in hydrolysing the empty fruit bunch fibres for cellulose nanocrystals isolation (Budhi et al., 2018), which could have several advantages in comparison to the liquid phase mineral acids such as ease of acid recovery, good thermal stability, and safe working environment (Lu et al., 2016). Researchers have introduced phosphotungstic acid (a kind of solid acid) from 65 to 85% in treating one gram of pulp in an Erlenmeyer at a temperature range of 80 to 100 °C under a continuous mechanical stirring for a duration of 25 to 35 h. The resulting solution (after the reaction process was stopped using a chilled water bath) was extracted using diethyl ether in excess to form a solution with 3 layers. The lowest layer of the solution consisted of phosphotungstic acid and diethyl ether, while the middle layer consisted of cellulose nanocrystals, water, and degraded sugar. The upper layer of the solution, however, consisted of mainly diethyl ether. According to the work, phosphotungstic acid and diethyl ether can be easily recovered from the solution using a distillation process at 45 °C, which is simpler in comparison to when mineral acid is used during the cellulose nanocrystals isolation. The middle layer can be centrifuged at 4,000 rpm for a duration of 15 min to recover the cellulose nanocrystals isolated from the empty fruit bunch fibres. The application of phosphotungstic acid in the isolation of cellulose nanocrystals can produce high crystallinity and yield at 73.3% and 44.8%, respectively.

From the economic point of view, the ease of phosphotungstic acid recovery could lead to lower reagent and separation costs required for the extraction process. Besides, the ease of phosphotungstic acid recovery also could minimize the costs involved in treating the waste reagent generated after the extraction of cellulose nanocrystals. However, the phosphotungstic acid isolation method is very time-consuming due to the limited contact between phosphotungstic acid and cellulose. Continuous mechanical mixing, long term operation at elevated temperature of around 100 °C for more than 25 h, expensive reagent cost and the requirement for additional steps to separate the cellulose nanocrystals from their aggregates can make this hydrolysis less attractive. Phosphotungstic acid hydrolysis also produced cellulose nanocrystals with irregular shapes (rod-like and spherical), while the sizes ranged from 22 nm to 35 nm (width).

3.2.4. Ionic liquid hydrolysis

In addition, cellulose nanocrystals preparation can proceed via ionic liquid hydrolysis. In general, the ionic liquid is a group of organic salts with a melting point of less than 100 °C (Kargarzadeh et al., 2017). It is commonly used due to its valuable properties such as low vapour pressure, non-flammability, chemically and thermally stable and environmental friendly (Shaheen and Emam, 2018). The ionic liquid is generally introduced to microcrystalline cellulose as a solvent and catalyst to produce cellulose nanocrystals. The typical ionic liquid utilised is 1-butyl-3-methylimidazolium hydrogen sulphate ($bmimHSO_4$) (Tan et al., 2015). Studies have found that $bmimHSO_4$ is capable of dissolving cellulose, which could be helpful in the extraction of cellulose nanocrystals from empty fruit bunches. Specifically, $bmimHSO_4$ causes hydrolytic cleavage of glycosidic bonds between two anhydroglucose units (Tan et al., 2015). Besides that, the esterification of hydroxyl groups on cellulose chemical structure happens due to sulphate groups in $bmimHSO_4$ (Shaheen and Emam, 2018). Hence, amorphous regions in microcrystalline cellulose are selectively removed, forming highly-crystalline cellulose nanocrystals after several cycles of centrifugation and sonication. The illustration of $bmimHSO_4$ catalysed hydrolysis is depicted in Fig. 4.

The ionic liquid was previously used in the extraction of cellulose nanocrystals from *Elaeis guineensis* empty fruit bunches. Based on the study (Mohtar et al., 2017), 1-butyl-3-methylimidazolium chloride ([bmim][Cl]) can be used to break the linkages between the cellulose, hemicellulose and lignin in the empty fruit bunches. Partial removal of the lignin and waxes from the carbohydrates was made possible due to the high solvating properties of the [bmim][Cl], without affecting other carbohydrates. The yield of cellulose obtained from the study was around 52.72%, while the maximum degradation temperature was 325.65 °C. However, the study has reported a relatively low crystallinity value of 16.69%. Recycling of the [bmim][Cl] in the dissolution and fractionation process was successfully conducted by mixing the concentrated ionic liquid with acetonitrile before the evaporating and drying process. The successful recycling of the [bmim][Cl] is an encouraging result of improving the hydrolysis of cellulose while minimizing the chemical wastes through recycling the ionic liquid. The recycling number of the ionic liquid after the hydrolysis process, however, requires further improvement in the future to minimize the generation of the chemical wastes further.

Another recent study was conducted using other types of ionic liquids during the hydrolysis of empty fruit bunches such as 1-butyl-3-methylimidazolium chloride ([BMIM]Cl), 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl), 1-ethyl-3-methylimidazolium diethyl phosphate ([EMIM][DEP]), 1-butyl-3-methylimidazolium acetate ([BMIM]Ac) and 1-ethyl-3-methylimidazolium acetate ([EMIM]Ac) (Liu et al., 2020). Researchers have found that the use of [BMIM]Ac is more effective in wax removal by transferring more depositional cellulose to the surface in addition to high glucose yield.

In brief, the main advantage of the ionic liquid treatment is that the ionic liquid will not be consumed at the end of the reactions as it can be recovered via ion exchange, reverse osmosis and evaporation method (Kargarzadeh et al., 2017). The recovered ionic liquid can be reused for another cycle of the microcrystalline cellulose hydrolysis process by removing the contaminants during a hydrolysis process. Recycling of ionic liquid exhibits the strength of ionic liquid as an eco-friendly compound with no hazardous product synthesized (Tan et al., 2015). The main disadvantages of the ionic liquid are the time-consuming treatment process and the high cost of ionic liquid, which can decrease productivity and increase the cost of production (Salminen et al., 2017).

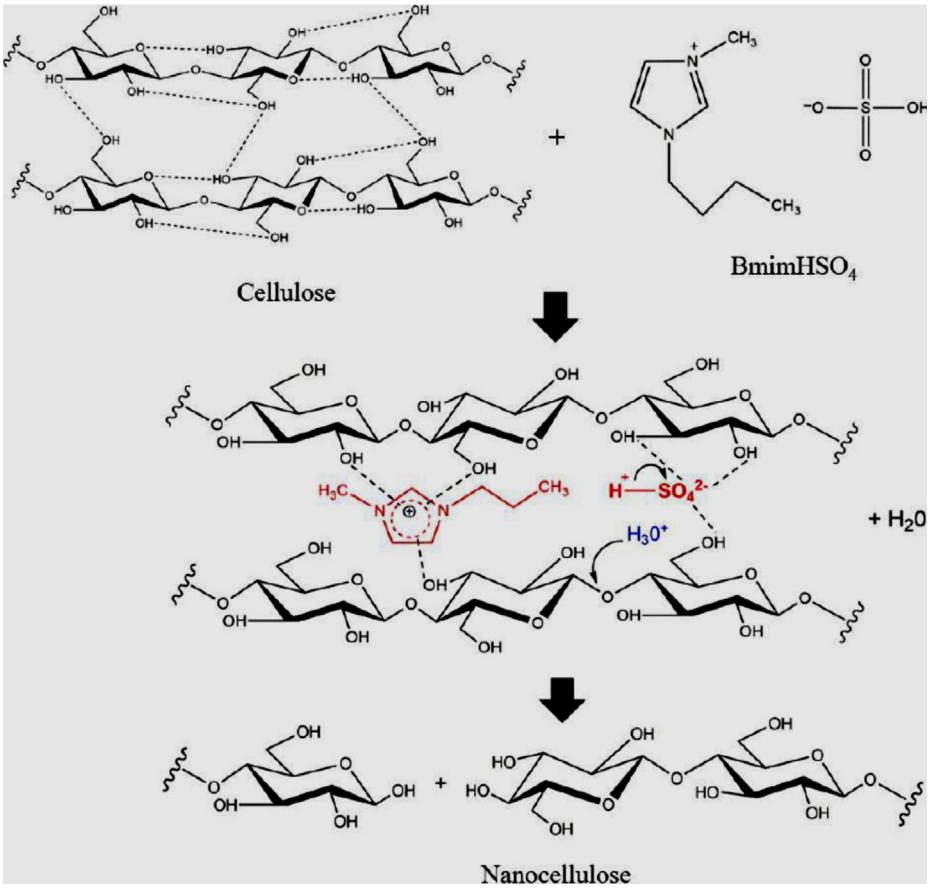

Fig. 4 Mechanisms of ionic liquid hydrolysis of cellulose. Adapted with permission from (Low et al., 2020).

3.2.5. Ammonium persulfate hydrolysis

The majority of the cellulose nanocrystals isolations from empty fruit bunch fibres have been dominated by acid hydrolysis. Recently, ammonium persulfate hydrolysis has been explored as a new method to isolate cellulose nanocrystals (Culsum et al., 2021) from empty fruit bunches (Wibowo et al., 2018). Given its high water solubility and low toxicity, ammonium persulfate has been considered as a potential candidate to be used to produce SO_4^{2-} free radicals and H_2O_2 at a high operating temperature and acidic condition, which are useful in solubilizing the lignin content and amorphous region of the celluloses (Leung et al., 2011).

Hydrolysis of empty fruit bunch fibres, with or without any pretreatment, have been conducted using 1 to 2 M of ammonium persulfate at 70 °C for 15 h in a refluxed round flask (Wibowo et al., 2018). Separation of the cellulose nanocrystals from the ammonium persulfate after the reaction was conducted using a vacuum filtration system. Based on the work, the average sizes of cellulose nanocrystals obtained from *Elaeis guineensis* empty fruit bunch fibres without pretreatment, *Elaeis guineensis* empty fruit bunch fibres with alkali-pretreatment, and *Elaeis guineensis* empty fruit bunch fibres with alkali-chloride pretreatment were 90, 85 and 25 nm, respectively. Ammonium persulfate hydrolysis has successfully isolated the cellulose nanocrystals with crystallinity values of 68, 75, and 78% from *Elaeis guineensis* empty fruit bunch fibres without pretreatment (at 2 M of ammonium persulfate), *Elaeis guineensis* empty fruit bunch fibres with alkali-pretreatment (at 1 M of ammonium persulfate) and *Elaeis guineensis* empty fruit bunch fibres with alkali-chloride pretreatment (at 1 M of ammonium persulfate), respectively.

This study has provided preliminary data on the cellulose nanocrystals extraction from empty fruit bunches using ammonium persulfate. Further study must be conducted on this work to better compare with other hydrolysis methods such as the optimum concentration for the cellulose nanocrystals extraction, recovery study on the ammonium persulfate, particle size distribution, surface charge analysis and yield analysis. This study also requires a lengthy reaction duration of 15 h, making the ammonium persulfate hydrolysis process less attractive from the commercial perspective.

3.2.6. Summary of cellulose nanocrystals extraction methods

Based on various cellulose nanocrystals extraction methods from empty fruit bunches that have been addressed, few critical considerations are needed in selecting the most suitable extraction method.

The extraction methods can be selected based on the desired properties of the final cellulose nanocrystals extracted from the empty fruit bunches. When a high yield of cellulose nanocrystals are to be obtained from the empty fruit bunches, the ionic liquid hydrolysis method could be selected, which could easily achieve 52.72%. However, when cellulose nanocrystals with high crystallinity (around 80.8%) and minimal width (1 to 3.5 nm) are required from the empty fruit bunches, sulphuric acid hydrolysis could be selected.

Besides, the extraction methods could be selected based on the feasibility of the operating conditions. When a short reaction duration is desired for the cellulose nanocrystals extraction method, sulphuric acid hydrolysis could be selected (which requires around 40 to 100 min), which is followed by hydrochloric acid hydrolysis (2 h), and ammonium persulfate hydrolysis (15 h). In addition, the cellulose nanocrystals extraction would favour sulphuric acid hydrolysis (reaction temperature 45 °C), followed by ammonium persulfate hydrolysis (reaction temperature 70 °C) and hydrochloric acid hydrolysis (reaction temperature 80 °C) when low operating temperatures are preferred.

3.3. Post-treatment of cellulose nanocrystals

Cellulose nanocrystals extracted from empty fruit bunch fibres may require modification depending on the applications of the cellulose nanocrystals. The post-treatment of the cellulose nanocrystals will typically involve the surface modification of the samples using various additives that can alter the surface properties of the cellulose nanocrystals. Cellulose nanocrystals can be functionalized by altering the surface hydroxyl groups, which can enhance their properties such as conductivity (Meulendijks et al., 2017), hydrophobicity (Mohanta et al., 2014), and thermal responsiveness (Zoppe et al., 2011). This section will discuss some of the reported works that employed post-treatment on cellulose nanocrystals extracted from empty fruit bunches.

3.3.1. Tannic acid (TA) and decylamine (DA) modification

Surface modification of cellulose nanocrystals extracted from *Elaeis guineensis* empty fruit bunches also has previously been conducted using TA and DA (Foo et al., 2019). The cellulose nanocrystals suspension was initially adjusted to pH 8 before 1 mg/ml of TA was added into the suspension and stirred for 6 h at room temperature. DA was subsequently added into the suspension at a concentration of 40 mg/ml and stirred for 3 h before centrifugation at 1,000 rpm for 10 min. The main objective of that study was targeted to improve the surface hydrophobicity of cellulose nanocrystals.

According to the work (Foo et al., 2019), tannic acid can be attached to the cellulose nanocrystals surfaces via catechol/pyrogallol-type phenol through oxidation under alkaline conditions. Oxidation of TA will lead to the formation of quinones, which are the highly reactive electrophilic entities to be attached to various compounds. The addition of decylamine caused the nucleophilic amines to react with the quinones, leading to the formation of a hydrophobic compound, which can be used to enhance their binding capability with curcumin or for other drugs delivery applications.

3.3.2. Aminosilane grafting

N-(2-aminoethyl)-3-aminopropyl-methyl dimethoxy silane, one of the main compounds used in carbon dioxide capture, was previously grafted onto cellulose nanocrystals isolated from empty fruit bunch fibres (Mohd et al., 2017). The silane coupling agent could interact with cellulose based on the reported work through a hydrolysis reaction by forming reactive silanol groups. The silanol groups could form polysiloxane structures by reacting with hydroxyl groups on the surfaces of cellulose fibres, which is used as the anchor points in silane-based grafting. According to the study, the cellulose nanocrystals were firstly isolated through sulphuric acid hydrolysis using 60% aqueous solution at a temperature of 45 °C before the modification by N-(2-aminoethyl)-3-aminopropyl-methyl dimethoxy silane in 80/20 (v/v) of solvent water/ethanol at 60 °C for 3 h. The modification of cellulose nanocrystals by N-(2-aminoethyl)-3-aminopropyl-methyl dimethoxy silane was evidenced by the presence of new peaks in the Fourier transform infrared results, which were NH_2 bending at 1600 cm_{-1}, Si-CH_3 at 1260 cm^{-1}, NH_2 wagging at 798 cm^{-1}, and the primary amine at around 3500–3300 cm^{-1}. Silanization modification, however, reduced the crystallinity of the cellulose nanocrystals into an amorphous structure.

The study has provided some helpful information on the potential application of cellulose nanocrystals through chemical modification (Mohd et al., 2017). However, several issues are not adequately evaluated in that study, including the effectiveness of the N-(2-aminoethyl)-3-aminopropyl-methyl dimethoxy silane grafted cellulose nanocrystals in the CO_2 capture, stability of the composite during the application, and stability of the composite for storage purposes. Thus, an extension of the similar study was previously carried out and the CO_2 capture capability was determined to be 0.20 mmol/g using 3-(aminopropyl) trimethoxysilane (APTMS) (Mohd et al., 2021). The aminated solid adsorbent aerogel developed using cellulose nanocrystals from the empty fruit bunches and APTMS can be used as an organic amine adsorbent in the CO_2 capture owing to its large surface area (21.6 m^2/g) and total pores volume (0.10 cm^3/g).

4. Characterisation of cellulose nanocrystals using different techniques

Various characterization techniques and instrumentations are introduced to investigate the surface morphology, topography, crystallographic structure, elemental and thermal properties of cellulose nanocrystals extracted from empty fruit bunches. Different characterization techniques reveal different information about the analyzed sample. Morphology and topography of the samples can be evaluated using transmission electron microscopy (TEM) and field emission scanning electron microscopy (FESEM) (Asad et al., 2018). As for crystallographic structures, elemental properties, and thermal stabilities, cellulose nanocrystals can be analyzed using an X-ray diffractometer (XRD), Fourier transform infrared spectroscopy (FTIR), and thermogravimetry, respectively. The dynamic light scattering (DLS) and zeta potential techniques can be used to determine the particle size distribution and zeta potential in cellulose nanocrystals (Naduparambath et al., 2018).

4.1. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is a common technique used to acquire images of cellulose nanocrystals at high magnification (Kumar et al., 2014). In TEM, a primary electron beam of high energy and intensity passes through a condenser to produce parallel rays impinge on the ultra-thin sample (Chorkendorff and Niemantsverdriet, 2003). It interacts with the sample as it passes through. The transmitted electrons form a two-dimensional projection of the sample mass. The image is then focused on an imaging device, including a

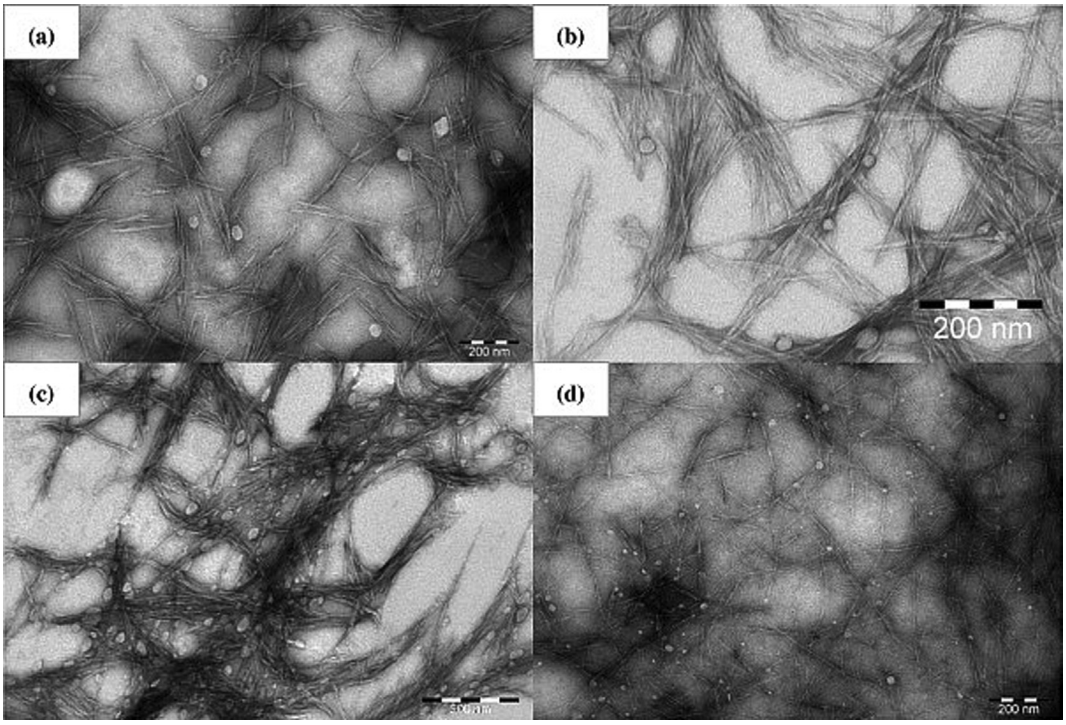

Fig. 5 TEM images of (a) cellulose nanocrystals prepared by sulphuric acid hydrolysis, (b) Cellulose nanocrystals prepared by combination of formic acid and hydrochloric acid hydrolysis, (c) Cellulose nanocrystals prepared by formic acid hydrolysis and (d) Cellulose nanocrystals prepared by TEMPO-mediated oxidation. Adapted with permission from (Li et al., 2015).

layer of photographic film and a fluorescent screen. Therefore, one can determine the sample particle size and inter-layer spacing of nanoparticles at a corresponding diffraction plane from the TEM image.

Due to small-sized cellulose nanocrystals in nature, consisting of hydrogen bonding and low electron density, individual cellulose nanocrystals are challenging to be imaged (Li et al., 2015). Thus, TEM with high resolution and magnification is commonly used to investigate the defined shapes and distribution of cellulose nanocrystals. Apart from that, the diameter of cellulose nanocrystals can be determined as well to identify the possible occurrence of agglomeration. Morphological characterisation using TEM in previous work revealed the appearance of needle-like shaped cellulose nanocrystals as depicted in Fig. 5 (Li et al., 2015), which also compared cellulose nanocrystals prepared by different approaches. TEM images presented individual needle-shaped nanocrystals and some agglomerates extracted from EFB, confirming that cellulose nanocrystals preparation from raw EFB was successful. In addition, the average aspect ratio gradually increased with further chemical treatment.

A similar analysis was also conducted on cellulose nanocrystals obtained through TEMPO-assisted oxidation of *Elaeis guineensis* empty fruit bunches in the presence of sonication treatment (Rohaizu and Wanrosli, 2017). Fig. 6 shows the TEM images of microcrystalline cellulose, TEMPO-oxidized microcrystalline cellulose, and cellulose nanocrystals isolated from *Elaeis guineensis* empty fruit bunches widths were measured to be 31, 15, and 4 nm, respectively. The enhanced fibrillation effect explained the size reduction observed in that study in the presence of TEMPO-oxidation and sonication, which replaced the hydroxyl groups with carboxylate groups that led to the formation of weak inter-fibrillar bonds.

4.2. Field emission scanning electron microscopy (FESEM)

FESEM, unlike an ordinary optical microscope, functions based on electrons instead of light (Chorkendorff and Niemantsverdriet, 2003). Electrons are negatively charged particles that can be released by the emission source field and subsequently accelerated due to the high electrical field gradient applied to them (Zhang et al., 2009). These liberated primary electrons will focus and deflect by electronic lenses in a high vacuum column to produce narrow electron beams that will bombard the sample. As a result, secondary electrons are liberated from the impacted spot on the sample. The angle and velocity of the liberated secondary electrons are then captured, thus, generating an electronic signal that enabling a video scan image to be perceived on the monitor (Wijeyesekera et al., 2016). In this way, the surface structures or topography of the cellulose nanocrystals produced can be observed and analysed.

The surface morphologies of raw, treated, and cellulose nanocrystals can be surveyed through the employment of FESEM. The utilisation of FESEM to capture cellulose nanocrystals preparation utilizing chemical treatments is suitable for assay the morphological and size changes of EFB after chemical treatment. Besides, it can couple with the DLS technique to further identify and clarify the particle size distribution of cellulose nanocrystals produced. Undoubtedly, the

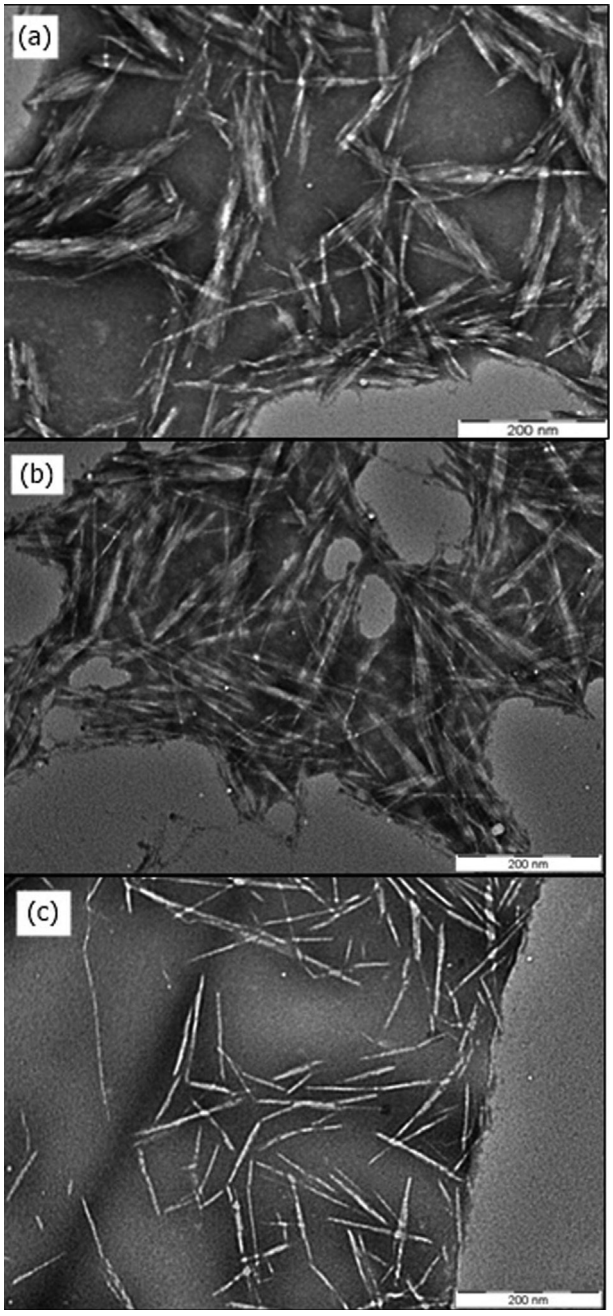

Fig. 6 TEM images of microcrystalline cellulose, TEMPO-oxidized microcrystalline cellulose, and cellulose nanocrystals isolated from *Elaeis guineensis* empty fruit bunches. Adapted with permission from (Rohaizu and Wanrosli, 2017).

diameter of cellulose nanocrystals has faced a reduction, which indicates the removal of non-cellulosic components, including hemicellulose and lignin, after performing the hydrolysis and bleaching treatments (Kamelnia et al., 2019). In addition, to achieve the adequate size and distribution of cellulose nanocrystals, which provides the separation and conversion of cellulose fibres into individual forms, ultrasound treatments could be introduced. cellulose nanocrystals can exist in different structures, which can exist in rod-like shapes and the spherical shape of nanoparticles. Hence, this information can be recorded using FESEM to evaluate the cellulose nanocrystals properties.

Comparison is made between SEM and FESEM. FESEM is far better than SEM in terms of resolution because the beam gun in SEM is thermionic while the beam gun used in FESEM is electromagnetic (Chorkendorff and Niemantsverdriet, 2003). FESEM can produce low-voltage images with a magnification factor up to 300,000× and can detect or measure samples as small as 1 nm. As cellulose nanocrystals are in the nano-sized range, FESEM could be one of the suitable instruments that can be used to obtain high-resolution images.

Fig. 7 shows the results of the morphological study conducted on raw empty fruit bunches, empty fruit bunch pulp (after went through pre-hydrolysis and soda pulping in a rotating digester), alkaline-treated empty fruit bunch pulp, and cellulose nanocrystals isolated through the acid hydrolysis process (Zianor Azrina et al., 2017). Based on the morphological study, smoother surfaces of the empty fruit bunch pulp can be observed after pre-hydrolysis and alkaline treatment due to the removal of lignin, hemicellulose, wax and impurities from the raw empty fruit bunches. In addition, cellulose nanocrystals in nano-sizes have been observed with some aggregations due to cohesion forces during the drying process.

Fig. 8 shows the FESEM images and particle size distribution charts of cellulose nanocrystals that were obtained at various concentrations of sulphuric acid, acid to pulp ratio (A/P), and duration of acid hydrolysis (Foo et al., 2020). The average width and length of the cellulose crystals ranged from 15 nm to 27 nm and 170 nm to 317 nm, respectively. The results demonstrated a considerable variation in the properties of the cellulose nanocrystals within a narrow variable range during the cellulose nanocrystals isolation process.

4.3. X-ray diffraction (XRD) analysis

XRD technology originated from physicist Max Von Laue in 1912. Max Von Laue discovered that crystalline materials could act as three-dimensional diffraction gratings for X-ray. The wavelengths are similar to the spacing of planes in a crystal lattice (Eckert, 2012). This discovery leads to the X-ray diffraction technique to characterise the crystallite size and orientation of crystallographic structure in powdered solid samples or polycrystalline. On top of that, X-ray diffraction can observe the variations in crystalline phases of the compound by lattice structural parameters means (Borchert, 2014). Generally, X-rays are produced by a cathode ray tube (Chorkendorff and Niemantsverdriet, 2003). It heated up the filament to generate a high concentration of electrons. Monochromatic radiation is produced as electrons, filtered by using the collimator, and the radiation will then pass through the sample. At this state, the electric vector of the radiation interacts with the electrons in the sample's atoms. When crystals scatter x-rays, destructive and constructive interference will result among the scattered rays.

The principles of XRD analysis are developed based on Bragg's Law. As X-ray strikes on the crystal structure, part of the beam is scattered, the unscattered beam will proceed to the next planes and so on. The successive planes are separated by interplanar distance, which will yield constructive interference. Hence, the lattice spacing, d, can be measured by angle 2θ obtained in the diffraction pattern and X-rays with

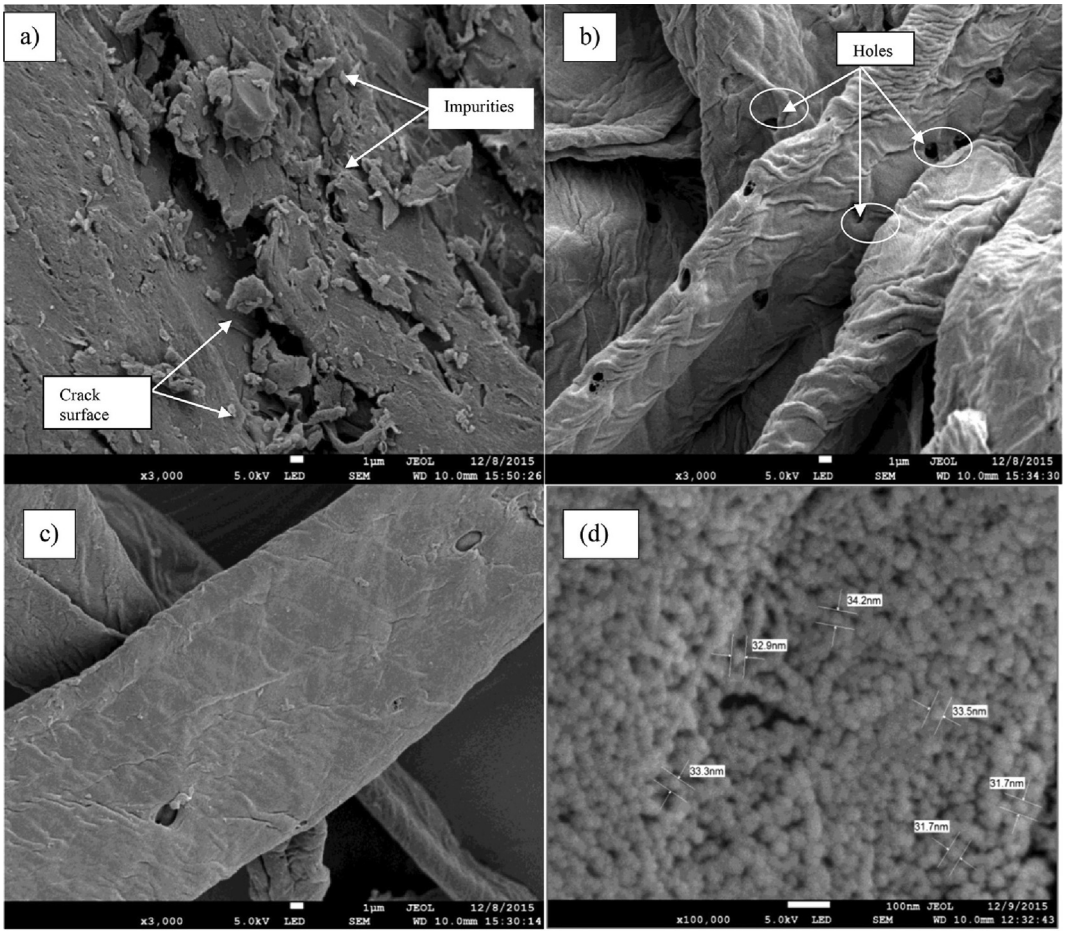

Fig. 7 FESEM images of raw empty fruit bunches, empty fruit bunch pulp, alkaline-treated empty fruit bunch pulp, and cellulose nanocrystals. Adapted with permission from (Zianor Azrina et al., 2017).

a wavelength, λ, leaving the crystal by applying the Bragg equation (Eq. (1)).

$$n\lambda = 2d\ \sin\theta \quad (1)$$

where
λ = Wavelength, nm
d = Lattice plane distance, nm
θ = Diffraction angle, °

XRD analysis can be used to study the crystallinity of the cellulose nanocrystals by calculating the crystallinity index (CrI) (Kargarzadeh et al., 2015) using either Segal's method (Eq. (2)), Revol's method (Eq. (3)) (Henrique et al., 2015), or peak deconvolution method with a Gaussian fit (Eq. (4)) (Cudjoe et al., 2017). I_{200} and I_{110} are the maximum intensities (in arbitrary units) of the 200 and 110 lattice diffractions, respectively. I_{am} and I_{15} are the intensities of diffractions in the same units at 2θ = 18° and 15°, respectively. I_{200} and I_{110} represent crystalline and amorphous regions, while I_{am} and I_{15} represent only the amorphous portion. For the peak deconvolution method, the amorphous and crystalline peaks in the diffractogram at 16°, 22.5°, 24°, and 36° need to be fitted using software by assuming Gaussian functions for each peak. In addition, the crystallite size of the cellulose nanocrystals can be calculated using the Scherrer formula (Eq. (5)), where D is crystallite size, K is Braggs constant, β is Full width at half maximum, θ is Bragg angle, and λ is X-ray wavelength (Pandi et al., 2021).

$$CrI = \frac{I_{200} - I_{am}}{I_{200}} \quad (2)$$

$$CrI = \frac{I_{110} - I_{15}}{I_{110}} \quad (3)$$

$$CrI = \frac{crystalline\ \ area\ \ of\ \ \left(1 - 10 + 110 + \frac{012}{102} + 200 + 004\right)}{crystalline\ \ area\ \ of\ \ \left(1 - 10 + 110 + \frac{012}{102} + 200 + 004\right) + amorphous\ \ area} \quad (4)$$

$$D = \frac{K\lambda}{\beta\cos\theta} \quad (5)$$

XRD analysis can be conducted to evaluate the crystalline structure of cellulose nanocrystals samples. Different specimens before and after treatment are analysed. Characteristic diffraction peaks were observed at approximately 16.2°, 22.4°, and 34.7°, corresponding to the (110), (002), and (004) crystallographic planes, respectively (Xiao et al., 2019). Hypothetically, the diffraction intensity at the main crystalline peak (22.4°) following chemical treatment compared to the raw material will increase, indicating that a higher crystallinity index will be observed after following chemical treatment. In

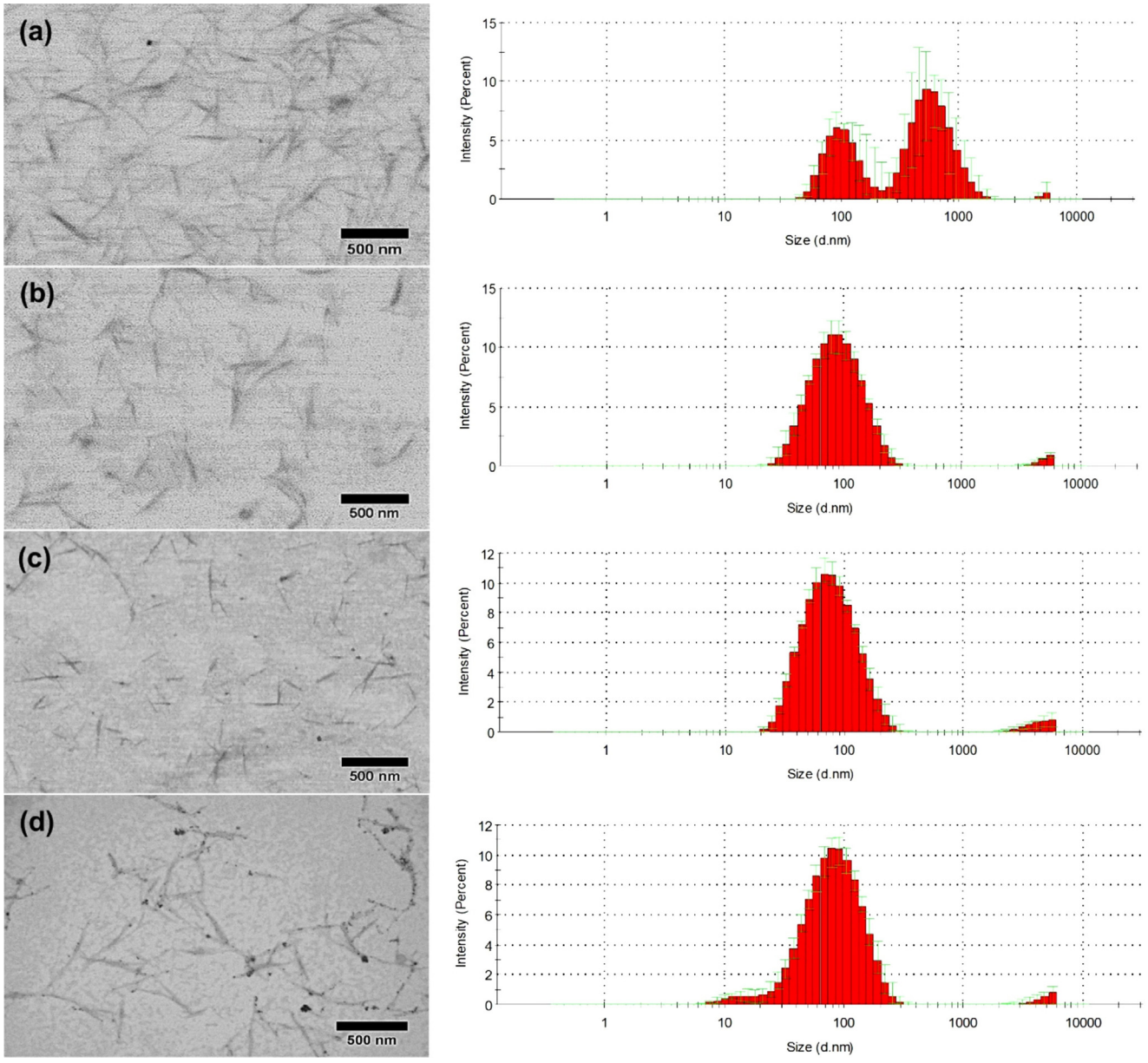

Fig. 8 FESEM images and particle size distribution charts of cellulose nanocrystals produced from (a) 56 wt% of H_2SO_4, A/P 15, 30 min, (b) 58 wt% of H_2SO_4, A/P 15, 45 min, (c) 60 wt% of H_2SO_4, A/P 15, 30 min, and (d) 57.88 wt% of H_2SO_4, A/P 20, 60 min. Adapted with permission from (Foo et al., 2020).

other words, chemically-treated cellulose nanocrystals will exhibit a higher crystallinity index compared to raw material. Previous research has reported that cellulose nanocrystals is highly crystalline, between 54 and 88%. It is evaluable under XRD analysis to depict the differences between chemically-treated cellulose nanocrystals extracted from EFB and raw EFB (Xiao et al., 2019). The crystallite size of cellulose was previously determined to be 9.8 nm (Nazir et al., 2013).

Similarly, XRD patterns have been used to differentiate the properties of raw EFB, purified fibre after chemical pretreatment, and cellulose nanocrystals extracted from EFB (Foo et al., 2019). This study has observed similar crystalline peaks (at around $2\theta = 22.6°$ and 34.6°) and the broad amorphous humps (at around 14.7° and 16.2°). These are the characteristic diffractograms of semi-crystalline materials (Rohaizu and Wanrosli, 2017). Chemical pretreatment of EFB can increase the CrI of the purified fibres from 38.8% to 66.1% (Fig. 9), which could be explained by the removal of amorphous lignin and hemicellulose. A higher crystallinity in the (002) plane could be obtained through the acid hydrolysis of pretreated empty fruit bunch fibres by the dissolution of the amorphous domains and hydrolytic cleavage of glycosidic bonds leading to the release of individual crystallites with a higher CrI (77.6%). In another similar work, a higher crystallinity of cellulose nanocrystals at 80% can be observed when the acid hydrolysis process was enhanced by the ultra-sonication application (Zianor Azrina et al., 2017), which is higher than sono-assisted TEMPO-oxidation of the empty fruit bunch fibres in

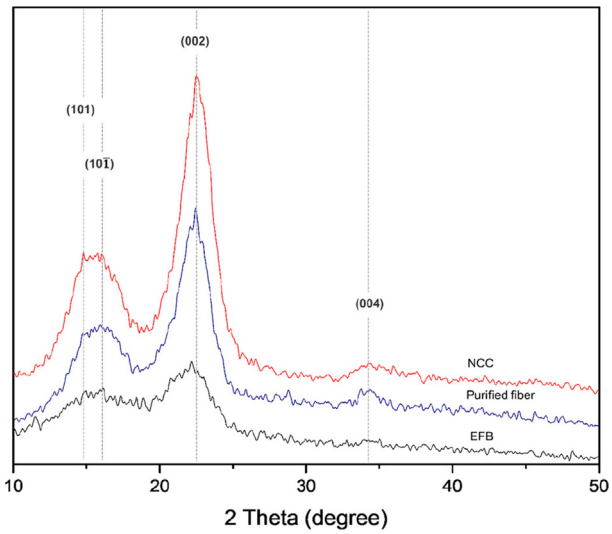

Fig. 9 XRD analyses conducted on raw empty fruit bunches, fibres after a chemical pretreatment, and cellulose nanocrystals. Adapted with permission from (Foo et al., 2019).

producing cellulose nanocrystals with a crystallinity of only 72% (Rohaizu and Wanrosli, 2017). Based on these works, it can be observed that the sonication-assisted isolation method can be used to enhance the chemical reaction rates but at the same time might deteriorate the crystallinity of the cellulose nanocrystals obtained. This can be explained by the non-selective sonication process that can disrupt the hydrogen bonds and the packing of cellulose fibrils.

Another similar study has reported slightly lower crystallinity for the cellulose nanocrystals obtained using sulphuric acid hydrolysis (65.3%) after pretreatment of the empty fruit bunch fibres using deep eutectic solvent (Gan et al., 2020). The crystallinity of bleached deep eutectic solvent-treated empty fruit bunch fibres has successfully improved from 38.7% to 51.2%, which demonstrated the effectiveness of the deep eutectic solvent in removing the lignin and hemicellulose before the sulphuric acid hydrolysis step.

4.4. Fourier transform infrared spectrometry (FTIR)

FTIR spectrometry has been used to study the absorption of infrared radiation (Zhang et al., 2009). Molecular absorption of the radiation will promote the transition between vibrational and rotational energy levels of the ground electronic energy state, inducing molecular vibration categorised by bending and stretching movement. The absorbed infrared radiation will produce a net change of radiation transmittance that passes through the sample, and the changes will be displayed on the spectrum (Jaggi and Vij, 2006). From the spectrum, identifying a specific functional group is possible based on the peak observed due to vibrational movement (Ng et al., 2020). FTIR variation is obtained through the interferometer rather than the grating used in the conventional IR spectrometers (Ismail et al., 1997). Also, FTIR has a more excellent resolution than dispersive IR, allowing the characterisation to be performed at much greater accuracy.

The chemical structures of raw empty fruit bunch, alkaline-treated empty fruit bunch, cellulose microcrystal, and cellulose nanocrystals samples have been analyzed by FTIR. Remarkably, all the samples displayed similar prominent peaks at specific wavenumber strongly associated with the cellulose structure, which is in good agreement with another reported work (Xiao et al., 2019). Apart from that, the absence of peaks in the spectra of the cellulose and all cellulose nanocrystals samples is possibly due to the significant elimination of hemicellulose and lignin by the purification process. FTIR spectrometry results can be used to determine the absence of

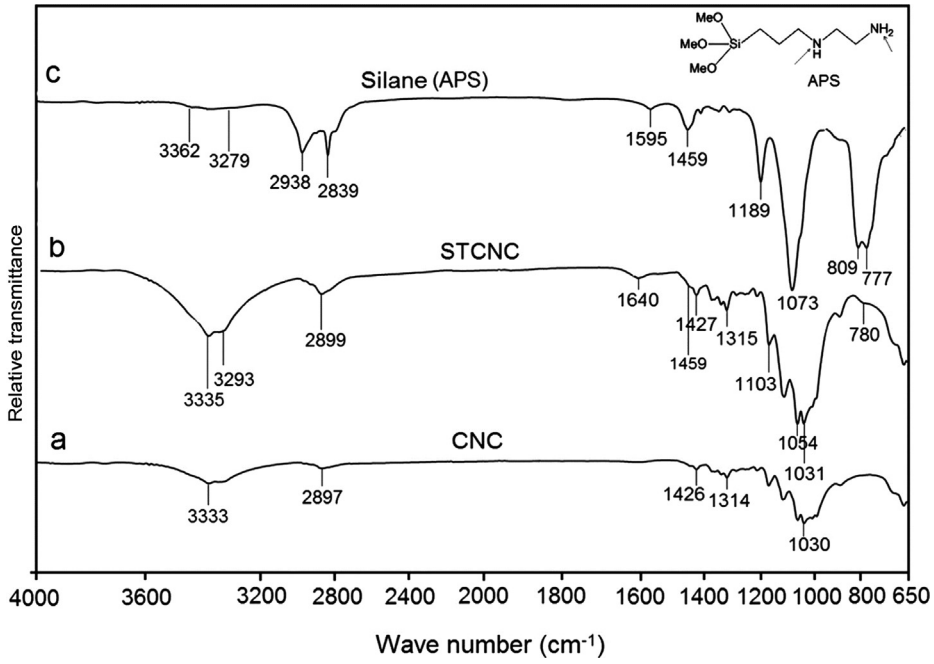

Fig. 10 Sample of FTIR spectra of cellulose nanocrystals produced by different treatments. Adapted with permission from (Kargarzadeh et al., 2015).

lignin and hemicellulose in cellulose nanocrystals isolated by acid hydrolysis (Mazlita et al., 2016). It distinguishes the differences of cellulose nanocrystals extracted from microcrystalline cellulose and cellulose. Hence, it can be used to evaluate the efficiency in the production of cellulose nanocrystals. Besides, the transmittance in the FTIR spectrum can provide a brief idea about the concentration of the sample (Griffiths, 1978). Fig. 10 displays various spectra of cellulose nanocrystals that are produced by different treatments. It can be observed that the stretching of the hydroxyl group of cellulose lies in the wavenumber range of 3350–3200 cm^{-1}. Remarkably, the absorbance peak of the C-H stretching group was recorded at around 3000–2840 cm^{-1}. The spectra of cellulose nanocrystals displayed the bending variations of C-H and C-O groups of the rings in polysaccharides and symmetrical bending of CH_2 at absorbance peak of 1315 cm^{-1} and 1426 cm^{-1}, respectively.

FTIR analysis was also used to determine the presence of carbonyl groups (at a wavenumber of 1746 cm^{-1}) in the cellulose nanocrystals obtained through TEMPO-oxidation (Rohaizu and Wanrosli, 2017). In addition, the disappearance of vibration bands within 1500–1600 cm^{-1} was observed in the cellulose nanocrystals extracted, which confirmed the complete removal of lignin from the raw and treated empty fruit bunch fibres before the isolation of cellulose nanocrystals (Al-Dulaimi and Wanrosli, 2017; Rohaizu and Wanrosli, 2017). On the other hand, the presence of sulfate groups in the cellulose nanocrystals isolated from empty fruit bunch fibres through sulphuric acid hydrolysis can be observed at a wavenumber of 1231 cm^{-1} (Al-Dulaimi and Wanrosli, 2017).

Undoubtedly, FTIR analysis helps determine the functionality of empty fruit bunch fibres and the extracted intermediates and cellulose nanocrystal samples. However, precise quantification of the components present in the samples such as lignin and cellulose content should be compensated with other analyses.

4.5. Dynamic light scattering (DLS) and zeta potential analyses

DLS is a technique that can be conveniently used to determine the average size distribution of particles contained in a sample (Ross Hallett, 1994). DLS technique is founded based on the light scattered by diffusing particles. DLS encompasses the Doppler broadening of the Rayleigh-scattered light resulting from the particle Brownian motion or translational diffusion. This thermal motion leads to time fluctuation in the broadening of the Rayleigh line depicted as Lorentzian shape and scattering intensity. The concentration of the fluctuation is significant in macromolecular solutions. Under these conditions, the Rayleigh line width will be directly proportional to the coefficient of translational diffusion. Subsequently, particle size distribution data can be generated from existing results. In the presence of an electrical potential, some DLS instruments also can provide zeta potential data for cellulose nanocrystals dispersions (Prathapan et al., 2016).

cellulose nanocrystals is well-known for its nanoscopic size range and rod-like structure. Determination of size distribution of rod-like cellulose nanocrystal particles could be proposed using the translational diffusion coefficient (measured by DLS) to obtain dimensional information of cellulose nanocrystals (Boluk and Danumah, 2014)

Spherical cellulose nanocrystals with a diameter of around 80–100 nm have previously been prepared, accompanied by similar aggregation behaviour (Okahisa et al., 2018). Such aggregation of cellulose nanocrystals is probably ascribed to their tiny size and high specific surface area, causing them to stick to each other via strong hydrogen bonds or van der Waals forces.

As the DLS technique can obtain size information within few minutes for particles with diameters ranging from few nm to 5 μm, it is suitable to be applied on the cellulose nanocrystals for size verification while at the same time it can determine the occurrence of agglomeration between cellulose nanocrystal particles. Besides, the DLS technique can be coupled with an electron microscope to determine the length and diameter of the particle in liquid to yield a more accurate result (Boluk and Danumah, 2014).

During acid hydrolysis using sulphuric acid at 58% and 45 °C, researchers have shown an increased zeta potential from −36.2 to −69.8 mV by increasing the reaction time from 40 to 100 min (Al-Dulaimi and Wanrosli, 2017) using DLS analysis.

Other researchers also have successfully employed DLS analysis in their study to obtain the average size and zeta potential of cellulose nanocrystals isolated from empty fruit bunches. An averaged size of 75 nm and zeta potential value of less than −10 mV were obtained from their study (Foo et al., 2019). They have successfully increased the zeta potential values of the cellulose nanocrystals isolated from empty fruit bunches to around −65 mV after modified the surface of cellulose nanocrystals using tannic acid and decylamine. This shows the importance of DLS analysis in verifying the surface modification and properties of cellulose nanocrystals based on the particle size distribution and surface charge data. DLS technique, however, is not highly accurate and has to be reported in addition to the information of the dispersing medium that the cellulose nanocrystals are placed in, which is aimed to enhance the interpretation of the data for future reference.

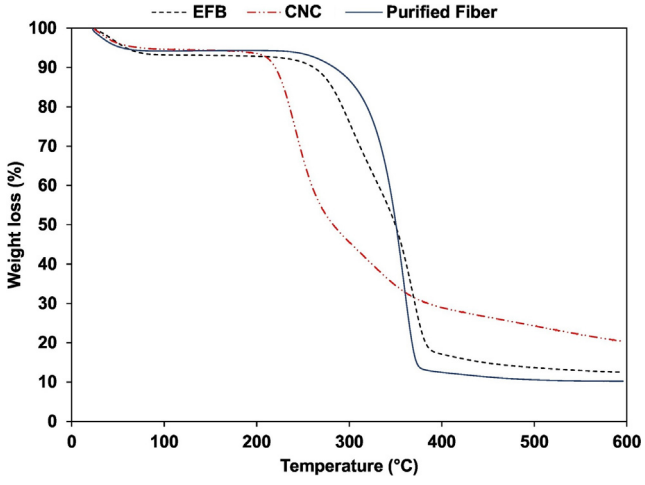

Fig. 11 Weight losses of empty fruit bunches (EFB), pre-treated empty fruit bunches (purified fibre) and cellulose nanocrystals isolated from empty fruit bunches (CNC). Adapted with permission from (Foo et al., 2019).

4.6. Thermogravimetric analysis (TGA)

Recently, TGA has been used to evaluate the thermal properties of empty fruit bunch fibres, pretreated fibres and cellulose nanocrystals produced from empty fruit bunches (Foo et al., 2019). TGA can be used to validate the presence of water molecules in all those samples at a temperature below 100 °C based on the weight losses observed from Fig. 11. In addition, TGA has been successfully used to verify the partial removal of pectin, lignin and hemicellulose in the empty fruit bunches (weight loss was observed at 280 °C) after the pretreatment process (weight loss only observed after 293C). By comparison, cellulose nanocrystals exhibited gradual weight loss at and above 200 °C due to the degradation of sulfated cellulose, which was introduced during the isolation of cellulose nanocrystals using sulfuric acid during the acid hydrolysis process. Cellulose nanocrystals also may produce higher amount of char residue due to their flame retardancy property. In another similar work (Zianor Azrina et al., 2017), cellulose nanocrystals isolated from empty fruit bunches also exhibited a higher thermal decomposition temperature of 403.09 °C compared to empty fruit bunch fibres (336.12 °C) and empty fruit bunch pulp (382.64 °C) obtained after alkaline pretreatment.

Table 5 Cellulose Nanocrystal Extraction methods using empty fruit bunches.

Method	Advantage	Disadvantage	Reference
Sulphuric Acid Hydrolysis	i. cellulose nanofibers of 1 to 3.5 nm in width but 100 nm to 2 μm in length ii. high yield of cellulose nanocrystals, as high as 37.1 % iii. the crystallinity of the cellulose can reach 80.8% iv. prevent cellulose nanocrystals from forming aggregates in the presence of sulfate esters v. require mild operating temperature (45 °C) vi. short reaction duration (40 to 100 min)	i. require thorough washing using water, successive centrifugations, or dialysis ii. require control mechanism to stop the acid hydrolysis iii. precise control of sulphuric acid concentration range is required iv. thermally sensitive process v. require corrosion-resistant equipment due to the highly corrosive condition vi. produce cellulose nanocrystals with lower thermal stability (maximum degradation temperature is around 200 °C)	(Al-Dulaimi and Wanrosli, 2017; Cheng et al., 2017; Fahma et al., 2010; Lin and Dufresne, 2013)
Hydrochloric Acid Hydrolysis	i. moderate crystallinity of around 53 to 65% ii. produce cellulose nanocrystals with higher thermal stability (maximum degradation temperature ranged from 346 to 358 °C) iii. cellulose nanofibers of 10 to 12 nm in width but 264 nm to 301 nm in length	i. require slightly higher reaction temperature at around 80 °C ii. yields of cellulose nanocrystals are slightly lower or about 18–21% iii. Require 2 h of reaction duration	(Al-Dulaimi and Wanrosli, 2017; Hastuti et al., 2018)
Phosphotungstic Acid Hydrolysis	i. acid can be easily recovered from the reaction (distillation process at 45 °C) ii. produce cellulose nanocrystals with high crystallinity or 84% iii. produce a high yield of cellulose nanocrystals (44.04%)	i. high concentration of acid is required (65 to 85%) ii. high operating temperature range (80 to 100 °C) iii. long reaction duration (25 to 35 h) iv. require extensive mechanical mixing due to the limited contact between the acid and pulp v. may form aggregates at the end of the process vi. require diethyl ether in the extraction process	(Budhi et al., 2018)
Ionic Liquid Hydrolysis	i. environmental friendly method that involves only ionic liquid and moderate operating condition ii. produce cellulose nanocrystal with moderate thermal stability (325.65 °C) iii. high yield of 52.72%	i. recovery of the ionic liquid may require the application of highly toxic chemicals such as acetonitrile ii. recovery of the ionic liquid requires a long duration (about 24 h) at about 60 °C iii. High extraction temperature is required (about 140 °C for 4 h)	(Liu et al., 2020; Mohtar et al., 2017; Shaheen and Emam, 2018)
Ammonium Persulfate Hydrolysis	i. chemical used is less toxic ii. low reaction temperature (about 70 °C) ii. produce cellulose nanocrystals with high crystallinity (as high as 68 to 78%) iii. the small width of cellulose nanocrystals can be obtained (25–31 nm) with the length to be in the range of 100–250 nm	i. moderate reaction duration or 15 h ii. require high concentration of the chemical (around 2 M) iii. less effective in the removal of lignin content from the cellulose nanocrystals (as high 20%)	(Wibowo et al., 2018)

In another similar study, cellulose nanocrystals produced from empty fruit bunch fibres showed higher thermal stability when acid hydrolysis duration was shorter (Al-Dulaimi and Wanrosli, 2017). According to the study, a longer hydrolysis duration using sulphuric acid enhanced the interaction between cellulose and the hydrogen ions, which led to more negatively charged sulfate groups on the cellulose structure (decomposition temperature at 120 to 200 °C). Displacement of the unsulfated ions from the empty fruit bunch fibres led to reduced thermal stability (decomposition temperature at around 290 to 370 °C was reduced to around 120 to 200 °C), which is in agreement with other reported study using the same raw material for cellulose nanocrystals isolation (Gan et al., 2020).

5. Future prospects and challenges

Cellulose nanocrystals extraction methods using empty fruit bunches have been summarized in Table 5. Different extraction methods may have different limitations and lead to the formation of cellulose nanocrystals with different properties. The main limitations in the sulphuric acid hydrolysis in obtaining cellulose nanocrystals from empty fruit bunches are the low yield of the cellulose nanocrystals and the extensive requirement for washing and centrifugations owing to the formation of cellulose nanocrystals with a small width. From the commercial production perspective, the sulphuric acid hydrolysis method consumes a large amount of water, which must be recycled using proper ceramic membranes to withstand the corrosive solution (Lanjewar et al., 2021).

Ionic liquid hydrolysis may produce a higher yield of cellulose nanocrystals from empty fruit bunches, around 15% more than the sulphuric acid hydrolysis, and the reagent used is environmentally friendly. Yet, this method has several main limitations that may make the process less attractive. Hydrolysis of empty fruit bunches using ionic liquid requires a long duration in recovering the ionic liquid (about 24 h) at an elevated temperature (60 °C). The extensive water washing step, recovery of ionic liquid, and the expensive ionic liquid used may make this hydrolysis process less cost-effective (Ovejero-Pérez et al., 2021). Besides, the recovery of ionic liquid may require the application of acetonitrile. Acetonitrile is a highly toxic compound, and its removal is an energy-intensive process owing to the azeotropic behaviour (Li et al., 2021).

Cellulose nanocrystals, however, also could be extracted using high-pressure homogenization in a homogenous media (Li et al., 2012) and enzymatic hydrolysis in combination with mechanical shearing (Henriksson et al., 2007). Applying these cellulose nanocrystals extraction methods using *Elaeis guineensis* empty fruit bunches as the raw materials is still not well-documented to date. Limited studies could be reasoned with the limitations in the methods, such as high production cost, complicated equipment setup, and low cellulose nanocrystals yield. However, collecting the cellulose nanocrystals extraction data using Elaeis guineensis empty fruit bunches as the source of raw materials is vital for comparing existing methods to identify the most cost-effective approach.

In addition, most of the reported studies have reported the cellulose nanocrystals isolation methods without optimizing the isolation conditions. Limited study on optimizing the isolation conditions could be because the effectiveness of the cellulose isolation steps is complicated by different pretreatment methods and different isolation approaches. Different pretreatment methods could affect the accessibility of the crystallites before they can be released in the following isolation step, which is dominated by acid hydrolysis. One of the recent studies has attempted to optimize the performance of the sulphuric acid hydrolysis method after the fibres were delignified using an acidic $NaClO_2$ solution made of an equal volume of acetate buffer (a mixture of NaOH and CH_3COOH at pH 4) (Foo et al., 2020). However, this study only evaluated the sulphuric acid concentration up to 60 wt% in addition to the acid hydrolysis time up to 60 min, which is much lower when compared to another recent study that has reported a slightly higher crystallinity value of around 80% (Al-Dulaimi and Wanrosli, 2017). In brief, the pretreatment and isolation of cellulose nanocrystals from the empty fruit bunches should be optimized within the same study using a suitable parameter range to produce a more effective optimum condition that can enhance the yield and characteristics of the cellulose nanocrystals.

There are limited methods reported on the cellulose nanocrystals isolation using *Elaeis guineensis* empty fruit bunch as the cellulose source. Comparison between the methods in cellulose nanocrystals extraction in terms of yield, reaction duration, and cellulose nanocrystals properties cannot be concluded before each method is evaluated thoroughly. Thus, the research gap should be supplemented with sufficient data through more experimental works using other cellulose nanocrystals isolation methods.

6. Conclusions

Despite being a promising feedstock for the isolation of cellulose nanocrystals, empty fruit bunches possess one major drawback, which is the presence of hemicellulose and lignin together with cellulose in plant fibres. So, the pretreatment step usually is necessary to obtain the final products of high purity cellulose nanocrystals. Several standard pretreatment methods have been evaluated in this review. Each method has its advantages and disadvantages. Among all the methods, chemical pretreatment is the most extensively studied pretreatment technique when empty fruit bunch fibres are used as the cellulose source. The chemical approach gives rise to high efficiency in removing impurities and relatively low energy consumption during the pretreatment step. However, recovery of the chemicals and hazards to the environment should be considered before a large scale of cellulose nanocrystals isolation is to be suggested. The selection of the pretreatment method may also affect the cellulose nanocrystals' yield and properties during the isolation step that follows.

Amongst all the extraction methods that have been evaluated in this study, sulphuric acid hydrolysis could be the most desired method for the cellulose nanocrystals extraction from empty fruit bunches. Technically, sulphuric acid hydrolysis can produce cellulose nanocrystals having a width in the range of 1–3.5 nm (the finest cellulose nanocrystals obtainable from empty fruit bunches) while staying in stable suspensions due to the presence of sulfate ester group. The sulphuric acid hydrolysis method also involves the diffusion of acid into the amorphous region of the lignocellulosic materials and subsequent cleavage of the glycosidic bonds by the protonation of

glycosidic oxygen or cyclic oxygen. The addition of water in the following step can break down the glycosidic bonds effectively. Unlike phosphotungstic acid hydrolysis, extensive mechanical stirring would be required to enhance the contact between the acid and the pulp. Sulphuric acid hydrolysis also can produce cellulose nanocrystals with a higher crystallinity of 80.8% than hydrochloric acid hydrolysis (only 53–65 %) and ammonium persulfate hydrolysis (only 68–78%).

From the economic point of view, sulphuric acid hydrolysis could offer more advantages for the cellulose nanocrystals extraction from empty fruit bunches than other methods. Sulphuric acid hydrolysis requires a short reaction duration, which is approximately 40 to 100 min only. By comparison, hydrochloric acid hydrolysis, phosphotungstic acid hydrolysis, ionic liquid hydrolysis and ammonium persulfate hydrolysis requires a reaction duration of 2 h, 25 to 35 h, 4 h and 15 h, respectively. Sulphuric acid hydrolysis could be amongst the most cost-effective method by comparing with phosphotungstic acid hydrolysis, ionic liquid hydrolysis and ammonium persulfate hydrolysis, which involve the applications of expensive reagents during the cellulose nanocrystals extraction, cellulose nanocrystals purification, and reagent recovery processes.

From the environmental point of view, sulphuric acid hydrolysis could offer more advantages for the cellulose nanocrystals extraction from empty fruit bunches than other methods. Sulphuric acid hydrolysis is the least energy-intensive method because the reaction can be carried out at 45 °C by comparing with hydrochloric acid hydrolysis (80 °C), phosphotungstic acid hydrolysis (80 to 100 °C), ionic liquid hydrolysis (140 °C) and ammonium persulfate hydrolysis (70 °C). Sulphuric acid hydrolysis also has avoided the application of highly toxic chemicals, such as acetonitrile as required by ionic liquid hydrolysis, to recover the expensive reagent used in the hydrolysis process.

There are some research gaps have been identified in this study. Some methods to isolate cellulose nanocrystals from other raw materials, such as high-pressure homogenization and enzymatic hydrolysis, are not used to isolate cellulose nanocrystals from *Elaeis guineensis* empty fruit bunches. Such data, however, is vital for future comparison with the cellulose nanocrystals extraction from *Elaeis guineensis* empty fruit bunches using acid hydrolysis and ionic liquid method, as discussed.

Characteristics of cellulose nanocrystals extracted, such as relative abundance, compositions, and crystalline structure, can be analysed through the employment of advanced analytical instruments. Characteristics of cellulose nanocrystals extracted can be used to determine the usefulness of cellulose nanocrystals generated for its downstream applications. In order to study the properties of cellulose nanocrystals extracted from empty fruit bunches, various instrumental analyses have been successfully employed, such as XRD, FTIR, TEM, FESEM and DLS.

Given the potential economic production of cellulose nanocrystals from empty fruit bunches, efforts from researchers are significantly required further to enhance the yield and quality of cellulose nanocrystals. Modern analytical instruments can be used in assisting researchers to achieve this goal more efficiently.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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