



Cellulose processing from biomass and its derivatization into carboxymethylcellulose: A review

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ABSTRACT

Many physical, chemical, and/or enzymatic treatments have been used to open the structure of lignocellulosic biomass, separate its components and obtain cellulose. The alkaline-bleaching treatment is most preferred in terms of reagent availability. In terms of cellulose yield and quality, however, there are inconsistencies with the alkaline-bleaching treatment. Similarly, the optimum conditions for carboxymethylcellulose (CMC) synthesis from cellulose mercerization and etherification are vague. This review paper investigates and compares the various conditions applied in CMC synthesis and recommends efficient processes and optimal conditions for increasing CMC yield and quality. Recommended mercerization parameters are 25–30% (w/v) NaOH, 1–1.5 h and 25–28 °C. Recommended etherification parameters are 1.2 g chloroacetic acid (CAA) or sodium chloroacetate (SCA)/g cellulose, 3–3.5 h and 50–55 °C. The source material and extraction process determines the quality of the cellulose produced. Therefore, identifying the most efficient methods and underlying conditions for various cellulose sources is important.

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Introduction

Cellulose is a plant material composed of a long chain of at least 500 glucose molecules, thus, a polysaccharide [43,71]. Cellulose has gradually acquired the status of a basic necessity in the modern world. It is widely used in many industries including fiber and clothing, paper, veterinary food, cosmetic and pharmaceutical industries.

Cellulose making is a two-century old industry in the world. Anselme Payen, a French chemist, is said to have discovered cellulose in 1838 after isolating it from plant materials and determining its chemical formula [108]. It is usually obtained

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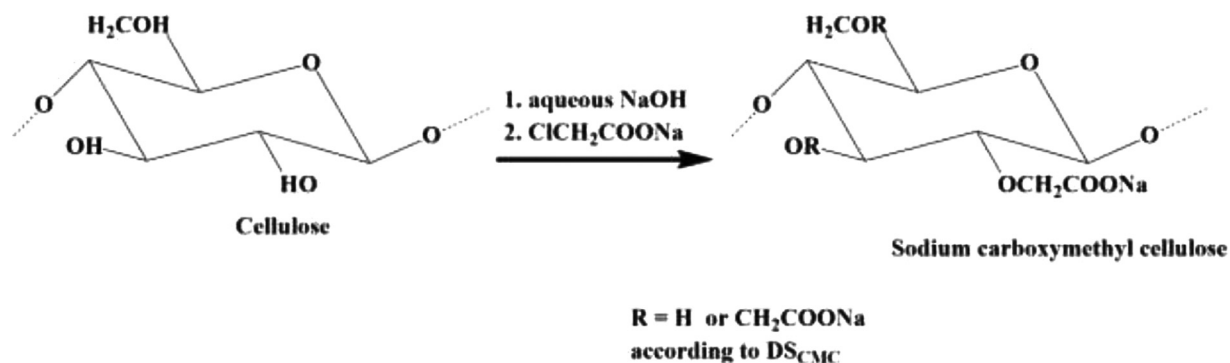


Fig. 1. Representation of the reaction scheme for the preparation of CMC.

through the physical, chemical, and/or enzymatic disintegration of plant material [94]. In plant material, cellulose is being enclosed by two main components: hemicellulose and lignin, which are amorphous [52],[48],[97].

A high percentage of cellulose can be found in agricultural residues such as palm bunch chaff, cocoa pods, plantain peels, banana leaves, maize cob, wood, sugar beet wastes, and many more. When these materials are mechanically reduced, the resultant fractions contain cellulose fibers, which when disintegrated provide crude cellulose [88]. Due to its large molecular weight and dense packing of the linear cellulose chains resulting in its crystalline form, cellulose is insoluble in water and has a poor ability to absorb water [24,94].

Recently, nanotechnology has provided opportunities to the development of a new class of materials known as nanomaterials. These are designed materials with at least one dimension in the 1–100 nm range that have unique physicochemical, optical, magnetic, and biological properties compared to bulk materials. Nanocellulose receives great attention due to its excellent characteristics such as nanoscale, non-toxicity, high mechanical strength/weight performance, high specific surface area, easy processing, large flexibility, good thermal stability, and desirable colloidal properties. They can be used in a variety of applications, including aerogels, catalyst and enzyme immobilization support, templates, liquid crystals, biomimetic materials, bio-imaging, biosensors, pharmaceutical binder, reinforcing polymer composites, low-calorie food additives, emulsion stabilizers, and energy storage [100,101].

There are several chemical modifications of cellulose based on the chemical reagents used and required properties. These cellulose derivatives may be classified into cellulose ethers or cellulose esters depending on the reagents. Carboxymethylcellulose (CMC), which is one of the derivatives of cellulose belongs to the class of cellulose ethers. As the name suggests, CMC is simply a cellulose derivative that is made up of the cellulose backbone comprising glucopyranose monomers and carboxymethyl groups attached to at least one hydroxyl groups of the cellulose [59,68]. It is generally prepared as an ionic compound, usually as sodium salt [36]. CMC is water soluble, unlike raw cellulose, and this is accomplished by adding ionic carboxymethyl groups to the cellulose chain, allowing the molecule to hydrate [16,81].

Throughout the 20th century, CMC has gained much recognition. Jasen was the first to prepare CMC in 1918 as a substitute for glue, tragacanth, agar-agar, gelatin and similar substances [38]. Soon afterwards, scientists discovered the use of CMC as thickening and film-forming agents [37]. In the early 1920s, CMC was manufactured at the IG Farbenindustrie AG (paint industry) in Germany [37]. Carboxymethylcellulose was first used in the 1940s as a fluid loss additive and bulk fluid viscofier [25].

The manufacturing of CMC involves two general reaction steps. The first is mercerization which involves reacting cellulose with an alkali in order to produce alkali-cellulose and water. The second is etherification which uses SCA or CAA to convert the alkali-cellulose into CMC [6,84,90,91]. The compound is synthesized by combining cellulose with SCA or CAA to generate a solid that is usually white to off-white in color, water-soluble, and odorless [16,81]. The reaction scheme for the preparation of CMC is shown in Fig. 1.

Carboxymethylcellulose has great importance to the modern industrial world and has many applications and scientifically proven benefits in the pharmaceutical, cosmetic, petroleum, lubricant, textile, adhesive, paper, detergent, ceramic and food industries. In a variety of products, including ice cream, the compound is employed as a viscosity modifier or thickening, as well as to stabilize emulsions. CMC is known for its excellent water retaining capacity [8,31]. It is good for stabilizing and plastering clay suspensions in drilling fluids, improving viscosity, limiting mud losses, and preserving suitable flow characteristics *in situ* [19,57].

Cellulose extraction from biomass has been a subject of intense research because of the great importance of cellulose in living organisms and the industry as well as of its high potential for accomplishing sustainable development goals and implementing industrial ecology principles [50]. In recent studies, cellulose is extracted from various plant materials including corn stover, sugarcane bagasse, cocoa pod husk, rice husk, coconut coir, soybean hulls, jute bast, banana leaves, oil palm residue and Ackee [1,15,51,60,77].

Conditioning of biomass, liberation of cellulose from ground fibers, and purification of cellulose are the three basic processes in the extraction of cellulose from lignocellulosic biomass. Water retting and mechanical size reduction treatment

are used to condition biomass, which is the first stage of the production process. Biomass is retted in water to remove dirt and pigment matter as well as soften lignin. Size reduction is done to enhance cellulose liberation [58]. Many different processes have been used to separate lignocellulosic biomass into its components- cellulose, hemicellulose and lignin [23,63]. These processes can be generally classified as physical (e.g. the ball-mill process), chemical (e.g. acid or alkaline pulping, solvents, ozone or peroxide bleaching) and physicochemical (e.g. steam explosion) processes [50,113]. Cellulose purification is achieved by bleaching to further remove lignin and hemicellulose [64].

In the Petroleum industry, there has been high demand for fluid-loss control agents such as CMC over the years. This is likely due to its impact on the rheological properties of water-based drilling fluids and the stability of clay suspensions, which helps to prevent water separation from suspensions and to improve surface or barrier properties [18,57].

Despite the fact that extensive research has been published on cellulose extraction and its use in the synthesis of CMC, little progress has been made on the processing procedure for producing good grade cellulose suitable for CMC manufacture. The purpose of this review paper is to present the advanced strategies for CMC synthesis from lignocellulosic biomass. Not only does the scope of the paper deal with a comprehensive discussion on the extraction and purification of cellulose, but it also provides insightful details of the synthesis and characterization of CMC. In addition, it gives an overview of the advantages, disadvantages and favorable conditions of the effective characterization methods for both cellulose and CMC compounds. The discussions in this paper include alkaline-bleaching treatment of cellulose fibers, cellulose characterization, mercerization and etherification of purified cellulose fibers (to form CMC), and CMC characterization.

Cellulose extraction

Cellulose extraction from lignocellulosic biomass can take different processes depending on the materials available, scale of production and quality of product [27,70]. The extraction methods of cellulose are discussed in the following sections.

Conditioning of biomass

Before the cellulose is extracted just upon reception, the biomass is thoroughly washed and sometimes scrubbed with short brushes. This is done either mechanically by a washer or manually by hand. They are then chopped to about 2 cm in length [58] and can be retted in distilled or deionized water with a solid to liquid ratio of 1:5 to 1:10 (w/v) (subject to density of solid). The retting is done to soften lignin and remove water-soluble products. In the first 6–8 h, much of the dirt and polar matter are removed by the water, after which the material is dried and ground to fine powder (say, millimeter level size). Screening can be done by separating particles into grades using size screens of choice [58]. For the subsequent alkali-bleaching treatment, the small size of finer fibers helps to increase the contact surface area between chemicals with active groups of cellulose fiber and even the rate of reaction.

Alkaline pretreatment

Although cellulose have been treated using a variety of treatment processes, cellulose obtained via alkaline treatment have been the primary focus of many researchers due to its advantages. The main advantages of alkaline treatment are: (a) the employment of relatively low temperatures and pressures than other pretreatment technologies, (b) in comparison with acid processes, alkaline processes cause less sugar degradation, and (c) many of the caustic salts can be recovered [52,54].

Alkaline hydrolysis is essentially a delignification process that also results in the solubilization of a considerable percentage of hemicellulose. The mechanism of this process is based on solvation and saponification, which induce depolymerization and cleavage of ester bonds cross-linking lignin and hemicellulose. The primary reactions that lead to the removal of lignin are the cleavage of α - and β - ether bonds in phenolic units and of β - ether linkages in nonphenolic units. Similarly, the hydrolysis of glycosidic bonds in hemicellulose releases the monomeric sugars and soluble oligomers from the fiber matrix into the hydrolysate. Typical reactions of lignin during alkaline pretreatment are shown in Fig. 2 (Supplementary data). Cellulose is extracted by exposing ground fibers to sodium hydroxide, which favorably and efficiently increases the accessibility of the cellulose [35]. The important modification done by alkaline treatment is the disruption of OH bonding in the fiber network structure by ionizing the hydroxyl groups of the various materials in the fibers to become alkoxide as shown in Eq. (1). This leads to the separation of the interfibrillar regions from the cellulose fibers. Even so, the detached cementing materials would be subjected to the alkali dissolution so that the bundles of cellulose fibrils can be separated with reducing cellulose fibers dimension [64].



The dissolution of non-cellulosic constituents in alkali creates voids in the fiber structure, resulting in significant swelling and changes in the physical structure, dimensions, morphology and mechanical properties [2,54,64].

The alkali treatment could be briefly categorized into two types of methods, which are alkali solution heating and alkali cooking by autoclave or digester. Alkali solution heating is carried out using a combination of relatively low temperature (70–90 °C) and mechanical stirring. However, cooking process or alkaline retting treatment of the fibers is done at high temperature (about 160 °C), high pressure (at the alkaline liquid autogenous vapor pressure) using chemicals such as alkaline sulfate and acid sulfite. These kind of treatment breaks or weakens the chemical bonds by chemical action to effectively

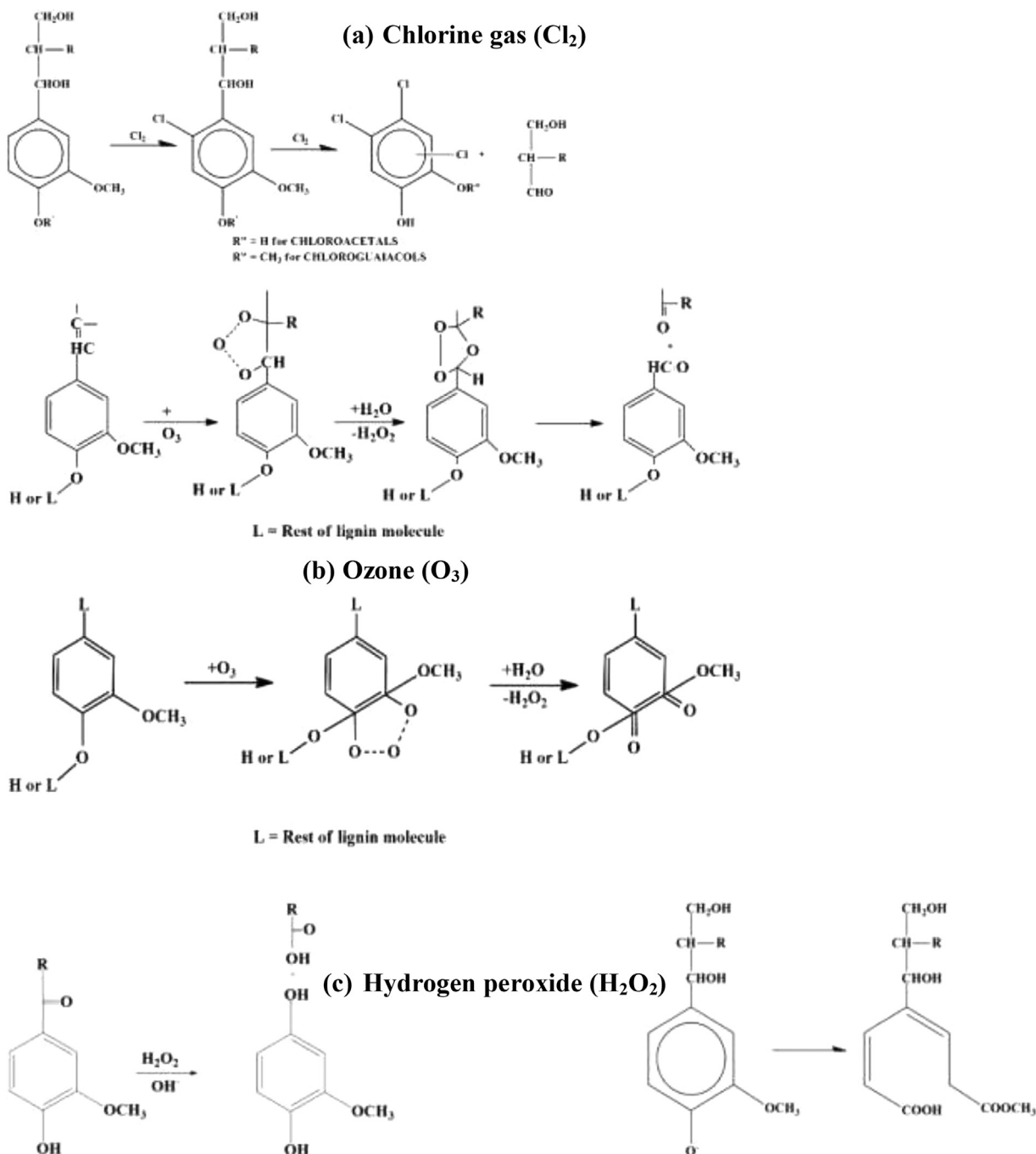


Fig. 2. Examples of reactions of bleaching agents with lignin: (a) Chlorine gas (Cl_2), (b) Ozone (O_3) and (c) Hydrogen peroxide (H_2O_2) [13,56].

degrade and dissolve lignin and hemicellulose. Simultaneously, a low-concentration anthraquinone solution (AQ), about 0.1% (w/v), is added to the alkali cooking liquor to enhance the delignification rate and also protect the cellulose fibers from alkali degradation, which is the so called end-wise degradation of cellulosic chains [64]. Paridah et al. [66] explored the characteristic potentials of alkaline sulfite anthraquinone and methanol (ASAM) pulping of bamboo culms (*Gigantochloa scorteichinii*). The studies revealed that at a constant ASAM pulping process at 170 °C, alkali ratio ($\text{Na}_2\text{SO}_3/\text{NaOH}$) of 80/20, 0.1% AQ and 15% (by vol) methanol, the optimum parameters were at 16% NaOH and 90 min cooking time.

Toğrul and Arslan [99] carried out an alkaline pretreatment of sugar beet pulp cellulose with 10% NaOH at 35 °C for 22 h, under agitation. In a study by Bacci et al. [10], different methods -chemical extraction, water retting, microbiological and enzymatic- were employed in the extraction of cellulose from nettle (*Urtica dioica*) stalks. The chemical retting consisted

Table 1
Alkali pretreatments (alkali solution heating) of cellulose fibers.

Source	Solution (% w/v) NaOH	Condition	^x Remark	Refs.
Cocoa pod husk	12	100 °C, 3 h	High temperature(65–70 °C)	[42]
Sugar beet pulp	10	35 °C, 22 h, continuous agitation	Long time (6–7 h)	[99]
<i>Eucalyptus grandis</i> wood chips	8	40 °C, 4 h	Low temperature (60 °C)	[105]
Palm kernel cake	7.5	Room temperature, 1 h, continuous agitation	Short time (4 h) and low temperature (60 °C)	[22]
Sugarcane bagasse	6	95 °C, 2 h, continuous agitation	Short time (2.5 h)	[109]
Newspaper	5	80 °C, 3 h	Good condition	[93]
Cocoa pod husk	2	80 °C, 5 h	Long time (3 h)	[112]
Cocoa pod husk	2	80 °C, 3 h	Good condition	[1]

^x Recommended operating condition based on the NaOH concentration is stated in bracket.

of a pretreatment with 0.35% sodium carbonate (Na_2CO_3) solution at 100 °C for 1 h, and a treatment with 2% NaOH at about 100 °C for 50 min [10]. This treatment produced higher cellulose (81.3%) fibers with lower lignin (2.2%) and hemicellulose (5.9%) content than the other methods. Rachtanapun and Rattanapanone [74] extracted cellulose from *Mimosa pigra* peels with 30% (w/v) NaOH at 100 °C for 3 h, resulting in a cellulose yield of $\approx 25\%$. The low cellulose yield could be attributed to high NaOH concentration and temperature. Hutomo et al. [42] performed caustic extractions of cocoa (*Theobroma cacao* L.) pod husk with 12% (w/v) NaOH at 100 °C for 3 h. Vena et al. [105] did an alkaline hemicellulose extraction of *Eucalyptus Grandis* wood chips in the ranges of 4–8% (w/v) NaOH, 2–4 h and 40–90 °C. They reported that wood chips yielding the best results was obtained with 8% (w/v) NaOH at 40 °C for 4 h. Hu et al. [40] extracted (crude) cellulose from argan press cake by a procedure involving alkaline treatment with 12 wt% NaOH and 8 wt% sodium sulfate (Na_2SO_4) solution at 80 °C for 90 min. This approach led to the extraction of cellulose with high purity, beyond 71%.

Jia et al. [46] conducted extraction of cellulose from corncob in the ranges of 20–70% NaOH at 170 °C and 0.7 MPa for 90 min. The results showed that the optimum concentration of NaOH was 50%. Rehman et al. [76] carried out an alkaline pulping of *Eucalyptus lenceolata* straw with 5% (w/v) NaOH at 35 °C and 2 atm for 30 min. Ye et al. [109] pretreated bagasse by an approach consisting of 6% NaOH at 95 °C for 2 h, increasing the cellulose content from 42.01% to 90.23%.

However, there are inaccurate and/or imprecise information with respect to the alkaline treatment of lignocellulosic biomass to obtain high yield cellulose with desired properties for various applications. Typical examples of alkali solution heating treatment of cellulose fibers have been listed in Table 1. After extraction, the resulting mixture is then subjected to filtration and the residue (pulp) is washed with large volume of deionized or distilled water until neutral pH is attained. Alternatively, acetic acid (96–99%) is used to neutralize the alkaline from the pulp, followed by using deionized water to wash the salt formed.

Modeling of alkaline pretreatment

The pretreatment employed strictly depends on the characteristics of the raw material as well as on the final purpose of the process itself (product application). The alkaline degradation chemistry and kinetics of cellulose have been studied in a number of research to understand and predict the relationship between alkaline pretreatment parameters and cellulose yield [29,32,89,92]. Vena et al. [105] reported a mathematical model that describes the xylan solubilization in the liquid fraction after extraction. They found that NaOH concentration has a high effect on xylan solubilization (and cellulose yield), followed by time and then temperature. High temperatures (> 140 °C) degrade cellulose.

In this review, the alkaline pretreatment mathematical model was obtained on the assumption that time is proportional to concentration but temperature is inversely proportional to concentration. Hence, a theoretical linear and logarithmic relationship to predict the alkaline hydrolysis time and temperature, respectively, based on the NaOH concentration was found to be represented by the following equations:

$$t(\text{h}) = 0.4369c + 0.7921 \quad (2)$$

$$T(^{\circ}\text{C}) = -54.87\ln(c) + 169.69 \quad (3)$$

In Eqs. (2) and (3), t is time, T is temperature and c is the concentration of NaOH (in% or g/100 ml) ≤ 20 .

Friebel et al. [32] carried out an alkaline extraction of beech wood sulfite pulp, which was delignified with oxygen in the ranges of 4–12% (w/v) NaOH and 20–80 °C. He reported that caustic extractions at about 80 °C with 60–80 g/L (1.5–2 M or 6–8%) NaOH were economically feasible, because pulp was obtained in good yield and an energetically moderate temperature profile was applied throughout the bleaching sequence. The dissolving pulp showed very good reactivity in viscose application tests, and its high purity makes it a promising candidate for further high-value products. Similarly, Taherdanak and Zilouei [92] reported that alkaline pretreatment of wheat plant at 75 °C with 80 g/L (2 M or 8%) NaOH significantly modified the wheat plant structure with an effective lignin and hemicelluloses removal. Therefore, the alkaline pretreatment mathematical model suggests that the optimum alkali solution heating parameters are in the ranges of 6–9% (w/v)

NaOH, 3.5–5 h and 46–76 °C, under mechanical stirring. This is due to lower fiber content, which might subject the cellulose fiber to chemical degradation and misuse of chemical reagents while excess fiber content might result in less efficiency of chemical treatment by reducing the effective reaction sites.

Cellulose purification (bleaching)

For the various purification techniques, cementing components that bind the fibril structure can be mostly removed to obtain cellulose-rich fibers or high purified cellulose fibers. In addition, purification of the cellulose fibers can clean the fiber surface, chemically modify the surface, stop the moisture absorption process, and increase the surface roughness [49]. Bleaching removes lignin and hemicellulose that was not removed during pretreatment, while maintaining the yield and integrity (strength) of the pulp fibers [64,95]. As lignin is a complex molecule with different types of linkages, chemical pulp bleaching (lignin-removing bleaching) is accomplished with various compounds containing chlorine or oxygen in several stages to break the various types of bonds within the lignin.

Bleaching chemicals can be divided into three groups according to their functions. The various groups of bleaching agents are: (a) Chlorine gas (Cl_2), Ozone (O_3) and Hydrogen peroxide (H_2O_2) (these react with the aromatic lignin units), (b) Chlorine dioxide (ClO_2) and Oxygen gas (O_2) (they react with lignin structures that have free phenolic hydroxyl groups) and (c) Hypochlorite (NaClO or $\text{Ca}(\text{ClO})_2$) and Hydrogen peroxide (H_2O_2) (they react with only certain functional groups such as α -carbonyls) ([13,56,86]). Typical reactions of bleaching agents with lignin are shown in Fig. 2.

Three chemical products are generally used to bleach cellulosic fibers - NaClO , sodium chlorite (NaClO_2) and H_2O_2 [17]. Many bleaching chemicals such as ClO_2 , Cl_2 , NaClO , and NaOH are reactive and hazardous to transport; they are produced on-site or nearby. Also, the use of hypochlorite in commercial pulp bleaching discontinues as it liberates organochlorine compounds and chloroform. Due to environmental concerns, chlorine-free agents have recently received more attention [40]. H_2O_2 and/or sodium dithionite or sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$) are cheap and safe (environmentally friendly) bleaching agents with their effectiveness dependent on the low content of lignin and extractives in wood species [9].

Hemicellulose bleaching stages are either acidic or alkaline treatments, the latter classified as cold caustic extraction (CCE) at temperatures of 25–45 °C and hot caustic extraction (HCE) at 70–120 °C. At higher temperatures, the treatments become rather nonspecific and lead to side reactions including acidic or alkaline cellulose degradation. Strong alkaline cellulose degradation, including hydrolysis begins only at temperatures exceeding 140 °C [32]. pH plays an essential role that brings about cellulose purification (bleaching). It controls the ions concentration of bleaching agent dissociated in water. These ions tend to react with cellulose fibers leading to cellulose purification and decolorization. Like other bleaching conditions, pH affects fiber properties (tensile and softness). Low pH levels cause fibers degradation; hence, reduce fiber strength [17]. The efficiency of peroxide bleaching can be affected substantially by pH. Under alkaline conditions, hydrogen peroxide is unstable and decomposes to produce reactive oxygen, which provides the bleaching effect. For the bleaching process, it is important to achieve the optimum degree of hydrogen peroxide stability, so that the full potential of the bleaching activity can be exploited [17,102]. In general, full brightness cannot be achieved in one bleaching process, instead several (three to seven) consecutive stages must be used to increase efficiency.

Typically, Cl_2 and O_2 are used at the first stage to remove lignin, followed by NaOH and sulfur dioxide (SO_2) to remove hemicellulose and then NaClO , ClO_2 , H_2O_2 , $\text{Na}_2\text{S}_2\text{O}_4$, and O_3 for brightening [13]. The essential part of bleaching is washing, for say 10 min, dissolving of lignin out of the pulp on the washer following the bleaching stage. For instance, washing with 95% ethanol, washing with distilled water and washing again with 95% ethanol, then drying at 60 °C in an oven until constant weight is achieved.

Bolio-López et al. [21] bleached cellulose fibers from Tó leaf petioles (*Calathea lutea*) with 3.5% NaClO , at 30 °C to pH 9.2, followed by 20% NaOH for 1 h, and finally 0.5% NaClO for 1 h, all under agitation. Hu et al. [40] purified crude cellulose from argan press cake in four bleaching stages, achieving 95% purity cellulose. The agent/condition used were: 1 wt% NaClO , solution pH about 12.55, at 45 °C for 1 h, followed by 2 wt% H_2O_2 , 0.5 wt% magnesium sulfate heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), and 3 wt% NaOH , pH about 12.8, at 60 °C for 1 h, and finally 1 wt% NaOH , and 0.5 wt% H_2O_2 , pH about 12.2, at 70 °C for 1.5 h. Zailani et al. [112] performed isolation of alpha-cellulose of cocoa (*Theobroma cacao* L.) pod husk with 50% H_2O_2 at 75 °C for 15 min and subsequently 12% w/v NaOH at 80 °C for 1 h. Bahrami et al. [11] extracted cellulose nanofibers from sugarcane bagasse fibers with a focus on the optimal design of ozone bleaching parameters in the ranges of 1–5 wt% pulp consistency, 1–6 h and 40–85 °C at 1.5 l/min air flow rate and 0.55 g/m³ ozone concentration. The results showed that the optimum conditions were 1 wt% pulp consistency, 2.5 h and 40 °C.

Rehman et al. [76] did a cellulose pulp bleaching of *Eucalyptus lanceolata* straw. The procedure involved totally chlorine free (TCF) treatment with 2% (v/v) H_2O_2 and 0.2% (w/v) ethylene diamine tetra-acetate (EDTA), pH 12, at 48 °C for 12 h, and then 80% (v/v) CH_3COOH and 65% (v/v) of HNO_3 at 120 °C for 30 min, both under agitation. Friebe et al. [32] extracted cellulose from beech wood sulfite pulp, which was delignified with oxygen. This was carried out with 10% consistency, pH 2.5, at 30 °C and 5 bar ozone, and subsequently 10% consistency, at 70 °C, 3 g NaOH and 3 g H_2O_2 per kg oven dried pulp. The test results proved the bleached pulp gave an overall yield of around 89.2%. The different performance of purification (bleaching) of cellulose fibers have been summarized in Table 2. The effect of NaClO_2 in acid treatment on pulp characteristics and nanocellulose yield have been described in a number of studies [17,32,61,83]. For instance, Ben Marzoug et al. [17] reported that the use of NaClO_2 must be in acidic conditions; however, cellulosic fibers are damaged in such conditions.

Table 2

Various purification (bleaching) of cellulose fibers.

Crude Cellulose	Agent/Condition	^x Remark	Refs.
Sugar beet	2% (w/v) NaCl, 10% CH ₃ COOH (acetic acid), 75 °C, 1 h	Short time (2 h)	[99]
Sago waste	0.94% (w/v) NaClO ₂ , Glacial acetic acid, 70 °C, 3 h	Low NaClO ₂ concentration (2%) and long time (2 h)	[72]
Sugar cane bagasse	2.52% (w/v) NaClO ₂ , Glacial acetic acid, 70 ± 5 °C, 1 h	Short time (2 h)	[82]
Cotton combing noil	0.3% (w/v) NaOH, 95 °C, 1 h	Low NaOH concentration (2%), high temperature (70 °C) and short time (1.5 h)	[96]
Palm kernel cake	0.26% H ₂ O ₂ , 0.4% (w/v) NaOH, 95 °C, 0.75 h	Good condition	[22]
Newspaper	2% (w/v) NaClO ₂ , Glacial acetic acid, 75 °C, 2 h	Good condition	[93]
Sugar cane bagasse	2.5% (w/v) NaClO ₂ , CH ₃ COOH, 80 °C	High NaOH concentration (2%), low temperature (70 °C) and long time (1.5 h)	[34]
Purun Tikus (<i>Eleocharis dulcis</i>)	1% H ₂ O ₂ , pH = 13.5, 55 °C, 3 h (Same amount of H ₂ O ₂ was added every 1 h)	Long time (2 h)	[90]
Agricultural wastes	4% (w/v) NaOH, 25 °C, 3 h	Low NaClO ₂ concentration (2%) and high temperature (70 °C)	[41]
Oil palm empty fruit bunch stalk	1.4% NaClO ₂ , pH = 3–4 (using CH ₃ COOH), 70 °C, 5 h	Low NaClO ₂ concentration (2%)	[65]
Baobab fruit shell	1% NaClO ₂ , CH ₃ COOH, 95 °C, 2h	Low temperature (70 °C)	[111]
<i>Posidonia oceanica</i> brown algae	0.7% NaClO ₂ , pH = 4 (with CH ₃ COOH), 70–80 °C, 2 h (5 times)	Short time (2 h)	[95]
	2% NaOH, Room temperature, 2 h (4 times)		
	2% NaClO ₂ , Room temperature, 2 h (4 times)		
	1.7% NaClO ₂ , pH = 3–4 (with CH ₃ COOH), 70 °C, 1 h (7 times)		

^x Recommended operating condition based on the NaClO₂ concentration is stated within bracket.

Based on the literature, the recommended NaClO₂ bleaching parameters should be in the ranges of 1.2–2.8% (w/v) NaClO₂, 1.5–2.5 h, 65–80 °C and 3–4 pH.

Process analysis

The purpose of the extraction is to enable the selective removal of lignin and hemicellulose, hence, isolating cellulose from plant materials. The best extraction method is one in which a maximum amount of lignin and hemicellulose is removed while simultaneously the yield and quality of the pulp is maintained. A dissolving pulp is a type of pulp that has high cellulose content (>90%), high purity, brightness, cellulose reactivity, and a uniform molecular weight distribution [12]. Therefore, the efficiency and yield of the extraction procedure must be determined, thus, the elimination of certain substances or the attack on fibers. High extraction yield indicates that the method is capable of eliminating other substances which are different from the cellulose.

When is further purification, such as soxhlet extraction, required? Soxhlet extraction may remove fat, wax, pectin, cutin and other non-aqueous extracts [26]. Some applications may need these and other byproducts removed to improve efficiency and reproducibility of product. There are already standard methods for determination of the contents -aqueous and non-aqueous extracts, moisture, lignin, cellulose and hemicellulose in samples. Some of these include laboratory analytical procedure offered by Association of Official Analytical Chemists (AOAC), Technical Association of the Pulp and Paper Industry (TAPPI), National Renewable Energy Laboratory (NREL), etc. [44,82,87,103,110]. Unfortunately, many scientists, for various reasons, do not experimentally determine chemical composition of raw material but refer to literature data or values, which has major effect on the cellulose yield. Also, the chemical composition of product after extraction and purification (processed biomass) should be checked to evaluate the effectiveness of cellulose extraction. Therefore, a lot of research works need to be done to review existing standard methods and/or develop quick, easy to use, and cost-effective protocols to determine the contents of solid biomass samples. The lignin (L) and hemicellulose (H) removal and cellulose recovery/yield is calculated as shown in the following equations:

In terms of mass composition;

$$L \text{ (or H) removal (\%)} = 100 - \left(\frac{L \text{ (or H) content in product (g)}}{L \text{ (or H) content in raw biomass (g)}} \times 100 \right) \quad (4)$$

$$\text{Cellulose recovery/yield (\%)} = \frac{\text{Cellulose content in product (g)}}{\text{Cellulose content in raw biomass (g)}} \times 100 \quad (5)$$

In terms of percentage composition;

$$L \text{ (or H) removal (\%)} = 100 - \left(\frac{L \text{ (or H) content in product (\%)}}{L \text{ (or H) content in raw biomass (\%)}} \times y_p \right) \quad (6)$$

$$\text{Cellulose recovery/yield (\%)} = \frac{\text{Cellulose content in product (\%)}}{\text{Cellulose content in raw biomass (\%)}} \times y_p \quad (7)$$

$$\text{Product yield, } y_p (\%) = \frac{\text{Mass of product (g)}}{\text{Mass of raw biomass (g)}} \times 100 \quad (8)$$

Cellulose characterization

The extraction treatments, purification conditions, and diversity of cellulose starting material influences the properties and behavior of product and hence the need for characterization before utilization [4,78,100]. Characterization of cellulose includes examination of physical, chemical and thermal properties as well as morphology. The following characterization methods are usually carried out on cellulose.

Fourier Transform-Infrared Spectroscopy (FTIR)- For identification and determination of the major chemical functional groups in lignin- hydroxyl (including aliphatic and phenolic), methoxyl, carbonyl and carboxyl groups. These are important structural characteristics of lignin which determine its optical properties, dispersion characteristics, and chemical reactivity [69]. FTIR spectra reflect the chemical structure of lignin. Common features and particular vibrations, specific to each lignin, are found in the spectra [73].

Scanning Electron Microscope (SEM)- For visualization and microstructural analysis on fiber and observation on the effect of the purification method in the removal of pectins, hemicelluloses, lignin and ash [28,55,80]. SEM is used to visualize the formation of lignin droplets at the fiber surface (i.e. area less than 20 μm in width) using high magnifications of 2700X or more as well as the separation of bundle fibers to individualize elementary fiber (i.e. area greater than 50 μm in width) using low magnifications of 950X or less.

Atomic Force Microscopy (AFM)- For dimensions and morphology analysis. It gives detailed true particle shape, dimensions, and size distribution/orientation. A significant portion of particle behavior can be attributed to particle shape and morphology [30,45].

Thermogravimetric Analysis (TGA)- For determination of the thermal stability of the cellulose material and its fraction of volatile components and change in mass as function of temperature [75]. The decomposition of lignin, hemicellulose and cellulose are at different temperature owing to the variations in their chemical structures. The thermal degradation of lignin is extremely slow with temperature ranging under 200 $^{\circ}\text{C}$ to above 700 $^{\circ}\text{C}$. However, hemicellulose thermal degradation is low, with temperature starting at 220 $^{\circ}\text{C}$ up to 315 $^{\circ}\text{C}$, due to the presence of acetyl groups. Cellulose thermal degradation is with temperature ranging at 315 $^{\circ}\text{C}$ to 400 $^{\circ}\text{C}$. Therefore, hemicellulose decomposes before cellulose and lignin hence, the low thermal stability of fibrous material [62,64].

X-Ray Diffraction (XRD)- For assessment of the treatments on fiber crystallinity and determination of the crystallinity index (CI), thus, the elimination of certain substances or the attack on fibers. High CI indicates that the method is capable of eliminating other substances which are different from the cellulose [3]. It is calculated using Equation 10 given by Nelson and O'Connor (1964),

$$\% I_C = \left[\frac{I_{(002)} - I_{am}/I_{(002)}}{I_{(002)}} \right] \times 100 \quad (9)$$

where $I_{(002)}$ is the Bragg peak height (Crystalline peak intensity at a 2θ angle close to 22°) and $I_{(am)}$ is the height for the amorphous background (Minimum peak intensity at a 2θ angle close to 16°). Empirically, these diffraction peak heights allow determining crystallinity. Degree of polarization is a measure of fiber damage [107].

Transmission Electron Microscopy (TEM)- For morphological analysis- Size, shape and structure determination. It has similar application as AFM. It offers the largest throughput, and is most desirable for rapid characterization of a large number of nanoparticles. TEM is capable of adequately characterizing nanoparticles having sizes between 10 nm and 1 μm [7,106].

Differential Scanning Calorimetry (DSC)- For measurement of enthalpy (heat flow) changes in a sample (liquid) due to a chemical process as a function of temperature or time. It is used in conjunction with differential thermal analysis (DTA) [33,79].

Dynamic Light Scattering (DLS)- For particle shape, dimensions, and size distribution profile. It has similar application as AFM or TEM but gives less detailed true profile to AFM or TEM. Nonetheless, DLS is an effective tool for measuring relative particle sizes and colloidal stability (i.e. the state of dispersion of particles) [7].

For the majority of applications, FTIR, TGA, XRD and microscopy (AFM or TEM with SEM), to characterize the physical and chemical properties of cellulose are recommended. These characterization methods with their recommended operating conditions, where applicable, have been summarized in Table 3.

CMC synthesis

Cellulose is swollen in a mixture of sodium hydroxide, about 15–50% (w/v) aqueous solution and an organic solvent (normally an alcohol, e.g. isopropanol), under vigorous stirring. By weakening the hydrogen bonds inside the cellulose crystallites, the alkali promotes or initiates the chemical process, making the individual polymer chains available for uniform chemical change. It also increases the nucleophilicity of the cellulose hydroxyl groups. The organic solvent functions as a

Table 3

Recommended operating conditions of various characterization methods.

CHARACTERIZATION METHODS	RECOMMENDED OPERATING CONDITIONS
FTIR	100:1 KBr to sample ratio (by weight); 4 cm ⁻¹ resolution; 4000–400 cm ⁻¹ spectral range; 64 (or 32) scans
SEM	1 (or 0.01%) suspension sample; 10 kV accelerating voltage; 100X (500 μm) - 10000X (5 μm) magnifications
AFM	0.01% suspension sample; 100000X (1000 nm) - 1000000X (100 nm) magnifications; tapping mode
TGA	5–10 mg sample weight; ambient - <1000 °C temperature range; 10 °C/min heating rate; 50 ml/min flow rate of N ₂ (N ₂ atmosphere prevents any thermo-oxidative degradation)
XRD	1.54 Å CuKα radiation; 40–45 kV voltage; 30–40 mA current; 0–40 ° 2θ range using a scan rate of 0.5–2 °/min

Table 4

Various synthesis of CMC.

Source of cellulose fibers	Agent/Condition	Degree of substitution (DS)	Refs.
Sugar beet	30% NaOH, Isobutyl, 25 °C, 1.5 h.	0.667	[99]
Sago waste	SCA, 70 °C, 6 h, continuous agitation		
	25% (v/v) NaOH, Isopropanol, 1 h.	0.821	[72]
Palm kernel	SCA, 45 °C, 3 h, continuous agitation		
	17.5% NaOH, Isopropanol, 30 °C, 1 h.	0.67	[22]
Cocoa pod husk	SCA, 50 °C, 2 h, continuous agitation		
	15% NaOH, Isopropanol, 25/30 °C, 1 h.	0.75	[42]
<i>Picea abies</i>	SCA, 55.93 °C, 3 h, continuous agitation		
	27.5% NaOH, Isopropanol, 20 °C, 1 h.	1.03	[6]
Corn husk	SCA, 60 °C, 1.5 h, continuous agitation		
Sugarcane bagasse	30% NaOH, C ₂ H ₅ OH, CAA, 55 °C, 3.5 h, c	2.41	[110]
	28.4% (w/v) NaOH, Isopropanol, 25 °C, 1.5 h.	1.085	[34]
	SCA, 57.85 °C, 4.01 h, continuous agitation		
Purun tikus	20% (w/v) NaOH, Isopropanol, Room temperature, 1 h.	0.2	[90]
	CAA, 55 °C, 3 h, continuous agitation		
Various agricultural waste	20% NaOH, Isopropanol, 50 °C, 1 h.	–	[41]
	SCA, 60 °C, 3 h, continuous agitation		
Oil palm empty fruit bunch stalk	30% (v/v) NaOH, Isopropanol, Room temperature, 1 h.	–	[65]
	SCA, 45 °C, 3 h, continuous agitation		
Sugarcane bagasse	5% NaOH, C ₂ H ₅ OH, 31.2 °C, 2 h.	–	[109]
	CAA, 57 °C, 2.4 h, continuous agitation		
Baobab fruit shell	35% NaOH, Isopropanol, Room temperature, 0.5 h.	0.94	[111]
	CAA, Room temperature, 0.5 h, then 55 °C, 3 h, continuous agitation		

diluent for effective polymer and alkali dispersal, heat transfer during the reaction, and acceleration of reaction product recovery [5,84,104]. Carboxymethylation of cellulose is achieved by slowly adding chloroacetic acid (CAA) or sodium chloroacetate (SCA) to the resultant solution while stirring continuously [53,67]. Normally, the alkylation agent hydrolyses causing reagent loss and formation of by-products. The reaction schemes during CMC synthesis are shown in Fig. SM2 (Supplementary data). The performances of the reactions under drastic reaction conditions (higher temperature, NaOH and SCA/CAA concentration) lead to more degradation of polymer chains and formation of side reaction products. At higher concentrations (>20%) of alkali, NaOH reacts with CAA or SCA to form sodium glycolate (HOCH₂COONa), resulting in the inactivation of the CAA or SCA and its consumption by the side reaction [72,84,90].

However, modification of the reaction conditions -the reactivity of the alkylating reagent, the amount of water, and addition of catalyst- can be used to sufficiently contain the side reactions, hence increase CMC characteristics and yield [36,110]. A number of research have examined the effects of chemical reagent concentration, duration, and temperature on CMC characteristics such as purity, viscosity, and water solubility [5,20,84,85,104]. Rachtanapun and Rattanapanone [74] investigated the effect of reaction temperature (30–60 °C) on the viscosity of CMC from *Mimosa pigra* peel cellulose. The viscosity of CMC decreased as temperature increased. The reason for this observation was that increasing temperature of a CMC solution reduces the cohesive forces while alongside increasing the rate of molecular interchange. Saputra et al. [84] submitted that slowly adding NaOH and SCA to the mixture while stirring at high speeds promotes the main reaction, resulting in less formation of byproducts such as sodium glycolate and less reagents misuse. At constant temperature, Alizadeh Asl et al. [5] discovered that the viscosity of CMC made from sugarcane bagasse cellulose increased with increasing NaOH concentration (20% to 30%). The reason for this observation was that greater DS causes the presence of greater hydrophilic groups in polymer structure which gives the polymer more ability to immobilize water in the aqueous system. Also, Youssif and Hassan [111] provided that the viscosity of CMC increased as the degree of substitution (DS) increased.

The subject of side reactions in CMC synthesis is of continuing interest in recent years, hence more exploration and exploitation using scientific models is needed at the present time. According to literature, the different performances of the synthesis of CMC have been summarized in Table 4. An essential part of CMC synthesis is purification. After the product has been filtered or decanted, the residue, for instance, is washed with absolute methanol, followed by a 70% ethanol solution,

and then washed again with absolute methanol. Washing is performed for several minutes under stirring in order to dissolve undesired products (e.g. NaCl). CMC is dried at 60 °C in oven until constant weight.

Degree of substitution is a key property affecting physical and chemical properties of CMC for many applications. Although the maximum theoretical value of substitution is 3, Holtzaple [39] reported that this value reached up to 1.4 for commercially available ones. CMC with DS less than 0.4 was insoluble. It was discovered that the DS increases significantly with temperature and time; however, the effect of time on DS is greater than that of temperature [98]. Pushpamalar et al. [72] reported that CMC synthesis from sago waste cellulose yielded a maximum DS of 0.768 when the cellulose to SCA ratio was 1:1.2 (g/g). Hutomo et al. [42] worked on the synthesis and characterization of CMC from cocoa (*Theobroma cacao* L.) pod husk cellulose. They reported that increasing the concentration of NaOH (11.59–28.41%) had a greater impact on DS than increasing the temperature (41–63 °C) or SCA (0.636–1.336 g/g cellulose). Yeasmin and Mondal [110] determined the optimized etherification parameters in the ranges of 20–40% (w/v) NaOH, 55–180% (w/v) CAA, 35–70 °C, and 1–5.5 h. The results provided that 30% (w/v) NaOH, 120% (w/v) CAA, 55 °C, and 3.5 h allowed to prepare CMC from corn husk cellulose with high DS and yield. Similarly, Joshi et al. [47] studied the effect of temperature and reaction time on etherification with respect to DS of CMC in the ranges of 40–70 °C, and 1–4 h, respectively. They reported that office waster paper yielding the best results, DS of 1.07, was obtained at 50 °C for 3 h with 0.376% (w/v) NaOH and 1.2582% (w/v) SCA. Due to the degradation of CMC under the influence of atmospheric oxygen, the DS value decreased with further increase in reaction temperature, which is in good agreement with those described in literature. Long reaction time improves diffusion and absorption of the reagents with the ultimate effect of improving contact between the etherifying agents and cellulose [72,110].

Golbaghi et al. [34] carried out a CMC production from sugarcane bagasse cellulose in the ranges of 10–40% (w/v) NaOH, 0.5–1.5 g SCA/g cellulose, 30–70 °C, and 1–6 h. The results provided that cellulose conversion to CMC at 28.4% NaOH, 1.14 g SCA/g cellulose, 57.85 °C, and 4.01 h obtained a maximum DS of 1.085. Alizadeh Asl et al. [5] worked on the synthesis and characterization of CMC from sugarcane bagasse cellulose and reported that the DS value decreased above 30%NaOH concentration. The reason for this observation was that the undesired side reaction happened which dominated the production. In this review, the recommended mercerization (or alkalinization) parameters are in the ranges of 25–30% (w/v) NaOH, 1–1.5 h, 25–28 °C, 1:20 (g/ml) cellulose to alcohol ratio and 1:4–5 (g/ml) cellulose to aqueous NaOH solution ratio. Isopropanol (C₃H₇OH) is the best alcohol of choice [72]. Similarly, the recommended etherification (or carboxymethylation) parameters are in the ranges of 1:1.2 (g/g) cellulose to SCA/CAA ratio, 3–3.5 h and 50–55 °C. This is due to lower fiber content, which might subject the cellulose fiber to the chemical degradation and misuse of chemical reagents while excess fiber content might result in less efficiency of chemical treatment by reducing the effective reaction sites.

CMC characterization

The ideality of CMC for a wide range of applications is based on its properties satisfying all general and/or specific regulatory requirements or meeting standards. CMC is divided into a variety of grades depending on the degree of purity, DS and intrinsic viscosity. A high quality or performance CMC is a CMC grade that has high purity (>90%), high DS (>0.88) and forms viscous solution with water completely but insoluble in ethanol. Depending on the purity, CMC is in the appearance of white or yellowish powder and soluble in cold and hot water. Ensuring white to off-white powder with no smell and taste is highly recommended. The average DS of carboxyl groups is a quantity which measures the average amount of substituted hydroxyl groups in an anhydroglucose unit by carboxymethyl. Hence, the higher the DS value of CMC is, the better the compatibility with salts will be. Solubility of CMC depends on the degree of polarization (DP) as well as the DS and the uniformity of the substitution distribution. Water solubility of CMC would increase with decreased DP and increased carboxymethyl substitution and substitution uniformity. DS, the distribution of carboxyl substituents along the polymer chains, and molecular weight are all important aspects in the many properties of CMC [53,67]. The viscosity of the CMC solution increases with increasing DP and increasing CMC concentration [14,47].

CMC reaction conditions, reactivity and amount of chemical reagents, and source of cellulose fibers influences the properties and behavior of product and hence the need for characterization before utilization [47,74,84]. FTIR, XRD, SEM, and TGA are various characterization methods used to examine the physicochemical and rheological properties, as well as morphology, of CMC. Other characterization methods also carried out on CMC includes water retention capacity, bulk density, colloidal stability, moisture content, molecular weight, foam formability, hygroscopicity, etc. There are already standard methods for the determination of properties and behavior of CMC. Some of these include laboratory analytical procedure offered by Association of Official Analytical Chemists (AOAC), American Society for Testing and Materials (ASTM) International, Codex Alimentarius Commission, American and European Pharmacopeia, etc. [5,22,34,65,110]. The results of CMC characteristics help improves product quality by altering its synthesis conditions. Various purity levels are applied in many areas of industry and human life. Typical applications of different CMC quality have been listed in Table SM1 (Supplementary data). Therefore, CMC products should be inspected or checked and tested by the various characterization methods and formula such that users can have a known and verified starting material prior to utilization.

Summary

Cellulose extraction and purification and its utilization as a raw material for CMC synthesis was discussed. The alkaline-bleaching treatment is extensively discussed for the extraction and purification of cellulose fibers. This comprises develop-

ing a theoretical relationship based on the NaOH concentration to estimate alkaline hydrolysis duration and temperature, as well as determining the stages to obtain dissolving pulp -high yield cellulose with desirable properties for diverse applications. The concentration of NaOH has the greatest impact on xylan solubilization (and cellulose production), followed by the length of alkaline hydrolysis and finally the temperature. Therefore, the optimum alkali solution heating parameters are in the ranges of 6–9% (w/v) NaOH, 3.5–5 h and 46–76 °C, under mechanical stirring. Also, based on the literature, the recommended NaClO₂ bleaching parameters should be in the ranges of 1.2–2.8% (w/v) NaClO₂, 1.5–2.5 h, 65–80 °C and 3–4 pH. Chemical composition analysis aids in assessing the efficacy of extraction methods. Extraction method with high lignin-hemicellulose removal and cellulose yield is good. Furthermore, the characterization methods of cellulose for diverse applications are described, with the recommended operating conditions for the feasible characterization methods -FTIR, TGA, XRD and microscopy (AFM or TEM with SEM) outlined. To ensure reliable test findings and therefore increase quality assurance, researchers should pay more attention to these methodologies and their recommended operating parameters.

For the synthesis of CMC, the mercerization and etherification processes of cellulose are the main methods involved in obtaining the CMC, despite side reaction challenges. More polymer chains are degraded and side reaction products are formed when cellulose reactions are performed under drastic conditions (higher reagents concentration and temperature). However, modification of the reaction conditions -the reactivity of the alkylating reagent, the amount of water, and addition of catalyst- can be used to sufficiently contain the side reactions, hence increase CMC characteristics and yield. Various characterization methods of CMC are summarized in this review. In this process, the general and/or specific standards for all CMC grades, independent of its application, are available to ensure that the physicochemical and rheological properties are known and verified before utilization. However, there are still some areas that need to be well-understood. Chemical composition analysis of solid biomass samples, for example, is inefficient and time-consuming, as well as a waste of energy and chemical reagents. As a result, more research is needed to make sure that the cellulose yield and purity of solid biomass samples can be easily validated. Existing standard procedures should be evaluated, or quick, easy-to-use, and cost-effective protocols should be established to determine the composition of solid biomass samples. Furthermore, more research utilizing scientific models should be focused on exploring and leveraging the subject of side reactions in CMC synthesis in order to reduce by-products and then increase the quality, yield and stability of CMC. Finding optimal purification parameters for both cellulose and CMC compounds to reduce chemical reagent usage will be critical for long-term sustainability and cost-effectiveness.

Conclusion

Cellulose is an earth abundant polymer usually derived from the disintegration of plant material or produced by the action of bacteria. It is obtained from lignocellulosic biomass that has been processed to open the structure of the cellulose source and make its microstructure more accessible. To separate lignocellulosic biomass into its constituents -cellulose, hemicellulose, and lignin-, a variety of physical, chemical, and/or enzymatic techniques have been used. Among the various purification methods, the alkaline-bleaching treatment is the most preferentially classical chemical process of cellulose fibers due to the availability of the bleaching reagents (NaOH/KOH, NaClO₂ and CH₃COOH) everywhere under the limited conditions. Carboxymethylcellulose (CMC) is a cellulose derivative that consists of the cellulose backbone made up of glucopyranose monomers and their hydroxyl groups bound to carboxymethyl moieties. Although significant research works have been published on cellulose extraction and its application in the synthesis of CMC, very little progress has been achieved in the processing procedure for producing high-quality cellulose suitable for CMC production. The goal of this review paper is to describe innovative methodologies for CMC production from lignocellulosic biomass. The recommended mercerization (or alkalization) parameters are in the ranges of 25–30% (w/v) NaOH, 1–1.5 h, 25–28 °C, 1:20 (g/ml) cellulose to alcohol ratio and 1:4–5 (g/ml) cellulose to aqueous NaOH solution ratio. The recommended etherification (or carboxymethylation) parameters are in the ranges of 1:1.2 (g/g) cellulose to SCA/CAA ratio, 3–3.5 h and 50–55 °C. More research utilizing scientific models should be focused on exploring and leveraging the subject of side reactions in CMC synthesis in order to reduce by-products and then increase the quality, yield and stability of CMC. The physical and mechanical qualities of both cellulose and CMC compounds are typically determined by the cellulose source and the extraction method used. Since these compounds are characterized to ensure that their performances are consistent before use, we considered the effective and efficient characterization methods and conditions that should be employed.

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Declaration of Competing Interest

The authors have no conflict of interest to declare.

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Supplementary materials

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