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Nanoparticle technology for separation of cellulose, hemicellulose and lignin nanoparticles from lignocellulose biomass: A short review

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ABSTRACT

This article addresses particle size reduction technologies currently available and their potential application in bioenergy production from waste biomass. It is believed the reduction of the particle size of biomass wastes to nano-scale will have a significant impact on the quality, quantity, and price of biofuels. Currently, these technologies have not been developed for commercial application due to lack of efficiency. They can only function on small scale operations with high energy consumption. Advancing particle size reduction technologies to produce nano-scale particles at a commercial level is an emerging need.

1. Introduction

Using biomass wastes for bio-energy production is expensive and requires different pre-treatment processes. Before fermentation, many of the following steps are required: milling, thermal, chemical, hydrolysis and/or irradiation pre-treatments. The main aim of the pre-treatment is to remove the lignin and hemicellulose, reduce cellulose crystalline, increase porosity and increase the internal surface area to alter the macroscopic structure into microscopic size [1]. The final stage, cellulose hydrolysis, is carried out using a cellulase enzyme, which converts cellulose to sugars. The major challenge for biofuel production is the inefficiency of separation lignin and cellulose biomolecules [2]. In addition, there are other challenges such as the formation of by-products that inhibit the fermentation process, large use of chemicals, high energy consumption, and considerable waste production [3]. Pre-treatment is one of the most expensive and least technologically mature steps in converting biomass to fermentable sugars [4]. In general, celluloses (crystalline) shows resistance toward fermentation as it has strong hydrogen bonds between cellulose molecules [5]. Therefore, the biofuel conversion efficiency of lignocellulose biomass largely depends on the capacity to break down the hydrogen bonds [6]. One way to improve biofuel production efficiency is through reducing the particle size of the biomass to micron-scale (mechanical milling) to create an adequate surface area for enzymatic hydrolysis [7].

This article presents and discusses the following hypothesis, reducing the particle size of biomass wastes to nano-scale using mechanical aid is the future of biofuel production from biomass. In addition, lignin, cellulose, and hemicellulose can be separated more efficiently at the nano-scale level. Biomass nanoparticles can be used directly in the fermentation processes. The fermentation process will not require neither enzymatic hydrolysis nor the expensive lignocellulose pre-treatment steps.

2. Lignocellulose biomass recalcitrance

Lignocellulosic biomass is the most abundant biopolymer in nature. The estimated annual lignocellulose biomass production is about 1.3×10^{10} metric tons. Therefore, its fractionation into reactive intermediates such as cellulose, hemicellulose, and lignin is important for the development of liquid fuels, chemicals, and other end products [8]. The lignocellulosic biomass structure is resistant to microbial or enzymatic degradation due to the presence of cross-links between cellulose and hemicellulose with lignin via ester and ether linkages which is known to be biomass recalcitrance [9].

3. Nanoparticle formulating processes

It has been well established that reducing the particle size of poorly water-soluble material will increase its surface area and improve its dissolution rate [10]. Nanoparticle formulating processes have been developed for the number of applications, including the pharmaceutical industry, to improve drug solubility [11]. The solubility increases significantly in reducing particle size below 0.5 μm in radius [12]. Another method, bio-milling, has been developed and capable of formulating nanoparticles that are

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less than 10 nm in size at ambient conditions. For example, Uddin et al. [13] developed nanoparticles using fungus *Saccharomyces cerevisiae* against the aqueous solution of Gd_2O_3.

It has been suggested that nanocellulose can be made, it is less expensive and safer to manufacture compared to synthetic nanoparticles [14]. Acid hydrolysis treatment [15]; high-pressure homogenizer[16]; enzyme assisted hydrolysis [17]; catalyzed oxidation [18] and ultrasonication technique [19] have also been used to create cellulose nanoparticles. However, methodology varied depending upon the type of raw material. Ball milling techniques have also been employed in dry and wet conditions. It helps to increase the amorphous content of cellulose and transform cellulose I to cellulose II and noncrystalline cellulose [6].

Cellulose is acquired once hemicellulose, lignin and other impurities are removed from the lignocellulose. Nanocellulose can be formulated from the natural cellulose with at least one dimension in the range of 1–100 nm. According to the dimensions, morphology, functions, and extraction methods, nanocellulose categorized into three key subgroups: cellulose nanofibers (CNF), cellulose nanocrystals (CNC), and microbial cellulose (BC) [20]. The extraction of nanocellulose from lignocellulose can be achieved by chemical, mechanical and enzymatic treatments.

3.1. Mechanical techniques

The mechanical methods can extract CNF from the primary and secondary cell walls, devoid of harshly degrading cellulose. Mechanical techniques involve high-pressure homogenization (HPH) [16], microfluidization [21], grinding [22], cryocrushing [23], high-intensity ultrasonication [19] and steam explosion [24]. The type of mechanical technique and level of applied mechanical force determine the degree of interfibrillar hydrogen bonding broken [25]. Mechanical techniques comes with high production costs for tools and materials and consume more energy than chemical techniques [26]. Therefore, chemical pretreatments are carried out before mechanical fibrillation agreeing to the processing and raw material [27], enhancing the reactivity of the cellulose fibers.

HPH is a commonly used technique for the extraction of CNF. In this process, cellulose slurry is passed under high pressure into a vessel through a small nozzle [28]. The resulting shear and impact forces on the fluid which reduces the size of the fibers to the nanoscale dimension. HPH is a simple effective nanoparticle separation technique, does not use organic solvents [29]. The main drawbacks of HPH technique are clogging problems, high energy intake and mechanical destruction to the crystalline structure of CNF [22]. Therefore various pretreatments are carried out before the use of HPH technique.

Microfluidization is another technique utilized to make CNF. A Microfluidizer consists of an intensifier pump to accelerate the slurry under high pressure into the interaction chamber. This technique defibrillates the fibers to nanoscale dimensions using a high shear rate and impact forces against colliding streams and channel walls [30]. These nanoparticles have uniform dimensions less than 100 nm. However, this process consumes high energy [21], pretreatments have been suggested to reduce energy consumption.

Grinding is another technique used to produce nanocellulose fibers. In this process, cellulose fiber is passed between static upper grinding stone and rotating lower grinding stone. The generated shearing forces breaking down the cell wall structure and fibers are individualized to nanofibers [31]. The degree of fibrillation determined by the distance between the grinding stones, morphology of the grinding stones and cycling number through a grinder [22]. Yet, the use of this technique mechanically damages the fibers [32].

Cryocrushing is a technique for mechanical fibrillation of frozen cellulose. In this process, water-swollen fibers are dipped in liquid nitrogen, subsequently crush with high impact and shear forces [21]. This leads to the liberation of nanofibrils with a diameter extending from 30 to 80 nm [23].

High-intensity ultrasonication (HIUS) is a mechanical technique that uses oscillating power to isolate cellulose fibrils by hydrodynamic forces of ultrasound [22]. During the process, cavitation leads to a formation of powerful oscillating high intensive waves. Once water molecules absorb this ultrasonic energy, microscopic gas bubbles are formed, expanded, imploded and breaking down cellulose fibers [20].

Steam explosion is a thermo mechanical process for the extraction of CNF. In this technique pulp is exposed to high-pressure steam for short time periods, followed by a sudden release of pressure, generating shear forces to the formation of CNFs. The steam explosion has significantly lower environmental impact since it uses fewer hazardous chemicals and consumes low energy [24].

3.2. Electrospinning

Electrospinning is a nanocellulose separation method, uses electrical force rather than mechanical force. Here, nanofibers are extracted from cellulose dispersion under high electric field. This is a simple and low-cost method. Nanofiber diameter and morphology depend on the electrospinning process, solution process rate, applied electric field, distance from the tip-to collector, and collector type [33].

3.3. Cellulose nanocrystals separation by acid hydrolysis

CNCs are the crystal-line area of cellulose and shows a rod-like shape having a low aspect ratio (length to diameter ratio) [23]. The particles have widths of 4 to 70 nm and lengths of 100 nm to several micrometers [34]. CNCs are produced from several cellulose materials such as wood, plants, bacteria, marine animals and fungi [35,36]. CNCs crystallinity changes from 54% to 88% [37]. The morphology, crystallinity, mechanical and thermal properties of CNCs depend on the origin of the cellulose, extraction conditions and technique used to extract. CNCs are typically extracted from cellulose fibers by acid hydrolysis. Acid hydrolysis removes the amorphous regions of cellulose while remaining crystalline regions intact [38]. The common acids used for this purpose are sulfuric and hydrochloric. But, sometimes hydrobromic and phosphoric acids have been used [39].

Recently, it has been reported that mechanical disintegration of the plant cell walls was yielded highly interconnected fibrils, size ranging from 10–100 nm in width and length. The delamination of cellulosic fibers under high mechanical shearing action is required to release nano fibrillated cellulose and to overcome interfibrillar hydrogen bonds into both crystalline and amorphous domains. Hakeem et al. [40] demonstrated that high-pressure homogenization (HPH) and microfluidization are the main methods that can be utilized to achieve nanoparticles. Ren et al. [41] showed that only with a combination of concentrated acid hydrolysis and HPH would rod-like cellulose nanoparticles form. The substrate used in this study was microcrystalline cellulose and the result was nanoparticles with a diameter of 10 nm and lengths in the range of 50–200 nm. The HPH treatment helped separate the nanofiber bundles.

Numerous studies have been reported regarding the conversion of cellulose to amorphous cellulose and cellulose II, however none of these studies has been focused on the use of ball milling for isolation of cellulose nanofibers [6]. Nuruddin et al. [6] have been able to separate cellulose nanofibers from kenaf fibers

Table 1
Pros and cons of different nanoparticle technologies.

Nanoparticle preparation method	Pros and Cons	References
High-Pressure Homogenization (HPH)	Produce nanoparticles with diameters between 20 and 100 nm. Use high energy, clogging of the homogenizer, and damage of the crystalline structure.	Wang et al. [42]
Microfluidization	Create nanoparticles less than 100 nm in diameter.	Rojas et al. [43]
Grinding	Particle size in the micrometer instead in the nanometer range. Damages the fiber structure.	Stelte and Sanadi [44]
Cryocrushing	Produce particles with diameters ranging from 30 to 80 nm.	Zheng [23]
High-intensity ultrasonication	Do not use any chemical treatment.	Cheng et al. [19]
Steam explosion	Lower environmental impact	Abraham et al. [24]
Acid hydrolysis	Low aspect ratio	Zheng [23]
Electrospinning	Simple and cost-effective process.	Frey [33]
Enzymatic hydrolysis	High cost due to the isolation process of the enzymes and the auspicious hydrolysis required long enzymatic treatment time.	Kalia et al. [45]

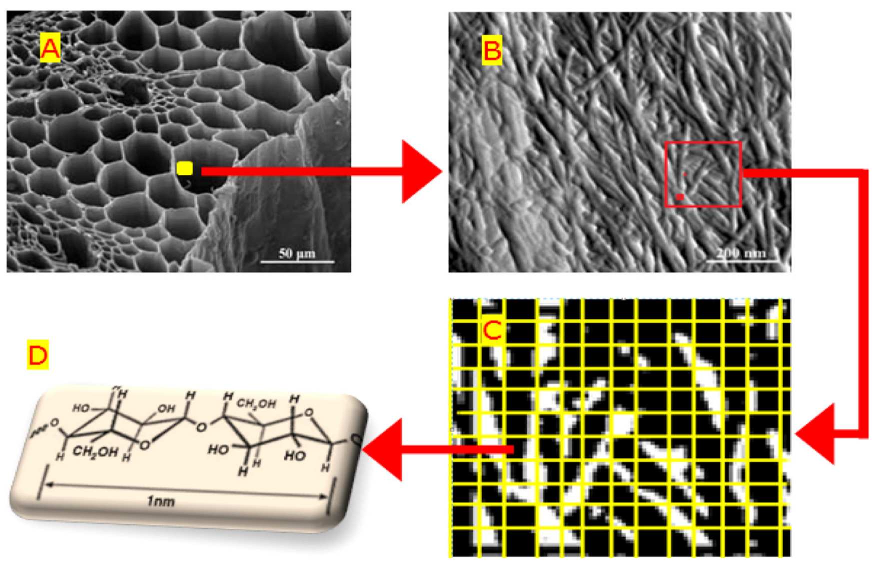

Fig. 1. Scenario of particle size reduction to around 20 nm, SEM/AFM figures for wheat straw retrieved from [46], A. thick-walled fiber cells, B. interwoven cellulose microfibrils of the primary wall largely unlignified but microfibrils (black spots) are partially embedded in what is believed to be hemicellulosic polymers (white spots), C. in case a square of 200 nm in length and width pulverized to 20 nm particle size, D. further grinding to 1 nm, size of two D-glucose units in the cellulose fiber.

and wheat straw. A number of pre-treatment techniques including chemical treatments with formic acid (FA)/acetic acid (AA), peroxyformic acid (PFA)/peroxyacetic acid (PAA), and hydrogen peroxide (H_2O_2) were used prior to ball milling. A homogeneous cellulose nanofiber of 8–100 nm in diameter was obtained from these processes. Most of these techniques that adopted milling, dispersion and separation of nanoparticles have not been utilized for the separation of cellulose from lignocellulosic materials. There is abandoned literature on the capacity of ball mill to achieve size reduction to nano-particals. For example, literature on a planetary ball mill manufactured by FRITSCH titled "Planetary Micro Mill PULVERISETTE 7 premium" claims that a final fineness of 100 nm hard, medium-hard and brittle materials can be achieved [47]. Also, a planetary ball mill manufactured by RETSCH titled "Planetary Ball Mill PM 100" is claimed to be capable of particle size reduction to around 100 nm [48]. It may be necessary to cryo-freeze the lignocellulosic material during ball-milling. Cryogenic grinding can help grind more effectively and efficiently, particularly for heat sensitive or tough-to-mill materials using liquid nitrogen. Radioisotopes (Cobalt-60 or Cesium-137) is usually used for gamma-ray production and it has been used to lignocellulostic pretreatment. The gamma radiation can penetrate through the lignocellulose and breakdown the crystal structure forming free radicals. These free radicals decay fast from the amorphous regions after the termination of radiation and biomass is degraded while decaying [49]. Gamma rays, ultrasonic waves, and liquid plasma have also been used for partial size reduction. These methods do not use chemical reducing substances, which is important for the elimination of impurities added to the nanoparticles [50]. Table 1 depicts the pros and cons of different nanoparticle technologies.

4. Separation of lignocellulose biomass

Cellulose is a semi-crystalline polysaccharide appearing in plant walls in the form of fibers, width range from 5 to 20 nm and length range from 0.5 up to several mm [40]. Fig. 1 shows lignocellulosic fiber arrangement and its potential to separate into three major components by size reduction to nano-scale. It is **hypothesized in this study that the three components could**

be and completely separated during size reduction to around 1 – 5 nm as the bindings between inter molecules are stronger than the bindings between intramolecular components in the lignocellulosic structure.

Due to powerful attractive interparticle forces (agglomeration) of nano-sized particles, lignocellulosic materials are hard to handle and separate. One approach is to fractionate the particles into a liquid. The difficulty of dissipating nanoparticles into a liquid varies and based on factors like particle size and shape, fluid type, presence of the dispersing agent, etc. Recent developments in the area of high-shear mixing technology can be adopted to disperse nanoparticles in liquid. A device titled "ultra-high shear mixers" available in the market delivers more vigorous mixing and greater throughput compared to traditional rotor/stator mixers, colloid mills and immersion mills [51]. One method of separating nanoparticles is based on their rate of migration through a viscous medium under centrifugal force. This method uses the differences in hydrodynamic behavior to separate objects; the medium of separation consists of zones of different viscosity (aqueous multiphase systems) [52]. The method of centrifugation of nanoparticles in aqueous multiphase systems, in a shorter time, provides resolution for separation of colloid particles of different compositions, in different size ranges, and of different aggregation states. The method is versatile, scalable, efficient, and non-destructive. Also, by comparison against standards, it provides a potential novel analytical method to identify the colloid size distribution in a suspension [53]. By varying the density of the medium where the nanoparticles are suspended, suitable medium properties can be identified for efficient separation.

5. Concluding remarks

To conclude, there is a great potential in converting waste lignocellulosic material to its three important components. More thoughtful research are required to advance the commercialization of such concept. The above discussed techniques can be used to pulverize biomass to nanoparticles, disperse it in liquids and separate the three components using centrifugation based on density gradient rate. In order to reduce the particle size below 100 nm, planetary ball mill is capable of achieving such range of size reduction. Other reduction methods may be required, such as gamma rays, ultrasonic waves, and liquid plasma. These different methods can be applied after dissipating the nanoparticles in liquids. If necessary, some chemicals such as hydrogen peroxide may be used in low concentration (combined with irradiation) to brake the hydrogen bonds.

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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