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An Overview of Recent Developments in Hetero-Catalytic Conversion of Cellulosic Biomass

Mohamed Rashid Ahmed-Haras¹, Nhol Kao^{1,*}, Md. Sakinul Islam¹, Liam Ward¹

¹ Department of Chemical and Environmental Engineering, School of Engineering, RMIT University, Melbourne, VIC 3000, Australia.

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ABSTRACT

In recent years, research activities involved in the production of nanocellulosic materials have grown substantially, rapidly stimulating the development of innovative production techniques. These materials are chemically extracted by acid-catalyzed Hydrolysis of the renewable and widely available cellulosic biomass. In this regard, sulfuric acid-catalyzed Hydrolysis of cellulosic biomass is a commonly known method for the production of nanostructured cellulose. However, this method may result in many disadvantages, including short catalyst-lifetime, corrosive to the reactor materials and managing the spent sulfuric acid resulted from the production process. This dictates the implementation of an eco-industrial alternative for the catalytic production of nanocrystalline cellulose (NCC). A viable and practical alternative is the application of heterogeneous (solid acids) catalysts, which can be more conducive in providing favorable platforms for efficient cellulose hydrolysis. This review highlights the current production methods of nanocrystalline cellulose. Further, recent literature on the heterogeneous-catalytic conversion of cellulosic biomass is briefly discussed. The limitations and disadvantages of these techniques are also described.

*Corresponding author: Nhol Kao, Department of Chemical and Environmental Engineering, School of Engineering, RMIT University, Melbourne, VIC 3001, Australia, E-mail: nhol.kao@rmit.edu.au Phone No.: +61 3 9925 3257, Fax No.: +61 3 9639 0138

1. Introduction

Nanostructured cellulose (nanocrystalline cellulose, NCC) has unique chemical, physical and optical characteristics, making it a beneficial and highly in-demand nanomaterial as a value-adding additive and reinforcing agent. These promising properties, together with its low cost and sustainability, have attracted growing interest and wide-opened its potential applicability as an effective nano-additive and nanofillers in cosmetics, polymer composites, functional materials and thermoplastic materials (Robles et al., 2017; Tan et al., 2019). The current NCC production are generally carried out by either chemical conversion, enzymatic conversion, or mechanical conversion, with the chemical conversion being the most widely used method (Thomas et al., 2018). Concentrated liquid acids mainly catalysis the recent chemical conversion of cellulosic biomass. However, this process generates a large volume of spent liquid acid or acidic waste, which is corrosive to the reactor and may result in adverse environmental impact. Handling and recycling those acidic wastes may incur additional production costs and required energy consumption (Xiu et al., 2019). Some industrial pilot plants had applied ultrafiltration and purification processes for recycling the spent liquid acid, which may also significantly add to the costs of existing NCCs production. The introduction of heterogeneous acid catalysts might greatly minimize such negative aspects.

On the contrary, heterogeneous solid acid catalysts are in practical terms more beneficial compared to homogeneous liquid acid catalysts in accordance with better catalyst activity, longer catalyst-lifetime and efficient reusability (Guo et al., 2012). The solid acid catalysts are also more conducive for large scale production, economic viability. More preferably, such catalysts may minimize environmental risks associated with the production of micro and nanostructured cellulosic materials. By definition, the solid acid catalyst is a solid substance that has acidic characteristics on its surface, allowing it to function as an acidic catalyst. Solid acids can be classified as either homogeneous or heterogeneous, based upon its solubility in any reaction medium. Homogeneous solid acids come in solid form, but they are soluble in the reaction medium, while the heterogeneous acids are mostly insoluble. Heterogeneous solid acids are industrially, economically and environmentally favorable for industrial-scale production in terms of processing residuals from cellulose depolymerization (Gaurav et al., 2016; Hara, 2010). Furthermore, many studies that have used heterogeneous acid catalysts for chemical hydrolysis of cellulose-based materials were focused more on bioenergy production (bioethanol and biodiesel). Such studies used cellulose multi-step degradation and often followed by enzymatic Hydrolysis, as highlighted in Table 2. This overview highlights the recent development in the heterogeneous catalysis of cellulosic biomass. It also outlines the main aspects of utilizing the potentials of this technique for the potential production of NCC.

2. Cellulosic Biomass

Cellulosic biomass, a complex natural material that often exhibits structural heterogeneity, is present in cell walls of most woody and non-woody plants. This structural and componential heterogeneity, in the cellular structure, can be attributed to the presence of carbohydrate biopolymers (cellulose and hemicellulose) and aromatic biopolymer lignin (Y. F. Huang et al., 2016). The carbohydrate biopolymers and lignin are bonded together to form the lignin-carbohydrate matrix, i.e., lignocellulose. Cellulosic biomass can be considered an abundant, inexpensive and renewable resource with an increasing trend in becoming the most promising feedstock essential for many modern industries (Anwar et al., 2014). In general, cellulosic biomass is widely acknowledged as a significant raw material for various applications such as eco-friendly biofuels, chemicals, biomaterials and many other value-added products (Watkins et al., 2015). This biomass is primarily generated as a waste during agricultural activities, or from the forest as forestry residues. Among these, agro-based waste quantities, rice husk (RH), or rice hull, which is produced in large quantities as a by-product of rice (paddy) plantations and processing. Another agro-based cellulosic biomass material is cotton linter, a by-product of the cotton and textile industry (Dhaliwal, 2019).

2.1 Rice husk

Rice is a cereal crop that is cultivated worldwide as an essential staple source of food. As one of the world's most consumable agriculture crops, rice is considered to play a significant role in the globe's food security (Gross, 2013). The food and agricultural organization of the United Nations (FAO), have determined that the global rice plantation area covers 160.8 million hectares containing 496 million tons of milled rice (Wu Leung, 1962).

Figure 1: Rice grain composition

The Australian rice industry has the capacity to produce more than 1 million tonnes of rice per year (RAG, 2016). Moreover, Australia has one of the world's highest yields of rice per hectare (10 t/ha) (Mushtaq, 2016). Analysis of the composition of a rice grain, as shown in Figure 1, reveals that while the most significant proportion (70%) is associated with white rice (endosperm) (Gul et al., 2015), a substantial portion is by-products such as 20% rice husk, 8% rice bran and 2% rice germ (Van Hoed et al., 2006). Generally, the main components (Figure 2) of RH are cellulose (35%), hemicellulose (25%) and lignin (18%) (Gupta & Balomajumder, 2016; Shukla et al., 2013).

Figure 2: Rice husk structure and composition

Due to its widespread abundance, Eco-friendly properties, and renewability, RH shows great potential for a wide range of very promising industrial applications such as construction materials, polymer composites, soil fertilization and bio-source of silica (Bodie et al., 2019). Consequently, a major focus of this study is to investigate the feasibility of extracting microcrystalline cellulose (MCC) from RH and thence producing spherical nanocrystalline cellulose (SNCC) as the main product of RH processing.

2.2 Cotton linter

Cotton (*Gossypium Hirsutum*), more specifically its linter, is considered to be an important natural source of cellulosic raw material. By definition, Cotton linter (CL) is the resulting short fibres that generate as a by-product of the textile industry and separated from cotton seeds by delinting machines, during the ginning processes. The quantity of CL produced globally is around 2.5 million metric tons, considering the 42 million metric tons of lint was produced in 2010, making it a widely available, low cost, renewable and biodegradable unique raw material for many manufacturing industries, for instance, carbon fiber (Bezerra et al., 2017; Dhaliwal, 2019; Zhou et al., 2016). In addition to lignocellulosic biomass, CL is considered to be an alternative cellulosic raw material. In contrast, the CL cellulose content accounts for more than 90% of its total composition (Estevinho & Rocha, 2018), compared to the woody biomass, which has cellulose content less than 50 % (Bharimalla et al., 2017; Ververis et al., 2004).

Noteworthy, since CL consists principally of cellulose, and hence it has no hemicellulose and lignin present, which are usually associated with cellulose and working as binding and structural materials (Palme et al., 2016). Unlike the lignocellulosic biomass, which has considerable amounts of lignin and hemicellulose, CL does not require excessive delignification and bleaching processes. Thus, it may reduce the time and production costs associated with processing cellulosic materials containing large amounts of lignin and hemicellulose. CL is therefore has a promising cost-effective candidate for the production of cellulose-based materials such as alpha-cellulose, methylcellulose, cellulose acetate, microcrystalline cellulose (MCC), nanofibrillated cellulose (NFC) and nanocrystalline cellulose (NCC). Together with

RH as raw material, MCC generated from CL was another focus of this study, as a precursor for potential NCC production via hetero-catalytic approach.

3. Cellulose and Microcrystalline Cellulose

Cellulose is the most abundant biopolymer on earth and it is the major component of plant cell walls. As a lignocellulosic renewable material, the structure of cellulosic macromolecular consists of long chains of repeatedly linked glucose molecules [Figure 3; (Tang et al., 2014)] which are linked together by β -(1 $\rightarrow$ 4) glycosidic bonds (C. Zhang et al., 2013). Cellulose consists of both amorphous (non-crystalline) and crystalline regions (Vendula & Miloslav, 2013). Cellulose by nature, as illustrated in Figure 3, is associated with hemicellulose and attached in the lignin-carbohydrate matrix. In Consequence, to effectively extract cellulose from lignocellulosic materials, lignin and hemicellulose have to be separated and removed by a two-stage chemical process, i.e., alkali extraction (delignification) and bleaching (whitening) (Syamani & Suryani, 2015). Once extracted, cellulose can be used as the precursor (intermediate material) for NCC production.

Figure 3: Chemical structure of cellulose, reproduced with permission (George & Sabapathi, 2015)

The none crystalline cellulose regions can be transformed into semi-crystalline or crystalline regions. Upon the improvement of cellulose crystallinity, while converted to its micro/nanostructured materials (MCC, NFC and NCC), cellulose amorphous region can be decreased or removed by applying acidic or enzymatic Hydrolysis.

The polymorphism occurs in the cellulose crystalline structure, whereby it can exist at different crystalline forms such as cellulose I, II, III, and IV (Rongpipi et al., 2019; Sunday Samuel & Mathew Adefusika, 2019; Wada et al., 2004). The formation degree of these different cellulose crystal structures typically depends on the intermolecular interactions, molecular orientations and chain arrangements (George & Sabapathi, 2015). From these cellulose crystallographic forms, cellulose I and cellulose II are the most widely observed cellulosic crystalline forms, as shown in Figure 4 (Mukarakate et al., 2016; Nam et al., 2016). Besides, cellulose I is often referred to as native cellulose and it exists as a parallel-chain molecular structure. In contrast, cellulose II is more thermodynamically stable with an antiparallel-chain molecular arrangement. Correspondingly, cellulose II is mostly regenerated from cellulose I via alkaline mercerization or less often by ionic liquids biomass treatment (Xi et al., 2013). However, few researchers have mentioned the co-existence of cellulosic crystalline mixtures in the extracted cellulose and/or cellulose derivatives (Ahmed-Haras et al., 2020; Yue et al., 2015).

Figure 4 Crystalline structures of Cellulose I and cellulose II, reproduced with permission (Mukarakate et al., 2016)

For the preparation of MCC, the cellulosic pulp needs to be first isolated from the hemicellulose and lignin matrix. After lignin and hemicellulose separation (the non-cellulosic materials) using consecutive Alkali extraction and bleaching methods (Syamani & Suryani, 2015). The extracted cellulosic-based material is then, most commonly, subjected to acid hydrolysis treatment to improve the crystallinity by which decomposing its amorphous region, thereby producing MCC. Typically, sulfuric acid (Camacho et al., 1996) and hydrochloric acid (Zhao et al., 2018) have been used as catalysts in conventional acid hydrolysis processes for MCC production. Recently, acidic ionic liquids have been used as catalysts for MCC production (Wu et al., 2017). Despite the good catalytic activities of mineral acids (H_2SO_4 and HCl), utilization is limited due to their corrosivity and costly processing being required for separation and disposal of the used acidic catalysts (Hara, 2010). In general, acidic ionic liquid catalysts are considered to be environmentally and economically undesirable for large scale MCC production (Rakita, 2003). Unlike the catalysts, as mentioned above, hydrogen peroxide (H_2O_2) can offer a more sustainable alternative as a green replacement for the toxic chlorine-based materials and corrosive acid catalysts. It is a strong oxidant and eco-friendly bleaching agent (chlorine-free bleaching agent). Therefore, oxidative Hydrolysis of cellulosic pulp, catalyzed by H_2O_2 , and concurrently utilizing the same bleaching agent may contribute to a more environmentally benign production process. As such, this may further lower the cost of MCC production.

Due to the considerable amounts of silica, lignin and hemicellulose present in RH, a large scale and commercial production of cellulosic-based materials (especially MCC) are not yet available. To date, most researchers are focused on the lab-scale production of RH-based alpha-cellulose, MCC and NCC. In the present study, RH will be subjected to sequential alkaline and oxidative hydrolysis processes through which the non-cellulosic components need to be removed. For CL, there is a lower emphasis on the need for successive delignification and bleaching pretreatments, due to the higher cellulose content. Thus, CL-based micro-sized cellulose (MCC-CL) is inexpensive and readily available in the market.

Another focus of this study is to investigate the development of MCC and NCC containing both cellulose I and cellulose II and porous microparticles, offering a novel class of cellulosic-based materials. The presence of these two different crystalline forms within the resultant structure may enhance thermal and mechanical properties and overall durability, widening their potential industrial applications. Besides, the development of porous microparticles has drawn great interest for their potential applications as drug carriers, absorbents, catalysts and biosensors (Cai et al., 2013; Gao et al., 2015). Developing MCC with structural porosity may potentially further improve its capability and functionality in many scientific and industrial sectors.

4. Nanocrystalline Cellulose

Nanocrystalline cellulose (NCC) is a term used when referring to nano-sized cellulose or cellulose on the nano-dimensional scale. Besides, NCC can be considered to be cellulose in its highest crystallinity form or its nanocrystalline domain, as shown in Figure 5.

NCC is classed as a renewable nanomaterial with unique properties compared with its cellulose counterpart that has great potential applications such as textiles, carbon nanotubes, nanocomposites, photonics, polymer nanocomposites, cosmetics, pharmaceuticals and in particular as value-added products for materials development (Peng et al., 2011). Nano-scaled cellulose has gained growing prominence along with rapidly increasing research interests, as it can be derived from bio-based inexhaustible raw materials.

The NCC is generally extracted from the widely available biopolymer (cellulose) via mechanical, biological, or chemical means (Isogai, 2013; Mishra et al., 2018). The extraction process involves isolating cellulose crystalline domains and removing most of the non-crystalline (amorphous) domains. Nano-cellulosic materials typically have much of cellulose yet with beneficial aspects over their basic material such as lightweight, high strength barrier characteristics and optical properties (Klemm et al., 2018; Sharma et al., 2019). Further benefits can be achieved through adjustment of the cellulose chains to form highly ordered domains, which can be subsequently extracted as nanoparticles, exhibiting unique characteristics due to their nano-scale size and large surface area (Foster et al., 2018; Shak et al., 2018).

The NCC individual nanoparticles can be produced with different morphological forms. The most commonly reported NCC shapes are needle-like or rod-like forms, where the nanostructured particles exhibit elongated shaped morphologies (Morais et al., 2013; Oun & Rhim, 2015; Theivasanthi et al., 2018). NCC can also exist as sphere-shaped nanocrystals (else known as elliptical nanocellulose), but to a lesser extent. As such, not many reported studies had been conducted on producing both monodispersed and polydispersed spherical nanocellulose from the wide spectrum of cellulosic-based starting materials. The monodisperse nanoparticles have a major advantage compared with the polydispersed

nanoparticles, which may be attributable to the consistency and uniform properties of individual nanoparticles, making the property of whole nanoparticles controllable and essential for applications such as pharmacy and drug delivery (Hwang et al., 2012; Robertson et al., 2016). That being so, none of these research studies, including in the aforementioned studies, to the best of our knowledge, have reported in the production of spherical nano-sized cellulose (SNCC) from cotton linter-based MCC and rice husk-based MCC via a

single-step heterogeneous catalysis process. The spherical morphology and structure of nanocelluloses may enhance their industrial applicabilities (Zheng et al., 2019), and thus making them excellent candidates as adsorbents for heavy metal removal from wastewater (Ram et al., 2018), nucleation agent for polymer nanocomposites (Lu et al., 2016), drug delivery (Evdokimova et al., 2018) and aerogels (X. Wang et al., 2018).

Figure 5 Structure of nanocrystalline cellulose, reproduced with permission (Börjesson & Westman, 2015)

5. Nanocrystalline Cellulose Production Methods

The increasing demands from today's society for nano-scaled cellulosic materials over the last few decades has stimulated the development of both emerging and current production techniques. Thereon, cellulosic materials can be scaled-down into their nano-dimensional materials through one of three major production methods, namely acid-catalyzed Hydrolysis (chemical process), enzyme-catalyzed Hydrolysis (biological process) and using a high-pressure homogenization process (HPH). Table 1 shows the advantages and limitations of each of these methods from the reported literature. In particular, attention has focussed on the use of strong mineral (commonly sulphuric) acids for Hydrolysis of cellulose-based and cellulose-containing materials. However, concentrated mineral acids are responsible for corrosion issues associated with production equipment. In addition, their disposal has caused environmental concerns (Ji et al., 2019). While these problems can be negated through Enzymatic Hydrolysis of cellulosic materials, whereby enzymes break down the cellulose glycosidic and intermolecular bonds. Of major drawbacks are the lengthy

hydrolysis times and low production yield (Y. Huang & Chen, 2013; Jeremic et al., 2019). Such hurdles might hinder potential commercialization and large scale production of nanocellulose derived using this process.

The major disadvantage of the HPH method is large energy consumption (Phanthong et al., 2018). Despite the problems associated with corrosion of the process equipment and environmental concerns, acid-catalyzed Hydrolysis is more preferable and therefore widely used for shorter operation times and less energy consumption. Notwithstanding, the introduction of less corrosive and recoverable acidic catalysts, in a solid form, may largely contribute to a further reduction in energy consumption and costs associated with equipment maintenance as well as enhancing environmental sustainability. Therefore, it would be desirable to investigate the feasibility of applying a recoverable heterogeneous acid catalyst for SNCC production.

Table 1: Common nanocrystalline cellulose production methods

Feedstock Material	Preparation Method	Advantage	Disadvantage	Nanocellulose Form	Reference
Soybean Straw	Enzymatic Hydrolysis using enzymatic cocktail Optimash™ VR.	Environmental Friendly	Low Yield	Cellulose Nanofibrils	Martelli-Tosi et al., 2016
Sugarcane Bagasse	High-Pressure Homogenization at 80 MPa	High Yield	High Energy Consumption	Nanocrystalline Cellulose	J. Li et al., 2012
Bacterial Cellulose	Enzymatic Hydrolysis using Cellulase from <i>Trichoderma reesei</i> ATCC 26921	Ecofriendly Approach	Long Hydrolysis Time	Cellulose Nanocrystals	Rovera et al., 2018
Cellulose Pulp	Acid Hydrolysis using 64% sulfuric acid	Low Hydrolysis Time	Equipment Corrosion	Nanocrystalline Cellulose	de Carvalho Benini et al., 2018
Cotton Linter	Acid Hydrolysis using 60% sulfuric acid	Mild Temperature	Equipment Corrosion	Cellulose Nanowhiskers	Morais et al., 2013

6. Acid-Catalyzed Production of NCC

6.1 Homogeneous Acid-Catalyzed Production of NCC

Previous studies have, in large measure, focused on the conversion of cellulose into its nano-dimensional materials (NCC and NFC) by liquid acid-catalyzed (homogeneous catalyst) hydrolysis methods. A range of homogeneous liquid acids has been used such as sulphuric acid (Tonoli et al., 2012), hydrochloric acid (Yu et al., 2013), formic acid (Li et al., 2015) and phosphoric acid (Frost & Johan Foster, 2020). By way of contrast and irrespective of their effectiveness in the catalytic downsizing of cellulose, most of the homogeneous acids are irretrievable, circumscribed reusability and hence considered environmentally unsustainable (Chen et al., 2016; W. Liu et al., 2019; S. Wang & Tian, 2016). Other industrial concerns are mainly related to the reaction vessels, particularly; the high corrosion rates of processing equipment. The excessive amounts of the acid (above 50 wt %) required for the NCC production, but yet with short catalyst-life (Z. Zhang & Zhao, 2009). As a result, the current processes produced spent sulphuric acid in large quantities, which is corrosive to the reactor and led to a negative environmental impact once being disposed. Despite that, there are current industrial production of NCC by CelluForce, InnoTech Alberta, FPInnovations and USDA's Forest Products Lab (Klemm et al., 2018; Rudie, 2017). Most of NCC large scale production had conducted in both pilot plants and batch reactors, using sulfuric acid-catalyzed Hydrolysis of wood-based pulp. These industrial approaches had applied different membrane filtration and recycling processes for the avoidance of huge management problems, generated from the spent sulphuric acid (Rudie, 2017). Unfortunately, such approaches may significantly add to the processing time and costs of the existing NCCs production. In this respect, solid acids have numerous and remarkable advantages over liquid acids regarding

catalyst activity, recovery, reusability, and catalyst lifetime (Guo et al., 2012).

6.2 Heterogeneous Acid-Catalyzed Hydrolysis of Cellulose

In recent years, there has been a substantial increase in research activities associated with cellulose hydrolytic conversion via heterogeneous solid acid catalysts, as summarized in Table 2. Certain aspects of these studies include catalytic Hydrolysis of cellulose into glucose and oligosaccharides using magnetic nanoparticulate ($\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-SO}_3\text{H}$) solid acid catalyst, aimed to produce fermentable sugars (glucose and oligosaccharides) for biofuel production (Xiong et al., 2014). Additionally, a magnetic Fe_3O_4 core encapsulated in a sulfonated carbon shell ($\text{Fe}_3\text{O}_4/\text{C-SO}_3\text{H}$) showed good catalytic activity as a recyclable acidic catalyst for cellulose hydrolysis (C. Zhang et al., 2013). Carbon- $\text{Fe}_2(\text{SO}_4)_3/\gamma\text{-Fe}_2\text{O}_3$ nanoparticles have used as a readily recoverable and reusable magnetic nanocatalyst for producing glucose from microcrystalline cellulose (Yamaguchi et al., 2016). A magnetic silica-supported solid acid catalyst ($\text{Fe}_3\text{O}_4\text{-SBA-SO}_3\text{H}$) has used for cellulose conversion into a 50% glucose production yield (Lai et al., 2011). Besides, in an aqueous medium and over a magnetic carbon-based solid acid (MMCSA) catalyst, corncob has depolymerized in a one-step reaction into 71% xylose with cellulose retention of 91% in the residue (Qi et al., 2019). For these processes and irrespective to their efficient catalytic conversion of cellulose, the magnetism followed by sulfonation of a carbon-based material requires a long operating time and good handling of the spent sulfuric acid used in catalyst preparation.

Furthermore, cellulose has converted with high yield (69%) to levulinic acid using Amberlyst 70 (acidic resin) as a heterogeneous acid catalyst (Alonso et al., 2013). The conversion of cellulose into glucose using

another acidic resin (Amberlyst 15) has successfully carried out with a production yield of 75% (Ishida et al., 2014). Cellulose has also depolymerized using zirconium dioxide (ZrO_2) to produce levulinic acid with a 53% production yield (Joshi et al., 2014). Levulinic acid (LA) is generated from cellulose decomposition and it is considered as a potential precursor for the production of chemicals and biofuel (Serrano-Ruiz et al., 2016). Sulfated Zirconia has also used for the hydrolytic conversion of cellulosic materials into glucose, which was later utilized as a biofuel production feedstock (Kristiani et al., 2015). Additionally, sulfonated activated-carbon ($\text{AC-SO}_3\text{H}$)

catalyst has used in the catalytic hydrothermal reaction of cellulosic material to produce glucose via heterogeneous Hydrolysis (Onda et al., 2009). The resin-activated carbon has also been used to hydrolyze cellulose into butyl Levulinate with a 31% yield (Liang et al., 2019). The above-cited heterogeneous depolymerization and downgrading of cellulose-based materials have mostly conducted using high processing temperature (120 °C or above) with uses of organic solvents and ionic liquids as reaction medium. However, these techniques may result in the disadvantages of higher energy consumption and insufficient separation of the final products.

Table 2: Solid acids catalyzed cellulose hydrolysis into different products

Catalyst	Raw Material	Final Product	Production Yield (%)	Targeted Application	Reference
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$	Cellulose	Glucose	73	Biofuel	Xiong et al., 2014
$\text{Fe}_3\text{O}_4@\text{C-SO}_3\text{H}$	Cellulose	Glucose	51	Biofuel	C. Zhang et al., 2013
Carbon- $\text{Fe}_2(\text{SO}_4)_3/\gamma\text{-Fe}_2\text{O}_3$	Microcrystalline Cellulose	Glucose	18-20	Biofuel Chemicals	Yamaguchi et al., 2016
$\text{Fe}_3\text{O}_4\text{-SBA-SO}_3\text{H}$	Cellulose	Glucose	50	Biofuel	Lai et al., 2011
MMCSA	Cellulosic Materials	Xylose	71	Biofuel	Qi et al., 2019
Amberlyst 70	Cellulose	Levulinic Acid	69	Biofuel Chemicals	Alonso et al., 2013
Amberlyst-15	Cellulose	Glucose	75	Biofuel Chemicals	Ishida et al., 2014
Sulfated Zirconia	Cellulosic Materials	Glucose	53	Biofuel	Kristiania et al., 2015
Sulfonated Activated-Carbon	Cellulose	Glucose	40	Chemical Feedstock	Onda et al., 2009
Resin-Activated Carbon	Cellulose	Butyl Levulinate	31	Chemical Feedstock	Liang et al., 2019
ZrO_2	Cellulose	Levulinic Acid	53	Biofuel	Joshi et al., 2014
$\text{H}_3\text{PW}_{12}\text{O}_{40}$	Cellulose	Glucose	50	Biofuel	Tian et al., 2010
$\text{Cs}_1\text{H}_2\text{PW}_{12}\text{O}_{40}$	Cellulose	Glucose	83	Biofuel	Tian et al., 2011
$\text{H}_5\text{BW}_{12}\text{O}_{40}$	Cellulose	Glucose	77	Biofuel	Ogasawara et al., 2011
Nafion-SAC-13	Cellulose	Levulinic Acid	72	Biofuel	Potvin et al., 2011
$\text{Ru}/\text{HZSM-5}$	Cellulose	Hexitols	39	Biofuel	H. Wang et al., 2015
Bimodal-HZ-5	Microcrystalline Cellulose	5-Hydroxymethylfurfural	46	Biofuel	Nandiwale et al., 2014
LiNbMoO_6	Cellulose	Hexanes	72	Biofuel	Y. Liu et al., 2015

Heteropoly acids (HPA) have applied as a solid acid catalyst for the hydrolytic conversion of cellulose. In detail, the heteropoly acid $\text{H}_3\text{PW}_{12}\text{O}_{40}$ has used as a catalyst for the Hydrolysis of cellulose to glucose with a 50% yield (Fu et al., 2015), although later studies revealed that the yield has increased to 83% (Tian et al., 2011).

Similarly, highly negatively charged heteropoly acid ($\text{H}_5\text{BW}_{12}\text{O}_{40}$) hydrolytically catalyzed the conversion of cellulose to glucose with a 77% yield (Ogasawara et al., 2011). Furthermore, Nafion-SAC-13 has used for glucose production, which was further converted to levulinic acid (72% yield) using a carbohydrate-based hydrolytic

conversion process (Potvin et al., 2011). Hydrolytic hydrogenation of cellulose to hexols (39% yield) has efficiently catalyzed using Ruthenium (Ru) metal loaded on mesoporous zeolite (HZSM-5) catalyst (H. Wang et al., 2015). In addition, microcrystalline cellulose (microsized cellulose) was hydrolyzed over Bimodal-HZ-5 zeolite; the hydrolytic conversion resulted in a 46% yield of 5-Hydroxymethylfurfural (Nandiwale et al., 2014). Y. Liu et al. (2015) have used a layered compound such as LiNbMoO_6 in hydrolysis-hydrogenation of cellulose to form hexanes with 72% production yield). As already been stated, achieving an efficient separation and quantification of the liquid hydrolysis products might potentially have identified as time and energy-consuming techniques. Besides, most of these studies focused on the production of glucose for biofuel productions. Hence, none of those cited studies have reported a direct heterogeneous catalysis production of nanostructured cellulosic materials.

6.3 Methods of Assisted Heterogeneous Catalytic Hydrolysis of Cellulose

Table 3 presents a summary of key papers on the use of heterogeneous catalysts, referred to as Catalytic-System 1, 2 and 3, for simplicity, for cellulose hydrolysis. All reported works had used heterogeneous catalysts assisted by methods that have already been efficiently proven for cellulose hydrolysis, to include; mineral acids, ultrasonication and hydrothermal conditions. However, by associating heterogeneous cellulose hydrolysis with the

conventionally used methods, many shortcomings of the traditional methods possibly could have concurred.

The proposed approach describes the production of spherical NCC via the cellulosic-materials Hydrolysis using heterogeneous acid alone and without applying any preparation methods of assistance, such as ultrasonication treatment, hydrothermal reaction conditions, microwave radiation nor mineral acids. Furthermore, most of the catalysts reported in Table 3 are not commercially available, as they are laboratory synthesized. Consequently, this may limit their technical and economic feasibility for future large-scale cellulose hydrolysis.

The main advantage which makes this proposed approach better, faster, applicable and cheaper is that cellulose hydrolysis can be conducted in a single-step reaction using only one heterogeneous catalyst. This process could be carried out under mild reaction conditions, while multi-step reactions at high temperature and pressure (hydrothermal, high energy consumption) have been used in the previously reported studies.

Furthermore, their long production time, high energy consumption and commercially unavailable catalysts may negatively be reflected in the manufacturing costs. In addition, none of the studies reported the production of cellulose nanospheres as a final product. Thus, the proposed method presents the production of renewable, high yield and thermally stable cellulose nanocrystals.

Table 3: Summary of solid acid catalysts assisted by mineral acids for cellulose hydrolysis

Catalyst	Reaction Conditions	Final Product	Production Yield (%)	Targeted Application	Reference
Catalytic-System [1]: Ru/AC in the presence of mineral acid (hydrochloric acid; HCl)	Hydrothermal reaction at about 180 °C for 20 min.	Soluble sugars; Glucose (88%) then converted by hydrogenation in the presence of hydrogen gas to 90 % Sorbitol	<u>Hydrolysis:</u> 88 % glucose <u>Hydrogenation:</u> 90 % Sorbitol	Not Mentioned	Shrotri et al., 2018
Catalytic-System [2]: Zeolite beta modified with alkali earth metals in a reaction medium contained hydrochloric acid (HCl)	Hydrothermal microwave-assisted at 210 °C for 30 min	Levulinic acid (LA), Glucose (G), 5-(hydroxymethyl) furfural (5-HMF), acetic acid (AA)	LA: 22.3 % G: 12.1 % 5-HMF: 14.6 % AA: 15.2 %	Chemical Feedstock	González-Rivera et al., 2014
Catalytic-System [3]: Sulfonated activated carbon fibres derived from lignin-based activated carbon	Hydrothermal reaction at 150 °C for 24 h	Glucose (G) and Cellulose Nanofibrils (CNF)	G: 64 % CNF: 8 %	Biofuel	Hu et al., 2015
List of heterogeneous catalysts assisted either the presence of mineral acids or conducted under ultrasonication	Hydrothermal and Under ultrasonication treatments	Mostly glucose with only two studies reported the production of nanofibrillated cellulose	Varied	Chemical feedstock	Lee et al., 2014

7. Conclusions

The nanocellulosic materials have gained a growing prominence with rapidly increasing research interests. In addition, these materials are particularly derived from bio-based inexhaustible raw materials. Among these, NCC which is a renewable nanomaterial with unique properties such as adaptable surface chemistry, biocompatibility, nontoxic and physicochemical and mechanical properties. This making NCC possess great potentials for diverse applications such as polymer nanocomposites, 3D printing materials, carbon nanotubes, photoelectronics, membrane, cosmetics, pharmaceuticals and most notably as value-added products for materials development (Peng et al., 2011; Shankaran, 2018). Those unique properties increased global demands aimed at expanding and developing NCC productions.

The sulfuric acid-catalyzed Hydrolysis of cellulose-based materials is the most commonly used method of NCC production. As yet, this method has greatly disadvantaged from the used concentrated acid, and a large quantity of the spent acid resulted from the production process. Refining and reusing the process effluents may not be cost-effective as well as energy-efficient. Recent hydrolysis techniques of cellulosic materials were involved in the application of heterogeneous catalysis with different types of heterogeneous acid catalysts. However, these techniques have mainly focused on biofuel and chemical productions, with major challenges and limitations are the time-consuming and insufficient separation of the final product. On the contrary, the introduction of heterogeneous solid acids, as an industrially viable green alternative, for the production of nanocellulosic materials may offer cost-effective production approaches.

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