Chapter 10
Producing Value-added Products from Organic Solid Wastes with Mechanochemical Processes

Haixin Guo, Xiao Zhang, and Feng Shen

Abstract Mechanochemical process is a versatile technique that is induced by mechanical forces such as shearing, friction, compression, stretching, and grinding. Recycling organic solid wastes (e.g. biomass) to value-added products from organic solid wastes *via* mechanochemical processes has received increasing interest due to its high efficiency, low cost and eco-friendly nature (solvent-less or solvent-free). In this chapter, a brief overview of the historical development of mechanochemistry, kinds of mechanochemistry equipment, the relationship between mechanochemistry and organic solid wastes (e.g. waste biomass) conversion into value-added products (chemicals, fuels, and carbon materials) will be introduced for the general reader. Emphasis is placed on typical mechanochemical processes for conversion of waste biomass to chemicals (glucose, xylose, furfural, 5-HMF, sorbitol, phenol, etc.) and functional carbon materials (adsorbents, catalysts, electrodes, etc.). The role and mechanism of mechanochemical technology on the waste biomass transformation into value-added products were also presented. Limitations and opportunities associated with the mechanochemical synthesis of valuable products from organic solid wastes (biomass) are highlighted.

Keywords Ball milling · Waste management · Biochar · Lignocellulose · Biorefinery

H. Guo
Graduate School of Environmental Studies, Tohoku University, Sendai, Japan

X. Zhang
School of Energy and Environmental Engineering, Hebei University of Technology, Tianjin, China

F. Shen (✉)
Agro-Environmental Protection Institute, Ministry of Agricultural and Rural Affairs, Tianjin, China
e-mail: shenfeng@caas.cn

10.1 Introduction

Mechanochemistry process technology refers to chemical reactions induced by the application of mechanical energy. Shear and compressive forces are developed through grinding and impacts [1]. The mechanochemical reaction process provides a new way to reduce or avoid the use of solvents. In solvent-free or solvent-less conditions, new synthetic is realized, improving the product selectivity, yield or reaction rate. Mechanochemistry, especially when implemented in a continuous process, has been identified by the International Union of Pure and Applied Chemistry (IUPAC) [2] as one of the ten world-changing technologies.

In 2000, Boldyrev, V. V and co-workers reported one of the earliest applications of mechanochemistry in the book "On Stones" in 315 B.C, which discussed the grinding of cinnabar and acetic acid with a mortar and pestle could produce elemental mercury (Hg) [3]. Since then, mechanochemical reactions were almost ignored by twentieth century scientists until the last few decades. In 1820, Faraday et al. [4] discovered that silver chloride could be reduced to its elemental form by a solvent-free grinding method. Then, M. Carey Lea (1823–1897) performed systematic investigations on the mechanochemical reaction and thus he is known as "the father of mechanochemistry." During the past two decades, mechanochemistry has been rapidly established as a green and environmentally friendly synthetic method.

Investigations using a mortar and pestle were the first to implement mechanochemical reactions since they are cheap and convenient tools [5]. However, manual grinding is susceptible to variable factors that are difficult to control, such as operator variability and laboratory environments. These factors frequently render results obtained by mortar and pestle unrepeatable. Today, machine-driven ball milling has become one of the most important tools for mechanochemical reactions. As shown in Fig. 10.1, laboratories typically implement two different kinds of ball milling equipment that represent different applications of mechanical force. These are the shaker (or mixer) mill and planetary mill. In shaker mills, the reaction jars are rapidly oscillated from side to side, or in complex paths which results in the enclosed ball bearings applying shear and compressive force to realize grinding [6]. While in the planetary mills (Fig. 10.1), the reaction vessels are spun at high speed,
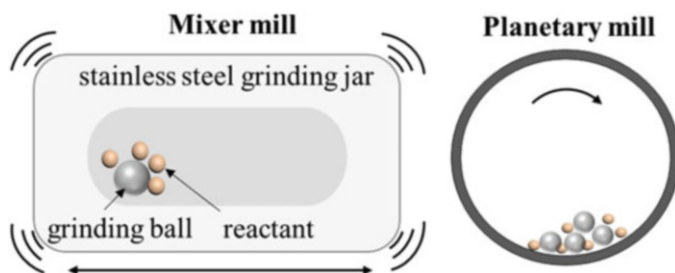
Fig. 10.1 Typical automatic ball milling equipment used for mechanochemical reactions

counter-rotatory to the main spinning "sun wheel" (thus, the term planetary) results in the balls grinding the solids within the jars.

Recently, mechanochemical reaction technology has been applied in various fields such as materials synthesis, industrial chemistry, extractive metallurgy, minerals engineering, and bioengineering [7]. Mechanochemical processing offers a lot of advantages such as ecological safety and process simplicity when compared to solution-based wet processing. Practically, the mechanochemical treatment processes not only avoid the complex post-treatment steps (e.g. reuse of solvent and separation of product) but also the use of large amounts of solvents. Importantly, most mechanochemical reaction systems are completed within minutes to hours. Another advantage of mechanochemistry is enabling applications under mild conditions (e.g. at ambient temperature). These factors make mechanochemical approaches an attractive solution for biomass waste management. Considering environmental and economic factors, mechanochemistry offers a time-saving, eco-friendly and labor-saving process for the conversion of waste biomass into sustainable platform chemicals, fuels, and functional carbon materials.

10.2   Chemicals from Waste Biomass

10.2.1   Reducing Sugars

The efficient hydrolysis of carbohydrates (e.g. cellulose and hemicellulose) of the biomass into reducing sugars (RS) is essential for the organic solid wastes transformation process. It is due to the RS (C5 sugars and C6 sugars) can be further transformed into value-added products (e.g. biofuels and chemicals) [8, 9]. However, the hydrolysis of biomass offers great challenges because raw biomass has a recalcitrant structure that protects its carbohydrate from degradation/attack by the enzymes [10]. Therefore, pretreatment is an essential step for waste biomass hydrolysis into reducing sugars, which can reduce the crystallinity of the cellulose and particle size of the biomass thus increasing the cellulose accessibility.

Pretreatment methods (e.g. chemical pretreatments including acid, alkaline and organic solvents, steam explosion, biological, and hydrothermal methods) have been used to promote the biomass hydrolysis into reducing sugars, however, these methods are usually limited by their corrosivity, recyclability of solvents, and waste generated. Most pretreatment methods of biomass limits the production of undesirable dehydration products (such as levoglucosan, levoglucosenone and 5-hydroxymethylfurfural) and improves susceptibility towards further hydrolysis through enzymatic processes [11]. Practically, chemical pretreatment methods limit further enzymatic hydrolysis [12]. So, it is necessary to develop environmentally friendly pretreatments methods that avoid strong acid and alkalis. Various equipment has been developed to implement mechanochemical processes such as automated mortar grinders, shaker mills, screw extruders and drum mixers [13].

Table 10.1 Effect of mechanical pretreatment on total reducing sugar (TRS) yields by biomass hydrolysis

Substrate	Milling time	TRS yields (%)		Ref.
	h	Without pretreatment	With pretreatment	
Bagasse	2	<150 mg/g	531.6 mg/g	[25]
Jatropha hulls	24	29.5	35.4	[26]
Plukenetia hulls	24	34.0	40.8	[26]
Rice straw	1	23.4	89.4	[19]
Cellulose	6	20.9	84.5	[27]
Oil palm	2	11.4	71.9	[28]
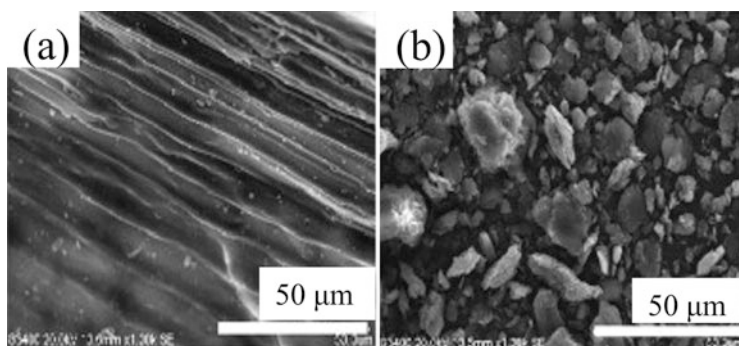
Fig. 10.2 Scanning electron micrographs of pretreated rice straws. (**a**) rice straw cutter milled to less than 2 mm and (**b**) rice straw ball milled for 60 min. (Reprinted with permission from [19]. Copyright © 2009, Elsevier)

Mechanical pretreatment processes enabled by the ball milling of raw biomass have appeared as an environmentally friendly, efficient, and economically feasible alternative the traditional pretreatment process. This approach was pioneered by Blair (dry) [14] and Schüth (wet) [15] for the realization of C5 and C6 sugars from cellulose and biomass. Larger scale experiments showed improved energy consumption [16–18]. Table 10.1 given the effect of mechanical pretreatment on the yields of total reducing sugar by hydrolysis of various raw biomass. Compared with direct hydrolysis of biomass, the TRS yields increasing 1.1–14.8% after ball pretreatment of biomass (Table 10.1). Gu et al. [12] reported that after pre-milled Douglas-fir forest residuals, the crystallinity of cellulose was reduced from 40% to 11%. The particle size of samples on D 90% decreased from 416 µm to 41 µm and on D 10% decreased from 20 µm to 3 µm after ball milled. Scanning electron microscopy (SEM) images result show that the particle size of rice straw after 60 min dry ball-milling pretreatment decreases from 500 µm to 2 mm to less than 30 µm (Fig. 10.2), and the surface changed from smooth to rough which lead to an increase in the overall surface area [19]. Wide-Angle X-ray Diffraction (WAXD) and ATR-FTIR analysis showed that both the mean size of the crystalline domains and crystallinity

index were decreased after 2–60 min of treatment with ball milling [20]. The average length of the fibers decreased to 12 μm from 200 μm after 60 min of ball milling. Proton NMR and ^{13}C NMR spectra were used to investigate the functional structure of the biomass during the ball milling process [21, 22]. It was shown that ball milling broke chains in cellulose (or hemicellulose), resulting in a disruption of the biomass structure and conversion into oligosaccharides or monosaccharides [22, 23]. Moreover, Zhang et al. [17] reported that the rolling mode (shear > compressive) promotes cellulose conversion into glucose, while the shaking mode (compressive>shear) promotes the levoglucosan formation. Wu et al. [24] reported that glucose yield from enzymatic hydrolysis of biomass greatly increased from 38.7% to 66.5% after the introduction of intermittent ball milling by enhancing the adsorption of enzymes into cellulose.

In conclusion, mechanical pretreatment (milling/grinding) is an efficient way to promote biomass hydrolysis into total RS. Mechanical pretreatment offers advantages through changes in the structure of biomass including the amorphization of biomass crystalline structures, breaking hydrogen bonding, decreasing the degree of polymerization (DP) of biomass and increasing the accessible surface area. Due to avoid strong acid and alkalis, the mechanical pretreatment (e.g. ball milling) as an environmentally friendly is also beneficial for enzymatic hydrolysis of biomass to reducing sugars.

10.2.2 Furfural and 5-HMF

Furfural and 5-hydroxymethylfurfural (5-HMF), which are obtained from the acid dehydration of C5/C6 sugars, are regarded as important biomass-derived platform compounds of the biorefinery [29–31], moreover furfural and 5-HMF offers a rich source of derivatives that are potential biofuel components such as ethyl levulinate (EL) [32], methyl tetrahydrofuran (MTHF) [29], 5-ethoxymethylfurfural (5-EMF) [32], 2,5-dimethylfuran (DMF) [33]. Extensive research has been carried out on direct preparation of furfural and 5-HMF from fructose and xylose with a homogeneous and heterogeneous acid catalyst such as modified biochar, zeolite, and $AlCl_3$ [30, 34, 35]. However, it is still a challenge to efficiently producing furfural and 5-HMF direct from raw biomass (e.g. long reaction times and harsh reaction conditions) so that the large-scale production of platform chemicals (furfural and 5-HMF) is still not feasible at reasonable prices. As shown in the above section, mechanical pretreatment (e.g. ball milling treatment) is beneficial for the hydrolysis of biomass into total RS (glucose, fructose and xylose), in this section the catalyst-assisted mechanochemical (or mechanocatalytic) process for the preparation of platform chemicals (furfural and 5-HMF) from raw-biomass (e.g. Cellulose, Bamboo powder) is discussed.

As shown in Table 10.2, compared with synthesis platform chemicals (5-HMF and furfural) single catalyst reaction, the objective product (5-HMF and furfural) yields increased *via* catalyst-assisted mechanochemistry reaction. As Fig. 10.3

Table 10.2 Conversion of C5/C6 sugars into furfural and 5-hydroxymethylfurfural *via* catalyst-assisted mechanochemical method (BM: ball-milling)

Substrate	Catalyst	Product	Without BM (%)	With BM (%)	Ref.
Cellulose	$Al_2(SO_4)_3$	5-HMF	39.8	44.6	[36]
α-cellulose	$AlCl_3$	5-HMF	–	79	[37]
C. japonica	[Py]Cl	5-HMF	<3 wt. %	6.9 wt.%	[39]
Pine sawdust	$AlCl_3$	Furfural	<82	85	[40]
Bamboo powder	Zeolite	Furfural	55	~65	[41]

Fig. 10.3 $Al_2(SO_4)_3$-assisted mechanochemical synthesis of 5-HMF from cellulose (Reprinted with permission from [36]. Copyright ©2020, Springer)

shows, Shen et al. [36] using ball-milling with $Al_2(SO_4)_3$-assisted pretreatment in preparation of 5-HMF from cellulose, in which $Al_2(SO_4)_3$ not only acts as a catalyst but also promotes cellulose comminution during the milling pretreatment step. Mechanochemical pretreatment also reduces reaction time, with ball milling, a 79% yield of 5-HMF and 80% yield of furfural were obtained after 9 min at 170 °C from glucan and xylan, respectively [37, 38]. This is due to soluble molecules obtained in the catalyst-assisted mechanochemical biomass pretreatment step. It is demonstrated that the catalyst-assisted mechanochemical method is an efficient technology in biomass transformation into furfural and 5-HMF, in which the objective product yield increase and short reaction time are possible compared to the traditional solution-based catalytic method.

10.2.3   *Sorbitol*

Sorbitol is notable among biomass-related materials, as it can be used for the production of pharmaceutical intermediates, monomers of polymers or fuels [42]. Sorbitol can be synthesized from cellulose *via* acidic hydrolysis into sugars and their further hydrogenation in the presence of hydrogen donor sources [43, 44]. Although some processes have succeeded in the conversion of cellulose

Table 10.3 Catalytic results for single ball-milling of biomass and mixed ball-milling

Catalyst	Conv. (%)	Sorbitol (%)	Ref.
Ru/AC	86	17	[50]
(Ru/AC)$_{mix}$	100	46	[50]
Ru/AC	88	42	[48]
(Ru/AC)$_{mix}$	89	69	[51]
Ru-Ni/AC	54.1	31.7	[51]
(Ru-Ni/AC)$_{mix}$	86.1	74.3	[51]
Ru-Ni/CNT	74.5	41.4	[51]
(Ru-Ni/CNT)$_{mix}$	99.3	70.8	[51]
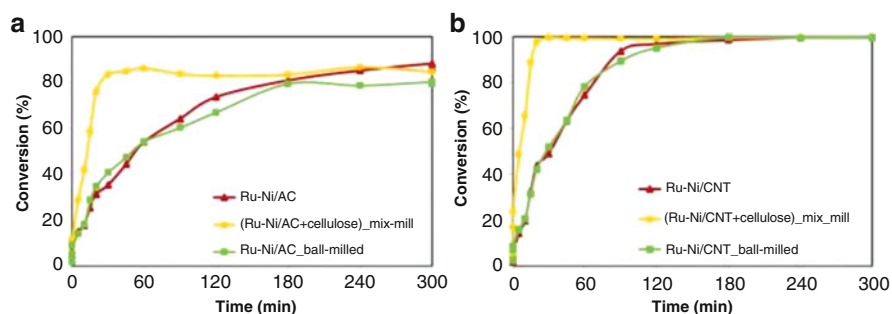
Fig. 10.4 Conversion of cellulose *via* a mixed feedstock/catalyst milling process. (**a**) Ru- -Ni/AC ball-milled together with cellulose and (**b**) Ru-Ni/CNT ball-milled together with cellulose. (Reaction conditions: cellulose 0.75 g, catalyst 0.3 g, water 300 mL, at 205 °C under 5 MPa H$_2$ (Reprinted with permission from [51]. Copyright © 2017, Springer)

into sorbitol with various metal catalysts such as Ru-containing composites [45, 46], there are still many challenges, such as the limit sorbitol selectivity and harsh reaction conditions.

In the previous section, mechanical pretreatment of biomass and acid catalyst-assisted mechanochemical ball milling pretreatment of biomass promoted biomass hydrolysis and dehydration. Results show that the selectivity of sorbitol and cellulose conversion can be increased after pretreatment by single ball milling [47] or catalyst ball-milling together with biomass (Table 10.3) [48–50]. Geboers et al. [47] reported a 27% yield of sorbitol with a 65% yield of sugar alcohol from ball milled cellulose. Ribeiro et al. [48, 51] reported that after milling cellulose with catalyst, the activity of catalyst and selectivity of sorbitol can be greatly increased. A 69% yield of sorbitol was realized by shaker milling a Ru/AC catalyst with cellulose without any acidic catalyst [51]. With cellulose ball-milled together with Ru-Ni/CNT catalyst, a yield of sorbitol of 70.8% was achieved from cellulose after just 1 h reaction time (Table 10.3). Based above section, the selectivity to sorbitol can be related to the improved physical contact between the catalyst and the solid substrate after ball-milling treatment. For both Ru-Ni/AC and Ru-Ni/CNT, the conversions of cellulose achieved with mixed-balling were higher than that without ball-milling pretreatment or single ball milling pretreatment (Fig. 10.4). The concurrent milling of catalyst and

cellulose gives a significant increase in the initial reaction rate (Fig. 10.4) that is due to mix-milling that can facilitate good solid-solid contact between substrate and active sites that become accessible to cellulose and promote the cellulose hydrolysis [50, 52]. In summary, the selectively and yield of sorbitol from hydrogenation of biomass can be increased if the reaction substrate is ball-milled together with catalyst.

10.2.4 Phenol

Phenol is a key feedstock in the chemical industry. It is mainly used for synthetic pharmaceuticals, herbicides, polymer precursors, resins, and plasticizers such as bisphenol-A [53–55]. Traditionally phenol is synthesized from petrochemical sources. However, there growing concerns about the environmental impact of petrochemical technologies and the declining reserves of such sources. Lignin has attracted much attention for supplanting petrochemicals for chemical precursors, due to it being a rich source of aromatics [56, 57]. Lignin (15–20%) along with cellulose (40–50%) and hemicellulose (25–35%) are the main basic structural components of lignocellulosic materials [58]. The procedure for the synthesis of lignin into phenol involves the separation of lignin from lignocellulosic materials and catalytic lignin depolymerization, dehydrogenation/oxidation into phenol [53, 59].

In the conversion of lignin into phenol, the most important step is mechanical milling (e.g. ball-milling and ultrafine grinding) of raw biomass (e.g. wood, corn stover, wheat straw) to disrupt the lignocellulosic cell wall polymers and promote the separation of lignin with cellulose/hemicellulose (Fig. 10.5) [22, 60–62]. The lignin in biomass is likely a branched polymer and cross-linked (Fig. 10.5) [63]. Some works have reported a schematic for heterogeneity of ball-milled treatment in lignin separation [64, 65]. In general, ball-milled pretreatment can reduce native cell wall
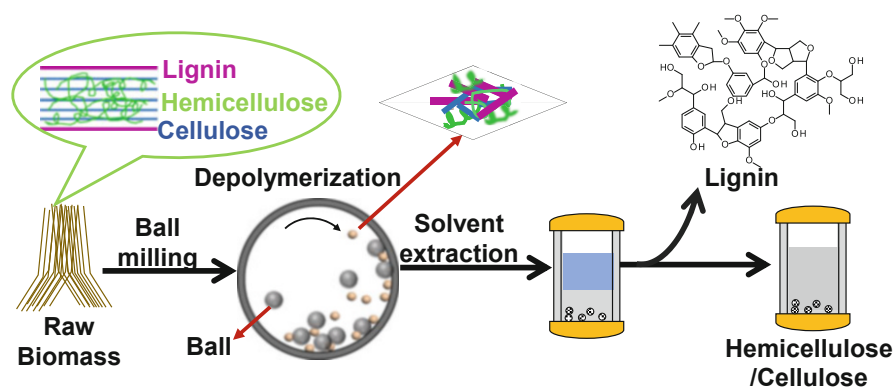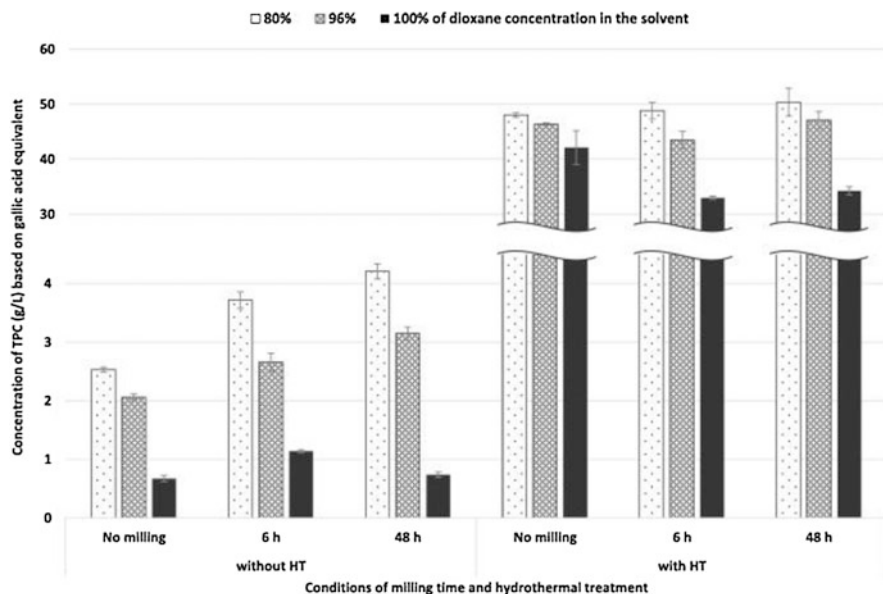

Fig. 10.5 Separation of lignin with cellulose and hemicellulose with ball-milling pretreatment

Fig. 10.6 Concentration of total phenolic compounds (TPC) (g/L) of hydrothermal conversion of lignin after ball-milling pretreatment (Reprinted with permission from [62]. Copyright © 2020, Springer)

recalcitrance, modify the supramolecular structure of the lignin-cellulose-hemicellulose matrix and depolymerization the cell wall of waste biomass (Fig. 10.5), which results in increasing the lignin separation.

The limited phenol yield from lignin is also due to the complex structure, heterogeneity and variety of lignin [66]. Mechanochemical processes (e.g. ball-milling) were also used in the second step to promote lignin depolymerization into lower molecular weight liquid products and further catalytic cracking into phenols [62, 67–70]. Chemical catalysis with mechanochemical treatment of biomass (*e.g.* ball milling treatment methods) has become a promising technology for lignin conversion into phenol. Bolm et al. [69] develop mechanochemical base-catalyzed degradation of lignin to the phenol derivatives under mild conditions. This was followed by Dabral *et al*,[71] who obtained excellent yields of phenol derivatives from lignin through mechanochemical-oxidation of lignin with HO-TEMPO/KBr in presence of ozone. Jang et al. [62] showed that that in the extraction of lignin, the total extracted phenolic compounds (TPC) concentration after ball milling pretreatment increased (Fig. 10.6). Moreover, Nair et al. [67] developed a combined mechanochemical and photocatalytic (titania consisting of anatase and rutile) oxidation process that transformed lignin into phenol. High yields of phenolic compounds from ball-milled lignin were obtained after 3–4 h of UV exposure and phenolic compounds formed even when milled without light. Compared to photocatalysis-assisted dry milling, catalysis of wet-milled mixtures with water or organic solvents (hexane) resulted in high yields of phenolics. Powder X-ray
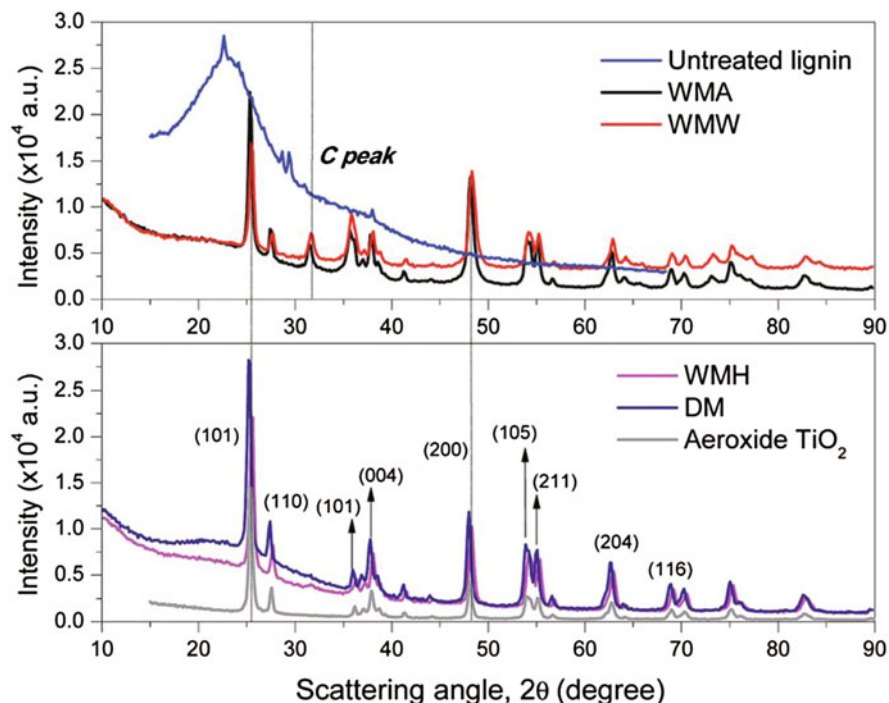
Fig. 10.7 Diffractograms of titania, lignin, and other milled samples under wet condition (Reprinted with permission from [67]. Copyright © 2016, Royal Society of Chemistry)

diffraction of pristine lignin milled with titania produced a new diffraction peak at 31.7 ° which was only realized after wet milling of lignin with acetone and water. This was attributed to the interaction between lignin and catalyst (Fig. 10.7).

Mechanochemical processes are highly effective that can be used in various waste biomass transformation steps, such as hydrolysis to reducing sugars, dehydration of reducing sugars to 5-HMF and furfural, hydrogenation for the realization of sorbitol, and lignin depolymerization, dehydrogenation-oxidation into phenol. Application of mechanochemical pretreatments (e.g. ball milling) can efficiently disrupt the crystalline structure of biomass, reduce particle sizes (comminution), break complex molecular and macromolecular networks. Many works have developed catalysis-assisted mixed mechanochemical processes to reduce the reaction time and improve product yields. This is due to the mechanochemical pretreatment not only produces comminution but also facilitates catalytic processes during the pretreatment step.

10.3   Functional Materials from Waste Biomass

Using waste biomass as a carbon source has emerged as an efficient way to synthesis high-value functional carbon materials. Mechanical ball milling technology has been widely used for the valorization of waste biomass to carbon-based materials such as adsorbents, catalysts, electrodes, flame retardants, and soil remediation agents.

10.3.1   Adsorbents

Carbon materials synthesized from waste biomass are potential substitutes for binder/filter media in adsorption areas. Generally, the adsorption capacity was observed to increase with higher surface areas, rich electrostatic interactions, and abundant functional groups. Mechanical treatment is an efficient way to improve the total surface area of functional carbon materials [72]. The physical- and chemical-properties of carbon material induced by ball milling are controlled by preparation temperatures of pristine biochar, pretreatment times, substrate-ball mass ratios (BPR), and milling media. After a ball milling pretreatment, the specific surface area can be greatly increased to ~350 m^2/g from 2 to 10 m^2/g [72]. With treatment by ball milling, high surface area carbon materials were obtained through particle size reduction of porous biochar [73]. Additionally, the ball mill pretreatment of biochar influences the oxygen-containing functional groups resulting in improved diffusion properties, the introduction of ionic defects, and the formation of graphitic structures [74].

Biochar or biochar-based composites materials synthesized *via* ball milling are efficient for the removal of inorganic and heavy metal pollutants (Ni, Hg, Cr, As and Cd) from wastewater [75]. For instance, the adsorption capacities of ball-milled bone biochar for Cd(II), Cu(II) and Pb(II) were 165.8 mg/g, 287.6 mg/g and 558.9 mg/g, respectively (25 °C, pH 5.0), which was much higher than that the un-milled biochar (75.2 mg/g, 163.8 mg/g and 389.5 mg/g, respectively) [76]. The mechanism investigated showed that the enhancement of the adsorption capacity of the biochar is due to the increased total surface area and oxygen-containing groups on the carbon frame after ball-milling treatment.

Carbon materials from waste biomass *via* ball-milling were reported to be effective in the adsorption and removal of antibiotics [77, 78]. For instance, negligible sulfonamide antibiotics were removed by biochars synthesized directly from raw bamboo, bagasse, and hickory chips. However, ball milling biochars prepared from the above waste biomass all showed high removal efficiencies of sulfamethoxazole from 33.4% to 83.3% and sulfapyridine from 39.8% to 89.6% [79]. The introduction of oxygen and nitrogen-containing groups into the biochar *via* ball milling resulted in improved adsorption capacities for antibiotics [80] which can be attributed to the interaction of the biochar functional groups with the adsorbate

through the formation of hydrophobic interaction, π-π interaction, and electrostatic interaction.

Ball milled carbon materials also show good adsorption performance for gaseous molecules due to internal pore structures developed during processing. The surface area of hickory wood biochar increasing to 285 m^2/g from ∼10 m^2/g after ball milling. The adsorbent had a high capacity for different VOCs (toluene, cyclohexane, chloroform, ethanol, and acetone) [81]. In addition to an improvement in the total surface area, the increased polarity of carbon materials induced by ball milling pretreatment also benefits adsorption of VOCs.

Hierarchical porous carbon adsorbents, with application in Hg^0 removal, can be fabricated mechanochemically using waste biomass rice straw. Large numbers of oxygen-containing functional groups were generated simultaneously after removal of a hard $CaCO_3$ template. The ball milled carbon adsorbent showed higher removal efficiency for Hg^0 from flue gas than that of conventional biochar (65% vs. 40) due to its hierarchical porous structures and oxygen-containing functional groups [82].

Ball milling is also a feasible method for the modification of biochar. Lyu et al. [83] obtained thiol-modified biochar from poplar wood biochar with 3-mercaptopropyltrimethoxysilane *via* the ball-milling treatment process. The thiol-modified biochar that has -SH groups, larger surface area and more negatively charged surface. It was demonstrated to be efficient for removal of CH_3Hg^+ and Hg^{2+} (CH_3Hg^+:104.9 mg/g and Hg^{2+}: 320.1 mg/g), which is much higher than the pristine biochar (CH_3Hg^+:8.21 mg/g and Hg^{2+}: 105.7 mg/g).[83].

10.3.2 Catalysts

Waste biomass-derived biochars/biochar-metal composites with catalytically-active groups introduced *via* mechanochemical processing have been used for photocatalysis [77], thermocatalysis [84], and electrocatalysis [85].

In a photocatalytic reaction system, the electrons of carbon defects in waste biomass derived-biochars were excited and shifted to oxygen-containing groups thus leading to the formation of $\cdot O_2^-$ and H^+. It was demonstrated that the milling process generally produced in more oxygen-containing functional groups as well as more reactive oxygen species on the carbon materials. Xiao et al. [86] reported that the concentrations of oxygen-containing groups including carboxyl, lactic, and phenolic hydroxyls of unmilled biochar were 0.1–0.3, 0–1.1, and 0.1–0.7 mmol/g, respectively. The concentrations of the above oxygen-containing groups increased to 0.2–0.5, 0.4–1.2, and 0.2–1.1 mmol/g, respectively after ball milling. The O/C ratio of biochar from poplar at 300 °C increased from 28.4% to 35.0% after ball milling. Photocatalysis experiments showed that the ball milled biochar exhibited a much higher enrofloxacin degradation rate (80.2%) compared with unmilled biochar (13.9%). Additionally, the mineralization ability improved from 0% to 66.4% after ball milling [86].
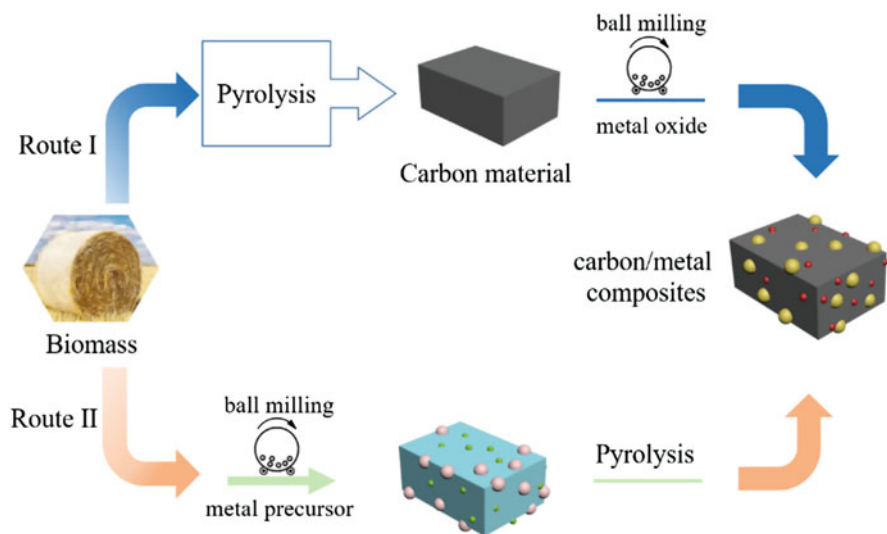
Fig. 10.8 Metal/biochar composites can be realized through the milling of catalysts with biochar or milling of precursors followed by pyrolysis (Reprinted with permission from [5]. Copyright © 2020, Springer)

When being used as thermal catalysis, waste biomass could be mechanochemically converted into biochar with more surface defects and rich catalytic sites such as heteroatoms (B, O, S). Due to the high stability of carbon materials under reaction conditions, catalytically active waste biomass-derived biochars could be employed as heterogeneous catalysts for different catalytic reactions. For example, surface-oxidized coke powder could be used as catalyst in the hydrolysis of cellulose [52, 87]. In conventional approaches, oxidation of biochar involves large amounts of liquid waste and requires high temperatures. Fukuoka et al. [88] reported a solvent-free ball milling strategy to fabricate -COOH rich biochars, in which the oxidant of persulfate salts (e.g. $KHSO_5$ and $(NH_4)_2S_2O_8$) was mixed with biochars by ball milling. By this way, highly carboxylated porous carbon materials were produced without the use of solvent. In this strategy, ball milling enhanced the contact between the biochar support and the persulfate salts and the mechanical processing gradually introduced surface defects in the carbons. The modified biochar obtained possessed a high-density of -COOH groups and showed good activity for the acid hydrolysis of cellulose into glucose with yields of 85% [68].

Metal/biochar composite catalysts can be directly synthesized *via* a physical solvent-free ball milling process. There are two ways to prepare metal/biochar composite as shown in Fig. 10.8. The first way is to prepare biochar and then ball mill the biochar with metal oxide. In another way, the waste biomass can be mixed with metal precursors by first milling a mixture of metal catalyst with waste biomass followed by pyrolysis to realize carbon/metal oxide composites.

In this way, the milling process can ensure complete dispersal of metal/metal oxides into waste biomass-derived biochars and facilitate carbon precursor particle refinement. He et al. [89] prepared an iron sulfide and biochar (FeS@BC) composite through ball milling and applied it to the to the oxidative degradation of tetracycline. The FeS@BC showed excellent performance which could be attributed to the fact that the milling process reduced the agglomeration of FeS, and increased the total surface area of the biochar.

Mechanochemically synthesized carbonaceous materials from waste biomass have also shown great potential in the electrocatalytic reactions. Lyu et al. [85] used ball- milled biochar as glassy carbon electrodes. These electrodes showed high electrocatalytic activity towards reduction of $Fe(CN)_6^{3-}$. The electrochemical properties including electrical conductivity, peak-to-peak separation, series resistance, and charge transfer resistance where are all improved after the milling pretreatment. Such properties play an important role in promoting electron transfer kinetics and reducing the interface resistance of carbon support materials [86].

10.3.3   Electrodes

Porous conductive carbons from waste biomass with a high surface area are desired materials for electrodes especially for electrical double-layer (EDL). The electrochemical performance is greatly affected by surface area since micropores provide abundant adsorbing sites for the electrolyte ions and mesopores promote diffusion of electrolyte ions [90]. Ball milling can greatly increase the surface area, pore-volume, oxygen-containing functional groups, hydrophilicity, crystallinity, and graphitization of waste biomass-derived carbons [74, 85]. This special structure facilitates electron transfer and reduces interface resistance of carbon materials as electrodes. To further improve the electrochemical performance of carbon electrodes, it is essential to increase the total microporous surface area of carbon materials. Mechanical ball milling could provide a powerful force for mixing waste biomass with other solid reagents. It can then be integrated into the chemical activation process to produce porous carbon materials from waste biomass and applied as electrodes for energy storage and electrochemical applications.

Traditional methods to prepare porous carbon materials are chemical activation *via* impregnation of waste biomass with KOH or $KHCO_3$ solutions and then pyrolysis at high temperatures [91, 92]. Mechanical ball milling provides an alternative solvent-free way to fabricate porous carbon materials. Zhai et al. [93] mixed the waste biomass of vinasse with the activating agent KOH *via* ball milling under solvent-free conditions. The ball milling process enhances homogenous contact between carbon precursor and KOH and improves pore production. Additionally, the ball milling process improves surface wettability of carbon materials since more surface defects are formed. In this way, porous carbons with surface area up to 3047 m^2/g have been obtained and have excellent characteristics for supercapacitor electrodes.

To further improve the electrochemical performance of carbon-based electrodes, heteroatom (N, S, B) doped porous carbon could be obtained from waste biomass *via* a one-pot ball milling method [94]. In this facile approach, waste biomass is employed as a carbon precursor, urea or melamine are used as heteroatom precursor, and K_2CO_3 (or $KHCO_3$) is used as the activator [95]. After ball milling and high temperature pyrolysis, high-surface porous carbons (up to 3000 m^2/g) with a high concentration of covalently modified heteroatoms are formed. In this way, the specific capacitances of the carbon materials can reach 302.7 F/g at a current density of 0.5 A/g in 6 M KOH.

10.3.4 Flame Retardants

Flame-retardants are a class of compounds that are added to combustible materials to prevent fires or slow the ignition of fire. Phosphorylation is one of the most important ways to fabricate flame-retardant carbon materials. Traditionally, phosphorylated carbons are obtained *via* the direct treatment of waste biomass with concentrated liquid phosphoric acid which is corrosive and difficult to recycle [96]. Fiss et al. [97] describe a facile, green, solvent-free and previously unreported way for direct phosphorylation of cellulose and lignin *via* ball milling method with solid phosphorus pentoxide (P_2O_5). Based on ^{31}P MAS NMR and TGA analysis, it was shown that phosphorus groups could be grafted onto the carbon support *via* mechanochemical treatment, and the obtained cellulose nanocrystals have high thermally stability.

10.3.5 Soil Remediation Agent

Because of the high content of carbon, large specific surface area and unique surface properties (i.e., more functional groups), carbon materials prepared from waste biomass *via* the mechanical milling process have been applied in the soil remediation. The biochar-soil composites prepared by sing-step dry ball milling wheat straw could be used for the retention of organic pollutants. Yan et al. [98] reported that the complexation of biochar with soil minerals was enhanced after ball milling of biochar due to its rich oxygen-containing functional groups. In this way, the sorption capacity and uptake rate of biochar-soil composites for phthalate esters in soil was greatly improved.

10.4 Conclusions and Future Outlook

Waste biomass as renewable and sustainable sources have a strong potential for supplanting traditional fossil sources in the production of platform chemicals, fuels and high-value carbon materials. However, it is still a challenging task due to the complex characteristics and robust structure of the waste biomass. This chapter has provided an overview of mechanochemical technology that can be developed into a green and efficient process for transformation of waste solid biomass. The mechanochemical treatment (*e.g.* ball milling) is an important step in conversion of waste biomass into chemicals and functional carbon materials, since it can disrupt the recalcitrant structure of biomass, break hydrogen bonding in biomass, decreasing the polymerization degree of biomass and facilitate the good solid-solid contact between catalyst and biomass substrate.

Generally, high yields of chemicals (e.g. reducing sugars, 5-HMF, furfural, sorbitol, phenol) can be obtained from waste biomass *via* mechanochemical pretreatment (e.g. ball milling) and selective hydrolysis, dehydration, hydrogenation or oxidation reactions. It is found that mechanochemical assisted conditions such as the type of ball milling method (single ball milling or mixed ball milling method), milling mode, milling time, ball material, ball size and other parameters, can greatly affect the yield of products. Practically, homogeneous catalyst ball-milled together with biomass prior to use in biomass transformation reactions, where the mechanical process promotes good physical contact between the catalyst and biomass, increases solid-solid mass transfer and increases chemical productivity.

Mechanochemistry provides a new way to design and fabricate functional carbon materials from waste biomass. Compared with conventional wet processing, the mechanochemical approach is solvent-lite or solvent-free, requires short reaction times, and can be performed at ambient temperatures. Highly porous carbon materials with surface area surface area up to 3047 m^2/g have been obtained by mechanochemically-assisted (ball-milling treatment) from waste biomass. The mechanochemical processing can promote the introduction of active sites such as oxygen-rich groups, metal oxides and heteroatoms into the carbon materials. The obtained functional carbon materials have a range of applications such as adsorbents, catalysts, electrodes and soil amendments.

Despite the outstanding contribution of mechanochemistry in waste biomass valorization, high consumption of energy limits its large-scale industrialization. Combining mechanical ball milling with other methods such as enzyme and cryoprocessing is a potential way to reduce energy input. Energy savings are also realized when processes are scaled beyond the laboratory. Unfortunately, such large-scale studies may be resource prohibitive. In addition, the impact of the mechanochemical process on the conversion of solid waste biomass at the molecular level is not yet fully understood and further investigations are needed to quantify and model frictional effects on reactive materials. As research in this field expands, many of these hurdles will be overcome and mechanochemical processing will become a mainstay in chemical plant design for sustainable society.

References

1. Bertran J. Mechanochemistry: an overview. Pure Appl Chem. 1999;71:581–6. https://doi.org/10.1351/pac199971040581.

2. Gomollón-Bel F. Ten chemical innovations that will change our world: IUPAC identifies emerging technologies in chemistry with potential to make our planet more sustainable. Chem Int. 2019;41:12–7. https://doi.org/10.1515/ci-2019-0203.

3. Boldyrev VV, Tkáčová K. Mechanochemistry of solids: past, present, and prospects. J Mater Synth Process. 2000;8:121–32. https://doi.org/10.1023/A:1011347706721.

4. Takacs L. The mechanochemical reduction of AgCl with metals. J Therm Anal Calorim. 2007;90:81–4. https://doi.org/10.1007/s10973-007-8479-8.

5. Shen F, Xiong X, Fu JY, Yang JR, Qiu M, Qi XH, Tsang DCW. Recent advances in mechanochemical production of chemicals and carbon materials from sustainable biomass resources. Renew Sust Energ Rev. 2020;130:109944. https://doi.org/10.1016/j.rser.2020.109944.

6. Tan D, García F. Main group mechanochemistry: from curiosity to established protocols. Chem Soc Rev. 2019;48:2274–92. https://doi.org/10.1039/C7CS00813A.

7. Howard JL, Cao Q, Browne DL. Mechanochemistry as an emerging tool for molecular synthesis: what can it offer? Chem Sci. 2018;9:3080–94. https://doi.org/10.1039/C7SC05371A.

8. Guo H, Lian Y, Yan L, Qi X, Smith RL. Cellulose-derived superparamagnetic carbonaceous solid acid catalyst for cellulose hydrolysis in an ionic liquid or aqueous reaction system. Green Chem. 2013;15:2167–74. https://doi.org/10.1039/C3GC40433A.

9. Rinaldi R, Schüth F. Acid hydrolysis of cellulose as the entry point into biorefinery schemes. ChemSusChem. 2009;2:1096–107. https://doi.org/10.1002/cssc.200900188.

10. Vyver SV, Peng L, Geboers J, Schepers H, Clippel F, Gommes CJ, Goderis B, Jacobs PA, Sels BF. Sulfonated silica/carbon nanocomposites as novel catalysts for hydrolysis of cellulose to glucose. Green Chem. 2010;12:1560–3. https://doi.org/10.1039/C0GC00235F.

11. Lee JW, Jeffries TW. Efficiencies of acid catalysts in the hydrolysis of lignocellulosic biomass over a range of combined severity factors. Bioresour Technol. 2011;102:5884–90. https://doi.org/10.1016/j.biortech.2011.02.048.

12. Gu BJ, Wang J, Wolcott MP, Ganjyal GM. Increased sugar yield from pre-milled Douglas-fir forest residuals with lower energy consumption by using planetary ball milling. Bioresour Technol. 2018;251:93–8. https://doi.org/10.1016/j.biortech.2017.11.103.

13. Szczesniak B, Borysiuk S, Choma J, Jaroniec M. Mechanochemical synthesis of highly porous materials. Mate Horiz. 2020;7:1457–73. https://doi.org/10.1039/D0MH00081G.

14. Hick SM, Griebel C, Restrepo DT, Truitt JH, Buker EJ, Bylda C, Blair RG. Mechanocatalysis for biomass-derived chemicals and fuels. Green Chem. 2010;12:468–74. https://doi.org/10.1039/B923079C.

15. Meine N, Rinaldi R, Schüth F. Solvent-free catalytic depolymerization of cellulose to water-soluble oligosaccharides. ChemSusChem. 2012;5:1322–9. https://doi.org/10.1002/cssc.201100770.

16. Kaufman RMD, Käldström M, Richter U, Schüth F, Rinaldi R. Mechanocatalytic depolymerization of lignocellulose performed on hectogram and kilogram scales. Ind Eng Chem Res. 2015;54:4581–92. https://doi.org/10.1021/acs.iecr.5b00224.

17. Zhang Q, Jérôme F. Mechanocatalytic deconstruction of cellulose: an emerging entry into biorefinery. ChemSusChem. 2013;6:2042–4. https://doi.org/10.1002/cssc.201300765.

18. Blair RG, Chagoya K, Biltek S, Jackson S, Sinclair A, Taraboletti A, Restrepo DT. The scalability in the mechanochemical syntheses of edge functionalized graphene materials and biomass-derived chemicals. Faraday Discuss. 2014;170:223–33. https://doi.org/10.1039/C4FD00007B.

19. Hideno A, Inoue H, Tsukahara K, Fujimoto S, Minowa T, Inoue S, Endo T, Sawayama S. Wet disk milling pretreatment without sulfuric acid for enzymatic hydrolysis of rice straw. Bioresour Technol. 2009;100:2706–11. https://doi.org/10.1016/j.biortech.2008.12.057.

20. Avolio R, Bonadies I, Capitani D, Errico ME, Gentile G, Avella M. A multitechnique approach to assess the effect of ball milling on cellulose. Carbohydr Polym. 2012;87:265–73. https://doi.org/10.1016/j.carbpol.2011.07.047.

21. Dornath P, Cho HJ, Paulsen A, Dauenhauer P, Fan W. Efficient mechano-catalytic depolymerization of crystalline cellulose by formation of branched glucan chains. Green Chem. 2015;17:769–75. https://doi.org/10.1039/C4GC02187H.

22. Liu H, Chen X, Ji G, Yu H, Gao C, Han L, Xiao W. Mechanochemical deconstruction of lignocellulosic cell wall polymers with ball-milling. Bioresour Technol. 2019;286:121364. https://doi.org/10.1016/j.biortech.2019.121364.

23. Ji G, Gao C, Xiao W, Han L. Mechanical fragmentation of corncob at different plant scales: impact and mechanism on microstructure features and enzymatic hydrolysis. Bioresour Technol. 2016;205:159–65. https://doi.org/10.1016/j.biortech.2016.01.029.

24. Wu Y, Ge S, Xia C, Mei C, Kim KH, Cai L, Smith LM, Lee J, Shi SQ. Application of intermittent ball milling to enzymatic hydrolysis for efficient conversion of lignocellulosic biomass into glucose. Renew Sust Energ Rev. 2021;136:110442. https://doi.org/10.1016/j.rser.2020.110442.

25. Da SAS, Inoue H, Endo T, Yano S, Bon EPS. Milling pretreatment of sugarcane bagasse and straw for enzymatic hydrolysis and ethanol fermentation. Bioresour Technol. 2010;101:7402–9. https://doi.org/10.1016/j.biortech.2010.05.008.

26. Su TC, Fang Z, Zhang F, Luo J, Li XK. Hydrolysis of selected tropical plant wastes catalyzed by a magnetic carbonaceous acid with microwave. Sci Rep. 2015;5:17538. https://doi.org/10.1038/srep17538.

27. Jiang LQ, Zheng AQ, Meng JG, Wang XB, Zhao ZL, Li HB. A comparative investigation of fast pyrolysis with enzymatic hydrolysis for fermentable sugars production from cellulose. Bioresour Technol. 2019;274:281–6. https://doi.org/10.1016/j.biortech.2018.11.098.

28. Zakaria MR, Fujimoto S, Hirata S, Hassan MA. Ball milling pretreatment of oil palm biomass for enhancing enzymatic hydrolysis. Appl Biochem Biotechnol. 2014;173:1778–89. https://doi.org/10.1007/s12010-014-0964-5.

29. Lange JP, Van DHE, Van BJ, Price R. Furfural-a promising platform for lignocellulosic biofuels. ChemSusChem. 2012;5:150–66. https://doi.org/10.1002/cssc.201100648.

30. Ramli NAS, Amin NAS. Kinetic study of glucose conversion to levulinic acid over Fe/HY zeolite catalyst. Chem Eng J. 2016;283:150–9. https://doi.org/10.1016/j.cej.2015.07.044.

31. Van PRJ, Van DWJC, De JE, Rasrendra CB, Heeres HJ, De VJG. Hydroxymethylfurfural, a versatile platform chemical made from renewable resources. Chem Rev. 2013;113:1499–597. https://doi.org/10.1021/cr300182k.

32. Guo H, Hirosaki Y, Qi X, Smith RL. Synthesis of ethyl levulinate over amino-sulfonated functional carbon materials. Renew Energy. 2020;157:951–8. https://doi.org/10.1016/j.renene.2020.05.103.

33. Qian Y, Zhu L, Wang Y, Lu X. Recent progress in the development of biofuel 2,5-dimethylfuran. Renew Sust Energ Rev. 2015;41:633–46. https://doi.org/10.1016/j.rser.2014.08.085.

34. Qi X, Guo H, Li L, Smith RL. Acid-catalyzed dehydration of fructose into 5-hydroxymethylfurfural by cellulose-derived amorphous carbon. ChemSusChem. 2012;5:2215–20. https://doi.org/10.1002/cssc.201200363.

35. Zhang L, Yu H, Wang P, Dong H, Peng X. Conversion of xylan, D-xylose and lignocellulosic biomass into furfural using $AlCl_3$ as catalyst in ionic liquid. Bioresour Technol. 2013;130:110–6. https://doi.org/10.1016/j.biortech.2012.12.018.

36. Shen F, Sun S, Zhang X, Yang JR, Qiu M, Qi XH. Mechanochemical-assisted production of 5-hydroxymethylfurfural from high concentration of cellulose. Cellulose. 2020;27:3013–23. https://doi.org/10.1007/s10570-020-03008-w.

37. Carrasquillo-Flores R, Kaldstrom M, Schuth F, Dumesic JA, Rinaldi R. Mechanocatalytic depolymerization of dry (ligno) cellulose as an entry process for high-yield production of furfurals. ACS Catal. 2013;3:993–7. https://doi.org/10.1021/cs4001333.

38. Schüth F, Rinaldi R, Meine N, Käldström M, Hilgert J, Rechulski MDK. Mechanocatalytic depolymerization of cellulose and raw biomass and downstream processing of the products. Catal Today. 2014;234:24–30. https://doi.org/10.1016/j.cattod.2014.02.019.

39. Yoshioka K, Yamada T, Ohno H, Miyafuji H. Production of furan compounds from Cryptomeria japonica using pyridinium chloride under various conditions. BioResources. 2018;13:208–19. https://doi.org/10.15376/biores.13.1.208-219.

40. Lappalainen K, Dong Y. Simultaneous production of furfural and levulinic acid from pine sawdust via acid-catalysed mechanical depolymerization and microwave irradiation. Biomass Bioenergy. 2019;123:159–65. https://doi.org/10.1016/j.biombioe.2019.02.017.

41. Yoshida K, Nanao H, Kiyozumi Y, Sato K, Sato O, Yamaguchi A, Shirai M. Furfural production from xylose and bamboo powder over chabazite-type zeolite prepared by interzeolite conversion method. J Taiwan Inst Chem Eng. 2017;79:55–9. https://doi.org/10.1016/j.jtice.2017.05.035.

42. Chen J, Wang S, Huang J, Chen L, Ma L, Huang X. Conversion of cellulose and cellobiose into sorbitol catalyzed by ruthenium supported on a polyoxometalate/metal-organic framework hybrid. ChemSusChem. 2013;6:1545–55. https://doi.org/10.1002/cssc.201200914.

43. Zhang X, Durndell LJ, Isaacs MA, Parlett CMA, Lee AF, Wilson K. Platinum-catalyzed aqueous-phase hydrogenation of D-glucose to D-sorbitol. ACS Catal. 2016;6:7409–17. https://doi.org/10.1021/acscatal.6b02369.

44. Rey-Raap N, Ribeiro LS, Órfão JJDM, Figueiredo JL, Pereira MFR. Catalytic conversion of cellulose to sorbitol over Ru supported on biomass-derived carbon-based materials. Appl Catal B Environ. 2019;256:117826. https://doi.org/10.1016/j.apcatb.2019.117826.

45. Gromov NV, Medvedeva TB, Rodikova YA, Timofeeva MN, Parmon VN. One-pot synthesis of sorbitol via hydrolysis-hydrogenation of cellulose in the presence of Ru-containing composites. Bioresour Technol. 2020;319:124122. https://doi.org/10.1016/j.biortech.2020.124122.

46. Mao F, Chen S, Zhang Q, Yang L, Fu Z. Ru/p-containing porous biochar-efficiently catalyzed cascade conversion of cellulose to sorbitol in water under medium-pressure H_2 atmosphere. Bull Chem Soc Jpn. 2020;93:1026–35. https://doi.org/10.1246/bcsj.20200095.

47. Geboers J, Van DVS, Carpentier K, De BK, Jacobs P, Sels B. Efficient catalytic conversion of concentrated cellulose feeds to hexitols with heteropoly acids and Ru on carbon. Chem Commun. 2010;46:3577–9. https://doi.org/10.1039/C001096K.

48. Ribeiro LS, Órfão JJM, Pereira MFR. Enhanced direct production of sorbitol by cellulose ball-milling. Green Chem. 2015;17:2973–80. https://doi.org/10.1039/C5GC00039D.

49. Ribeiro LS, Delgado JJ, Órfão JJM, Pereira MFR. Direct conversion of cellulose to sorbitol over ruthenium catalysts: influence of the support. Catal Today. 2017;279:244–51. https://doi.org/10.1016/j.cattod.2016.05.028.

50. Almohalla M, Rodríguez-Ramos I, Ribeiro LS, Órfão JJM, Pereira MFR, Guerrero-Ruiz A. Cooperative action of heteropolyacids and carbon supported Ru catalysts for the conversion of cellulose. Catal Today. 2018;301:65–71. https://doi.org/10.1016/j.cattod.2017.05.023.

51. Ribeiro LS, Delgado JJ, Órfão JJM, Pereira MFR. Carbon supported Ru-Ni bimetallic catalysts for the enhanced one-pot conversion of cellulose to sorbitol. Appl Catal B Environ. 2017;217:265–74. https://doi.org/10.1016/j.apcatb.2017.04.078.

52. Kobayashi H, Yabushita M, Komanoya T, Hara K, Fujita I, Fukuoka A. High-yielding one-pot synthesis of glucose from cellulose using simple activated carbons and trace hydrochloric acid. ACS Catal. 2013;3:581–7. https://doi.org/10.1021/cs300845f.

53. Wang M, Liu M, Li H, Zhao Z, Zhang X, Wang F. Dealkylation of lignin to phenol via oxidation-hydrogenation strategy. ACS Catal. 2018;8:6837–43. https://doi.org/10.1021/acscatal.8b00886.

54. Rinaldi R, Jastrzebski R, Clough MT, Ralph J, Kennema M, Bruijnincx PCA, Weckhuysen BM. Paving the way for lignin valorisation: recent advances in bioengineering, biorefining and catalysis. Angew Chem Int Ed. 2016;55:8164–215. https://doi.org/10.1002/anie.201510351.

55. Tejado A, Peña C, Labidi J, Echeverria JM, Mondragon I. Physico-chemical characterization of lignins from different sources for use in phenol-formaldehyde resin synthesis. Bioresour Technol. 2007;98:1655–63. https://doi.org/10.1016/j.biortech.2006.05.042.

56. Zakzeski J, Bruijnincx PCA, Jongerius AL, Weckhuysen BM. The catalytic valorization of lignin for the production of renewable chemicals. Chem Rev. 2010;110:3552–99. https://doi.org/10.1021/cr900354u.

57. Wang Y, Wang Q, He J, Zhang Y. Highly effective C-C bond cleavage of lignin model compounds. Green Chem. 2017;19:3135–41. https://doi.org/10.1039/c7gc00844a.

58. Bertella S, Luterbacher JS. Lignin functionalization for the production of novel materials. Trends Chem. 2020;2:440–53. https://doi.org/10.1016/j.trechm.2020.03.001.

59. Verboekend D, Liao Y, Schutyser W, Sels BF. Alkylphenols to phenol and olefins by zeolite catalysis: a pathway to valorize raw and fossilized lignocellulose. Green Chem. 2015;18:297–306. https://doi.org/10.1039/C5GC01868D.

60. Qu T, Zhang X, Gu X, Han L, Ji G, Chen X, Xiao W. Ball milling for biomass fractionation and pretreatment with aqueous hydroxide solutions. ACS Sustain Chem Eng. 2017;5:7733–42. https://doi.org/10.1021/acssuschemeng.7b01186.

61. Mittal A, Katahira R, Donohoe BS, Pattathil S, Kandemkavil S, Reed ML, Biddy MJ, Beckham GT. Ammonia pretreatment of corn Stover enables facile lignin extraction. ACS Sustain Chem Eng. 2017;5:2544–61. https://doi.org/10.1021/acssuschemeng.6b02892.

62. Jang SK, Lee HJ, Jung CD, Yu JH, Choi WJ, Choi IG, Kim H. High yield solvent extraction of hydrothermal and ball-milling treated lignin prior to enzymatic hydrolysis for co-valorization of lignin and cellulose in Miscanthus sacchariflorus. Fuel. 2020;269:117428. https://doi.org/10.1016/j.fuel.2020.117428.

63. Balakshin M, Capanema EA, Zhu X, Sulaeva I, Potthast A, Rosenau T, Rojas OJ. Spruce milled wood lignin: linear, branched or cross-linked? Green Chem. 2020;22:3985–4001. https://doi.org/10.1039/D0GC00926A.

64. Ahmed MA, Lee JH, Raja AA, Weon CJ. Effects of gamma-valerolactone assisted fractionation of ball-milled pine wood on lignin extraction and its characterization as well as its corresponding cellulose digestion. Appl Sci. 2020;10:1599–611. https://doi.org/10.3390/app10051599.

65. Sapouna I, Lawoko M. Deciphering lignin heterogeneity in ball milled softwood: unravelling the synergy between the supramolecular cell wall structure and molecular events. Green Chem. 2021;23:3348–64. https://doi.org/10.1039/D0GC04319B.

66. Biannic B, Bozell JJ. Efficient cobalt-catalyzed oxidative conversion of lignin models to benzoquinones. Org Lett. 2013;15:2730–3. https://doi.org/10.1021/ol401065r.

67. Nair V, Dhar P, Vinu R. Production of phenolics via photocatalysis of ball milled lignin-TiO$_2$ mixtures in aqueous suspension. RSC Adv. 2016;6:18204–16. https://doi.org/10.1039/C5RA25954A.

68. Sun C, Zheng L, Xu W, Dushkin AV, Su W. Mechanochemical cleavage of lignin models and lignin via oxidation and a subsequent base-catalyzed strategy. Green Chem. 2020;22:3489–94. https://doi.org/10.1039/D0GC00372G.

69. Kleine T, Buendia J, Bolm C. Mechanochemical degradation of lignin and wood by solvent-free grinding in a reactive medium. Green Chem. 2013;15:160–6. https://doi.org/10.1039/C2GC36456E.

70. Brittain AD, Chrisandina NJ, Cooper RE, Buchanan M, Cort JR, Olarte MV, Sievers C. Quenching of reactive intermediates during mechanochemical depolymerization of lignin. Catal Today. 2018;302:180–9. https://doi.org/10.1016/j.cattod.2017.04.066.

71. Dabral S, Wotruba H, Hernández JG, Bolm C. Mechanochemical oxidation and cleavage of lignin β-O-4 model compounds and lignin. ACS Sustain Chem Eng. 2018;6:3242–54. https://doi.org/10.1021/acssuschemeng.7b03418.

72. Peterson SC, Jackson MA, Kim S, Palmquist DE. Increasing biochar surface area: optimization of ball milling parameters. Powder Technol. 2012;228:115–20. https://doi.org/10.1016/j.powtec.2012.05.005.

73. Lyu H, Gao B, He F, Zimmerman AR, Ding C, Huang H, Tang J. Effects of ball milling on the physicochemical and sorptive properties of biochar: experimental observations and governing mechanisms. Environ Pollut. 2018;233:54–63. https://doi.org/10.1016/j.envpol.2017.10.037.
74. Huang L, Wu Q, Liu S, Yu S, Ragauskas AJ. Solvent-free production of carbon materials with developed pore structure from biomass for high-performance supercapacitors. Ind Crop Prod. 2020;150:112384. https://doi.org/10.1016/j.indcrop.2020.112384.
75. Lyu H, Gao B, He F, Ding C, Tang J, Crittenden JC. Ball-milled carbon nanomaterials for energy and environmental applications. ACS Sustain Chem Eng. 2017;5:9568–85. https://doi.org/10.1021/acssuschemeng.7b02170.
76. Xiao J, Hu R, Chen G. Micro-nano-engineered nitrogenous bone biochar developed with a ball-milling technique for high-efficiency removal of aquatic cd(II), cu(II) and Pb(II). J Hazard Mater. 2020;387:121980. https://doi.org/10.1016/j.jhazmat.2019.121980.
77. Xiao Y, Lyu H, Yang C, Zhao B, Tang J. Graphitic carbon nitride/biochar composite synthesized by a facile ball-milling method for the adsorption and photocatalytic degradation of enrofloxacin. J Environ Sci. 2021;103:93–107. https://doi.org/10.1016/j.jes.2020.10.006.
78. Xiang W, Wan Y, Zhang X, Tan Z, Gao B. Adsorption of tetracycline hydrochloride onto ball-milled biochar: governing factors and mechanisms. Chemosphere. 2020;255:127057. https://doi.org/10.1016/j.chemosphere.2020.127057.
79. Huang J, Zimmerman AR, Chen H, Gao B. Ball milled biochar effectively removes sulfamethoxazole and sulfapyridine antibiotics from water and wastewater. Environ Pollut. 2020;258:113809. https://doi.org/10.1016/j.envpol.2019.113809.
80. Zhang Y, Miao X, Xiang W, Zhang J, Cao C, Wang H, Hu X, Gao B. Ball milling biochar with ammonia hydroxide or hydrogen peroxide enhances its adsorption of phenyl volatile organic compounds (VOCs). J Hazard Mater. 2020;403:123540. https://doi.org/10.1016/j.jhazmat.2020.123540.
81. Xiang W, Zhang X, Chen K, Fang J, He F, Hu X, Tsang DCW, Ok YS, Gao B. Enhanced adsorption performance and governing mechanisms of ball-milled biochar for the removal of volatile organic compounds (VOCs). Chem Eng J. 2020;385:123842. https://doi.org/10.1016/j.cej.2019.123842.
82. Shi Q, Wang Y, Zhang X, Shen B, Wang F, Zhang Y. Hierarchically porous biochar synthesized with $CaCO_3$ template for efficient Hg^0 adsorption from flue gas. Fuel Process Technol. 2020;199:106247–54. https://doi.org/10.1016/j.fuproc.2019.106247.
83. Lyu H, Xia S, Tang J, Zhang Y, Gao B, Shen B. Thiol-modified biochar synthesized by a facile ball-milling method for enhanced sorption of inorganic Hg^{2+} and organic CH_3Hg^+. J Hazard Mater. 2019;384:121357. https://doi.org/10.1016/j.jhazmat.2019.121357.
84. Yang X, Yu I, Tsang D, Budarin VL, Yong SO. Ball-milled, solvent-free Sn-functionalisation of wood waste biochar for sugar conversion in food waste valorisation. J Clean Prod. 2020;268:122300. https://doi.org/10.1016/j.jclepro.2020.122300.
85. Lyu H, Yu Z, Gao B, He F, Huang J, Tang J, Shen B. Ball-milled biochar for alternative carbon electrode. Environ Sci Pollut Res. 2019;26:14693–702. https://doi.org/10.1007/s11356-019-04899-4.
86. Xiao Y, Lyu H, Tang J, Wang K, Sun H. Effects of ball milling on the photochemistry of biochar: enrofloxacin degradation and possible mechanisms. Chem Eng J. 2020;384:123311. https://doi.org/10.1016/j.cej.2019.123311.
87. Anh TT, Chung P, Katz A. Weak-acid sites catalyze the hydrolysis of crystalline cellulose to glucose in water: importance of post-synthetic functionalization of the carbon surface. Angew Chem Int Ed. 2015;54:11050–3. https://doi.org/10.1002/ange.201504865.
88. Shrotri A, Kobayashi H, Fukuoka A. Mechanochemical synthesis of a carboxylated carbon catalyst and its application in cellulose hydrolysis. ChemCatChem. 2016;8:1059–64. https://doi.org/10.1002/cctc.201501422.
89. He J, Tang J, Zhang Z, Wang L, Liu Q, Liu X. Magnetic ball-milled FeS@biochar as persulfate activator for degradation of tetracycline. Chem Eng J. 2021;404:126997. https://doi.org/10.1016/j.cej.2020.126997.

90. Xia K, Gao Q, Jiang J, Hu J. Hierarchical porous carbons with controlled micropores and mesopores for supercapacitor electrode materials. Carbon. 2008;46:1718–26. https://doi.org/10.1016/j.carbon.2008.07.018.

91. Qu J, Wang Y, Tian X, Jiang Z, Deng F, Tao Y, Jiang Q, Wang L, Zhang Y. KOH-activated porous biochar with high specific surface area for adsorptive removal of chromium (VI) and naphthalene from water: affecting factors, mechanisms and reusability exploration. J Hazard Mater. 2021;401:123292. https://doi.org/10.1016/j.jhazmat.2020.123292.

92. He X, Li J, Meng Q, Guo Z, Liu Y. Enhanced adsorption capacity of sulfadiazine on tea waste biochar from aqueous solutions by the two-step sintering method without corrosive activator. J Environ Chem Eng. 2020;9:104898. https://doi.org/10.1016/j.jece.2020.104898.

93. Shi C, Hu L, Guo K, Li H, Zhai T. Highly porous carbon with graphene nanoplatelet microstructure derived from biomass waste for high-performance supercapacitors in universal electrolyte. Adv Sustain Syst. 2017;1:1600011. https://doi.org/10.1002/adsu.201600011.

94. Schneidermann C, Jackel N, Oswald S, Giebeler L, Presser V, Borchardt L. Solvent-free mechanochemical synthesis of nitrogen-doped nanoporous carbon for electrochemical energy storage. ChemSusChem. 2017;10:2416–24. https://doi.org/10.1002/cssc.201700459.

95. Qi J, Zhang W, Xu L. Solvent-free mechanochemical preparation of hierarchically porous carbon for supercapacitor and oxygen reduction reaction. Chemistry. 2018;24:18097–105. https://doi.org/10.1002/chem.201804302.

96. Cao L, Yu I, Tsang D, Zhang S, Sik OY, Kwon EE, Song H, Sun PC. Phosphoric acid-activated wood biochar for catalytic conversion of starch-rich food waste into glucose and 5-hydroxymethylfurfural. Bioresour Technol. 2018;267:242–8. https://doi.org/10.1016/j.biortech.2018.07.048.

97. Fiss BG, Hatherly L, Stein RS, Friščić T, Moores A. Mechanochemical phosphorylation of polymers and synthesis of flame-retardant cellulose nanocrystals. ACS Sustain Chem Eng. 2019;7:7951–9. https://doi.org/10.1021/acssuschemeng.9b00764.

98. Yan J, Quan G. Sorption behavior of dimethyl phthalate in biochar-soil composites: implications for the transport of phthalate esters in long-term biochar amended soils. Ecotoxicol Environ Saf. 2020;205:111169. https://doi.org/10.1016/j.ecoenv.2020.111169.