Green Chemistry

Accepted Manuscript

Volume 1 | Number 1 | Jan 2013 | Pages 1–100

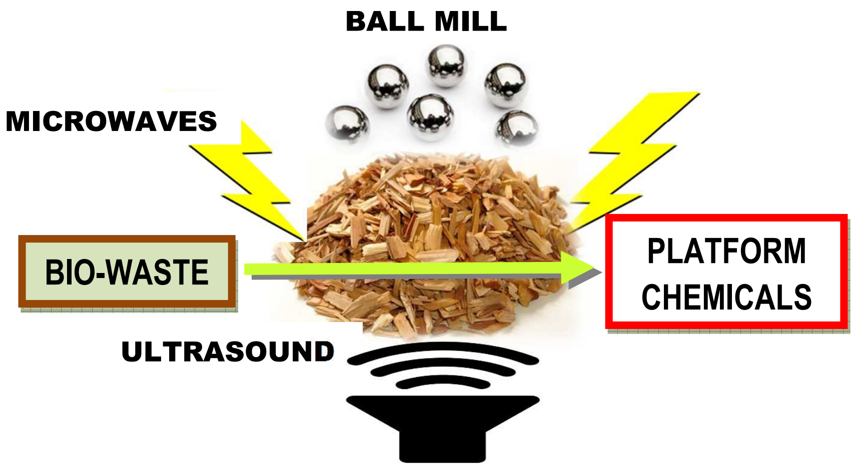
Green Chemistry

Cutting-edge research for a greener sustainable future

www.rsc.org/greenchem

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/greenchem


BALL MILL
MICROWAVES
BIO-WASTE
PLATFORM CHEMICALS
ULTRASOUND

Green Chemistry RSCPublishing

ARTICLE

Microwave, ultrasound and ball mill procedures for bio-waste valorisation

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

S. Tabasso,[a] D. Carnaroglio,[b] E. Calcio Gaudino[b] and G. Cravotto[b]*

Bio-waste valorisation has been one of the hottest research topics worldwide over the last decade. Following the biorefinery concept, the main goals are the search for inexpensive renewable resources for the production of chemicals, materials and energy, the transformation of bio-waste into useful by-products and the development of new technologies for process intensification to make all these conversions economically profitable. Bio-waste is generally a negative-cost feedstock for the potential production of high value-added chemicals and bioenergy. The present review has the aim of describing existing studies and applications of non-conventional energy sources such as microwaves, ultrasound and ball milling within this field. We have focused our attention on suitable protocols for the conversion of biomass into fine chemicals. Comparisons with classic procedures are a good means with which to highlight the huge advantages and potential scalability of these so-called "enabling technologies".

Introduction

Waste is currently a major worldwide issue and is becoming more and more important in both developing countries and the industrialized world. For this reason, alternatives to disposal and/or land filling are being increasingly considered attractive approaches for coping with both the environmental issues and the increasing global demand for energy, chemicals and materials. Bio-waste is an important source of lipids, carbohydrates, mineral acids, inorganic compounds (i.e. silica), dietary fibres and phytochemicals, including phenolics, carotenoids and tocopherols. Main bio-waste sources are agricultural residues, animal waste, municipal solid waste, tree forest residues and food waste. The inherent chemical complexity of food waste makes it a very attractive source for the conversion of crop residues and agro-industrial by-products into value-added chemicals. Food waste (FW) can be defined as the "end products of various food processing industries that have not been recycled or used for other purposes".[1] Most of the biomass on earth is found in the form of lignocellulose. The term lignocellulosics refers to woody and herbaceous plants and major crop residues such as sugar cane bagasse, wheat straw, and rice straw. Lignocellulosic materials are mainly composed of cellulose, hemicellulose and lignin. Theoretically, lignocellulosic material is an ideal source of raw sugars for industrial processes since it does not affect food supplies and price. Other sources of carbohydrates are chitin biomass, produced as the industrial waste material of fisheries and the seafood industry. Only a negligible amount of the chitin biomass generated is used in (e.g. formulations for skin moisturizers) joint-pain relievers, anti-cancer and antimicrobial agents and in most cases it is after its partial deacetylation to chitosan. Therefore, it would be of huge economic and environmental interest for this sustainable chitin biomass waste to be transformed into high value fuel and chemical products.

Biomass can be used in a number of different ways to deliver valuable feedstock materials for industry. Building-block

---

[a] Dipartimento di Chimica, University of Turin, Via P. Giuria 7, I-10125 Turin, Italy.
[b] Dipartimento di Scienza e Tecnologia del Farmaco and NIS – Centre for Nanostructured Interfaces and Surfaces, University of Turin, Via P. Giuria 9, I-10125 Turin, Italy. E-mail address: giancarlo.cravotto@unito.it; Fax: +39 011 6707687

chemicals, as considered in this paper, are molecules that contain multiple functional groups and which have revealed themselves as potential sources of new families of useful molecules after treatment. All building block chemicals can further be converted into a wide spectrum of derivatives *via* chemical processes, such as reduction, oxidation, dehydration, hydrogenolysis and direct polymerization. Sugars and polyols (e.g. glucose, sorbitol, glycerol), organic acids (e.g. succinic, levulinic, itaconic, lactic acids) and furans (e.g. furfural and 5-hydroxymethylfurfural - HMF) are some of the key biomass-derived platform molecules that can be obtained from the various types of feedstock. Several generic types of bio-based chemical products fall into the following categories:[2]

- Carbohydrate polymers of natural origin
- Plant based fats and oils (and to a lesser extent from animal sources)
- Terpene based materials
- Chemicals from carbohydrate containing materials

The US Department of Energy submitted a list of 12 potential bio-based platform chemicals that are obtained from sugars (Table 1).[3] The 12 building blocks can be subsequently converted to a number of high-value bio-based chemicals or materials.

Table 1. Bio-based platform chemicals

C3	glycerol
	3-hydroxypropionic acid
C4	1,4 di-acids (succinic, fumaric and malic acid)
	aspartic acid
	3-hydroxybutyrolactone
C5	levulinic acid
	glutamic acid
	itaconic acid
	xylitol/arabinitol
C6	sorbitol
	glucaric acid
	2,5-furan-di-carboxylic acid

In addition, furan derivatives such as 5-hydroxymethyl-furfural (HMF), furfural and 2,5-furandicarboxylic acid are mentioned as they hold great promise in their role of primary building blocks for the biorefinery.[4] Over the last three decades, significant amounts of effort have been put into in the development of environmentally friendly procedures that involve the generation of high energy micro-environments by means of non-conventional energy sources such as microwaves (MW)[5] and ultrasound (US).[6] Mechanochemical activation, mainly by ball mill reactors, also generates high energy micro-environments due to the localized pressures and frictional heating provided by the kinetic energy that it produces. The use of mechanical forces to induce chemical reactivity is the oldest and simplest technique used by mankind, and one which has existed since before the dawn of science. Mechanochemistry and sonochemistry share some striking similarities and numerous reactions can be rationalized, in both cases, purely in terms of mechanical effects.[7]

The peculiar properties of MW as a source of volumetric and selective dielectric heating can be efficiently exploited for the extraction of natural matrices, the hydrolysis of biopolymers and materials' further conversion into highly valuable fine chemicals.

US irradiation can also be regarded as a special type of energy input into a system. Heat transfer can be improved using MW selective heating, while US can provide hotspots and strong mechanical effects. US is transmitted through a medium *via* pressure waves and the main advantages it offers are directly linked to the physical effect of acoustic cavitation. Acoustic waves can break the cohesion of a liquid and create micro-cavities. These cavities are actually micro-bubbles which respond to the sound wave by growing until they become unstable. At that point, bubbles violently collapse creating drastic conditions inside the medium on a very short time scale; temperatures of 2000-5000K and pressures of up to 1800 bar are created inside the collapsing cavity. Shock waves, generated by cavity collapse, induce mechanical effects, such as the splitting of large molecules to smaller fragments, particle size reduction, surface cleaning and intensive mixing and heating. Sonochemical methods are also used in carbohydrate chemistry,[8] not only for biomass pre-treatment, but also for the hydrolysis and cleavage of oligo- and polysaccharides. The first report that dealt with US-assisted carbohydrate chemistry, published in 1933, qualitatively described the hydrolysis of aqueous starch, arabic gum and agar. Shorter chain molecules are produced at a frequency of 722 kHz as indicated by viscosity measurements.[9,10] It was later demonstrated that the treatment of aqueous solutions of chitosan and starch under US (360 kHz) significantly reduced the molecular weight of polysaccharides.[11] The effect that US had on their degradation was caused by the formation of OH• radicals and mechanochemical effects. Indeed, scission was accompanied by side reactions which led to the formation of carbonyl groups. The sonochemical yield of this process was shown to depend on polymer concentration, US power and the gas used to saturate the solution. Compared to chitosan, the US-induced chain scission of starch gives lower yields, probably because the chain conformation of starch is different to the rod-like chitosan macromolecules.

Several studies have looked into the conversion of biomass under non-conventional methods, with various catalytic systems and solvents.

Mineral acid catalysts

The first attempt to convert monosaccharides into platform chemicals under MW-irradiation was the conversion of fructose into HMF. The latter is formed *via* the acid-catalysed hydrolysis of hexoses, while pentoses afford furfural (Fig. 1). Further dehydration of HMF yields levulinic and formic acid.

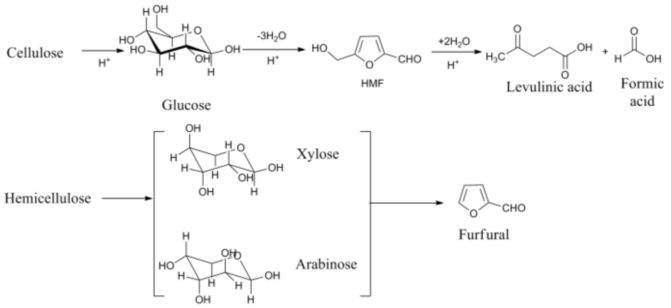


Fig. 1 Production of furfural and hydroxymethyl furfural from xylose and fructose.

HMF holds enormous potential as a raw material for the production of chemicals, polymers and biofuels as it can be converted to γ-valerolactone (GVL) and furan-2,5-dicarboxylic acid (FDCA), a potential building block for polyesters. HMF, levulinic acid (LA) and GVL are of interest as precursors of hydrocarbon fuels. In 1977, Kuster and Temmik studied the influence of pH (1-6) on fructose conversion into HMF under MW irradiation.[12] The conversion rate of d-fructose passes through an inflexion point at pH 3.1, whereas no HMF formation occurred at pH 3.9 and no LA formation occurred at pH 2.7. Isomerisation to d-glucose is observed at pH 4.5. More recently, a highly concentrated aqueous fructose solution (27 wt.%) was dehydrated to 5-HMF in a MW-assisted process[13] and the influence of numerous parameters was studied. At a 0.01 M HCl concentration, high temperatures favoured the dehydration reaction to HMF in a flash process (1 min). A fructose conversion of 95% was achieved with a 53% HMF yield. Higher acid concentrations yielded a mixture of formic acid, LA and HMF. The authors showed that the presence of the catalyst strongly influenced the HMF yield, while an increase in the initial MW power had no effect. When a shorter reaction time of only 1s was applied, a 52% fructose conversion value with 63% 5-HMF selectivity was obtained. On the other hand, glucose dehydration yielded 49% HMF with 10 wt % sulphuric acid under MW irradiation for 1 min.[14] In most cases, monosaccharides, such as fructose or glucose, have been used to produce HMF instead of biomass, as the depolymerisation of cellulose is perhaps one of the most difficult hurdles that the conversion of lignocellulose into HMF and furfural must overcome. The dilute acid hydrolysis of cellulose in a batch MW reactor was first published in 2007.[15] The recourse to dilute phosphoric acid led to the production of a mixture of simple monosaccharides (xylose, arabinose and glucose) whose respective yields were modulated by the appropriate setting of reaction conditions (i.e. acid concentration and MW irradiation conditions). On the other hand, starch was easily depolymerized to glucose under sonochemical conditions when sulphuric acid was used as a catalyst[16] even at 23 °C.[17,18] Phosphoric acid was also used for the hydrolysis of municipal solid waste for ethanol production: [19] α-cellulose and grass clippings were treated at 160 °C yielding Phosphoric acid can be used under milder conditions to form cellulose oligomers at 50 °C under conventional heating in a two-step acid-catalysed hydrolysis process.[20] Deep hydrolysis was obtained in the second-step where the oligomers were heated under MW irradiation up to 160 °C with dilute sulphuric acid. Yield and conversion selectivity to glucose increased up to 73.3% and 80.1%, respectively, under MW irradiation. These values are much higher than the figures obtained using the classic hydrolysis process. By comparison, only 20.3% glucose yield and 48.9% selectivity were obtained using the one-step MW methodology.

The mechanical depolymerisation of cellulosic fibres proved to be an efficient solution for enhancing oligosaccharide yields. Milling treatments are able to break hydrogen bonds, thus facilitating the access of the acid catalysts. Indeed, the solvent-free milling of the cellulosic fibres that are impregnated with HCl or H_2SO_4 produces water-soluble oligosaccharides (WSOs) in quantitative yields in 2 h. Lignocellulosic materials (e.g., beechwood, pinewood, and sugar cane bagasse) are also transformed by the mechano-catalytic method into soluble products within 2-3 h. WSOs undergo acid hydrolysis in aqueous solutions under MW irradiation with full conversion at 403 K after only 10 min.[21]

Potato peel can be considered a suitable source of sugars which are obtained from starch depolymerisation. Acidic solutions of potato starch, wet potato sludge and dry potato sludge were irradiated with US and MW separately, or better simultaneously, by means of a pyrex horn inserted into a multimode MW oven from the top.

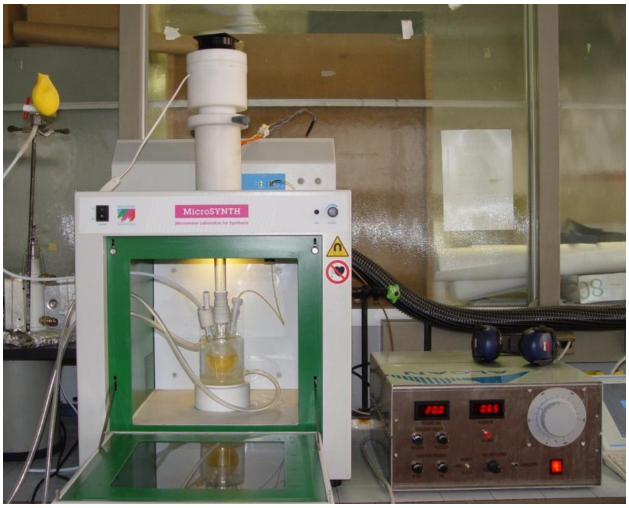


Fig. 2 Hybrid US/MW reactor developed at the University of Turin in collaboration with Danacamerini.[22]

The combined US/MW reactor, equipped with a 20 kHz probe with a non-metallic horn, was applied in dual irradiation mode at 60 °C for 120 min.[23] A synergistic effect, due to the optimal heat and mass transfer in the reaction mixture, on the depolymerisation rate was observed, which furnished a higher yield and a shorter reaction time. In fact, the highest reducing sugar yield (57%) from complex dry potato sludge was obtained under US/MW irradiation. Sonication separated the granules from the biomass debris, while MW enhanced the reaction, giving potatoes starch depolymerisation of up to 77%.

Different types of biomass can be used to produce HMF and furfural in MW-assisted processes that enhance cell structure disruption and cause the release of cell constituents and a higher reaction rate. Studies into the direct production of HMF and furfural from biomass showed that the acid-catalysed conversion of wheat straw using hydrochloric acid *via* the MW-assisted process yielded furfural as the major product.[24] The highest furfural yield from wheat straw treatment was 51.3%. HMF was produced from the acid-catalysed conversion of wheat straw *via* the MW-assisted process in low yields. This may be due to the temperature being limited by the maximum temperature of the MW-assisted heating system, which was only 200 °C. The temperature range used for the production of furfural was not suitable for HMF production from wheat straw *via* acid-catalysed conversion. Glucose was also released during the acid-catalysed conversion of wheat straw *via* the MW-assisted process. The maximum glucose yield was 43.6% of the glucan content in wheat straw.

The auto-hydrolysis of corn cobs with water in a stainless steel pressure reactor afforded liquors which were rich in xylans and which could be converted into furfural under MW irradiation.[25] Corn cobs, an abundant agricultural waste, show high hemicelluloses content (about 30-40 wt.% of dry material). A 37% furfural yield, with respect to total hemicellulose content in the raw material, was obtained using HCl as catalyst. The oligomers contained in corncob hydrolysates were rapidly converted into monomers under MW irradiation. Besides HMF and furfural preparation, a rapid and selective MW-assisted synthesis of 5-chloromethyl furfural (CMF), starting from a range of carbohydrates (biphasic reaction mixture HCl/dichloroethane), has recently been described.[26] CMF is a new multifunctional bio-platform molecule of great potential value as it can be converted into several valuable furan moieties (Fig. 3).

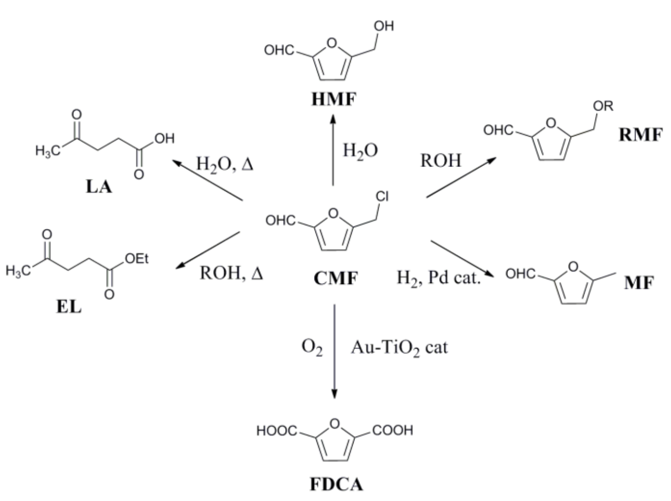


Fig. 3 Chloromethyl furfural (CMF) as a bio-platform molecule. Reproduced from ref 26 with permission of The Royal Society of Chemistry.

Of the different types of biomass investigated, inulin yielded 70% CMF with 98 % selectivity when irradiated at 80°C for 15 min.. This was of particular interest as it paved the way for the use of non-food polysaccharides for the formation of an interesting and valuable bio-platform molecule in extremely high yield and selectivity. The selective MW heating of the acidic aqueous layer of the biphasic mixture (different dissipation factors) led to excellent selectivity observed over the earlier preparation of this molecule.

Further dehydration of HMF gave LA and formic acid. LA can also be produced from hemicellulose in a 3 steps process in which furfural and furfuryl alcohol are intermediates.[27,28] LA, a sugar derived keto-acid (4-oxopentanoic acid), is a key intermediate for the production of fine chemicals and biofuels.

The hydrolysis of corn starch in a combined US-MW reactor afforded 23% LA with HCl.[29] Polysaccharides of both plant and animal origin were successfully converted to LA in the presence of mineral acids under dielectric heating. Cellulose afforded 31% LA when treated with 2 M HCl at 190 °C for 50 min, while 22.7 % LA was achieved from chitosan.[30]More recently, we achieved full conversion and high LA yields (90% from cellulose and 95% from chitosan) *via* a MW-assisted flash reaction with 1M HCl.[31] In addition, tomato plant waste, which was collected at the end of the crop harvest season, was selectively converted into LA (63% yield) under the same conditions. It is important to highlight the role of reaction temperature, in fact, the hydrolysis of polysaccharides selectively afforded simple monosaccharides at around 150 °C.

Other carbohydrate-rich biomass residues, i.e. sugar beet molasses, whey powder, wine yeast, potato peel sludge, spent hops, malt dust and apple marc have been oxidized or hydrolysed under acidic or alkaline conditions and MW irradiation to yield other marketable chemicals such as aliphatic acids, sugar acids and mono-/disaccharides.[32] Various different acidic reaction products were obtained, according to the composition of the starting materials, in a MW-assisted digestion procedure with 30% HNO_3. Potato peel sludge afforded glucaric acid, while wine yeast offered advantages for the production of tartaric acid. The oxidation of whey powder yielded acetic acid that was produced in large amounts. Alternatively, hydrolysis (100 °C) led to monosaccharides at lower HCl concentrations and high pressure. The combination of HCl hydrolysis and MW-assisted digestion converted up to 45% of the dry matter content of malt dust into monosaccharides, giving glucose as the main product. The composition and yields of products formed from MW-assisted residue digestion were almost identical to those generated *via* conventional methods. However, the former provides a considerable reduction in reaction time and reagent demand.

Ionic liquids

Some ionic liquids facilitate cellulose dissolution by disrupting the hydrogen bonding between molecules. Because ionic liquids consist of anions and cations, they strongly absorb MW irradiation and can be used in lignocellulosic biomass conversion either alone or in combination with other catalysts. Some ionic liquids behave as Brønsted acid catalysts, for example 3-allyl-1-(4-sulfobutyl)imidazolium trifluoromethane sulfonate, and others as Lewis acid derivatives, such as 3-allyl-1-(4-sulfurylchloride-butyl)imidazolium trifluoromethane sulfonate. Fructose dehydration has been performed in DMSO under MW irradiation in the presence of these two catalysts, yielding 85% and 88% HMF at full conversion, respectively.[33] Yield and selectivity increased with increasing temperatures. This effect was stronger for the Brønsted acid, which was significantly less active than the Lewis acid at lower temperatures. The combination of ionic liquid/MW irradiation is an efficient mean of carrying out the dehydration of highly concentrated fructose to form HMF; highly concentrated fructose was dissolved in [C_4mim]Cl and irradiated in a MW reactor for a time ranging from 1 to 30 minutes yielding ca. 57-97% HMF.[34] SO_3H-functionalized ionic liquids, such as 1-methyl-3-(3-sulfopropyl)imidazolium hydrogen sulfate ([C_3SO_3Hmim] HSO_4) were applied in the direct conversion of cellulose into LA.[35]

Ionic liquids and Lewis acids

Because some ionic liquids have been widely used to dissolve carbohydrates such as fructose, glucose and cellulose, they have been studied in combination with acid catalysts, such as Lewis acids, for the conversion of biomass into added-value chemicals. For example, the $CrCl_3$-catalysed MW-assisted conversion of glucose into 5-HMF has been investigated in a series of ionic liquids, namely [BMIM][Cl], 1-ethyl-3-methyl imidazolium chloride ([EMIM][Cl]), 1-hexyl-3-methyl imidazolium chloride ([HexylMIM][Cl]), 1-methyl imidazolium hydrogen sulfate ([HMIM][HSO_4]) and 1-butyl-3-methyl imidazolium hydrogen sulfate ([BMIM][HSO_4].[36] The results show that ionic liquids that include a Cl^- anion, in the presence of $CrCl_3$, were the most effective for converting glucose into 5-HMF. This was probably due to the formation of [BMIM][$CrCl_4$] whose basic properties probably accelerated the isomerization of glucose to fructose and the dehydration of fructose into 5-HMF.

HMF yields of between 53% and 62% were obtained from different types of cellulose after 2 min using $CrCl_3$. [Bmim]Cl was also used in combination with $ZrCl_4$ for the direct conversion of cellulose into HMF.[37] [Bmim]Cl showed excellent dielectric properties for MW absorption and enabled the complete dissolution of cellulose. In addition, the combination of [Bmim]Cl and $ZrCl_4$ formed a series of complex ions such as $[ZrCl_5]^-$ and $[ZrCl_6]^{2-}$ which played an important role in the isomerization of glucose into fructose, followed by dehydration, to produce HMF. To minimize the use of expensive ionic liquids, DMA that contains LiCl has been utilized as a solvent for purified cellulose. Despite the good solubilisation properties of this system, the [BMIM]Cl additive was proven to be essential for the conversion of sugarcane bagasse to 5-ethoxymethyl-2-furfural (EMF), a promising biofuel, in the presence of the $Zr(O)Cl_2/CrCl_3$ catalyst under MW irradiation[38] On the contrary, HMF was converted into EMF in the absence of the [BMIM]Cl additive without affecting EMF yield and selectivity.

The highest HMF yields achieved from cellulose and sugarcane bagasse were 57% and 42%, respectively. The enhanced HMF yield in the presence of [BMIM]Cl additive is due to the increase in Cl^- ion concentration, which promotes cellulose hydrogen bond disruption.

Ionic liquids and solid acid catalysts

The application of solid acid catalysts in cellulose hydrolysis is seen to be more environmentally friendly as it is able to simplify the downstream processes and circumvent waste acid and water disposal. The solid acid-promoted hydrolysis of cellulose in ionic liquids can be accelerated by MW heating. Of the solid acid catalysts used for this purpose, zeolites are very commonly used as they are non-toxic and easily recovered from the solution. Being microporous, aluminosilicate minerals, they can accommodate a wide variety of cations, which can be released into solution where they exhibit different types of catalytic activity. Ionic liquids were able to improve the catalytic activity of zeolites and increase contact between cellulose and zeolites. Zhao and Zhang proposed a new route to cellulose hydrolysis using HY zeolite and [C_4mim]Cl under MW irradiation which was used to accelerate hydrolysis rates.[39]

Other types of solid acids such as Amberlyst-15 and NKC-9 (macroporous styrene-based sulfonic acid resin) were tested for furfural production in [BMIM]Cl under MW irradiation from D-xylose, xylan and lignocellulosic biomass.[40]

The HMF and furfural yields obtained from the various types of untreated biomass and catalysed by various solid acids are shown in Table 2.

Biomass itself can be used to synthesize solid acid catalysts for MW-assisted 5-HMF production. Six catalysts were prepared by carbonization, at 400 °C, and sulfonation, at 150 °C, of raw biomass materials, such as glucose, fructose, cellulose, lignin, bamboo and Jatropha hulls.[41]

Carbon carriers are amorphous carbons consisting of polycyclic aromatic carbon sheets where all the S atoms in the carbon materials are in the form of $–SO_3H$, as active sites.[42] The lignin-derived solid acid catalyst (LCC) proved to be the most effective in the conversion of sugars to HMF in a combined solvent system formed of DMSO and [BMIM][Cl] and MW irradiation.

Table 2 Furfural and HMF yields from untreated biomass

Entry	T (°C)	Time (min)	Sample	Catalyst	Dosage (g)	Yield (%)	
						HMF	Furfural
2	160	10	corncob	Amberlyst-15	0.3	7.2	11.6
3	160	10	corncob	NKC-9	0.3	11.8	13.3
5	160	10	pine wood	Amberlyst-15	0.3	15.4	20.1
6	160	10	pine wood	NKC-9	0.3	17.9	19.7
8	160	10	grass	Amberlyst-15	0.3	18.6	22.5
9	160	10	grass	NKC-9	0.3	22.6	24.3
10	170	5	corncob	Amberlyst-15	0.3	12.5	13.9
12	170	5	corncob	NKC-9	0.3	12.8	13.6
13	160	3	corncob	Amberlyst-15+$AlCl_3$	0.3+0.015	16.3	17.5
15	160	3	corncob	NKC-9 $AlCl_3$	0.3+0.015	16.9	15.7

Green Chemistry RSCPublishing

ARTICLE

Metal chlorides

As shown earlier, the conversion of glucose to HMF is more difficult than the conversion of fructose. Indeed, it requires an additional step; the isomerization of glucose to fructose. This is followed by the dehydration of fructose in the presence of a catalyst. Metal chlorides have proven to be efficient catalysts for the conversion of glucose as they effectively catalyse not only the dehydration step but also the isomerization. $AlCl_3{\cdot}6H_2O$ is abundant and inexpensive and has been shown to catalyse the isomerization of glucose to fructose in aqueous solution.[43] Yang, Hu and Abu-Omar reported the synthesis of 5-hydroxymethylfurfural (HMF) from different types of biomass (pine wood, grass and poplar) in a biphasic medium of water/tetrahydrofuran under MW irradiation with $AlCl_3{\cdot}6H_2O$ as the catalyst. Despite low HMF yields, high furfural yields (51-66%) can be obtained from raw biomass in a one-pot reaction in this system. In addition to 5-HMF, 1-(furan-2-yl)-2-hydroxyethanone was also identified in the process of cellulose degradation as it can be produced from the chemical conversion of cellulose in a $ZnCl_2$ solution of high concentration.[44]

An explanation of the mechanism, that is, the process by which a combination of $ZnCl_2$ and MW results in the conversion of cellulose to 1-(furan-2-yl)-2-hydroxyethanone, is depicted in Figure 4.

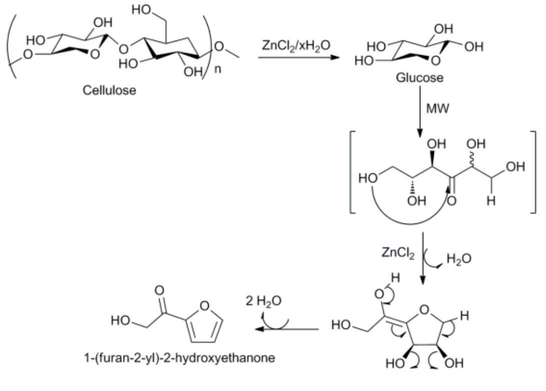


Fig 4 Direct conversion of cellulose to 1-(furan-2-yl)-2-hydroxyethanone in concentrated $ZnCl_2$ solution under MW irradiation. Reprinted from ref. 44 with permission from Elsevier.

The aldohexose formed from the action of MW irradiation over the zinc-oxygen coordination species rearranges into an enolate molecular intermediate structure with a carbonyl group at C-3 position. The oxygen atom on C-6 then induces a nucleophilic attack on the C-3 carbonyl carbon atom and forms a five-carbon ring *via* dehydration and the action of $ZnCl_2$, which functions as a Lewis acid. This proposed mechanism explains how MW energy can promote cellulose degradation into the aldohexose intermediate and how the five-carbon ring continuously dehydrates and eventually forms 1-(furan-2-yl)-2-hydroxyethanone.

Polyoxometalates

Polyoxometalates (or heteropolyacids) have attracted much attention in recent years because of their particular physicochemical properties. For example, $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$, in aqueous solutions exhibit stronger acidity than typical mineral acids such as H_2SO_4, HNO_3 and HCl. For this reason, they have been widely used in catalytic systems for biomass conversion.[45] Polyoxometalates exhibited excellent performance in the hydrolysis of cellulose to glucose. In addition, after extraction with organic solvents, the heteropoly acids can be separated from the homogeneous solution, dried and reused. Li et al. described cellulose hydrolysis, under MW irradiation at low temperatures (80-100 °C), which was catalysed by concentrated solutions of $H_3PW_{12}O_{40}$ (50%–88%, w/w). 88% HPW solutions yielded 75.6% glucose for the hydrolysis of cellulose at 90 °C for 3 h under MW irradiation.

Corncob, corn stover and bagasse were also used as feedstock under MW irradiation, giving 37.2%, 43.3% and 27.8% glucose yield, respectively. Furfural was also detected as a side product in these processes in yields of 11.6%, 7.26% and 7.47%, respectively. The reusability of HPW in corn stover was also investigated and it was shown that the yield of glucose gradually decreased, probably because of the presence of impurities and by-products which can damage catalytic active sites.

Solid catalysts

The large-scale use of acids suffers from several drawbacks, including reactor corrosion, catalyst recovery and waste disposal. The use of heterogeneous acids is a marked improvement which overcomes these limitations thanks to easy solid catalyst separation. In solid acid catalysed dehydration, the reaction rate is limited by surface reaction and mass transfer. For this reason, most hydrolysis processes with solid acids require the pre-treatment of cellulose, *via* ball milling, for example. In addition, catalytic activity can be improved by MW heating.[46] As many catalysts that are commonly used for carbohydrate conversion are toxic to the environment, immobilized catalysts can be used to overcome this problem.

For example, the use of $CrCl_3$, that has been immobilized on hydroxyapatite, has been proposed for the conversion of glucose under MW irradiation. [47]. In another example, Yepez *et al.* reported the use of supported Cu nanoparticles on aluminosilicate materials for the conversion of glucose to valuable products *via* tandem formic acid-promoted dehydration (to HMF) and further selective hydrogenation to 5-methylfurfuryl alcohol (MFA), under MW irradiation.[48] Formic acid acts as both the hydrogen-donating reagent (*via* decomposition into hydrogen and CO + CO_2) and the dehydration co-catalyst, promoting the formation of HMF and furfural as well as other products, including reduced species such as methyl furfural. Cu was present mostly in the form of copper oxide (Cu_2O). These species are reduced *in situ* and hydrogen is evolved from formic acid decomposition to provide Cu^0 reduced species which are responsible for the hydrogenating sites in the catalytic system.

Ion-exchange resins can also be used for fructose → HMF conversion. The treatment of fructose in water/acetone mixtures in the presence of a strongly acidic resin (DOWEX 50WX8-100) under MW irradiation yielded over 70% HMF.[49] 180 °C Combined mixtures of DMSO and acetone were also used for sulphated zirconia mediated fructose dehydration under MW heating. [50] The ZrO_2 and TiO_2 catalysed conversion of d-fructose and d-glucose produced moderate HMF yields (38.1% and 18.6% respectively) in an aqueous medium under MW irradiation at 200 ˚C.[51,52] To develop a more energy efficient heterogeneous catalyst, self-assembled mesoporous titania nanoparticles, synthesized using sodium salicylate as a template, were used in the efficient catalytic dehydration of carbohydrates to HMF under MW heating.[53] As self-assembled TiO_2 nanoparticles that contain mesoscopic void spaces and possess Lewis acidity proved to be efficient catalysts in the MW assisted conversion of carbohydrates into HMF, mesoporous titanium phosphate with framework acid sites should play a crucial role in this catalytic reaction. For example, a hierarchically macro/mesoporous titanium phosphate material, MTiP-1, with aggregated particles has been used as an active catalyst for the dehydration of biomass derived carbohydrates.[54] Fructose, glucose, mannose, sucrose, cellulose and sugarcane bagasse were converted into HMF under MW-assisted heating in various solvents, with yields ranging from 29 to 44%.

Of the solid acids available, HNb_3O_8 has been widely studied as a layered heterogeneous catalyst. However, a pre-exfoliation process is necessary to expose its acid sites and make them accessible to reactants. The dielectric heating abilities of MW have proven to be efficient in the *in situ* exfoliation of HNb_3O_8 and in catalysing carbohydrate dehydration in a pure aqueous solution.[55]

A series of biomass-derived carbohydrates with mono-, di- and polysaccharide structures, such as glucose, xylose, sucrose and inulin were used to investigate the applicability of HNb_3O_8 for their dehydration, showing that layered HNb_3O_8 gives high activity for sucrose hydrolysis, which simultaneously produces a large amount of fructose and glucose. Inulin can also be hydrolysed completely to form fructose and glucose. The high activity of HNb_3O_8 in both polysaccharide hydrolysis and the dehydration of obtained fructose makes the consecutive reaction smooth and HMF can be produced directly from inulin. Biomass itself can be made into activated carbon materials by carbonization to be used as catalyst supports. For example, the sulphonated bio-char acid catalyst (BC-SO_3H), obtained from lignocellulosic biomass such as bamboo, wood and coconut shells has been proven to accelerate the activation of cellulose molecules in the MW-assisted hydrolysis of cellulose in water.[56] Carbonaceous solid acids, derived from different types of biomass, which bear -SO_3H, -COOH and phenolic hydroxyl (OH) groups in the framework of the amorphous carbon, have been proven to be excellent candidates for cellulose hydrolysis.[57] These types of solid acids were prepared from hydrolysed corn cob residue and were used for the hydrolysis of the corn cob itself, with only a small amount of water under MW irradiation. Both the cellulose and hemicellulose in the corn cobs was converted into the corresponding sugars using the self-derived carbonaceous solid acid catalyst at a considerably low temperature (403 K). In addition, the solid catalyst can be prepared from the solid waste of hydrolysed biomass residue, which not only completely utilizes the unconverted component of the lignocellulosic biomass and reduces the cost of the catalyst, but also reduces pollution.

It is well known that when monosaccharides are treated in aqueous alkaline solutions, lactic acid is formed, [58] due to the mechanism reported in the scheme reported in Figure 5:[59]

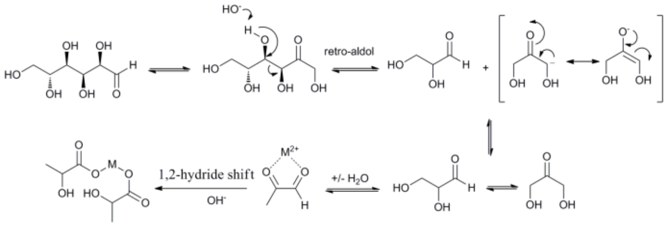


Fig. 5 Hypothesis of reaction mechanism for lactic acid formation. Reprinted from ref. 59 with permission from WILEY-VCH.

Lactic acid is a feedstock with a growing market. It is used in the food and pharmaceutical industries and has potential to be used in the production of biodegradable polymers, such as poly(lactic acid). Limits concerning the use of alkaline solutions are related to the release of a broad excess of by-products and the high concentration of alkali used. To overcome these problems, alumina supported KOH has recently been used in a MW-assisted solvent-free process to directly convert glucose into lactic acid,[60] while yields were four times lower in the absence of the solid support. MW heating makes it convenient to perform reactions very efficiently in dry media conditions, thus providing reaction rate enhancements and differing selectivity compared to conventional conditions.

Miscellanea

Supercritical water has proven its efficiency in the non-catalysed conversion of fructose to HMF at a temperature range which varied from 180 to 250 °C, yielding 47% HMF.[61] A lower HMF yield (30%) was obtained when glucose was used as the substrate and its reaction rate was about 8 times slower than in the case of fructose.

The mechano-catalytic depolymerisation of cellulose has also been studied.[62] High-energy processing in a shaker mill resulted in the production of levoglucosan, fructose and glucose.

The levoglucosan fraction decreased in size under continued high-energy milling and other dehydration products were observed - levoglucosenone and 5-hydroxymethyl furfural (HMF), as well as furfural, the retro-aldol condensation product (Fig. 6).

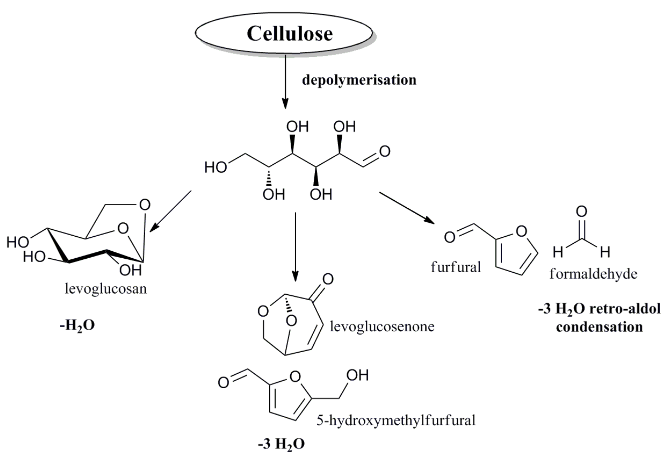


Fig. 6 Products of the mechano-catalytic depolymerisation of cellulose, reproduced from ref 62 with permission of The Royal Society of Chemistry.

As far as bio-waste conversion is concerned, the valorization of citrus peel residues is currently the object of increasing interest as it is one of the most underutilized and geographically widespread biowaste residues on the planet. A MW assisted process has thus recently been developed for the conversion of this type of bio-waste into valuable products such as d-limonene, α-terpineol, pectin and a novel type of mesoporous cellulose.[63] The advantage and superiority of the MW protocol compared to other techniques lies in its ability to simultaneously produce several valuable products coupled with a unique *in situ* flexibility. In a single MW treatment a number of marketable products, including limonene, pectin and sugars as well as a novel and unique form of porous cellulose can be easily and conveniently produced. During the experiment, the *in situ* conversion of d-limonene to α-terpineol was observed at temperatures above 180°C.

A wide range of cellulose rich biomasses and municipal wastes have also been investigated for conversion into valuable products. In particular, waste office paper containing up to 80% cellulose, obtained from recycling, was found to be one of the best candidates for MW hydrolysis.[64] Waste paper is virtually free from hemi-cellulose and lignin. The remainder is made up of water (5%) and an inorganic filler (15%) (e.g. calcium carbonate). Although it is likely to be contaminated with inks and other foreign material, waste paper is nevertheless a strong model waste material. The glucose yield under MW irradiation was more than 60 times higher than under conventional heating. At temperatures above 180°C, real biomass, cellulose and cellulose related waste (e.g. waste office paper), were converted to sugars without the need to add an acid or base. The short reaction times should also allow a move from batch to continuous processing, thus removing the sugar in the optimum concentration from the active zone before secondary breakdown reactions can occur.

Conclusions

This comprehensive literature survey highlights the great potential that enabling technologies, such as MW, US and ball milling, possess in the field of bio-waste valorisation *via* conversion to high added-value fine chemicals. In particular MW technology offers intriguing future perspectives in bio-waste valorisation. The observed energy saving, efficiency, selectivity and sustainability of these non-conventional protocols have all shed light onto the attractive potential scalability of these techniques and their profitable large scale applications. High-throughput applications of enabling technologies would entail the use of flow US[65] and MW flow-reactors.[66]

Acknowledgements

This work is funded by the University of Turin (fondi ex 60% 2013).

References

[a] Dipartimento di Chimica, University of Turin, Via P. Giuria 7, I-10125 Turin, Italy.
[b] Dipartimento di Scienza e Tecnologia del Farmaco and NIS - Centre for Nanostructured Interfaces and Surfaces, University of Turin, Via P. Giuria 9, I-10125 Turin, Italy

1 L. C. Sze Ki, L.A. Pfaltzgraff, L. Herrero-Davila, E.B. Mubofu, S. Abderrahim, J.H. Clark, A.A. Koutinas, N. Kopsahelis, K. Stamatelatou, F. Dickson, S. Thankappan, Z. Mohamed, R. Brocklesbyc, R. Luque, *Energy Environ. Sci.* 2013, **6**, 426.
2 R.L. Bain, W.P. Amos, M. Downing, R.L. Perlack, 2003. NREL Report, No. TP-510-33123, U.S. Department of Energy Laboratory.
3 T. Werpy, G. Petersen, (Eds.), 2004. U.S. Department of Energy Laboratory, 2004. http://www.nrel.gov/docs/fy04osti/35523.pdf
4 J.J. Bozell, G.R. Petersen, *Green Chem*. 2010, **12**, 539.
5 A. De La Hoz, A. Loupy A. (Eds.). Microwaves in Organic Synthesis, 3rd Edition, 2012, **1**, 541. Springer Science, New York.
6 G. Cravotto, P. Cintas. *Chem. Soc. Rev*., 2006, **35**, 180.
7 G. Cravotto, E. Calcio Gaudino, P. Cintas, *Chem. Soc. Rev*., 2013, **42**, 7521.

8 N. Kardos, J.L. Luche, *Carbohydr. Res*., 2001, **332**, 115.

9 A. Szalay, *Z. Phys. Chem*., 1933, **A164**, 234.

10 A. Szent-Gyo, *Nature*, 1933, **131**, 278.

11 R. Czechowska-Biskupa, B. Rokita, S. Lotfy, P. Ulanskia, J.M. Rosiak, *Carbohyd. Polym.*, 2005, **60**, 175.

12 B.F.M. Kuster, H.M.G. Temmink, *Carbohydr. Res.*, 1977, **54**, 185.

13 T.S. Hansen, J.M. Woodley, A. Riisager, *Carbohydr. Res.*, 2009, **344**, 2568.

14 C. Li, Z. Zhang, Z. K. Zhao, *Tetrahedron Lett.*, 2009, **50**, 5403.

15 A. Orozco, M. Ahmad, D. Rooney, G. Walker, *Process Saf. Environ.*, 2007, **85**, 446.

16 J.H. Choi, S. B. Kim, J. Chem. Eng., 1994, **11**, 178.

17 S. Akiya, S. Okui, *J. Pharm. Soc. Jpn.*, 1951, **71**, 182.

18 P. Tomasik, M.F. Zaranyka, *Ad. Carbohydr. Chem. Biochem.*, 1995, **51**, 302.

19 A.M. Orozco, A.H. Al-Muhtaseb, A.B. Albadarin, D. Rooney, G.M. Walkera, M.N.M. Ahmad, *RSC Advances*, 2011, **1**, 839.

20 J. Ni, H. Wang, Y. Chen, Z. She, H. Na, J. Zhu, *Bioresour. Technol.*, 2013, **137**, 106.

21 R. Carrasquillo-Flores, M. Käldström, F. Schüth, J.A. Dumesic, R. Rinaldi, *ACS Catal*., 2013, **3**, 993.

22 G. Cravotto, P. Cintas, *Chem. Eur. J.*, 2007, **13**, 1902.

23 A. Hernoux-Villière, U. Lassi, T. Hu, A. Paquet, L. Rinaldi, G. Cravotto, S. Molina-Boisseau, M.F. Marais, J.M. Lévêque, *ACS - Sustainable Chem. & Eng*., 2013, **1**, 995.

24 O. Yemis, G. Mazza, G., *Bioresour. Technol.*, 2012, **109**, 215.

25 C. Sánchez, L. Serrano, M.A. Andres, J. Labidi, *Ind. Crop. Prod.*, 2013, **42**, 513.

26 S.W. Breeden, J.H. Clark, T.J. Farmer, D.J. Macquarrie, J.S. Meimoun, Y. Nonnec, J.E.S. Reida, *Green Chem.*, 2013. **15**, 72.

27 R. Weingarten, J. Cho, R. Xing, W.C. Jr. Conner Jr., G. W. Huber, *ChemSusChem*, 2012, **5**, 1280.

28 G.M. Gonzalez Maldonado, R.S. Assary, J. Dumesic, L.A. Curtiss, 2012, *Energy Environ. Sci.*, **5**, 6981.

29 K. Zhou, H. Qian, H. Zhou, K. Zhu, *Sci. Technol. Food Ind.*, 2008, **2**, 74.

30 A. Szabolcs, M. Molnár, G. Dibó, L.T. Mika, *Green Chem.*, 2013, **15**, 439.

31 S. Tabasso, E. Montoneri, D. Carnaroglio, M. Caporaso, G. Cravotto, *Green Chem.*, 2014, **16**, 73.

32 K. Fischer, H.P. Bipp, *Bioresour. Technol*, 2005, **96**, 831.

33 Q. Bao, K. Qiao, D. Tomida, C. Yokoyama, *Catal. Commun.*, 2008, **9**, 1383.

34 C. Li, Z.K. Zhao, H. Cai, A. Wang, T. Zhang, T, *Biomass bioenergy*, 2011, **35**, 2013.

35 H. Ren, Y. Zhou, L. Liu, *Bioresour. Technol.*, 2013, **129**, 616.

36 X. Qi, M. Watanabe, T.M. Aida, R.L. Smith, *ChemSusChem*, 2010, **3**, 1071.

37 B. Liu, Z. Zhang, Z.K. Zhao, *Chem. Eng. J.*, 2013, **215**, 517.

38 A. Dutta, A.K. Patra, S. Dutta, B. Saha, A. Bhaumik, *J. Mater. Chem.*, 2012, **22**, 14094.

39 Z. Zhang, Z.K. Zhao, *Carbohydr. Res.*, 2009, **344**, 2069.

40 L. Zhang, H. Yu, P. Wang, *Bioresour. Technol.*, 2013, **136**, 515.

41 F. Guo, Z. Fang, T.J. Zhou, *Bioresour. Technol.*, 2012, **112**, 313.

42 M.H. Zong, Z.Q. Duan, W.Y. Lou, T.J. Smith, H. Wu, *Green Chem.*, 2007, **9**, 434.

43 C. Rasendra, I.G.B.N., Makertihartha, S. Adisasmito, H. Heeres, *Top. Catal.* 2010, **53**, 1241.

44 L. Yang, G. Li, F. Yang, S.M. Zhang, H.X. Fan, X. Na, *Carbohydr. Res.*, 2011, **346**, 2304.

45 W. Deng, Q. Zhang, Y. Wang, *Dalton Trans.*, 2012, **41**, 9817.

46 H. Yao-Bing and F. Yao, *Green Chem.*, 2013, **15**, 1095.

47 Z.H. Zhang, Z.K. Zhao, *Bioresour. Technol.*, 2011, **102**, 3970.

48 A. Yepez, A. Pineda, A. Garcia, A.A., Romero, R. Luque, R., *Phys. Chem. Chem. Phys.*, 2013, **15**, 12165.

49 X. Qi, M. Watanabe, T.M. Aida, R.L. Smith, *Green Chem.*, 2008, **10**, 799.

50 X. Qi, M. Watanabe, T.M. Aida, R.L. Smith, *Catal. Commun.*, 2009, **10**, 1771.

51 M. Watanabe, Y. Aizawa, T. Iida, R. Nishimura, H. Inomata, *Appl. Catal. A: Gen.*, 2005, **295**, 150.

52 X. Qi, M. Watanabe, T.M. Aida, R.L. Smith, *Catal. Commun.*, 2008, **9**, 2244.

53 S. Dutta, S. De, A.K. Patra, M. Sasidharan, A. Bhaumik, B. Saha, *Applied Catalysis A: General*, 2011, **409**, 133.

54 S. Dutta, S. De, M.I. Alam, M.M. Abu-Omar, B. Saha, *J. Catal.*, 2012, **288**, 8.

55 Q. Wu, Y. Yan, Q. Zhang, J. Lu, Z. Yang, Y. Zhang, Y. Tang, *ChemSusChem*, 2013, **6**, 820.

56 Y.Y. Wu, Z.H. Fu, D.L. Yin, Q. Xu, F.L. Liu, C.L. Lu, L.Q. Mao, *Green Chem.*, 2010, **12**, 696.

57 Y. Jiang, X. Li, X. Wang, L. Meng, H. Wang, G. Peng, X. Wang, X., Mu, 2012, *Green Chem*., **14**, 2162.

58 B.Y. Yang, R. Montgomery, *Carbohydr. Res.*, 1996, **280**, 27.

59 D. Esposito, M. Antonietti, *ChemSusChem*, 2013, **6**, 989.

60 G. Epane, J.C. Laguerre, A. Wadouachi, D. Marek, Green Chem., 2010, **12**, 502.

61 M. Moeller, F. Harnisch, U. Schroeder U., *Biomass Bioenerg.*, 2012, **39**, 389.

62 S.M. Hick, C. Griebel, D.T. Restrepo, J.H. Truitt, E.J. Buker, C. Bylda, R.G. Blair, *Green Chem.*, 2010, **12**, 468.

63 A.M. Balu, V. Budarin, P.S. Shuttleworth, L.A. Pfaltzgraff, K. Waldron, R. Luque, J.H. Clark, *ChemSusChem*, 2012, **5**, 1694.

64 J. Fan, M. De Bruyn, Z. Zhu, V. Budarin, M. Gronnow, D.L. Gomez, D. Macquarrie, J.H. Clark, *Chem. Eng. Process*, 2013, **71**, 37.

65 L. Alexandru, G. Cravotto, L. Giordana, A. Binello, F. Chemat, *Innov. Food Sci. Emerging Technol.*, 2013, **20**, 167.

66 I. Choedkiatsakul, K. Ngaosuwan, S. Assabumrungrat, S. Tabasso, G. Cravotto, Biosource Bioen. (in press).