

Recent Trends in Catalytic Hydrolysis of Waste Lignocellulosic Biomass for Production of Fermentable Sugars

S. Chatterjee and R. Chakraborty

Abstract This article presents a comprehensive comparative assessment of the reaction conditions employed in the heterogeneous and homogeneous catalytic hydrolysis of waste lignocellulosic biomass (WLB) for the production of fermentable sugar (FS) for its subsequent conversion to renewable bioethanol. The effects of catalyst type and reaction conditions on the selectivity of FS in catalytic hydrolysis of low-cost WLB have been meticulously assessed. Moreover, representative radar plots demonstrating FS (substrate for bioethanol) yield in both homogeneous and heterogeneous catalytic protocols have been elucidated. An intensive global attention has recently been paid for the improvement of catalytic technologies pertaining to efficient pretreatment and hydrolysis for conversion of WLB to FS. Cellulose [$(C_6H_{10}O_5)_n$], the foremost component in WLB materials, is a biodegradable polymer of simple carbohydrates, consisting of β (1, 4)-linkage of D-glucose units, which can be depolymerized to FS for the subsequent sustainable synthesis of renewable biofuels. In this article, a critical assessment of the production of FS through catalytic pretreatment and subsequent hydrolysis of WLB resources has been elucidated. The abundant presence of low-cost WLB and their potential application for synthesis of FS (D-glucose) and other derivatives (xylose) for subsequent bioethanol, biobutanol, bio-H₂ production can provide an economically sustainable and environmentally benign avenue to mitigate energy crisis and global climate change.

The present study reveals the effects of important process parameters, viz. hydrolysis time, catalyst concentration, temperature and water to WLB ratio on the selectivity of D-glucose in both homogeneous and heterogeneous catalytic hydrolysis of WLB along with various advanced pretreatment intensification protocols. In order to improve the existing drawbacks, recent efforts have been made to develop advanced methods through utilization of ionic liquid, microwave, and infrared irradiation as well as ultrasonication to make the overall process more efficient and environmentally benign.

Keywords Lignocellulosic biomass • Hydrolysis • Fermentable sugar • Heterogeneous catalysts • Homogeneous catalysts • Process intensification

S. Chatterjee • R. Chakraborty (✉)
Jadavpur University, Kolkata, West Bengal, India
e-mail: ch.rajat@gmail.com

1 Introduction

The major constituents of natural waste lignocellulosic biomass (WLB) are lignin, cellulose and hemicelluloses (Somerville et al. 2004). The percentage of the constituents may vary according to the nature of the WLB (Carrier et al. 2011). Owing to the widespread networks of inter- and intramolecular hydrogen bonding, cellulose is insoluble in water. It is, therefore, problematic to process and hydrolyze in solution (Murakami et al. 2007). Thus, it is necessary to carry out economic and effective pretreatment of WLB to convert it into accessible cellulose and hemicelluloses for subsequent catalytic hydrolysis leading to the formation of fermentable sugar (FS) for subsequent bioethanol production (Kumar et al. 2009; Mosier et al. 2005).

The main objectives of the pretreatment process are (Somerville et al. 2004) to disrupt the crystalline structure of the cellulose present in WLB, (Carrier et al. 2011) to break down the complex polymer chains of lignin as well as hemicelluloses and (Murakami et al. 2007) to increase the porosity and the surface area of cellulose for better accessibility and high productivity of desired product for subsequent hydrolysis step (Lynd et al. 1999; Li et al. 2010). In this article, both homogeneous and heterogeneous catalytic pretreatment processes have been discussed. Moreover, recent pretreatment process intensification protocols such as the application of microwave radiation, ionic liquids (ILs) and ultrasound wave have been meticulously reviewed.

Furthermore, the catalytic conversion of WLB to valuable chemicals faces additional difficulties owing to the inert chemical structure and complex molecular distribution of carbon, oxygen and hydrogen present in the WLB. In this context, it is necessary to develop new highly activated, recyclable low-cost eco-friendly heterogeneous solid catalysts for the yield of desired product FS (D-glucose) (Abadi et al. 1998; Dhepe et al. 2005; Stocker 2008). To date, most of the research works related to kinetics of heterogeneous catalyzed conversion of WLB are based on the lignocellulosic model compounds such as synthetic crystalline cellulose, commercial cellobiose and xylan (Bootsma and Shanks 2007; Lai et al. 2011; Rick et al. 2012).

The present review mainly concerns about the production of FS (D-glucose) through catalytic pretreatment and subsequent hydrolysis of naturally available WLB resources, incorporating the significant effects of corresponding process parameters. The abundant presence of low-cost WLB and their potential application for synthesis of FS can provide sustainable environmentally benign avenue overcoming energy crisis and mitigating global environmental problems. Additionally, growing endeavours are being made to integrate the multistep batch pretreatment and hydrolysis processes into a continuous conversion of WLB employing well-designed multifunctional low-cost environmentally friendly heterogeneous solid catalysts to achieve the desired sustainable yields of valuable products (Yan et al. 2006).

2 Pretreatment of WLB

In last few years, many procedures have been employed for cellulose pretreatment prior to hydrolysis (Hamelinck et al. 2005; Sousa et al. 2009); selected works have been discussed in the following sections. In Fig. 1, a schematic for pretreatment and subsequent processes for FS synthesis has been depicted. Moreover, various new advanced pretreatment processes and their different technical aspects have been highlighted in comparison with the existing processes in the following sections.

2.1 Homogeneous Acid-Catalyzed Pretreatment

In recent years, in addition to physical pretreatments, e.g. grinding and milling, many researchers applied physicochemical homogeneous acid (HCl, H₃PO₄)-catalyzed pretreatment on various types of WLB (corn stover, *Achyranthes aspera*, *Sida acuta*) to produce FS (86.2 wt. %, 85.4 wt. %) which typically involves moderate reaction time of 40 min to 1 h at a moderately high temperature range of 60–120 °C (Siripong et al. 2016; Zu et al. 2014). Nonetheless, owing to requirements of elevated temperature (Kim et al. 2014; Kundu and Lee 2015) and lengthy time, the process involved high energy consumption in addition to equipment corrosion and generation of the massive acidic waste stream and difficulties in product separation. Thus, to augment the efficiency of the pretreatment process, heterogeneous catalyst(s) must be applied to overcome the difficulties pertaining to homogeneous acid-catalyzed pretreatment processes.

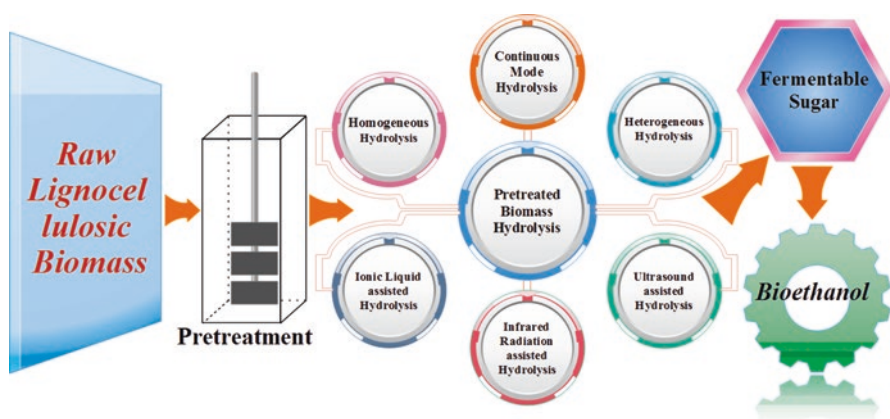


Fig. 1 Schematic for the hydrolysis of WLB to synthesize FS and subsequent bioethanol production

2.2 Heterogeneous Acid-Catalyzed Pretreatment

Recently, Tan and Lee (2015) reported maximum 99.8 wt. % FS (D-glucose) from macroalgae cellulosic residue using Dowex™ Dr-G8 as a heterogeneous solid catalyst at 120 °C for 30 min. Although solid-catalyzed pretreatment demonstrated remarkable performance, however, all these catalysts were synthesized using reagent-grade chemicals rendering expensive catalyst, which, in turn, made the process cost-intensive.

2.3 Intensification of Pretreatment Using Recent Protocols

Recently, several researchers have reported improved new processes such as ultrasonication and applications of the microwave to intensify the pretreatment of the raw WLB; these are precisely discussed in the following sections.

2.3.1 Pretreatment Using Ionic Liquid (IL)

Pretreatment employing ILs has gained much interest in the field of WLB hydrolysis (Perez-Pimienta et al. 2016). Recently, Farahania et al. (2016) reported the pretreatment of poplar biomass with IL (1-ethyl-3-methyl-imidazolium acetate) at a lower temperature of 50 °C for 24 h rendering significant (80 wt. %) FS (glucose) yield. However, the application of ILs in WLB hydrolysis is not economically attractive due to its high cost, handling difficulties and problems in product separation.

2.3.2 Ultrasonication- and Microwave Irradiation (MI)-Assisted Pretreatment

In recent years, new green-pretreatment technologies were applied to augment the WLB hydrolysis process such as ultrasonication (Ramadoss and Muthukumar 2014) and microwave irradiation (MI) (Diaz et al. 2015).

In ultrasonication process, ultrasound energy was employed to disrupt hydrogen bonds between WLB components enabling mass transport and, thus, causing improved WLB digestion (Li et al. 2015). In spite of being a green technology, owing to the higher power consumptions (400–600 W) and relatively poor FS (glucose) yields (Chen et al. 2011) made the overall process economically less attractive.

On the other hand, another new eco-friendly pretreatment technique, viz. MI, has been applied over the last few years to intensify and enhance FS and subsequent bioethanol production (Ninomiya et al. 2014). Recently, Gabhane et al. (2014) used

banana agricultural waste for obtaining maximum FS yield around 47.33 wt. % at 50 °C in 15 min. However, the high power requirement of MI system made the overall process economically unattractive for scale-up purposes.

3 Hydrolysis of WLB

The next step after pretreatment in the synthesis of FS is hydrolysis of oligosaccharides, cellulose and hemicelluloses components. Various industrially important chemicals like FS, 5-HMF, furfural, etc. are synthesized in this step. To intensify the hydrolysis of WLB and to augment the desired product selectivity, various advanced cutting-edge technologies like ultrasonication, microwave radiation and different types of green solid heterogeneous solid catalysts (synthesized or commercially available) have been employed in the hydrolysis. The characteristics of the emerging hydrolysis processes have been enunciated in following sections.

3.1 *Homogeneous Acid-Catalyzed Hydrolysis of WLB*

Many industrially important fermentative products such as bioethanol, levulinic acid, furfural, etc. can be obtained from waste WLB hydrolysate (Jönsson et al. 2013). The most well-established, extensively used procedure, e.g. acid hydrolysis (Gütsch et al. 2012), has been found effective for WLB hydrolysis. Nonetheless, homogeneous acid hydrolysis has several limitations such as elevated reaction temperature (170–240 °C), equipment corrosion, difficulty in product separation and high reaction time (Taherzadeh and Karimi 2007) making the overall process problematic.

3.2 *Heterogeneous Solid Acid-Catalyzed Hydrolysis of WLB*

Over recent past, the applications of green solid acid heterogeneous catalysts such as supported metals, acid resins, H-form zeolites, carbonaceous acids, functionalized silica, metal oxides, etc. had gained widespread interest in the WLB hydrolysis process. For WLB hydrolysis, Amberlyst-15, a solid acid catalyst (Meena et al. 2015), was found very much effective (Onda et al. 2008; Pang et al. 2010), and owing to the presence of the SO₃H group, the catalyst could selectively allow penetration of hydrogen ions of reactants during the hydrolysis reaction.

Notably, most of the heterogeneous solid acid catalysts applied for WLB hydrolysis were developed from cost-intensive reagent-grade chemicals besides requiring prolonged hydrolysis time and relatively elevated temperature in comparison with homogeneous WLB hydrolysis. Notably, the economic sustainability of hydrolysis

process is greatly dependent on the efficacy, reusability and cost-effectiveness of the heterogeneous catalyst. In this context, low-cost catalysts which have been preliminary derived from waste biomass resources like carbon-based solid acid catalysts (CBSAC) are noteworthy (Suganuma et al. 2008). This catalyst rendered hydrolysis of untreated cellulose yielding 4 wt. % glucose at 100 °C for 3 h.

However, most of the previously mentioned research works have been performed on lignocellulosic model compounds, i.e. commercially available microcrystalline cellulose, synthetic cellobiose and xylan (Lai et al. 2011; Rick et al. 2012). Recently, Nata et al. (2015) achieved approximately 19.91 mg/mL of FS from hydrolysis of corn starch at elevated temperature (150 °C) over prolonged (6 h) reaction time using C_4 -SO₃H as the solid acid catalyst. Very recently, Hu et al. (2016) have prepared a magnetic carbonaceous solid acid containing chlorine (–Cl) groups as cellulose-binding sites and sulfonic (–SO₃H) groups as cellulose-hydrolyzing sites; the catalyst was used for hydrolysis of rice straw in presence of ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) at high reaction temperature of 130 °C for 4 h resulting in maximum 78.5 % of FS. Additionally, Zhong et al. (2015) and Sakdaronnarong et al. (2016) also investigated the efficacy of various carbon-based catalysts on hydrolysis of wheat straw and sugarcane bagasse, respectively.

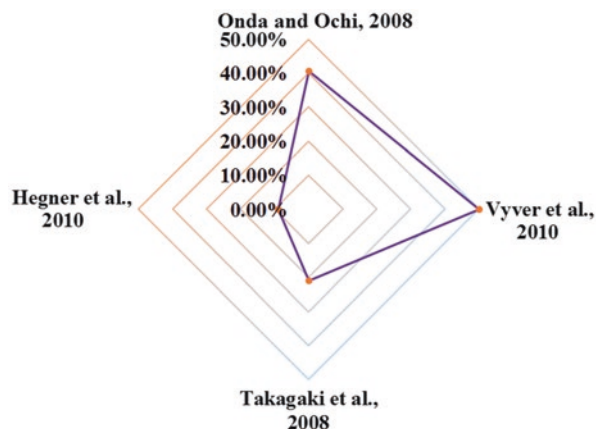
The effects of reaction conditions on the selectivity of FS are presented in Table 1 for heterogeneous solid acid-catalyzed systems. The yield of FS varies significantly from 9 wt. % to 50 wt. % through application of different types of heterogeneous catalysts. A poor selectivity of FS was observed using Nafion/silica catalyst, whereas using sulfonated silica/carbon nanocomposites, considerable improvement in sugar selectivity could be achieved.

On the other hand, the usage of AC-SO₃H, as well as HNbMoO₆, exhibited a moderate selectivity to FS. However, in general, high temperature and long reaction time remain as the major drawbacks to solid-catalyzed hydrolysis. Figure 2 demonstrates the deviation in FS selectivity in accordance with select references.

Table 1 Overview of reaction conditions and selectivity of FS using heterogeneous catalysts

Catalyst	Reaction condition		FS selectivity (%)	References	Remarks
	Temperature (K)	Time (h)			
AC-SO ₃ H	423	24	40.5	Onda et al. (2008)	Elevated reaction temperature; long reaction time; poor FS selectivity
Sulfonated silica/carbon nanocomposites	423	24	50.0	Vyver et al. (2010)	
HNbMoO ₆	403	12	21.0	Takagaki et al. (2008)	
Nafion/silica	463	24	9.0	Hegner et al. (2010)	

Fig. 2 Radar plot depicting selectivity of fermentable sugar through the heterogeneous catalytic protocol in concurrence with select references



3.3 Intensification of Hydrolysis Using Recent Protocols

In recent years, several research works have been reported involving applications of the microwave, ultrasound and ILs to intensify the hydrolysis of the WLB for possible enhancement of FS yield. These have been briefly discussed in the following sections.

3.3.1 Ultrasound-Assisted (US) Hydrolysis of WLB

US hydrolysis of WLB has gained remarkable attention in the recent past. Werle et al. (2013) reported acid hydrolysis of waste palm leaves (*Roystonea oleracea*) by ultrasound obtaining maximum 74 % yield of FS at 65 °C for 300 min using phosphoric acid as catalyst. Silva et al. (2015) reported the application of ultrasound in enzymatic hydrolysis of sugarcane bagasse attaining maximum FS of 217 g kg⁻¹ for 4 h at 47 °C. On the other hand, Borah et al. (2016) reported ultrasound-assisted enzymatic hydrolysis of various types of WLB such as *Eichhornia crassipes* and *Saccharum spontaneum*, to achieve maximum 40.02 % of FS. Nonetheless, the overall process was economically unattractive due to the high equipment and energy cost for ultrasonication.

3.3.2 Microwave Irradiation (MI)-Assisted Hydrolysis of WLB

In recent past, MI was applied to WLB hydrolysis to enhance the hydrolysis rate and to augment the yield of FS and consequent bioethanol production (Xue et al. 2011). Recently, Villière et al. (2013) reported maximum 46 wt. % FS yield from wet potato sludge (industrial waste) in 2 h at 60 °C using combined MI and ultrasonication and sulphuric acid as catalyst. Moreover, the research group also stated

that, during hydrolysis, rapid heat transfer was observed due to the application of MI, whereas mass transfer was increased at the interfacial boundary layers of solid-liquid hydrolysis system. Nevertheless, high microwave energy requirements (1 kW) might be a concern for the overall process economy.

3.3.3 Ionic Liquid (ILs)-Assisted Hydrolysis of WLB

Recently, Wang et al. (2014) reported hydrolysis of bamboo biomass using six different types of metal ions including Mg^{2+} , Ca^{2+} , Na^+ , K^+ , Cu^{2+} and Fe^{3+} obtaining 67.1 wt. % of FS at 100 °C in 4 h with $CuCl_2$ as co-catalyst. On the other hand, Ramli and Amin (2014) reported usage of 1-butyl-3-methylimidazolium bromide (BMIMBr) as ILs for oil palm frond and empty fruit bunch direct hydrolysis that resulted in maximum 27.4 wt. % and 24.8 wt. % FS yield (120 °C, 4 h) using solid Fe/HY catalyst. Nonetheless, the process has limitations in terms of use of high-cost ILs and difficult product separation with lower FS yield.

3.3.4 Hydrolysis WLB Carried Out in Continuous Mode Reactors

Most of WLB hydrolyses were carried out in batch reactors. Some pioneer research works have been conducted in continuous-type reactors (CTR) resulting augmented yield of FS at mild reaction conditions using shorter residence time (Kumakura and Kaetsu 1978; Church and Wooldridge 1981). Kim et al. (2005) reported hydrolysis of glucans from pretreated corn fibre obtaining around 90 wt. % of glucose at 160 °C in 3.5 min residence time in a packed-bed reactor using a cation exchanger. Importantly, they observed that the cost of catalyst had a significant influence on the overall production cost of FS and subsequent bioethanol production. To date, very scanty reports are available for conversion of WLB into FS in CTR (Kim et al. 2005) using heterogeneous catalysts. Future works should focus on enhancing the capacity of the FS production using continuous catalytic reactor.

3.3.5 Fast Pretreatment-Hydrolysis WLB Using Energy-Efficient Infrared Radiation

More recently, our research group (Chatterjee et al. 2016) has successfully achieved a promising high 89.87 mol% glucose (FS) yield from waste watermelon (*Citrullus lanatus*) peel at 60 °C applying energy-efficient far-infrared radiation in presence of heterogeneous Amberlyst-15 catalyst in one-pot pretreatment-hydrolysis system in much shorter time.

4 Prospects and Conclusion

Waste lignocellulosic biomass is the most abundant renewable bioresource on earth. It has been considered as one of the most significant natural resources for the production of industrially valuable products such as glucose, fructose, 5-HMF as well as bioethanol and biobutanol. In the past years, several pretreatments and subsequent hydrolysis processes have been developed. Generally, the heterogeneous pretreatment and hydrolysis processes are preferable over homogenous processes mainly due to the ease of product separation and reduced corrosion, leaching and handling problems. However, the invention of the heterogeneous solid catalysts with high catalytic activity for both pretreatment and subsequent hydrolysis processes still faces a challenging issue mainly owing to the solid-solid contact between the insoluble waste lignocellulosic biomass and solid catalyst.

However, the application of ionic liquids as a solvent or as a catalyst can be considered as an alternative solution; nonetheless, high cost and difficulties associated with separation and recovery have made such process economically unattractive. On the other hand, other eco-friendly intensification protocols such as the application of microwave and ultrasound on pretreatment and consequent hydrolysis steps rendered superior yields of desired products at comparatively milder operating conditions in comparison with conventional heated reactors. Nevertheless, microwave and ultrasound processes usually require high energy inputs; the consequent increment in production cost makes the overall process economically unpleasant. Furthermore, the most economically sustainable avenue in terms of feedstock should be augmented utilization of waste lignocellulosic biomass rather than pure cellulose.

The present study reveals that the usage of both homogeneous and heterogeneous catalysts in conventional pretreatment and hydrolysis steps of waste lignocellulosic biomass involve high reaction time, temperature and significantly low selectivity towards desired product. In order to improve the existing protocols, effort must be made to develop newer advanced technology involving process intensification protocol such as energy-efficient infrared radiation. Besides, more research needs to be conducted on continuous mode of catalytic pretreatment and subsequent hydrolysis for enhanced throughput of fermentable sugar in such a way that the overall process remains environmentally benign as well as energy-efficient and economically viable to render a sustainable protocol.

References

- Abbadi A, Gotlieb KF, Bekkum H (1998) Study on solid acid catalyzed hydrolysis of maltose and related polysaccharides. *Starch/Staerke* 50(1):23–28
- Bootsma JA, Shanks BH (2007) Cellobiose hydrolysis using organic–inorganic hybrid mesoporous silica catalysts. *Appl Catal A* 327:44–51

- Borah AJ, Agarwal M, Poudyal M, Goyal A, Moholkar VS (2016) Mechanistic investigation in ultrasound induced enhancement of enzymatic hydrolysis of invasive biomass species. *Bioresour Technol* 213:342–349
- Carrier M, Loppinet-Serani A, Denux D, Lasnier JM, Ham-Pichavant F, Cansell F, Aymonier C (2011) Thermogravimetric analysis as a new method to determine the lignocellulosic composition of biomass. *Biomass Bioenergy* 35(1):298–307
- Chatterjee S, Barman S, Chakraborty R (2016) Far infrared radiated energy-efficient rapid one-pot green hydrolysis of waste watermelon peel: optimization and heterogeneous kinetics of glucose synthesis. *RSC Adv* 6:74278–74287
- Chen WH, Tu YJ, Sheen HK (2011) Disruption of sugarcane bagasse lignocellulosic structure by means of dilute sulfuric acid pretreatment with microwave assisted heating. *Appl Energy* 88:2726–2734
- Church JA, Wooldridge D (1981) Continuous high-solids acid hydrolysis of biomass in a 11/2-in. Plug flow reactor. *Ind Eng Chem Prod Res Dev* 20:378–382
- Dhepe PL, Ohashi M, Inagaki S, Ichikawa M, Fukuoka A (2005) Hydrolysis of sugars catalyzed by water-tolerant sulfonated mesoporous silicas. *Catal Lett* 102(3–4):163–169
- Diaz AB, Moretti MMS, Bussoli CB, Nunes CCC, Blandino A, Silva R, Gomes E (2015) Evaluation of microwave-assisted pretreatment of lignocellulosic biomass immersed in alkaline glycerol for fermentable sugars production. *Bioresour Technol* 185:316–323
- Farahania SV, Kimb Y, Schalla C (2016) A coupled low temperature oxidative and ionic liquid pretreatment of lignocellulosic biomass. *Catal Today* 269:2–8
- Gabhane J, William SPMP, Gadhe A, Rath R, Vaidya AN, Wate S (2014) Pretreatment of banana agricultural waste for bio-ethanol production: individual and interactive effects of acid and alkali pretreatments with autoclaving, microwave heating and ultrasonication. *Waste Manag* 34:498–503
- Gütsch JS, Nousiainen T, Sixta H (2012) Comparative evaluation of autohydrolysis and acid-catalyzed hydrolysis of *Eucalyptus globulus* wood. *Bioresour Technol* 109:77–85
- Hamelinck CN, Hooijdonk GV, Faaij APC (2005) Ethanol from lignocellulosic biomass: techno-economic performance in short-, middle- and long-term. *Biomass Bioenergy* 28(4):384–410
- Hegner J, Pereira KC, Boef BD, Lucht BL (2010) Conversion of cellulose to glucose and levulinic acid via solid-supported acid catalysis. *Tetrahedron Lett* 51(17):2356–2358
- Hu L, Li Z, Wu Z, Lin L, Zhou S (2016) Catalytic hydrolysis of microcrystalline and rice straw-derived cellulose over a chlorine-doped magnetic carbonaceous solid acid. *Ind Crop Prod* 84:408–417
- Jönsson LJ, Alriksson B, Nilvebrant NO (2013) Bioconversion of lignocellulose: inhibitors and detoxification. *Biotechnol Biofuels* 6:16
- Kim Y, Hendrickson R, Mosier N, Ladisch MR (2005) Plug-flow reactor for continuous hydrolysis of glucans and xylans from pretreated corn fiber. *Energy Fuel* 19:2189–2200
- Kim I, Lee B, Park J, Choi S, Han J (2014) Effect of nitric acid on pretreatment and fermentation for enhancing ethanol production of rice straw. *Carbohydr Polym* 99:563–567
- Kumakura M, Kaetsu I (1978) Radiation-induced degradation and subsequent hydrolysis of waste cellulose materials. *Int J Appl Radiat Isot* 30:139–141
- Kumar P, Barrett DM, Delwiche MJ, Stroeve P (2009) Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuels production. *Ind Eng Chem Res* 48:3713–3729
- Kundu C, Lee J (2015) Optimization conditions for oxalic acid pretreatment of deacetylated yellow poplar for ethanol production. *J Ind Eng Chem* 32:298–304
- Lai DM, Deng L, Li J, Liao B, Guo QX, Fu Y (2011) Hydrolysis of cellulose into glucose by magnetic solid acid. *Chem Sus Chem* 4(1):55–58
- Li C, Nierim B, Manisseri C, Arora R, Scheller HV, Auer M, Vogel KP, Simmons BA, Singh S (2010) Comparison of dilute acid and ionic liquid pretreatment of switchgrass: biomass recalcitrance, delignification and enzymatic saccharification. *Bioresour Technol* 101:4900–4906
- Li J, Zhang X, Zhang M, Xiu H, He H (2015) Ultrasonic enhance acid hydrolysis selectivity of cellulose with HCl–FeCl₃ as catalyst. *Carbohydr Polym* 117:917–922

- Lynd LR, Wyman CE, Gerngross TU (1999) Biocommodity engineering. *Biotechnol Program* 15(5):777–793
- Meena S, Navatha S, Prabhavathi Devi BLA, Prasad RBN, Pandey A, Sukumaran RK (2015) Evaluation of Amberlyst15 for hydrolysis of alkali pretreated rice straw and fermentation to ethanol. *Biochem Eng J* 102:49–53
- Mosier N, Wyman C, Dale B, Elander R, Lee YY, Holtzapple M, Ladisch M (2005) Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresour Technol* 96(6):673–686
- Murakami M, Kaneko Y, Kadokawa J (2007) Preparation of cellulose-polymerized ionic liquid composite by in-situ polymerization of polymerizable ionic liquid in cellulose-dissolving solution. *Carbohydr Polym* 69(2):378–381
- Nata IF, Irawan C, Mardina P, Lee C (2015) Carbon-based strong solid acid for cornstarch hydrolysis. *J Solid State Chem* 230:163–168
- Ninomiya K, Yamauchi T, Oginoc C, Shimizua N, Takahashi K (2014) Microwave pretreatment of lignocellulosic material in cholinium ionic liquid for efficient enzymatic saccharification. *Biochem Eng J* 90:90–95
- Onda A, Ochi T, Yanagisawa K (2008) Selective hydrolysis of cellulose into glucose over solid acid catalysts. *Green Chem* 10:1033–1037
- Pang J, Wang A, Zheng M, Zhang T (2010) Hydrolysis of cellulose into glucose over carbons sulfonated at elevated temperatures. *Chem Commun* 46:6935–6937
- Perez-Pimienta JA, Flores-Gómez CA, Ruiz HA, Sathitsuksanoh N, Balan V, Sousa LC, Dale BE, Singh S, Simmons BA (2016) Evaluation of agave bagasse recalcitrance using AFEX™, autohydrolysis, and ionic liquid pretreatments. *Bioresour Technol* 211:216–223
- Ramadoss G, Muthukumar K (2014) Ultrasound assisted ammonia pretreatment of sugarcane bagasse for fermentable sugar production. *Biochem Eng J* 83:33–41
- Ramli NAS, Amin NAS (2014) Catalytic hydrolysis of cellulose and oil palm biomass in ionic liquid to reducing sugar for levulinic acid production. *Fuel Process Technol* 128:490–498
- Rick O, James RK, Joby M (2012) Hemicellulose hydrolysis using solid acid catalysts generated from biochar. *Catal Today* 190(1):89–97
- Sakdaronnarong C, Saengsawang A, Siriyutta A, Jonglertjunya W, Nasongkla N, Laosiripojana N (2016) An integrated system for fractionation and hydrolysis of sugarcane bagasse using heterogeneous catalysts in aqueous biphasic system. *Chem Eng J* 285:144–156
- Silva JRF, Cantelli KC, Soares MBA, Tres MV, Oliveira D, Meireles MAA, Oliveira JV, Treichel H, Mazutti MA (2015) Enzymatic hydrolysis of non-treated sugarcane bagasse using pressurized liquefied petroleum gas with and without ultrasound assistance. *Renew Energy* 83:674–679
- Siripong P, Duangporn P, Takata E, Tsutsumi Y (2016) Phosphoric acid pretreatment of *Achyranthes aspera* and *Sida acuta* weed biomass to improve enzymatic hydrolysis. *Bioresour Technol* 203:303–308
- Somerville C, Bauer S, Brininstool G, Facette M, Hamann T, Milne J, Osborne E, Paredes A, Persson S, Raab T, Vorwerk S, Youngs H (2004) Toward a system approach to understanding plant cell walls. *Science* 306(5705):2206–2211
- Sousa LC, Chundawat SPS, Balan V, Dale BE (2009) ‘Cradle-to-grave’ assessment of existing lignocellulose pretreatment technologies. *Curr Opin Biotechnol* 20(3):339–347
- Stocker M (2008) Biofuels and biomass-to-liquid fuels in the biorefinery: catalytic conversion of lignocellulosic biomass using porous materials. *Angew Chem Int Ed* 47(48):9200–9211
- Suganuma S, Nakajima K, Kitano M, Yamaguchi D, Kato H, Hayashi S, Hara M (2008) Hydrolysis of cellulose by amorphous carbon bearing SO₃H, COOH, and OH groups. *J Am Chem Soc* 130:12787–12793
- Taherzadeh MJ, Karimi K (2007) Enzyme based hydrolysis process for ethanol from lignocellulosic materials: a review. *Bioresour Com* 2:707–738
- Takagaki A, Tagusagawa C, Domen K (2008) Glucose production from saccharides using layered transition metal oxide and exfoliated nanosheets as a water-tolerant solid acid catalyst. *Chem Commun* 42:5363–5365

- Tan IS, Lee KT (2015) Solid acid catalysts pretreatment and enzymatic hydrolysis of macroalgae cellulosic residue for the production of bioethanol. *Carbohydr Polym* 124:311–321
- Villière A, Lassi U, Hu T, Paquet A, Rinaldi L, Cravotto G, Molina-Boisseau S, Marais M, Lévêque J (2013) Simultaneous microwave/ultrasound-assisted hydrolysis of starch-based industrial waste into reducing sugars. *ACS Sustain Chem Eng* 1:995–1002
- Vyver V, Peng L, Geboers J, Schepers H, Clippel F, de Gommès CJ, Goderis B, Jacobs PA, Sels BF (2010) Sulfonated silica/carbon nanocomposites as novel catalysts for hydrolysis of cellulose to glucose. *Green Chem* 12:1560–1563
- Wang N, Zhang J, Wang H, Li Q, Wei S, Wang D (2014) Effects of metal ions on the hydrolysis of bamboo biomass in 1-butyl-3-methylimidazolium chloride with dilute acid as catalyst. *Bioresour Technol* 173:399–405
- Werle LB, Garcia JC, Kuhn RC, Schwaab M, Foletto EL, Cancelier A, Jahn SL, Mazutti MA (2013) Ultrasound-assisted acid hydrolysis of palm leaves (*Roystonea oleracea*) for production of fermentable sugars. *Ind Crop Prod* 45:128–132
- Xue J, Chen HZ, Kadar Z (2011) Optimization of microwave pretreatment on wheat straw for ethanol production. *Biomass Bioenergy* 35:3859–3864
- Yan N, Zhao C, Gan WJ, Kou Y (2006) Polyols: a new generation of energy platform? *Chin J Catal* 27(12):1159–1163
- Zhong C, Wang C, Huang F, Wang F, Jia H, Zhou H, Wei P (2015) Selective hydrolysis of hemicellulose from wheat straw by a nanoscale solid acid catalyst. *Carbohydr Polym* 131:384–391
- Zu S, Li W, Zhang M, Li Z, Wang Z, Jameel H, Chang H (2014) Pretreatment of corn stover for sugar production using dilute hydrochloric acid followed by lime. *Bioresour Technol* 152:364–370