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BIODEGRADABLE MUNICIPAL SOLID WASTE AS SUBSTRATE FOR ETHANOL PRODUCTION: A REVIEW

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Abstract

Biodegradable Municipal Solid Waste is the most abundant renewable bioresource as an alternative of traditional resources for ethanol production. It is primarily composed of cellulose, hemicellulose, and lignin, which are strongly associated with each other. Pretreatment processes are being used for separation of these complex interlinked fractions to make the accessibility of cellulose and hemicellulose for hydrolysis into fermentable sugars. A major hurdle is the separation of complex and rigid lignin component which is highly resistant to solubilization. It is also a major inhibitor for hydrolysis of cellulose and hemicellulose. Moreover, other factors such as lignin content, crystalline, and rigid nature of cellulose, production of post-pretreatment inhibitory products and size of feed stock particle limit the digestibility of lignocellulosic biomass. There is need of extensive research in the development of various pretreatment processes. The major pretreatment methods include physical, chemical, and biological approaches. Integrated processes combining two or more pretreatment techniques is better than conventional single pretreatment process in reducing the number of process operational steps which minimize the production of undesirable inhibitors. However, an extensive research is still required for the development of new and more efficient pretreatment processes for Biodegradable Municipal Solid Waste yielding promising results.

Introduction

Municipal solid wastes are the residue or rubbish generated from household and commercial activities from municipalities. It excludes wastes generated from hospitals, industries and other electrical and electronic wastes. Fast urbanization, over population, change in life style and unscientific disposal of wastes caused problem to health and environment. Collection of municipal solid waste creates health problem by providing shelter to rodents and insects which are vectors of disease organism. Mosquitoes growth is responsible for dengue, malaria fevers and other communicable diseases such as typhoid, cholera etc. Mixing with soil and water and generation of leach ate from illegal dumping cause environmental problem by polluting air, soil and water. Piles in the streets makes nuisance by unpleasant odour. Co-disposal with hazardous materials cause LF site problem. In India, Municipal Solid Waste management (MSWM) scheme is there which undertake many objectives to protect health of the public, to provide sanitation. The solid waste management has been the subject of local bodies as per Municipal Corporation Act. MSWM include planning, engineering, organization, administration, financial and legal aspects of activities associated with generation, storage, collection, transportation, processing and disposal of wastes in an environmentally compatible manner adopting principles of economy, aesthetics and energy conservation. Bio-Process Innovation, Inc., and Universal Entech, LLC collaborated on a pilot scale project to demonstrate bio-ethanol production from MSW-derived waste paper. The project consisted of separating paper from MSW using a unique pulverizer-air classifier, taking the collected light-fraction waste paper stream and pulping the entire unsorted fraction using a low-shear mechanical pulper to produce a clean paper pulp fiber stream, and enzymatically/fermentatively converting the pulp fiber to bio-ethanol using a 100 L pilot scaled Continuous Multi-stage Stirred Reactor Separator (CMSRS). The CMSRS employs gas stripping of ethanol along with the simultaneous saccharification and fermentation of the cellulose fibers and allows recycle of the fermentation broth/cellulase enzyme.

MSW generation status and bioethanol production in India

India, the second largest populated and one of the fastest urbanising countries is a land of climatic, social and cultural diversity. Wastes generation varies from villages to cities 0.1 to 0.6 kg per head. There are 23 metro cities generating 30, 000 ton per day and class I cities generating 50, 000 per day. Whereas, 28% of urban population produces approximately 1, 76,530 Tons of garbage with all kinds of litter is a common site in urban India. Nair *et al.* (2017) have reported bioethanol production has been increased from 2004 to 2013 that acknowledged by global community for providing energy security, thereby reducing the dependence on fossil fuels. Bioethanol is the dominating biofuel for transportation, with an annual world production increasing from 28.5 million m3 in 2004 to 87.2 million m3 in 2013. Out of that, our India has produced 2 million m^3ethanol in 2004 and 8 million m3 in 2013. Waste biomass in the form of lignocellulosic or starch-based origin is a potential source of free fermentable sugars that could be effectively used for ethanol fermentation.

Characteristics of MSW

Constituents of MSW are compostable organics, inert debris, paper, plastics, leather, textile, glass, household hazardous and metals. Generally, MSW in India consists of 40-55% of compostable organics, 8% of paper and 20% of recyclables. The typical composition of municipal solid waste is like wet waste (53.7%), dry waste (10%) and inert waste (22%).

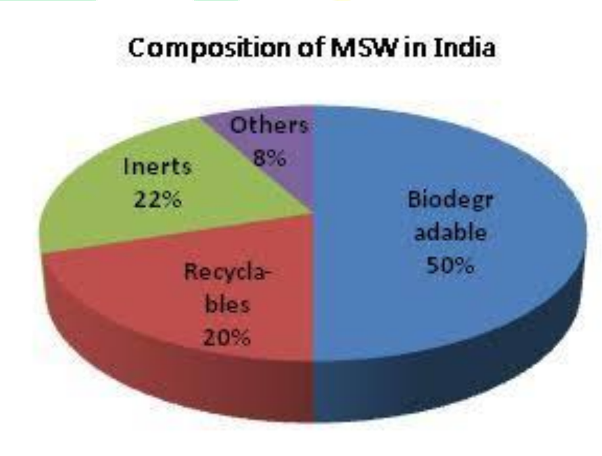

Fig 1 Composition of MSW in India

Municipal solid waste also includes lignocellulosic feedstock represents an extraordinarily large amount of renewable bioresource available in surplus on earth known as Biodegradable Municipal Solid Waste (BMSW) which is emerging as an alternate biomass for large-scale production of second-generation bioethanol for human sustainability. Utilization of BMSW can lead to environmental advantages particularly in terms of solid and liquid waste management, reduction in CO_2 level, improvement in water quality, land use, biodiversity *etc*.Continuous supply and sufficient availability of BMSW along with long term price stability makes it a promising biomass source however the conversion yield to bioethanol is currently too low to make it economically viable. Oke, M. A.*et al* (2016) reported that Lignocellulosic ethanol production so far, has been based mainly on single feedstocks while the use of mixed feedstocks has been poorly explored. Previous studies from alternative applications of mixed lignocellulosic biomass (MLB) have shown that their use can bring about significant cost savings when compared to single feedstocks. Although laboratory scale evaluations have demonstrated that mixed feedstocks give comparable or even higher ethanol yields compared to single feedstocks, more empirical studies are needed to establish the possibility of achieving significant cost savings.The main composition of lignocellulosic feedstocks is cellulose, hemicellulose, and lignin. Many obstacles are associated with effective utilization of lignocellulosic materials. Some of the major factors are the recalcitrance of the plant cell wall due to integral structural complexity of lignocellulosic fractions and strong hindrance from the inhibitors and byproducts that are generated during pretreatment. Based on the type of the treatment process involved, lignocellulosic biomass pretreatment methods are broadly classified into two groups: Non-biological and biological. Non-biological pretreatment methods do not involve any microbial treatments and are roughly divided into different categories: physical, chemical, and physico-chemical methods.

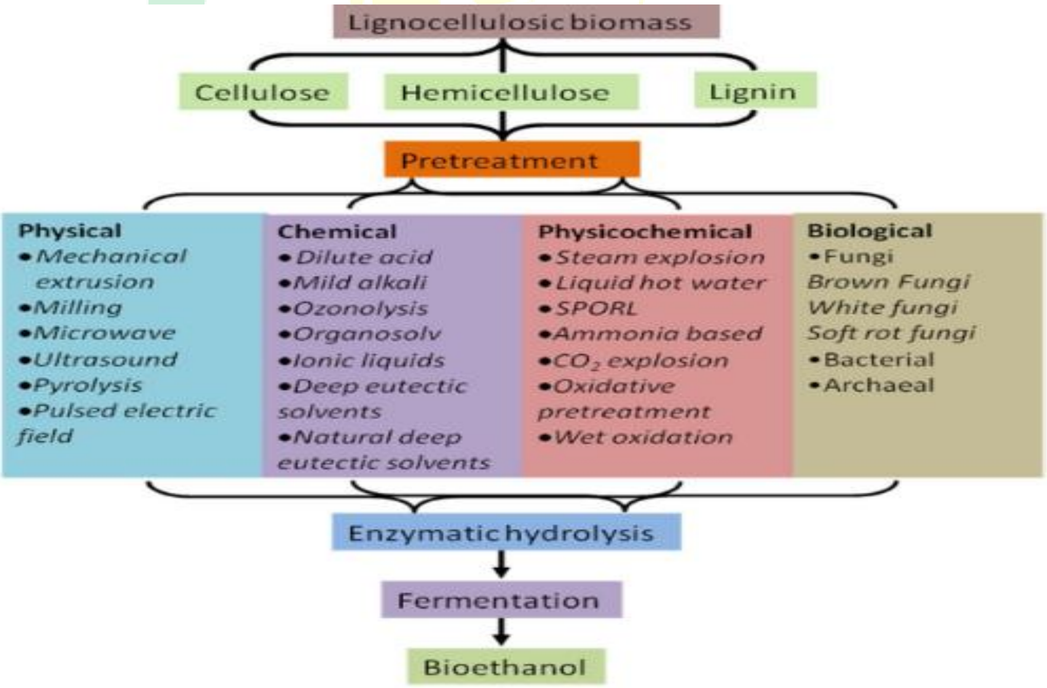

Fig. 2 Overview of different pretreatment processes

Physical pretreatment

Mechanical extrusion

It is the most conventional method of biomass pretreatment where the feedstock materials are subjected to heating process (>300 °C) under shear mixing. This pretreatment process results mainly in production of gaseous products and char from the pretreated lignocellulosic biomass residues. Karunanithy *et al.* (2013) selected different varieties of warm season grasses viz. switch grass, big bluestem, and prairie cord grass and studied the effect of different screw speeds (100, 150, and 200 rpm), barrel temperatures (50, 75, 100, 150 and 200 °C) and different concentrations of cellulose with β-glucosidase (1:1 to 1:4). The reducing sugar yields from big bluestem pretreated at screw speed of 200 rpm and 150 °C barrel temperature produced 66.2% and with prairie cord grass pretreated at 150 rpm and 100 °C produced 49.2%. Different parameters of mechanical extraction process were studied by Zheng and Rehmann (2014).

Milling

Mechanical grinding (milling) is used for reducing the crystallinity of cellulose. It mostly includes chipping, grinding, and/or milling techniques. Chipping can reduce the biomass size to 10–30 mm only while grinding and milling can reduce the particle size up to 0.2 mm. Better results were obtained when milling was combined with alkaline pretreatment method. As compared to wet milling process, alkaline milling treatment increased the enzymatic hydrolysis efficiency of corn stover by 110%.Three different milling methods i.e., ball, attrition and planetary milling were compared by Kim *et al.* (2013). Attrition and planetary mills were found to be more effective in reducing the size of biomass as compared to ball milling. Planetary mill produced highest amount of glucose and galactose than other milling methods. All the milling pretreatment methods do not produce any toxic compounds like levulinic acid.In another study, oil palm frond fiber when pretreated through ball mill produced glucose and xylose yields of 87 and 81.6%, respectively, while empty fruit bunch produced glucose and xylose yields of 70 and 82.3%, respectively (Zakaria *et al.* 2014).

Microwave

Microwave irradiation is a widely used method for lignocellulosic feedstock pretreatment because of various reasons such as easy operation, low energy requirement, high heating capacity in short duration of time, minimum generation of inhibitors and degrades structural organization of cellulose fraction. Xu *et al.* (2011) developed an orthogonal design to optimize the microwave pretreatment of wheat straw and increased the ethanol yield from

2.678 to 14.8%. Microwave pretreatment of oil palm empty fruit bunch fiber in the presence of alkaline conditions showed 74% reduction in lignin (Nomanbhay *et al.* 2013).Alkali pretreatment along with microwave was carried out by Meenakshi *et al* (2016) and found that low energy process cause significant delignification (89%) of sugarcane bagasse.

Ultrasound

Sonication is a new technique used for the pretreatment of lignocellulosic biomass. The studies in the laboratory have found sonication a feasible pretreatment process. Ultrasound waves produce both physical and chemical effects which alter the morphology of lignocellulosic biomass.Ultrasound treatment leads to formation of small cavitation bubbles cause rupturing of the structures of cellulose and hemicellulose fractions result in increasing the accessibility to cellulose degrading enzymes for effective breakdown into simpler reducing sugars. Duration of sonication has maximum effect on pretreatment of biomass. Rehman *et al.* (2013) observed that continuous sonication for long time beyond a certain limit has no additional effect in terms of delignification and sugar release. Most of the researchers have used ultrasound frequency of 10–100 kHz for the pretreatment process which has been enough for cell breakage and polymer degradation (Gogate *et al.*, 2011).

Pyrolysis

Pyrolysis has also been employed for the pretreatment of lignocellulosic biomass and in biorefinery processes also. Unlike bioethanol applications, pyrolysis treatment is used for production of bio-oil from lignocellulosic feedstocks.Pyrolysis is found to be more efficient when carried out in the presence of oxygen at lower temperatures (Kumar *et al.*, 2009). Zwart *et al.* (2006) used Biomass to liquid (BtL) route for the production of transportation of fuels from biomass which includes conversion of biomass to syngas to high-quality Fischer – Tropsch (FT) fuels.

Pulsed-electric field

Pulsed-electric field (PEF) pretreatment creates the pores in the cell membrane to expose the cellulose present in the biomass hence, allowing the entry of agents that will break the cellulose into constituent sugars. In PEF pretreatment, the biomass is subjected to a sudden burst of high voltage between 5.0–20.0 kV/cm for short durations (nano to milliseconds). Luengo *et al.* (2015) reported that electric field strength and pulse duration are the two interdependent processing parameters affecting electroporation through PEF. Two different durations in the range of milliseconds and microseconds were applied to *Chlorella vulgaris* and found irreversible electroporation at >4 kV/cm in the millisecond range and at ≥10 kV/cm in the microseconds range. Yu *et al.* (2016) optimized pressure, electric field strength, and pulse number on the juice expression yield, total polyphenols, and total proteins content in the expressed juices of rapeseed stem biomass. The optimum conditions of electric field strength $E = 8$ kV/cm, pressure $P = 10$ bar and pulse number tPEF = 2 ms increased juice yield from 34 to 81%. Total polyphenols and total proteins content increased significantly after PEF pretreatment.

Chemical pretreatment

Dilute acid

Acid treatment is the most commonly used conventional pretreatment method of lignocellulosic feedstocks, it is less attractive due to the generation of high amount of inhibitory products such as furfurals, 5-hydroxymethylfurfural, phenolic acids, and aldehydes. The corrosive and toxic nature of most acids requires a suitable material for building the reactor which can sustain the required experimental conditions and corrosive nature of acids. Different acids were used for delignification like sulphuric acid, hydrochloric acid, nitric acid and maleic acid. The most common commercially used acid is dilute sulphuric acid (H_2SO_4). Pretreatment liquor of *Eulaliopsis binata* (a perennial grass commonly found in India and China) with diluted H_2SO_4 at optimum conditions resulted in 21.02% total sugars, 3.22% lignin, and 3.34% acetic acid with the generation of low levels of inhibitors (Tang *et al.*, 2013). Due to its low cost, pretreatment of lignocellulosic biomass through sulfuric acid is a conventional method.

Dicarboxylic acids are being tested by researchers in order to overcome the drawbacks associated with sulfuric acid. Such acids have higher pKa values than sulfuric acid and therefore have a higher solution pH as compared to sulfuric acid which is a type of mineral acid. Lee and Jeffries (2011) reported that dicarboxylic organic acids exhibit two pKa values which make them more efficient for carrying out the hydrolysis of the substrate over a range of temperature and pH values. Oxalic acid can also be used for the pretreatment of corn cobs that were heated to 168 °C and kept for 26 min. A total sugar yield of 13% was obtained through oxalic acid pretreatment with production of very less amount of inhibitors (Lee *et al.*, 2011). Raud *et al.* (2014) investigated the potential of Woody and non-woody vegetation for bioethanol production which contained grass, twigs, and leaves. Dilute acid was used for pre-treatment at temperature of 130°C in order to compare yields from different methods. Waste from urban greening had the highest cellulose content of 22.96% and gave the best glucose and ethanol yields, 154.5 g kg-1 and 62.5 g kg-1, respectively when the sample was pre-treated with dilute H_2SO_4.

Mild alkali

In comparison to acid treatment, alkali pretreatment methods can be performed at ambient temperature and pressure. The most commonly used alkali reagents are the hydroxyl derivatives of sodium, potassium, calcium, and ammonium salts. Among these hydroxyl derivatives, sodium hydroxide was found to be most effective. Mild alkali pretreatment can be successfully carried out at ambient conditions whereas, higher temperature is required if the pretreatment is needed to be carried out for longer duration. The lime pretreatment method was modified by neutralizing the lime with carbon dioxide before hydrolysis. This eliminated the solid–liquid separation step resulting in 89% glucose recovery from leafstar rice straw. Mondal and Banerjee (2015) showed the consequences of calcium hydroxide or lime digestion on organic fraction of municipal solid waste of Varanasi, India. The different concentrations (0.1, 0.2, and 0.5%) of calcium hydroxide was blended separately to substrates (10% total solid) at 30-35 °C in 3 different beakers denoted by A1, A2 and A3, respectively of 2 L capacity. Initially COD value increases with time and reaches a maximum value and after this it starts decreasing. Both TOC and TKN content of the samples at the end are less than those of initial values.sugarcane bagasse was subjected to different alkaline pretreatments for lignin removal. Sugarcane bagasse of three particle size *viz* unscreened (as comes from factory) and screened (0.5 and 2 mm) was treated with 1 and 5% sodium hydroxide with boiling, autoclaving and microwaving treatments. Bagasse of different particle size was also treated with lime (4%) at 70^0C for different time intervals. In all the pretreatments, delignification varied with treatment time and alkali concentration. Delignification of sugarcane bagasse was found to be increased with increasing concentration of sodium hydroxide from 1 to 5% and reduction in particle size to 0.5mm. Maximum 81.42 % delignification was achieved when bagasse of 0.5 mm particle size was subjected to boiling for 60 min in 5% NaOH. Lime pretreatment to sugarcane bagasse of different particle size also removed lignin but it was found to be less effective in comparison with sodium hydroxide pretreatment. Based on efficiency of delignification, bagasse (0.5 mm) boiled in 5% NaOH for 60 min was found to be best pretreatment for lignin removal. Patra, J. *et al* (2017) used dilute acid (H2SO4, 3%) and alkali (NaOH, 3%) pretreatment methods have some potential how ever to date, these methods effectively increase ethanol production of municipal solid waste (MSW). Enzymatic hydrolysis was carried out with *Aspergillus niger, Aspergillus fumigatus* and *Trichoderma reesei*. Finally, the fermentation was done by sugar three ethanologenic yeasts, *Saccharomyces cerevisiae, pichia stipitis, canida shehatae* for bioethanol production.The highest ethanol yield (22.32%) v/v. was obtained with a pre-hydrolysis treatment consisting of NaOH at 3% concentration, followed by *Pichia stipitis* and enzymatic hydrolysis with *Aspergillus niger*.

Ozonolysis

Ozone treatment is mainly used for reducing the lignin content of lignocellulosic biomass as it mainly degrades lignin but negligibly affects hemicellulose and cellulose (Kumar *et al.*, 2009). The important factor which affects the ozone pretreatment is the moisture content of the biomass, higher the moisture content, lower the lignin oxidization.

Organosolv

Organosolv is the process that involves addition of aqueous organic solvents such as ethanol, methanol, ethylene glycol, acetone etc. to the biomass under specific condition of temperature and pressure (Ichwan and Son 2011). Bajpai (2016) performed this process in the presence of an acid, base or salt catalyst. Park *et al.* (2010) studied the effect of different catalysts (H_2SO_4, NaOH, and $MgSO_4$) on pine and found H_2SO_4 as the most effective catalyst in terms of ethanol yield. But in terms of digestibility, NaOH was found to be effective when its concentration was increased by 2%. H_2SO_4 has high reactivity therefore has proven to be a very strong catalyst but at the same time it is toxic, corrosive and is inhibitory in nature.

Panagiotopoulos *et al.* (2012) treated poplar wood chips with steam followed by organosolv treatment for separating hemicellulose, lignin, and cellulose components. Lignin extraction was found to increase to 66%, while 98% of the cellulose was recovered by two stage pretreatment process and 88% of cellulose was hydrolyzed to glucose after 72 h. Similarly, horticultural waste was pretreated by a modified method using ethanol under mild conditions for bioethanol production. Pretreatment resulted in hydrolysate containing 15.4% reducing sugar after 72 h, which after fermentation produced 1.169% ethanol in 8 h using *Saccharomyces cerevicae* (Geng *et al.* 2012). Hideno *et al.* (2013) reported utilization of alcohol-based organosolv treatment in combination with ball milling for pretreatment of Japanese cypress (*Chamaecyparis obtusa*). They observed that combination of alcohol-based organosolv treatment in mild conditions and short time ball milling had a synergistic effect on the enzymatic digestibility.

Ionic liquids

Ionic liquids have received great attention in last decade for the pretreatment of lignocellulosic biomass. Ionic liquids are comparatively a new class of solvents which are entirely made of ions (cations and anions), have low melting points (<100 °C), negligible vapor pressure, high thermal stabilities, and high polarities (Behera *et al.*, 2014). L. et al. (2017) developed sixteen cellulose rich municipal solid waste (MSW) blends and screened using an acid assisted ionic liquid (IL) deconstruction process. Corn stover and switchgrass were chosen to represent herbaceous feedstocks; non-recyclable paper (NRP) and grass clippings (GC) collected from households were chosen as MSW candidates given their abundance in municipal waste streams. The most promising MSW blend: corn stover/non-recyclable paper (CS/NRP) at 80/20 ratio was identified in milliliter-scale screening based on the sugar yield, feedstock cost, and availability. A successful scale-up (600-fold) of the IL-acidolysis process on the identified CS/NRP blend has been achieved. During the scale-up experiment under the same conditions lower glucose yield (from 65% to 58%) and xylose yield (from 61% to. 35%) were obtained compared to small scale results.

Deep eutectic solvents

These are relatively a new class of solvents having many characteristics similar to ionic liquids. A deep eutectic solvent (DES) is a fluid generally composed of two or three cheap and safe components that are capable of self association, often through hydrogen bond interactions, to form a eutectic mixture with a melting point lower than that of each individual component (Zhang *et al.* 2012 a). Most of the DESs have used choline chloride (ChCl) as hydrogen bond acceptor. ChCl is low-cost, biodegradable, and non-toxic ammonium salt which can be extracted from biomass. ChCl is able to synthesize DESs with hydrogen donors such as urea, carboxylic acids, and polyols. Although DESs are similar to Ionic Liquids in terms of physical behavior and physical properties, DESs cannot be considered as ionic liquids due to the fact that DESs are not entirely composed of ionic species and can be obtained from non-ionic species (Zhang *et al.* 2012 b).

Natural deep eutectic solvents (NADES)

Recently, a large number of natural products have been brought into the range of Ionic Liquids (ILs) and DES. These products include choline, urea, sugars, amino acids, and several other organic acids (Dai *et al.* 2013). As compared to ILs, NADES are cost effective, easier to synthesize, non-toxic, biocompatible, and highly biodegradable. NADES are prepared by the complex formation between a hydrogen acceptor and a hydrogen bond donor. Due to the charge delocalization of the raw individual components result in decrease in melting point of the prepared solvent mixtures. After seeing the potentiality of NADES in diverse applications, these solvents are regarded as the solvents for the twenty first century (Paiva *et al.* 2014). When lignocellulosic feedstock were pretreated with NADES reagents showed high specificity towards lignin solubilisation and extraction of high purity lignin from agricultural residue such as rice straw (Kumar *et al.* 2016). The dilution effect on the physicochemical properties of NADES was studied by FT-IR and 1H NMR techniques (Dai *et al.*, 2015). These studies showed that there were intense H-bonds between the two components of NADES system. But the dilution with water weakened the interactions.

Physico-chemical pretreatment

Steam explosion

Steam pretreatment is the most common physicochemical method which used for pretreatment of lignocellulosic biomass. This method was known as steam explosion. Steam pretreatment is typically a combination of mechanical forces (pressure drop) and chemical effects (autohydrolysis of acetyl groups of hemicellulose).Biomass is subjected to high pressure (0.7–4.8 MPa) in this process saturated steam at elevated temperatures (between 160 and 260 °C) for few seconds to minutes which causes hydrolysis and release of hemicellulose. The steam enters the biomass expanding the walls of fibers leading to partial hydrolysis and increasing the accessibility of enzymes for cellulose. After this the pressure is reduced to atmospheric condition (Rabemanolontsoa and Saka, 2016).Several biomasses have shown positive effects on pretreatment with steam such as pine chips, French maritime pine (*Pinus pinaster*), rice straw, bagasse, olive stones, giant miscanthus (*Miscanthus giganteus*), and spent Shiitake mushroom media (Jacquet *et al.* 2012).The possibility of formation of fermentation inhibitors at high temperature, incomplete digestion of lignin-carbohydrate matrix and the need to wash the hydrolysate which decreases the sugar yield by 20% are few disadvantages associated with steam pretreatment (Agbor *et al.* 2011).

Liquid hot water

Liquid hot water also known as hot compressed water is similar to steam pretreatment method and it uses water at high temperature (170–230 °C) and pressure (up to 5 MPa) instead of steam. This leads to hydrolysis of hemicellulose and removes lignin making cellulose more accessible. Abdullah and coworkers (2014) investigated the process of LHW and carried out the hydrolysis. The optimization could not be carried out at same severity due to the difference in rate of hydrolysis of cellulose and hemicellulose. Therefore, a two-step hot compressed water treatment was proposed. First stage is carried out at low severity for hydrolyzing the hemicelluloses while second stage is carried out at high severity for depolymerization of cellulose and increase sugar yield. Ogura *et al.* (2013) and Phaiboonsilpa (2010) applied two-step hydrolysis (I step: 230 °C-10 MPa-15 min; II step: 275 °C-10 MPa-15 min) to Japanese beech, Japanese cedar, Nipa frond and rice straw. They found to solubilize 92.2, 82.3, 92.4, and 97.9% of the starting biomass, respectively. Rabemanolontsoa and Saka (2016) also proved that LHW is capable of acting on a large variety of biomass including softwoods.

SPORL treatment

Sulfite pretreatment to overcome recalcitrance of lignocelluloses (SPORL) is a efficient pretreatment method for lignocellulosic biomass (Xu *et al.*, 2016). It can be performed in a combination of two steps: First, the biomass is treated with calcium or magnesium sulfite that removes hemicellulose and lignin fractions. In the second step, the size of the pretreated biomass is reduced significantly using mechanical disk miller. Idrees *et al.* (2013) applied Sodium sulfide and sodium sulfite along with sodium hydroxide for pretreatment of corncob, bagasse, water hyacinth and rice husk. Pretreatment under optimized conditions resulted in removal of 97% lignin and 93% hemicellulose from water hyacinth, whereas, 75% lignin and 90% hemicelluloses were removed from bagasse and rice husk. It has the capacity to process a variety of biomass and has excellent scalability for commercial production by incorporating into existing mills for production of biofuels.

Ammonia based pretreatment

Methods like Ammonia fiber explosion (AFEX), Ammonia recycle percolation (ARP) and Soaking Aqueous Ammonia (SAA) used liquid ammonia for the pretreatment of lignocellulosic biomass. More than 90% of celluloses and hemicelluloses can be converted to fermentable sugars if pretreated with AFEX under optimized conditions of ammonia loading, temperature, pressure, moisture content and pretreatment time (Uppugundla *et al.*, 2014).In ARP process, aqueous ammonia (5–15 wt %) is passed through a reactor containing biomass. The temperature range is between 140 and 210 °C with a reaction time of 90 min and percolationrate is 5 mL/min after which the ammonia is recycled (Kim *et al.* 2008). Alvira *et al.* (2010) conducted ARP process and found that it is capable of solubilizing hemicellulose but cellulose remains unaffected. Thus, both AFEX and ARP have been found to effective for herbaceous plants, agricultural residues and MSW.

CO2 explosion

This process carries out the pretreatment of biomass through supercritical CO2 which means the gas behaves like a solvent. The supercritical CO2 is passed through a high pressure vessel containing the biomass. The vessel is heated to the required temperature and kept for several minutes at high temperatures (Hendricks and Zeeman 2009). Low cost of carbon dioxide, low temperature requirement, high solid capacity, and no toxin formation makes it an attractive process. However, high cost of reactor which can tolerate high pressure conditions is a big obstacle in its application on large scale (Agbor *et al.*, 2011).

Oxidative pretreatment

It involves treatment of lignocellulosic biomass by oxidizing agents such as hydrogen peroxide, ozone, oxygen or air. This process causes delignification by converting lignin to acids, which may act as inhibitors. Therefore, these acids need to be removed (Alvira *et al.*, 2010). Cao *et al.* (2012) performed pretreatment of sweet sorghum bagasse through different pretreatment processes and found the highest yield with dilute NaOH followed by H_2O_2 pretreatment. The highest cellulose hydrolysis yield was 4.3%, total sugar yield was 90.9% and ethanol concentration was 0.61% which was 5.9, 9.5, and 19.1 times higher as compared to control.

Wet oxidation

Wet oxidation is a simple method for pretreatment of lignocellulosic and waste water treatment and soil remediation (Chaturvedi and Verma 2013). This pretreatment method is unlikely to reach industrial scale of biomass pretreatment because of the high cost of the hydrogen peroxide and the combustible nature of the pure oxygen (Bajpai, 2016). Alkaline Peroxide-Assisted Wet Air Oxidation (APAWAO) treatment on rice husk resulted in solubilization of 67 and 88 wt% of hemicellulose and lignin, respectively. The glucose amount increased 13-fold as compared from untreated rice husk (Banerjee *et al.*, 2011).

Biological pretreatment

Biological pretreatments are considered as efficient, environmentally safe and low-energy process, when compared with conventional chemical and physical pretreatment methods.Nature has abundant cellulolytic and hemicellulolytic microbes which can be specifically targeted for effective biomass pretreatment (Vats *et al.*, 2013). The white-rot fungi species commonly employed for pretreatment are *Phanerochaete chrysosporium, Ceriporia lacerata, Cyathus stercolerus, Ceriporiopsis subvermispora, Pycnoporus cinnarbarinus* and *Pleurotus ostreaus.* Kumar *et al.* (2009) studied other basidiomycetes species also for breakdown of several lignocellulosic feedstocks. Among these *Bjerkandera adusta, Fomes fomentarius, Ganoderma resinaceum, Irpex lacteus, Phanerochaete chrysosporium*, *Trametes versicolor*, and *Lepista nuda* are well studied. These species have been reported to show high delignification efficiency. To make biological pretreatment at par with other pretreatment methods, more basidiomycetes fungi should be tested for its ability to delignify the biomass effectively at a faster rate. Bhatia *et al* (2012) shown that lignocellulolytic microorganisms, especially fungi, have attracted a great deal of interest as biomass degraders for large-scale applications due to their ability to produce large amounts of extracellular lignocellulolytic enzymes. Process integration has also been considered for the purpose of decreasing the production cost, which was partly achieved by performing hydrolysis and fermentation in a single reactor (SSF) using one or more microorganisms (co-culturing).

Combined biological pretreatment

The studies are going on to find a combination of another pretreatment process with biological pretreatment process is more effective as compared to a single pretreatment process. Wang *et al.* (2012) used combination of biological pretreatment with liquid hot water pretreatment method for better enzymatic saccharification of *Populus tormentosa*. This combination resulted in highest hemicelluloses removal (92.33%) that increase 2.66-fold in glucose yield as compared to pretreatment carried out with liquid hot water alone. The combination of mild acid pretreatment (0.25% H_2SO_4) and biological pretreatment using *Echinodontium.taxodii* on water hyacinth was found more effective than one step pretreatment. The reducing sugars yield doubled as compared to single step acid pretreatment method (Ma *et al.*, 2010).

Enzymatic Hydrolysis

Jenson *et al.* (2010) investigated an enzymatic liquefaction of MSW organics, paper and cardboard for biogas p[roduction. Degradable material with a particle size above 1 mm after treatment was evaluated using Scanning Electron microscopy. The results showed that paper particles were the main obstacles needing additional treatment in order to become fully liquefied.

Abdullah, *et al.*(2016) optimized cellulase activity of *Trichoderma reesei* (26.10 ± 3.09 FPU/g) at 30°C with a moisture content of 60% with an inoculums of 0.5 million spores/g and incubation for 168 hours. Crude enzymes produced from MSW by *T. reesei* were evaluated for their ability to release glucose from MSW. A cellulose hydrolysis yield of 24.7% was achieved, which was close to that obtained using a commercial enzyme. Results demonstrated that MSW can be used as an inexpensive lignocellulosic material for the production of cellulase enzymes. Rosander, *et al.* (2016) investigated the potential of MSW as a carbon and energy source for *Escherichia coli*. For this purpose, MSW was initially fractionated and processed to yield a liquid (LMSW) and a dry solid fraction (DSMSW). In contrast to DSMSW, the liquid fraction had a natural high sugar content of 21 g L-1. By further applying enzyme-catalyzed hydrolysis to DSMSW, a hydrolyzate concentration of 114 g L-1 was achieved. Abdullah, *et al.*(2018)used two commercial cellulase enzymes, Cellic® and CTec2, and a fresh prepared fungal filtrate was also used to hydrolyse MSW. Results revealed that CTec2 displayed the best hydrolysis efficiency. An assessment of the efficacy of addition of surfactants revealed that addition of tween 80 or polyethylglycol had a no significant effect on release of sugars. Results revealed that by increasing the solid liquid ratio the amount of glucose increased. Vaurs, A. P. *et al* (2018) carried out enzymatic hydrolyses of the different paper streams and found that glucan conversions differ depending on the type of paper. Office paper and cardboard showed similar hydrolysis performances with virtually the same glucan conversions. The glucan conversion of newspaper was approximately 30 % lower, while that of magazines was only 25.0 ± 3.1 %. Surprisingly, the paper mixture showed very good conversion, close to that of office paper and cardboard.

Fermentation

Lignocellulosic biomass can be transformed into bioethanol via two different approaches. Both routes involve degradation of the recalcitrant cell wall structure of lignocellulose into fragments of lignin, hemicellulose and cellulose. Martin, M. and Ignocio, E. C. (2011) proposed the optimal conditions for the production of bioethanol from switchgrass, via hydrolysis. Two technologies were considered for switchgrass pretreatment, dilute acid and ammonia fibre explosion (AFEX) so that the structure of the grass is broken down. Next, enzymatic hydrolysis follows any of the pretreaments to obtain fermentable sugars, mainly xylose and glucose. Ethanol is obtained by fermentation of the sugars. In order to obtain fuel quality ethanol, water must be removed from the water-ethanol mixture. The production capacity of Bioethanol plants from lignocellulosic biomass is limited by the availability of biomass in the region. Current trends as well as NREL reports suggest values in the range of 40 to 60 Mgal ethanol/ yr from pilot scale reactor.

Matsakas *et al.* (2014) utilized household food wastes as raw material for the production of ethanol at high dry material consistencies. This substrate led to an increase of 13.16% in the ethanol production levels achieving a final ethanol yield of 107.58 g/kg dry material. Garbers, M. H. (2015) processed wastes from nearby industries for ethanol production. Residues from ethanol production are used as animal feed, fertilizer or solid biomass fuel and 85% pure ethanol is centrally collected for dehydration in Hamina. The storage and blending with gasoline were done at nearby petrol pumps and their distributions are being taken over 1.200 fuel stations. Hence, a large scale bioethanol using BMSW are being searched for compensating the demand of world. Simultaneous saccharification and fermentation of sodium hydroxide pretreated sugarcane bagasse was carried out by using commercial enzyme and *Candida utilis* and was optimized with respect to temperature, inoculum size, nitrogen supplementation, enzyme loading, substrate concentration and incubation period. Optimum conditions for simultaneous saccharification and fermentation of pretreated sugarcane bagasse were 1.0% (w/v) inoculum size, 2.0% (v/v) enzyme loading, temperature 35°C, 10%

substrate concentration, pH 6.0, supplementation of 0.3% urea and 72 h incubation period. Yeast strain *Candida utilis* produced 2.2% ethanol under optimized conditions and production of ethanol can further be improved by co-fermentation of pentose sugars in the substrate.

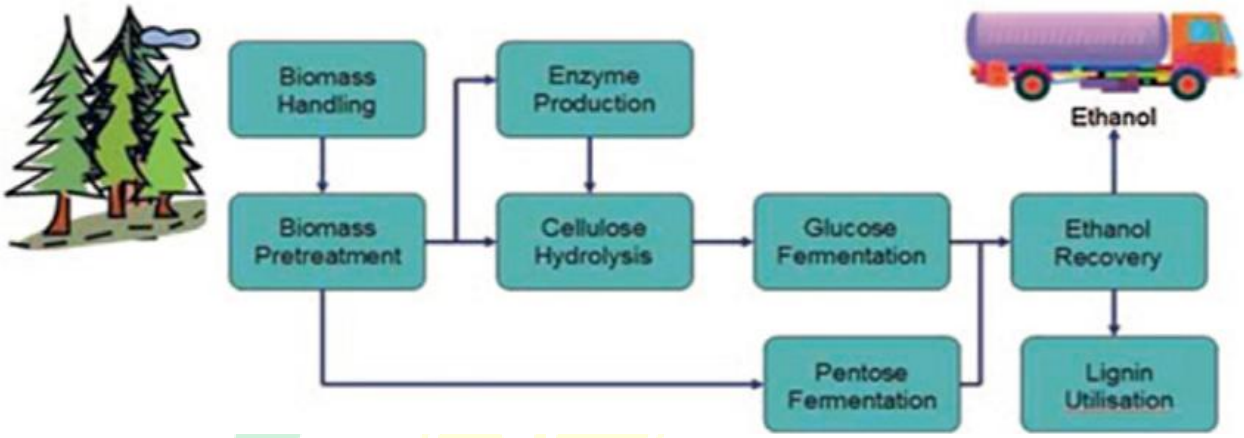

Fig. 2 Schematic of a biochemical cellulosic ethanol production process

Thapa, B. *et al*. (2017) collected, dried, and crushed food waste to produce ethanol in this study. Two experiments were carried out in series (i.e. hydrolysis and fermentation). Varying acid concentration and temperature were considered for optimization in hydrolysis. The maximum reducing sugar yield obtained was 32.63 g/100 g of dry food waste at 7.5 % acid concentration at 135 ºC. The ethanol yield was 13.78 g/100 g of dry food waste from MSW of Kathmandu Valley and Delhi respectively.

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