

Pretreatments to enhance the digestibility of wheat straw

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To cite this article:

Zahoor, Yuanyuan Tu. Pretreatments to Enhance the Digestibility of Wheat Straw. *International Journal of Renewable and Sustainable Energy*. Vol. 3, No. 1, 2014, pp. 26-34. doi: 10.11648/j.ijrse.20140301.15

Abstract: Wheat straw is a sufficient agricultural by-product with a low market price. The biofuel produced from lignocellulosic material exhibits energetic, economic and environmental benefits in contrast to bio-ethanol from starch or sugar. Until now, physical and chemical difficulty caused by the close connection of the main components of lignocellulosic biomass, discourage the hydrolysis of cellulose and hemicellulose to fermentable sugars. The main purpose of pretreatment is to enhance the enzyme accessibility improving digestibility of cellulose. Every pretreatment has a particular effect on the fraction of cellulose, hemicellulose and lignin, thus different pretreatment methods and conditions should be selected for the development of subsequent hydrolysis and fermentation steps. This paper reviews the most importance technologies for ethanol production from lignocellulose and its represent several vital qualities that should be marked for low-price and promote pretreatment processes.

Keywords: Wheat Straw, Lignocellulosic, Cellulose, Hemicelluloses, Lignin

Introduction

The pretreatment methods are The utilization of biomass energy has attracted more concentration from the governments around the world. The “Aggressive Biofuels Growth” scenario aims to restore 10% of gasoline production with biofuels by 2010, 15% by 2015, and 20% by 2020 all over most of the world [40]. Due to the Chinese government law of renewable energy published on January 1st, 2006, showed that biofuels from renewable sources would account for 5% of primary energy by 2010 and 10% by 2020 [31, 4]. The increase in largely ethanol yields in ethanol production from agricultural residues (e.g. Wheat straw), which include high amounts of hemicelluloses and cellulose, it is essential to utilize both hexoses and pentoses. The utilization of biomass for biofuels such as ethanol and butanol decrease our need on fossil fuels and decline the emissions of greenhouse gases such as carbon dioxide [54]. About 21% of the world’s food depending on the wheat crop and its global production needs to be increased to satisfy the growing demand of human consumption [49]. The main components of wheat straw are cellulose ~34-43%, hemicelluloses ~26-35% and lignin around ~14-21%, which differ slightly in composition owing to dissimilar

varietal, geographical, and climatic influences in the growth of wheat straws [57]. Therefore, wheat straw would provide as a vast potential feedstock for production of ethanol in the 21st century.

Pretreatment is a vital role in practical cellulose conversion processes, and it is the subject to this review. Pretreatment is required to modify the structure of cellulosic biomass to make cellulose more reachable to the enzymes that convert the carbohydrate polymers into fermentable sugars. The aim is to break the lignin seal and disrupt the crystalline structure of cellulose. Pretreatment has been viewed as one of the most luxurious processing steps in cellulosic biomass-to-fermentable sugar conversion with high costs. Pretreatment also has the huge potential for enhancement of efficiency and lowering of cost through research and development [43]. Lignocellulosic biomass has the polymeric and complex structure. It generates difficulty in bioethanol production. To achieve the efficient conversion, a number of pretreatment methods have been examined [38]. Due to the complex structure of lignin, which is linked with cellulose and hemicelluloses, the structure created more difficulties in its removal. By the complex

structure, bio-ethanol production from wheat straw needs at least four most important steps, pretreatment, hydrolysis, fermentation and distillation [93].

The pretreatment methods are divided as physical, physico-chemical, chemical and biological processes. Physical application is size reduction of milling-grinding and chipping. Decrease material sizes develop the efficiency of following processing due to greater specific surface area of the material. Physicochemical methods are adapted to solubilize lignocellulosic components of the material structure based on pH, temperature and moisture content and create the material exposed easily for the subsequent processing step.

The availability of more cellulosic materials to hydrolysis needs, a pretreatment process is making to decrease the cellulose crystallinity and increase the cellulose porosity [54, 38]. Different pretreatment methods can be used to improve the digestibility of cellulosic materials [7, 41]. Acid, wet oxidation, solvent, metal complex and lime pretreatments are efficient, but more expensive compared to the importance of glucose [7]. Acid pretreatment usually requires corrosion resistant materials of construction and some mineral acids produce degradation products [42], but also its cost is more. The liquid hot water, ammonia fiber explosion and steam explosion pretreatments have high potential, but it needs high temperature or high pressure [41]. Therefore, the pretreatments have a great potential to develop the efficiency and lowering of cost during ethanol production from wheat straw.

The main aim of this paper is to review the published investigations on wheat straw conversion to bioethanol and to demonstrate the recent advances of the technology, future perspective and challenges come across throughout pretreatment methods.

Wheat straw Production and potential feedstock for 2nd generation bio-ethanol.

Wheat (*Triticum aestivum* L.) is the world's most widely grown Crop. Wheat straw is one of the most abundant agricultural by-products, shows a low commercial value and most of it is being used for cattle feed and waste material. In terms of total production, wheat is the second most important grain crop in the world. FAO statistics reported a world annual wheat production in 2009 of 682 million tons and, in average, the harvesting of 1.3 kg of grain is accompanied by the production of 1 kg of straw; this gives an estimation of about 524 million tons of wheat straw in 2009. Therefore, wheat raw material is a rich source for the production of bio-ethanol [3]. The straw produced has left on the field, plowed again into the soil, burned or even removed from the land depending on the decision made by the landowner. By burning of wheat straw, the air pollution problems increase day by day including, CO and NO₂ [36].

The main benefit of using a biomass source for fuel production is its renewability. It is the fourth biggest source of energy in the world after coal, petroleum and natural gas. Biomass is a complex mixture of organic materials, however, the most important components of plant biomass are

polymeric carbohydrates (approximately 75%, dry weight) including celluloses and hemicelluloses with lignins which main purpose is strength to the plant structure and holding the fibers together [53]. Cellulose, hemicellulose and lignin build up about 90% of the whole composition of lignocelluloses [47]. Cellulose have protected and sheathed by lignin and hemicellulose, and also lignin have covalently bonded to carbohydrates [41]. Cellulose, hemicellulose and lignin content of wheat straw have including 33–40, 20–25, and 15–20 (%w/w), respectively [60]. Due to this structural complexity of the lignocellulosic matrix, ethanol production from wheat straw requires pretreatment, which is very important for its degradation.

The potential pretreatment methods are developed, which decreases the costliest in the biological conversion and successive hydrolysis and fermentation process [45]. A huge number of physical (cutting, chopping, milling and grinding), chemical (acid, alkali, oxidizing agents, and organic solvents), physico-chemical (steam explosion, ammonia fiber explosion), biological, or a combination of these pretreatment approaches and different feedstock material have been investigated [47, 41].

To make cellulosic materials more vulnerable to hydrolysis, pretreatment methods are very important to reduce the cellulose crystalline and increase the cellulose porosity [54, 38]. Different pretreatment methods are investigated to enhance the digestibility of cellulosic materials [7, 41]. Acid, wet oxidation, solvent, metal complex and lime pretreatments are effective, but too luxurious compared to the value of glucose [7]. Therefore, the pretreatment have a great potential for improvement of effectiveness and decreasing the cost of wheat straw digestibility for conversion to available sugar.

1. Pretreatment of Wheat Straw

The main goal of the pretreatment of lignocellulosic material is to remove lignin and hemicelluloses, changed the crystalline structure of cellulose, and increase the porosity of the materials, thus enhancing the accessibility of enzymes to cellulose. Pretreatment is one of the most crucial steps in the overall conversion of biomass-to-ethanol as it directly impacts the further steps of enzymatic hydrolysis, fermentation and downstream processing [41]. There are several review articles on various pretreatment approaches with different feedstocks which provide a general overview of the field [23, 7, 39, and 9]. Different physical (combination, hydro-thermolysis), chemical (acid, alkali, solvents, ozone), physico-chemical (ammonia fiber explosion, steam explosion), and biological pretreatment techniques have been developed to improve the accessibility of enzymes to cellulosic fibers [41]. A number of researchers have attributed feasible explanation for the enhancement in sugar recovery in extrusion pretreatment includes to enhance in surface area [12,13,14,15], specific surface area [64,65,80], pore size [75,61], and pore quantity [62], a reduction in cellulose crystallinity [8,62], and induction of micro/nano fibrillation [61].

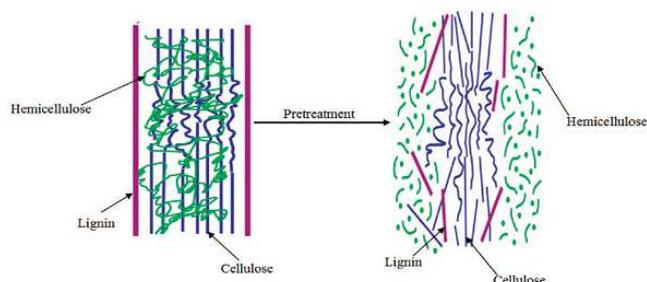


Figure 1. Schematic of the role of pretreatment in the conversion of biomass to fuel. [47].

1.1. Physical

The most essential step in wheat straw for ethanol production is size decreasing through milling, grinding or chipping, which can increase the efficiency of further processing. However, the use of very small particles also makes some problems, etc more energy and time consumption. Initial and ultimate particle size, moisture content and material properties are among the variables that influence both energy consumption and the effectiveness of succeeding process. Smaller particle size and higher moisture content of straw will lead to higher specific energy consumption. The wheat straw degradability has improved by the decrease of particle size until a limit of 100 μm , up to 36% total carbohydrate and 40% glucose hydrolysis yields. The ball milling samples sweep away this limit up to 46% total carbohydrate and 72% glucose yields and also decreases cellulose crystallinity from 22% to 13% [26]. A number of other studies have shown that ball milling potentially decreases cellulose crystallinity [2,28,6]. The first essential step in grinding experiments, CM2mm (760 μm), has comparable to ordinary particle size decline on biomass (0.2– 2 mm) as reviewed [89]. Its median particle has also similar to those observed [44] and [58] using a high sized sieve-grinder (3.2 mm-hammer mill) showed suitable particle sizes \sim 760 and 640 μm . Ball milling disrupted partially the crystalline structure of cellulose. Ball milling showed very efficient pretreatment of wheat straw increasing its degradability then steam explosion pretreatment [26].

1.2. Physico-Chemical

The solubilization of lignocellulose material required temperature, pH and moisture content. Hemicellulose compounds has beings to solubilize into the water at a temperature higher than 150 $^{\circ}\text{C}$ and among various components, Xylan can be extracted the most easily [7]. Liquid hot water (LHW), steam explosion (SE) and ammonia fiber explosion (AFEX) are among physicochemical methods investigated for pretreatment of wheat straw.

Liquid hot water (Fig.3) is a hydrothermal pretreatment, where use the pressure for maintaining water in the liquid state, a particular temperature. LHW pretreatment can remove up to 80% of the hemicellulose and also increase the enzymatic digestibility of pretreated material wheat straw [69, 33]. LHW pretreatment at 180 $^{\circ}\text{C}$, the glucose has re-

lease to some extent increases in the later enzymatic hydrolysis period. Such as, the conversion of cellulose to glucose at 72 h of enzymatic hydrolysis enhanced from 75.97% to 83.39% with only a variation of 7.42% after 48 h [37]. The development of environmentally friendly pretreatments that do not involve chemicals one is liquid hot water pretreatment [17, 16]. When the pretreatment temperature has been rising from 170 to 200 $^{\circ}\text{C}$, corresponding glucose yield in enzymatic hydrolyzate has increased from 24.67 to 34.12 g [78]. A maximum overall sugar recovery of fermentable sugars in a LHW pretreatment of wheat straw, it would be necessary to carry out the process in two stages. At first time, pretreatment stage had maximizing hemicelluloses derived sugars recovery and a second stage a maximum glucose recovery. Due to this process maximum of 80% of xylose and 91% of glucose content in raw material could be recovered and would be available for fermentation [33].

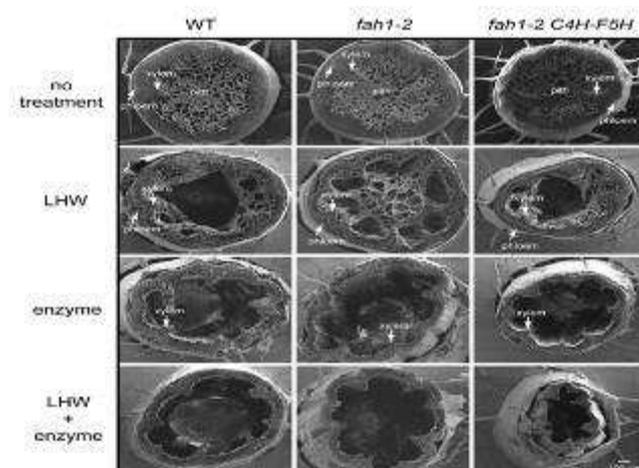


Figure 2. Scanning electron microscopy (SEM) of *Arabidopsis* stem cross-sections subjected to different treatments. etc Wild-type, *fah1-2* and *C4H:F5H* stems were cross-sectioned and fasten to a glass slide. Sections expected either no treatment or one of the following treatments: liquid hot water (LHW) pretreatment, enzyme digestion, or LHW pretreatment in addition enzyme digestion. Afterwards, they were imaged by SEM. [84].

Steam explosion (Fig.3) auto-hydrolysis is one of the large amounts used cost-effective pretreatment methods for wheat straw. Therefore, by this way, the biomass size-reduced is rapidly heated by high pressure steam for a period of time, and subsequently the pressure is rapidly reduced, which creates the materials endure an explosive decompression. Temperatures from 160–230 $^{\circ}\text{C}$ for several seconds to a few minutes are normally used in the SE of wheat straw. Steam explosion has effective and extensively used pretreatment method [22, 30]. After steam explosion pretreatment, the tight physical structure of the straw was disrupted. As the outcome, the fractionation of straw becomes easy, and approximately 80% of the hemicelluloses were decomposed into soluble sugars such as xylose and oligo-saccharides [30]. At the higher temperatures ranging from 170 $^{\circ}\text{C}$ to 220 $^{\circ}\text{C}$, the pretreatment can efficiently increase in amount of cellulose and lignin, and a relative

decline occur in the hemicellulose content [66,48,35]. Higher glucose yields upon enzymatic hydrolysis were obtained after pretreatment at 210 °C for 10 min [35] and also the steam explosion without an acid catalyst is a good pretreatment method for saccharification of wheat straw [35]. Steam-explosion pretreatment make together high pressures and temperatures and has the most commonly used methods for pretreatment of lignocelluloses [32, 1]. This pretreatment has some weakness, which makes it less efficient for biomass containing higher lignin content (e.g. softwood newspaper) as well as solubilization of very small fraction of solid materials, mostly hemicellulose [89]. More experimental works are required to find the feasibility and efficiency of the SE pretreatment method for wheat straw.

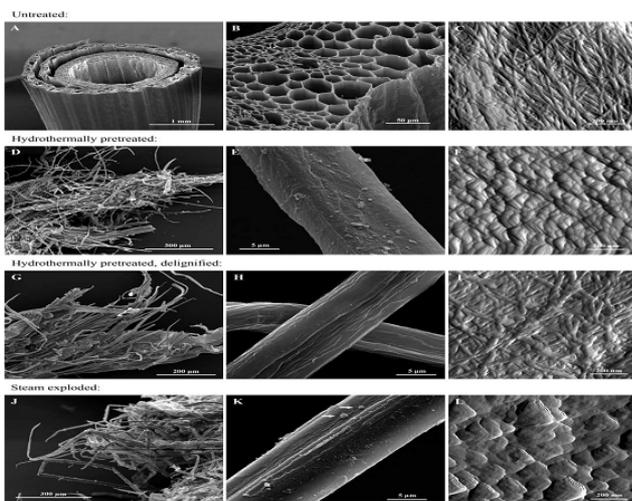


Figure 3. Microscopy images: The SEM and AFM images of untreated (A)-(C), hydrothermally pretreated (D)-(F), delignified hydrothermally pretreated (G)-(I) and steam-exploded wheat straw (J)-(L), [94].

1.3. Ammonia Fiber Expansion (AFEX)

The ammonia fiber expansion/explosion treatment parameters include temperature, moisture content, ammonia loading and residence time. (AFEX) process is been found to be an effective pretreatment for promoting enzymatic hydrolysis [24]. AFEX can achieve greater than 90% conversion of cellulose and hemicellulose to fermentable sugars for a variety of lignocellulosic materials, including alfalfa, barley straw, corn residue, wheat straw, rice straw, corn fiber, sugarcane bagasse, switchgrass, coastal bermudagrass, and rye grass straw [11]. AFEX reduces the degree of polymerization of cellulose and hemicellulose to increase enzyme accessibility for hydrolysis [24]. AFEX-centered cellulosic technology simplifies production stages, decreases the requirement for nutrient supplementation, increases the diversity of co-products and potentially enhances the environmental benefits beyond the direct impact of the pretreatment processes AFEX, a dry-to-dry pretreatment process, completely preserves lignin and carbohydrate [83]. This process decrystallises the cellulose, hydrolyses hemicellulose, eliminates and depolymerises lig-

nin, and raises the size and quantity of micropores in the cell wall, thus significantly increasing the rate of enzymatic hydrolysis [41]. In previous studies, AFEX treatment resulted in near theoretical yields of glucose in different types of agricultural residues [24] and energy crops [29,71]. In particular, previous work has shown conversions of over 90% of the glucan and 70% xylose on switchgrass, however again, the cultivar/ecotype and harvest time was not specified [27].

1.4. Microwave Pretreatment

A thermal pretreatment based on microwave heating, which provide a rapid heating in bulk material with reduced thermal (Fig.4). Such a volumetric heating reduces also the processing times with considerably energy saving. The microwave pretreatment consisted of three stages: (i) the ramp time to reach the targeted temperature, (ii) holding time at targeted temperature and (iii) the time to cool down until 90C° in order to allow being safe open the vessels. The improvement of anaerobic digestibility of the wheat grass by microwave pretreatment is related mainly to structure modifications of the matrix of wheat straw [20]. The microwave-assisted process was a very effective method for the xylose production from wheat straw by diluted acid catalysis [88] the use of microwaves as an energy source provides an up to 85-fold savings in energy [18]. The more efficient solubilisation was found by microwave heating of sludge to 175 C; in that situation 54% of the ultimate chemical solubilisation ratio was achieved. Sludge irradiated at 175C had the highest cumulative biogas production, which was about 31% higher than the control [56].

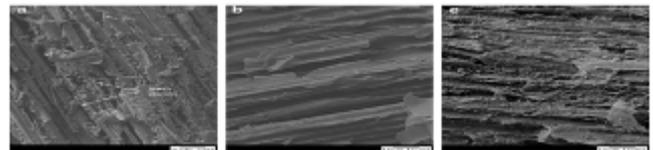


Figure 4. Scanning electron microscopy images of sweet sorghum biogas: a: before pretreatment showing starch granules; b: after microwave pretreatment without lime showing clean cellulose fibrils on cell walls, free from starch granules; c: after microwave pretreatment with lime, showing degraded cell walls and eroded fibers[95].

2. Chemical Pretreatment

2.1. Acid

Acid pretreatments involve the application of sulfuric, nitric, or hydrochloric acids to remove the hemicellulose components and expose the cellulose for enzymatic digestion [19]. Agricultural residue, such as corncobs and stovers, is particularly well suited to dilute acid pretreatment [51,73]. A maximum sugar yield of 541.2 mg g⁻¹ wheat stubble was obtained by pretreatment at 2% H₂SO₄/90 min/121 °C followed by enzyme saccharification. Using dilute acid pretreatment to extract oligoxylans and lignin while simultaneously improving cellulose hydrolysis may be a means of consolidating the economic viability of a bio-

refinery [70]. The most favorable conditions for sugar recovery were temperature 147°C, acid concentration 1.53% and retention time 30 min [63]. Hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid have been tested for use in biomass pretreatment. Dilute sulfuric acid is commonly used as the acid of choice [43,55].

2.2. Alkali

Alkali pretreatment refers to the application of alkaline solutions to remove lignin and various uronic acid substitutions on hemicellulose that lower the accessibility of an enzyme to hemicellulose and cellulose [74]. Generally, alkaline pretreatments are more effective on agricultural residues and herbaceous crops than on wood materials [68]. Sodium hydroxide makes the biomass to swell through solvation and saponification reactions, increases the porosity of the material thus increases enzymatic hydrolysis rate [7]. Effective delignification and chemical swelling of the fibrous cellulose [10, 86], cause condensation of lignin and modification of the crystal structure, which can introduce unwanted effects for lignin removal and cellulose degradation [34, 50]. Therefore alkaline pretreatment has been studied on different types of lignocellulosic biomass containing switchgrass, corn stover, rice straw, wheat straw, and rice hulls [92], the majority of the investigate on alkaline pretreatment has focused on optimization of the process parameters to improve substrate digestibility [92,59]. The maximum relative amount of arabinose was detected in the hydrolysate obtained from pre-treatment with 1.5% NaOH for 6h at 20°C and also optimal conditions for delignification and dissolution of hemicellulosic polysaccharides were found to be pre-treatment with 1.5% sodium hydroxide for 144 h at 20°C [72].

2.3. Lime Pretreatment

Lime provides a lower cost alternative than additional alkalis, and lime pretreatment also needs lower temperatures and pressures. while the NaOH pretreatment, the weakness of the lime pretreatment are lengthy residence time, a huge amount of wash water, or time consuming neutralization process and the formation of large quantities of salts, such as $\text{Ca}(\text{SO})_4$. Lime pretreatment has the following advantages: lime is the least expensive alkali at \$0.06/kg; is safe to handle; and can be simply recovered. The mechanism is similar to the NaOH pretreatment. When using over lime ($0.5\text{g Ca}(\text{OH})_2/\text{g biomass}$) to pretreated corn stover at 25–55°C, lignin and hemicellulose were selectively uninvolved, so the degree of crystallinity slightly increased from 43% to 60% with delignification, but cellulose was not affected [73]. Both sodium hydroxide and lime have very effective at higher temperatures [79,52].

3. Wet-Oxidation

The wet oxidation process (water, oxygen and elevated temperature) was investigated under alkaline conditions for

fractionation of hemicellulose, cellulose, and lignin from (Fig. 5a, b). At higher temperature and longer reaction time, a purified cellulose fraction (69% w/w) was produced with high enzymatic convertibility to glucose. At 185°C, nearly three times more hemicellulose was solubilized than at 150°C [67]. Wet oxidation (WO) has proven itself to be an efficient pretreatment method of wood and wheat straw; WO dissolves the hemicellulosic fraction and makes the solid cellulose fraction susceptible for enzymatic hydrolysis and fermentation [25, 5, 67]. Wet oxidation operates with water and requires the addition of oxygen. When oxygen is omitted, the process is essentially a hydrothermal pretreatment [46].

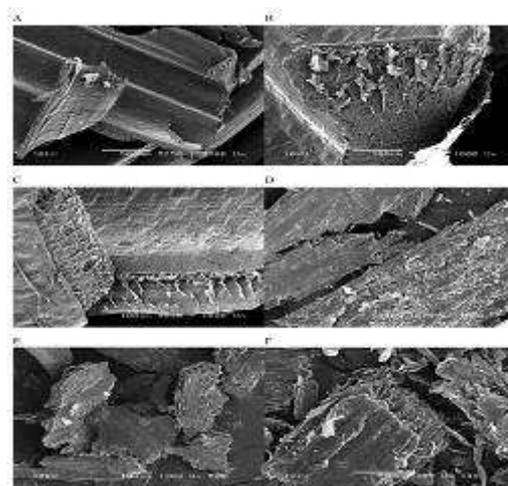


Figure 5a. SEM images of wheat straw samples (not wet oxidized). Numbers in parentheses correspond to magnification. (A) Reference substrate sample (50); (B) Reference substrate sample (250), (C) Reference substrate sample (250), (D) 707–1,000 μm (100), (E) 250–500 μm (100), (F) 53–149 μm (500). Sizes of the particles can be measured by the bars given in the bottom of each SEM image [96].

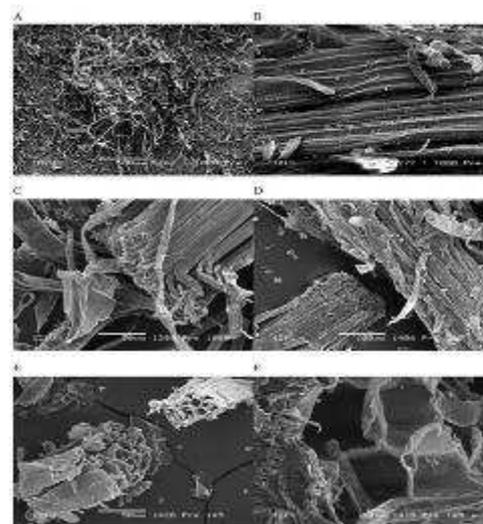


Figure 5b. SEM images of wet oxidized wheat straw samples. Numbers in parentheses correspond to magnification. (A) Reference substrate sample (50), (B) Reference substrate sample (500), (C) 707–1,000 μm (500), (D) 250–500 μm (250), (E) 53–149 μm (500), (F) 53–149 μm (1,000). Sizes of the particles can be measured by the bars given in the bottom of each SEM image [96].

4. Organosolv

The organosolv pretreatment process covers a broad range of organic solvents such as methanol, ethanol, acetic acid, peracetic acid, and acetone, and so on. The organosolv process is a delignification process, with varying simultaneous hemicelluloses solubilization. In this practices, an organic or aqueous organic solvent mixture with or without an acid or alkali catalyst is used to break the internal lignin and hemicelluloses bonds [89, 85, 39]. For economic reasons, the use of low-molecular-weight alcohols such as ethanol and methanol has been favored [21]. The usual operation temperature of organosolv is in the range of 150-200. However, due to low cost and ease of recovery, methanol and ethanol seem to be the most favored alcohols for alcohol-based organosolv pretreatment. On the other hand, some polyhydric alcohols also can be employed for pre-treating biomass under atmospheric pressure with or without catalysts. Ethanol is a renewable solvent and its volatility facilitates the extensive recycling required [87]. Wheat straw (Fig.6) has been successfully pulped and pretreated using aqueous ethanol in previous studies [82,90,91]. A maximum enzymatic digestibility of 86% with a lignin yield of 84% was reached without the use of a catalyst (organosolv at 210 C, 50% w/w aqueous EtOH) [77]. A drawback of the organosolv process is that the conditions required to delignify lignocellulosic feedstocks may lead to low yields of hemicelluloses sugars due to degradation and subsequent formation of humans and condensation products with lignin [82,87]. In earlier work on autocatalytic acetone-based organosolv pretreatment of wheat straw, were illustrated that, at conditions yielding maximum enzymatic digestibility (205C°), the yield of the major hemicellulose sugar xylose was only 4% of its theoretical maximum or 1% w/w raw wheat straw [81].

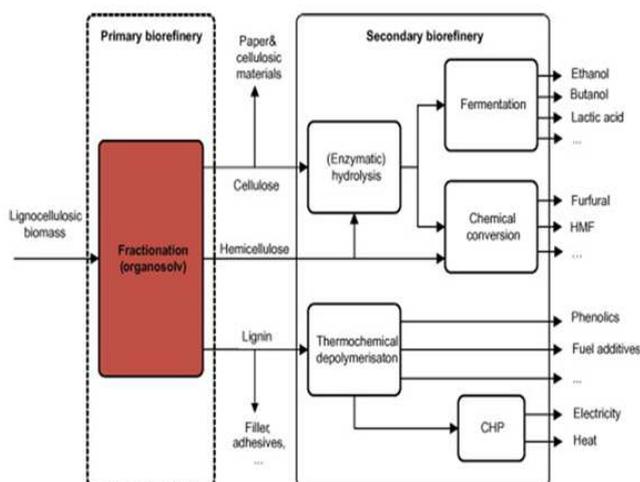


Figure 6. Organosolv- based lignocellulosic biorefinery [97].

The ethanol-based organosolv fractionation of wheat straw for the production of lignin and enzymatically digestible cellulose.

5. Conclusion

There are various pretreatment strategies that have been building up for the pretreatment of lignocellulosic biomass. This review has summarized some of the main strategies that are presently being used and has provided several ways as to which biomass types have been shown to be more suitable with each pretreatment. There are several other pretreatment approaches that have also find out, several of which are dissimilarity of the processes described here. The selection of pretreatment is basically related on biomass properties, availability to materials required for the process, expenditure of reagents desired, and the price of equipment to operate for that procedure. Further more efficient methods can be established, so they will more decrease the cost of these processes, decrease energy requires, and creates more fuels produced from lignocellulosic biomass cost-competitive with fossil fuels.

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