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Bioethanol Production from Straw

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ABSTRACT

Straw is one of the most abundant renewable resources, and if utilized efficiently can provide appropriate feedstocks for competitive energy production. Liquid fuels in particular may be advantageously produced from straw, and of such fuels, bioethanol fuel may be the most important.

The processes involved in bioethanol production include an appropriate pre-treatment, hydrolysis of the straw to convert the cell walls to simple sugars, anaerobic fermentation to convert the sugars to ethanol, and finally distillation. Ethanol production from straw could also be performed by direct microbial conversion. In addition, the straw may be converted to bio-oil by fast pyrolysis.

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Introduction

During the last fifty years or so, and almost within living memory, man has witnessed an almost imperceptible change in the energy situation from surplus and cheap availability to scarcity and rising fuel prices. Depleting world reserves have made the continued reliance on fossil fuel energy resources unsustainable. Renewable sources of energy have to be found in order to meet the continuously rising demand and decreasing energy reserves. A further incentive for the search for energy sources other than the high-carbon fossil fuels is the environmental concern particularly over acid rain and emissions of so-called greenhouse gases such as carbon and sulphur dioxides and other exhaust gases.

Of the available renewable sources of energy, sources of biomass can no longer be neglected. Bioenergy from biomass is estimated to contribute about 10–14% of the primary energy supply of the world or about 38% of that of the developing countries. The utilization of biomass for energy production can also lead to significant reduction of CO2 and SO2 emissions.

Of the available biomass sources, plant biomass and agricultural waste products stand paramount. An estimated 90% of greenhouse gas emissions can be avoided by replacing coal by straw in power generation plants. A further advantage of plant biomass in general is that plant biomass evolved to be difficult for microorganisms to take apart. As a result, trees can last thousands of years, and even straw can hang around for years.

Biofuels are liquid fuels that can be widely produced from biomass. Biofuels are potentially renewable and carbon neutral. They are essentially the only petroleum alternatives that provide potential large-scale economic and environmental advantages. A major factor that contributes to make biofuel an attractive and possibly essential alternative to fossil fuel is related to the environmental consequences and rising levels of greenhouse gases in the atmosphere resulting from the combustion of fossil fuels; the combustion of biofuel on the other hand does not increase the net 2 atmospheric levels of carbon dioxide as it is a plant and not petroleum-derived fuel.

According to Bruce Dale, the area of society's greatest current vulnerability, particularly in the developing world, is in liquid transportation fuels. In effect, he maintains, we do not have an energy crisis but rather a mobility, specifically a liquid transportation fuels, problem. Research is being conducted world-wide to develop new technologies for the generation of liquid transportation biofuels from biomass. The production of liquid transportation biofuels from biomass has been mostly production of bioethanol and biodiesel.

beet and maize. The use of such crops, however, may place an enormous strain on world food markets. In order to address this problem, non-food crop feedstocks and lignocellulosic agricultural by-products and forest residues may be used to produce second-generation biofuels. Various methods for using non-food biomass have already been developed at both laboratory and industrial scales. On the other hand, to reduce food surplus, the Agricultural Policy of the European Union (EU) obliges the European farmers to leave a percentage of the arable land as set-aside, where can be grown, as an exception, vegetables for non-food purposes, i.e. energetic ones [1-23].

Straw

Of the agricultural by-products available in large quantities, straws in particular can provide if utilized efficiently appropriate feedstocks for competitive energy production with consequent reduction of dependence on fossil fuels [6]. Straw is one of the most abundant renewable resources. In China alone, it is estimated that 400 million tonnes of wasted straw could be used as a substitute for 200 million tonnes of coal [16]. Straws may also be mixed with

other ligneous and waste materials such as paper mulberry, sawdust and livestock excretions to provide biomass material suitable for energy production.

Straws include in general both grain and grass straws. Grain straws are the dry stalks of cereal plants, after the grain and chaff have been removed. Straws make up about half of the yield of cereal crops such as barley, canola, corn, oats, rice, rye, sorghum and wheat. Of these straws rice and wheat straws are abundant agricultural residues with low commercial value [15].

The utilization of straw for energy production, however, must be considered with regard to its many actual or potential uses in agriculture or for fodder or other uses. Furthermore, as the produced straw is in most cases dispersed over a wide area, the problems and costs associated with its collection and transport must also be considered. In addition, energy consumption would be required for the preliminary preparation of the straw prior to transportation. After separation of unwanted leaf and stem and drying, the collected straw has to be cut or pulverized and screened to obtain straw powder [8, 14]. Alternatively, the straw may be compressed into bundles to obtain straw bricks, irradiated and finally pulverized and sieved [13].

Straw is a complex lignocellulosic material consisting predominantly of celluloses and hemi-celluloses (60 per cent or more) in which sugars are locked up as five- and six-carbon sugars. Other materials contained in straws include lignins (15 to 20 per cent), water-soluble substances (also known as extractives) (5 to 12 per cent), mineral matter or ash and proteins which are usually present in very small amounts (2.2 to 3.0 per cent) and moisture. [11]. In general, straw is a low carbon material and its sulphur content is low (about 0.24% in wheat straw), but the overall chemical composition of straw could slightly differ depending on straw species, soil, and climate conditions. Among the three natural macromols that constitute straws, only lignin has the mole ratio of C : H : O (1 : 1.3 : 0.3) close to that of crude petroleum (1 : 1.6 : 0.05) [3]. Straws may also have high contents of silica and chlorine, and straw, especially wheat straw, may have high contents of potassium and other alkali metals.

In lignocellulosic materials such as straw, hemicellulose is the most thermal-chemically sensitive fraction and hemicellulose compounds start to solubilize into the water at temperatures higher than 150°C, and among various components, xylan can be extracted the most easily [4].

The hemicellulose serves as a connection between lignin and cellulose fibres. The dominant hemi-cellulose polymer in wheat straw is xylan consisting of D-xylose backbone with different side groups including Larabinose, D-galactose, acetyl, feruloyl, p-coumaroyl and glucuronic acid residues [25].

The cellulose strains in straws are tightly surrounded by hemicellulose and lignin and tightly packed in such a way that neither water nor enzyme can penetrate through the structure.

The cellulose content of the straw can be increased by a liquefying process in which a mixture of straw powders including rice, corn and wheat straw powders is mixed with a phenol compound such as phenol, o-cresol, m-cresol, o-chlorophenol, o-nitrophenol, resorcinol, hydroquinone or polyethylene glycol. The resulting mixture is then subjected to a treatment involving heating, adding an organic or inorganic acid catalyst such as hydrochloric acid, nitric acid, sulphuric acid, phosphoric acid or benzene sulphonic acid, oxalic acid, acrylic acid, salicylic acid, formic acid and acetic acid, washing with an organic solvent, neutralizing, filtering and drying to obtain finally a solid with increased cellulose content [20].

Lignins are steric network macromolecules composed of phenyl propane monomers linked by chemical bonds and are covalently linked to cellulose. They have thermosetting properties and a low melting point of about 140ºC. The lignin content of straw may be determined by spectrophotometry [26].

Table 1 shows the average chemical composition of barley, canola, oat, wheat and rice straw samples and Table 2 gives the composition of rye straw at different stages of growth [26-30].

Table 1. Chemical Composition of Selected Straw Samples.

Composition (% dry matter)	Barley straw [27]	Canola straw [27]	Oat straw [27]	Wheat straw [27]	Rice straw [28]	Rice straw [29]
Cellulose	33.25	42.39	37.60	34.20	34.3	41.0
Hemicellulose	20.36	16.41	23.34	23.68	21.7	20.0
Lignin	17.13	14.15	12.85	13.88	17.6	17.8
Ash	2.18	2.10	2.19	2.36	12.5	12.0
Starch	0.11	0.34	0.12	2.58	-	9.2
Fat	1.91	0.69	1.65	1.59	1.6	
Protein	3.62	6.53	5.34	2.33	9.2	

Table 2. Composition of Rye Straw at different Stages of Growth on a dry Basis [30].

No. Of sample	Moisture at time of harvest	Ash	Nitrogen	Pentosans	Cellulose	Lignin
1	80.0	7.3	2.39	15.9	17.2	9.9
2	78.8	5.7	1.76	20.5	26.1	13.5
3	57.4	4.9	1.01	22.7	30.6	19.0
4	60.2	5.9	2.20	22.7	20.1	16.0
5	15.0	3.2	1.22	11.9	4.6	13.4
6	15.0	3.7	0.22	21.7	34.6	18.8
7	-	-	0.55	26.6	37.7	21.0

Utilization of Straw

The utilization of straw for energy production includes combustion and the production of liquid, gaseous and solid fuels.

The use of straw in large-scale biomass power plants is becoming widespread in countries of the European Union, with several facilities already online, particularly in Denmark where straw is the most abundant biomass resource. A new generation of small scale (less than 20 MWe) biomass-fuelled power plants has also been developed based on a gas turbine (Brayton cycle) prime mover. These power plants were expected to increase the efficiency and lower the cost of generating power from straws and other biomass fuel [24].

The calorific value of straw has always been the focus when exploring the utilization of straws for energy production. The heating values of straw come mainly from the combustion of organic matter, i.e., cellulose, hemicellulose, lignin and starch.

Determination of the calorific value of straw needs in general delicate and expensive calorimeter, and is time-consuming. It would be extremely useful, therefore, if the calorific value of straw can be accurately predicted by regression from ultimate or proximate analysis. Several such formulae for the calculation of the calorific value of biomass have already been proposed including correlations between calorific values and lingocellulosic contents. Although the equations based on the ultimate analysis are believed to be more accurate than correlations based on proximate analysis, the instrument for ultimate analysis may cost even more than the calorimeter method [31].

The models proposed which provide satisfactory estimation of the calorific value of straw by regression from proximate analysis, or moisture, ash, and volatile matter contents, can be either multiple linear regression equations or they may be based on the near infrared spectroscopy technology [192]. Two equations were derived for the estimation of the calorific value of wheat and rice straw samples by Huang et al [31].

Heating value = - 2737 – 160.43 × Moisture + 266.76 × Volatile matter Heating value = 18655.03 – 154.73 × Moisture – 206.17 × Ash

Energy Production from Straw

Energy production from straws can be achieved by either of two processes, namely fermentation and pyrolysis.

Straw may be used for the production of bio-liquid fuel, but the oilproducing characteristics of straw may in general be inferior to that of wood feedstocks such as Pterocarpus indicus, Cunninghamia lanceolata and Fraxinus mandshurica [39]. Furthermore, the quality of the bio-oil produced may be poor and its direct utilization difficult, but it may be possible to blend bio-oil and diesel oil by a simple emulsion method to obtain emulsion oil that is more stable than bio-oil [29].

Liquid fuels that may be advantageously produced from straws include bioethanol, bio-butanol and butane diol glycol. These, like other products of biomass conversion, capture, contain and recycle the excess carbon dioxide and methane effluents that contribute to global warming.

Of such liquid fuels, bioethanol fuel may be the most important. Straw is particularly suited for bioethanol production for it has several characteristics, such as high cellulose and hemicellulose content; and cellulose, in particular, is a major source of glucose that can be readily hydrolyzed into fermentable sugars [11]. Cellulosic-based ethanol far exceeds corn in energy balance, pollution reduction and farm availability. The abundance and high carbohydrate content of barley straw make it a good candidate for bioethanol production in Europe [17].

Bioethanol

Ethanol (C_2H_5OH, 34.7 wt. % oxygen) is a partially oxidized fuel compared to gasoline (C4-C12, 0 wt. % oxygen), resulting in a lower stoichiometric air-fuel-ratio. Therefore, a larger mass or volume of ethanol compared to gasoline is required to yield the same caloric output from combustion. The volumetric energy fraction of ethanol is approximately 66% that of gasoline, suggesting a one-third reduction in the total kilometres per volume of ethanol consumed. However, ethanol has a higher octane number, permitting the fuel to be burned at a higher compression ratio resulting in higher power output and efficiency. Furthermore, as a result of the significantly higher latent heat of vaporization for ethanol (1177 kJ/kg compared to 348 kJ/kg at 60°C) there is an effective engine cooling leading to significant reductions in CO and NOx emissions. However, the emission of reactive aldehydes, including acetaldehyde and formaldehyde, is increased [18].

Only minor modifications to engines are needed for cars to run on fuel blends of gasoline with up to 30% ethanol. There is evidence to indicate that under proper fine tuning of engine parameters, the use of ethanol–gasoline blends in cars will lead to enhanced engine performance and reduced emission of CO. New cars can also be made with engines designed to run on pure ethanol [6].

Bioethanol is non-toxic and with its high oxygen content and octane no. is presently the cleanest and may be the only real renewable alternative to gasoline. In the considered opinion of many researchers, bioethanol today may be the most dominant biofuel. The global production of bioethanol showed an upward trend over the last 25 years with a sharp increase from 2000. Worldwide annual production capacity in 2005 and 2006 were about 45 and 49 billion litres, respectively and total output in 2015 was forecast to reach over 115 billion litres [7]. Brazil was for a time the largest bioethanol producing country, but in 2005, the United States passed Brazil and became the world's number one ethanol producer. Bioethanol production from straw and other non-food biomass resources as feedstock is of particular relevance in countries with large populations and growing gasoline consumption such as Brazil, Egypt, China and India. About 3.9 billion litres of ethanol can be produced from rice straw and bagasse in China and India [10].

Bioethanol Production

The efficient utilization of straw for bioethanol production is critically dependent on the chemical constituents of the straw as well as the desired bioethanol properties. It may also be possible to couple bioethanol production to biogas production with beneficial ecological consequences.

The processes involved in bioethanol production by fermentation include an appropriate pre-treatment (to open up the cell wall materials for enzymatic attack), hydrolysis of the straw to convert the cell walls to simple sugars, anaerobic fermentation to convert the sugars to ethanol, and finally distillation. Hydrolysis and fermentation may be accomplished separately or simultaneously, or ethanol production from straw could be performed by direct microbial conversion. In addition, the straw may be converted to bio-oil by fast pyrolysis and the bio-oil steam-reformed for the production of hydrogen [6,11].

Pretreatment

Pre-treatment of straw for bioethanol production is estimated to account for 33% of the total cost of bioethanol production [6]. The objectives of pre-treatment are to open up the cell wall materials for enzymatic attack, increase the surface area and porosity of the substrate, reduce the crystallinity of cellulose and disrupt the heterogeneous structure of cellulosic materials [7]. By modifying the structure of cellulosehemicellulose-lignin matrix by the application of pre-treatment methods, the natural binding characteristics of lignocellulosic biomass can be enhanced [5].

The selection of an appropriate pre-treatment technique is one of the major challenges in developing technologies for bioethanol production from straw. The choice of pre-treatment methods plays an important role in increasing the efficiency of enzymic digestibility and enzymic saccharification of the straw thereby making the whole process economically viable [12]. The factors that are most relevant in this choice include solid loading, reaction temperature and energy balance, reaction time and minimum use of chemicals as well as some environmental factors such as wastewater treatment, catalyst recovery and solvent recycling. Higher reaction temperatures are generally accompanied with shorter reaction times [7,12].

After separation of unwanted leaf and stem and drying, the straw is cut or pulverized and screened to obtain straw powder [8, 14]. Alternatively, the straw may be pressed to obtain straw bricks, irradiated with 6Co-γ ray or electron beam accelerator, and finally pulverized and sieved [13]. For pre-treatment the straw may be subjected to mechanical pre-treatment, irradiation, chemical, fungal or hot water treatment [6,7,8].

Mechanical pre-treatment in the form of size reduction through chipping (10-30 mm), grinding or milling (0.2-2 mm) can lead to significant improvement of enzymatic hydrolysis of straw [6]. On the other hand, mechanical size reduction requires almost prohibiting amount of energy which may preclude its widespread use for the production of bioethanol from straw; and the use of very small particles may not therefore be desirable.

Irradiation can be very effective as a form of pre-treatment for enzymic hydrolysis of straw [9]. For the chemical pre-treatment of straws, different chemicals may be employed including acids, alkalis and oxidizing agents such as peroxide and ozone [6]. Solid-state pre-treatment with sodium hydroxide can greatly alter the internal structures of the lignin and lignin-carbohydrate complex resulting in the separation of cellulose from lignin and the decomposition of lignin from large molecules with three-dimensional network structures to small molecules with linear structures.

The high energy consumption along with the high consumption of chemicals and the corrosion problems associated with some of the chemical methods may be major impediments to their selection as appropriate pre-treatment techniques and may preclude their widespread use for the production of bioethanol from straw.

Fungal pre-treatment of lignocellulosic materials is an important biological pre-treatment method in which microorganisms are used for selective degradation of lignin and hemicelluloses. It is a safe, environmentally friendly and less energy intensive method compared to other pre-treatment methods. The overall attractiveness of the fungal method is, reduced, however, by the substantial loss in cellulose and hemicellulose during the fungal pre-treatment step and the very slow rate of hydrolysis reaction [6].

Other methods investigated for the pre-treatment of straws include liquid hot water and steam explosion [6]. Liquid hot water is a hydrothermal pretreatment, where pressure (> 5 MPa) is applied to maintain water in the liquid state at elevated Temperatures (170-230°C). It has potential to release high fraction of hemicellulosic sugars mostly in the form of oligomers contributing to reduction of undesired degrading products [4,7]. Steam explosion is one of the most cost-effective and widely used pretreatment methods for straw. It is probably the most suitable method for pre-treatment of straw in terms of lower reaction time, higher solid loading and minimum use of chemicals [7].

By acid-catalyzed steam explosion, hemicelluloses can be effectively removed from the straw, providing high yields of fermentable sugars. The yields of mono saccharides produced by enzymic hydrolysis of the straw pretreated by this pre-treatment method were found to be 46 g/l. Pre-treatment by ammonium fibre explosion, on the other hand, is distinctly different from other pre-treatment methods in that it does not significantly solubilise hemicelluloses. The yield of monosaccharides produced by enzymic hydrolysis of the pre-treated straw in this case was found to be 37 g/l [21].

Hydrolysis and Saccharification

After pre-treatment the straw is hydrolyzed or saccharified. Cellulose and hemicellulose in straw are tightly surrounded by lignin and must be hydrolyzed or saccharified into reducing sugar to be utilized by bacteria for bio-fuel production. Saccharification is a crucial step to release fermentable sugars before biological fermentation. By hydrolysis of the straw, the cell walls are converted to simple sugars (pentoses and hexoses) and a hydrolyzate is obtained with a relatively high concentration (12-15%) of glucose and xylose. Glucose is mainly obtained from the enzymatic hydrolysis of cellulose, and xylose is the main C5 sugar derived from hemicellulose. From hemicellulose degradation, other sugars including galactose, arabinose and mannose are also mainly obtained. The amount of biofuel produced depends mainly on the sugars production during the hydrolysis step.

Straw is saccharified by the use of alkalis, acids or with the addition of an appropriately selected enzyme in enzymatic hydrolysis, which can be membrane-facilitated [8]. The hemicellulose is readily hydrolyzed by dilute acid or base, as well as hemicellulase enzyme [7]. According to some researchers, total hydrolysis of cellulose into glucose, which could be fermented into ethanol, is not yet economically feasible. This, however, is likely to change as a result of higher fossil fuel prices.

Acids catalyse the hydrolysis of cellulose and hemicellulose to produce sugars that organisms can ferment to ethanol. For acid hydrolysis either of two acids, H2SO4 or HCl may be used.

The H2SO4 hydrolysis is a two-stage process, a pre-hydrolysis step with diluted acid of less than 1% concentration and at 120-200°C under corresponding increased pressures followed by hydrolysis in concentrated H2SO4. Fermentable sugar formed may be partly destroyed by the prolonged exposure to acid at high temperatures. The HCl process is a gas-phase hydrolysis followed by a liquid-phase concentrated acid hydrolysis. The sugar concentrations obtained may be in the range 3-4% and 7-9%, respectively [40].

The addition of Tween 20 increased the enzymatic saccharification yield of H2SO4 pre-treated wheat straw from 488 to 520 (mg/g) [50]. Similar results were also obtained with lime pre-treated

wheat straw, while no improvement was observed with alkaline peroxide pre-treated wheat straw [50-52].

Saccharification of straw for making bioethanol may also be achieved by enzymatic hydrolysis without the use of chemicals such as acids or alkalis. Enzymatic hydrolysis using appropriate enzymes represents the most effective method to liberate simple sugars from cellulosic materials. Enzymatic hydrolysis is applied widely because of its mild reaction conditions, lack of corrosion, and positive environmental profile [41,42]. This Method, however, is characterised by low accessibility of enzymes to the cellulose due to the complex structure of lignocelluloses [43, 44]. Consequently, the efficiency of enzymatic saccharification of the straw is very much dependent on its composition and lignocellulosic structure. Lignin in particular plays a major role in this process as it shields the cellulose from the cellulolytic enzymes and the enzymes irreversibly adsorb to the lignin.

Enzymatic hydrolysis of the straw is catalyzed by a class of appropriately selected enzymes known as cellulases and hemicellulases including such enzymes as glucanase, xylanase, pectinase or amylase. The conjugated action of cellulase and hemicellulase results in a higher ultimate sugar production. At least three major groups of enzymes namely, endo-glucanase, exo-glucanase and β-glucosidase are involved in hydrolysis of cellulose to glucose and their action is synergistic. Endo-glucanase attacks regions of low crystallinity in the cellulose fibre and creates free chain-ends. Exoglucanase degrades the molecule further by removing cellobiose units from the free chain-ends, which is then cleaved to glucose by the action of βglucosidase. In addition to substrate and end-product concentrations, enzymatic hydrolysis can be influenced by other hydrolysing conditions such as temperature and pH as well as by the method of pre-treatment of the cellulosic materials. Most cellulose enzymes show an optimum activity at temperatures in the range of 45–55ºC, pH 4–5 and 48 h residence time [7,8,40,45,46].

The cellulase system is used to hydrolyse cellulose to glucose for fermentation to ethanol. The action of cellulolytic enzymes occurs through three steps of adsorption, biodegradation and desorption. Addition of surfactants may improve the enzymatic cellulose conversion into monomeric sugars [47]. Various mechanisms have been proposed for the positive effect of surfactant addition on enzymatic hydrolysis. The surfactant could modify the nature of cellulose surface properties, reduce irreversible binding of cellulase on cellulose or prevent enzyme denaturation as well as unproductive binding of enzymes to lignin residues [7].

In general, non-ionic surfactants such as Tween 20 were shown to be most effective for enhancing enzymatic hydrolysis [49, 53]. The addition of small amounts of MgSO4 and Tween 80 was found also to increase the activity of cellulase.

Trichoderma viride cellulase was used for the degradation of straw [28,48]. Treatment of the straw powder with Phanerochaete chrysosporium by solid state culture and liquid state crude enzymes is also carried out in order to achieve lignin degradation [14].

Recent developments in the energy sector underline the relevance of Archaea in industrial bioethanol production by using their enzymes in the production process.

Kristensen et al. investigated the effects of enzymatic hydrolysis of five different types of pre-treated wheat straw. They found that the addition of different non-ionic surfactants showed increased cellulose conversion in all cases. The highest increase obtained was 70% with sulphuric acid treated straw when Berol 08 was used as surfactant. The optimum surfactant concentration was approximately 0.05 (g/g dry mass) and was found to be similar, irrespective of pre-treatment type [49].

In many cases, the cost of cellulase enzymes to saccharify cellulose to glucose can be a major hindrance. An enzyme production process may be necessary for the production of the cellulase system, which may be a continuous or batch operation. In the continuous process, a 48-h residence time to produce an active cellulase system is utilized. Compared to batch operation, the overall protein yield is less using a continuous system, but the productivity per unit time is higher. The continuous enzyme production process could be made cost effective by the use of inexpensive medium components and substrates [54]. Enzyme production and fermentation may also be combined in a single organism in a process called consolidated bioprocessing, a process which may provide more opportunities for improvement and processing cost reduction [1].

Enzymes may be generated by adding glucose, NH4Cl and water to the dry straw powder, sterilizing at 121ºC for 2 h, inoculating 5% Phanerochete chrysosporium into a specific medium, and culturing at 37-39ºC for 30 days. The generated enzymes including xylanase, Mn-dependent peroxides and laccase are able to degrade xylogen [19].

Cellulases can be produced by fungi such as Trichoderma reesei and Aspergillus niger or bacteria such as Clostridium cellulovorans. Most research for commercial cellulase production has focused on fungi since the majority of relevant bacteria are anaerobes with very low growth rates [55].

Fermentation

The final process in the production of ethanol is the fermentation of the saccharified liquid using appropriate microorganisms including fungi, bacteria and yeasts. The ideal microorganism should have broad substrate utilization, high ethanol yield and productivity, tolerance to inhibitors present in the hydrolyzates and to high concentrations of ethanol, cellulolytic activity and ability for sugar fermentation at high temperatures [56]. In this fermentation step, the economy of bioethanol production could be improved by simultaneous fermentation of hexose and pentose sugars.

Fungi are commonly too slow for a competitive industrial xylosefermentation process [69].

In the presence of sufficient nitrogen and other minerals the celluloses and hemi-celluloses undergo rapid decomposition. Lignins are in general more resistant to decomposition, but under suitable conditions, aerobic organisms are capable of decomposing lignin in straws, the rate of decomposition being as great as that of cellulose and hemicellulose.

Straws can be subjected to the action of a culture of an aerobic cellulose decomposing organism (Spirochoeta cytophaga), whose activities are found to depend on the mineral substances present in the culture fluid. The fermentation is aerobic; the breakdown of the straw is most rapid in a neutral or slightly alkaline medium in the presence of sufficient available nitrogen.

The ethanol yield of anaerobic bacteria capable of fermenting

xylose is low and they are inhibited at low sugar and ethanol concentrations.

Ethanol fermentation at elevated temperatures using various anaerobic thermophilic bacteria such as Clostridium sp. and Thermoanaerobacter sp. has been proposed [7,57,70,71]. This process has a number of advantages including high production rates, facilitated product recovery, utilization of a wide range of substrates and low risk of contamination [72]. The main drawbacks are low tolerance to ethanol and the production of other products besides ethanol such as volatile fatty acids and lactate. Recently, two novel ethanol-tolerant facultative anaerobic thermophilic strains of Geobacillus thermoglucosidasius were isolated from compost [73]. A mixed bacterial culture dominated by Thermoanaerobacter, Thermoanaerobacterium and Caldanaerobacter was recently found to produce simultaneously ethanol and hydrogen from glucose under extreme thermophilic conditions [74].

Zymomonas mobilis is an efficient ethanol-producing bacteria and it is advantageous over Saccharomyces cerevisiae with respect to ethanol 11 productivity and tolerance. Z. mobilis possesses nearly 100% ethanol conversion rate on glucose-based media.

Other appropriate microorganisms that may be used for ethanol production include Fusarium oxysporum, Candida shehatae and the yeasts Kluyveromyces marxianus and Pachysolen tannophilus [14,19,40,64,65]. K. marxianus is a thermotolerant yeast, but it has been shown to be inhibited by compounds originated during steam-explosion [66]. Zayed and Meyer used Pachysolen tannophylus for the fermentation of xylose and glucose resulting from the hydrolysis of delignified wheat straw with 86% ethanol yield [67]. The use of some of these microorganisms, however, is characterized by low ethanol yields and a tendency to re-assimilate the produced ethanol [68].

Recombinant bacteria with deletions of genes responsible for production of by-products have been also considered for ethanol production. A recombinant bacterium (E. coli) was tested for ethanol production from pretreated wheat straw and showed the highest ethanol yield among the bacteria studied for bioconversion of wheat straw derived feedstocks [51]. Immobilized recombinant Zymomonas mobilis could also be used for efficiently fermenting the hydrolyzate produced from straws and cellulosic feedstocks [48,57]. There is, however, a practical drawback for the wide implementation of recombinant ethanologens, since the plasmids carrying xylose conversion genes are often rejected by the host [75]. Finding new wild-type ethanologens or construction of new promising genetic manipulated organisms with higher ethanol tolerance, productivity and yield will create a basis for future development of commercial lignocellulose-based bioethanol production from straw [7].

The yeast Saccharomyces cerevisiae is one of the best-known microorganisms for ethanol production from hexoses offering high ethanol yields and high ethanol tolerance in fermentation medium [13,57]. The main disadvantage of the native strains of S. cerevisiae is their inability to utilize pentose sugars [58, 59]. Ethanol yield of 99%, based on initial glucose concentration, was obtained recently with native S. cerevisiae strain [60]. Genetically modified strains of S. cerevisiae capable of fermenting both hexoses and pentoses have been developed [61]. However, those strains showed a low productivity with respect to the conversion of xylose to ethanol [62].
A mixed culture of S. cerevisiae and fungal strains T. harzianum and P. Chrysosporium may also be used for ethanol production [63]. S. cerevisiae and T. harzianum were found to grow mutually together in liquid and solid media and proved to be excellent in producing ethanol compared to other combinations [63].

The saccharified hydrolyzate may be anaerobically fermented to obtain an acetic acid mixture which is esterified with methanol under the action of a first catalyst to form mixed esters, followed by hydrogenation under the action of a second catalyst to obtain fuel ethanol with high oxygen content and octane no. and good combustibility [76].

The fermentation spent wash and residues could be anaerobically digested to produce CH4 which could be used for process heat requirements.

Simultaneous Saccharification and Fermentation
In the simultaneous saccharification and fermentation process, the sugars produced during hydrolysis are immediately fermented into ethanol and the problems associated with sugar accumulation and enzyme inhibition as well 12 as contamination can therefore be avoided [46, 77]. The use of continuous simultaneous saccharification and fermentation alters the rate of hydrolysis by removal of end-product inhibition and enhancing the overall yields of ethanol [54]. Furthermore, the use of one reactor leads to cost reduction. In addition, with simultaneous saccharification and fermentation the total time for the conversion process can be very much reduced. This was demonstrated by Alfani et al. who reported that the time needed for the bioconversion of steam-exploded wheat straw by the simultaneous process was reduced from 96 h for the separate process to 30 hours, but the final ethanol yield was at the same time reduced from 81% to 68% [78]. The main drawback of the simultaneous process, however, is the different optimum temperatures of the hydrolysis and fermentation processes. Whereas most fermenting yeasts have an optimal temperature around 30–35□C, hydrolyzing enzymes show optimal activities around 45–55ºC [79]. The simultaneous process is usually conducted at temperatures inferior to the optimum of the cellulolytic enzymes. It may be possible however to ferment ethanol at temperatures close to the optimum of enzymatic hydrolysis (between 38 and 45°C) by using thermos-tolerant yeast such as Kluyveromyces marxianus [80].

The performance of K. marxianus was evaluated by García-Aparicio et al. during simultaneous saccharification and fermentation process of steamexploded barley straw for an incubation period of 72 h with a moderate enzyme dosage and using the washed solid fraction as substrate [81].

Distillation
Distillation is the final step in ethanol production. Due to the current limitation of solid loading in enzymatic hydrolysis and fermentation stages, the resultant ethanol concentration is commonly low which dramatically increases the cost of distillation [7].

Pyrolysis
Pyrolysis of straw for the production of bio-oil may be a slow or fast pyrolysis [29,82,83].

Fast pyrolysis is a thermal decomposition process in which organic materials are rapidly heated at 450–600^{0}C in the absence of air. This process, which has been progressively designed and optimized for producing bio-oils, requires lower process temperatures and

efficient quenching of the condensable vapours in order to prevent their cracking and hence maximize oil production [84, 85]. The bio-oil produced by such a process may contain large molecules derived from lignin which adversely affects the bio-oil properties [86,87].

For the fast pyrolysis of straw, a bubbling fluidized bed with discontinuous feed may be applied. The calorific value of the bio-oil produced from corn straw was 16-18 MJ/kg [88].

A flash pyrolysis process was developed by Longanbach and Bauer to produce liquid fuels, chars and gases from grass straw and other biomass materials. In this process, the biomass material is heated by contact with hot recycle char and carried in gas stream through a reactor where pyrolysis occurs at very short residence times and heat-up rates [83].

Conclusion

Straw is one of the most abundant renewable resources and is particularly suited for bioethanol production. Bioethanol is non-toxic and with its high oxygen content and octane no. is presently the cleanest and 13 may be the only real renewable alternative to gasoline. Production of Bioethanol from straws can be achieved by either of two processes, namely fermentation and fast pyrolysis. The processes involved in bioethanol production by fermentation include an appropriate pre-treatment, hydrolysis of the straw to convert the cell walls to simple sugars, anaerobic fermentation to convert the sugars to ethanol, and finally distillation. Ethanol production from straw could also be performed by direct microbial conversion.

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