Chapter 1

Introduction

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Straw, the above-ground part of the cereal plant that remains after the nutrient grain or seed has been removed, comprises about half the total dry weight of the crop. For many centuries, straw was valued as the most useful by-product of cereal production, and it has been used for feeding livestock, bedding, growing mushroom, and so on [1]. However, with the development of science and technology in the recent decades, especially with the exploitation of petroleum, straw is regarded as little more than an embarrassing companion to the grain crop. Farmers in many of the chief cereal-growing countries of the world burn or plough the straw into the field directly as a fertilizer. For instance, in the United Kingdom, approximately half (6 million tons) of the annual production of recoverable cereal straw in England and Wales are disposed of by burning [2]. It was reported that only a little of the straw remaining from the nearly 230 million hectares of wheat grown annually in the world was used as a fodder for animals [3].

However, as petroleum is currently one of the most important natural resources and a raw material for the synthesis of various chemicals, a series of issues has arisen, such as the diminishing world reserves of petroleum, the resultant pollution from the processing and utilization of petroleum, the sensitive petroleum market, and so on. Especially, the problem of global warming requires severe reductions in the use of fossil fuel [4]. In addition, the straw burning should be avoided, as it causes serious environmental pollution. These problems have led researchers to pay attention to the value of biomass, which is both sustainable and CO₂-neutral. Agricultural crop residues, such as straws of wheat, barley, rice, maize, oats, rye, and cotton, as well as sugarcane bagasse and other residues, represent an enormous underutilized energy resource, which has a great potential as feed for ruminants and also as raw materials for paper, chemicals, and other technical products [5]. Generally, for every ton of cereal production worldwide, about 1.5 tons of straw is obtained as a by-product. World production of cereals exceeds 1000 million tons per annum, which means about 1500 million tons of cereal straw is produced each year, in which China produce more than 700 million tons cereal straws per year [6]. Straw and other fibrous by-products from cereals available in the world amount to approximately 3000 million tons per year [7]. Because of the enormous quantity of straw, utilization of straw to the utmost extent is now demanding attention in the major cereal-growing areas of the world.

One of the most traditional utilizations of straw is as feed for livestock. Unfortunately, we notice that even though straw contains enough cellulose, which makes it an excellent source of energy for ruminants, it is a poor-quality feed in its natural state. The limited use of straw as feed is due to its low rate of degradation in the rumen, low digestibility, and low voluntary intake [8, 9]. This is caused by the chemical structure of the straw, which limits the digestion of cellulose and hemicelluloses. The chemical factors include lignification [10, 11], silicification, crystallinity of cellulose, and other factors [12]. The problem of straw being used for livestock feeding is discussed in detail by Han et al. [12] and Morrison [13].

Various physical, chemical, and biological treatments have been applied to improve utilization of straws. Physical treatment is carried out mainly to increase the surface area, which would enhance the attachment of bacteria. Processes such as milling, grinding, chopping, and steaming have long been used to improve the feed value (digestibility) of straw [14]. Chemical methods have been used to improve the digestibility of wheat straw [15, 16]. Alkaline treatment of lignocellulosic substances such as wheat straw disrupts the cell wall by dissolving hemicelluloses, lignin, and silica, by hydrolyzing uronic and acetic acid esters and by swelling cellulose, and by decreasing the crystallinity of cellulose [9]. This increase of the biodegradability of the cell walls is also due to the cleavage of the bonds between lignin and hemicelluloses or lignin and phenolic acids. In general, ammonium hydroxide (NH₄OH) usually produces a positive response [17–20] but is generally less effective than
Advantages of NH$_4$OH over the mineral hydroxides are excess of evaporation, elimination of mineral imbalances, and supply of supplemental N [9, 22]. The most promising results have been obtained from biological methods of degrading lignin. The use of intact microorganisms or their enzymes for the conversion of straw into animal feed has been an active area of research [23–26]. One of the major ligninolytic organisms, the white rot fungus, has been used extensively in this area of research. Although a huge potential is found in the utilization of straw as an animal feed, we need to consider the ways in which the carbohydrates and lignin in straw are degraded and how these components interact with each other to prevent degradation.

The demand for paper has increased significantly in recent years, so much so that the Food and Agriculture Organization (FAO) has predicted an increase in the worldwide use of paper and cardboard from the 210 million tons of 1988 to about 350 million tons by 2010 [27]. Paper consumption in the world in 2004 amounted to an average 52.45 kg per person per year and was 16.32% higher than in 1991. The current annual production of pulp cannot meet the increasing demand, which continues to grow at a dramatic rate [28, 29]. This steady increase in the demand of paper is gradually leading to a worldwide shortage of wood fiber supplies. The virgin forests from which most of the pulp for paper has been obtained for the past 100 years are shrinking. In addition, environmental and population growth pressures are contributing to long-range changes in forest-land management practices, which reduce the harvest of wood for wood products and for pulp and paper manufacture [30]. One possible solution to this problem lies in the use of annual and nonwood plants [31–35].

A number of nonwood fibers are in use all over the world for making paper and other products. In 1970, pulp from nonwood fibers accounted for only 6.7% of the overall worldwide production. By 1993, the proportion had increased to 10.6% and, sometime in the future, it will be predictably double that of pulp made from woody materials [27, 36]. Straw materials are by far the largest source of nonwood fibers, followed by bagasse and bamboo. Straw was used for the first time as a raw material for paper in 1800, and in 1827, the first commercial pulp mill began operations in the United State using straw [37]. In many countries, straw has been used for paper and board production, and interest in this field continues to grow. This is particularly important in these countries where the pulp wood availability is extremely limited [38]. Wheat and rye straws are used in some European countries, such as Bulgaria, Denmark, Greece, Holland, Hungary, Italy, Rumania, Spain, and Yugoslavia, where pulpwod supplies are limited, and the purchase of wood pulp from outside sources is too expensive to support local paper production. The growing utilization of cereal straws has received the attention of many developing countries, particularly Algeria, Argentina, China, Egypt, India, Indonesia, Mexico, Pakistan, Sri Lanka, Syria, and Turkey. In these countries, corrugating medium, board, and packaging paper are produced from high-yield unbleached straw pulps; bleached straw pulp is used as a major furnish for fine-quality writing, printing, and other paper grades [39]. The greatest part of this increase is attributed to the developing market economies, especially in Asia [40]. Most of the world’s increased use of nonwood plant fibers has been attributed to the tremendous increase in nonwood pulping capacities in China. At present, China produces more than two-thirds of nonwood pulp produced worldwide [41]. Major agriculture residues used in China’s pulp and paper industry include wheat straw and bagasse. Straw is a major source of fiber for the paper industry in China, which is mainly due to its ready availability.

The main drawbacks that are considered to limit the use of nonwood fibers are the difficulties in collection, transportation, and storage [42, 43]. Besides, straw contains significant amounts of silica, ranging approximately from 3 to 13.3%, which creates potential problems in conventional chemical recovery systems [39]. Despite these drawbacks, the use of straw shows potential as a means of addressing the shortage of raw materials for paper manufacture. Furthermore, the production of pulp from nonwood resources has many advantages such as easy pulping capability, excellent fibers for the special types of paper, and high-quality bleached pulp. Finally, we should note that the analysis of fiber morphology and chemical composition of plant material has been useful in searching for candidate fiber crops. This has provided an indication of the papermaking potential of various species [44]. Morphological characteristics, such as fiber length and width, are important in evaluating the pulp quality of fibers [45], and the chemical composition of the candidate plant gives an idea of the feasibility of using the plant as a raw material for papermaking.

The rapidly growing demand for energy, a dwindling and unstable supply of petroleum, and the emergence of global warming by the use of fossil fuels have rekindled a strong interest in pursuing alternative and renewable energy sources [46]. Biomass as a renewable resource has received more interest. The recovery of energy from biomass has centered thermochemical and biochemical conversion processes. Mechanical extraction (with esterification) is the third technology for producing energy from biomass, for example, rapeseed methyl ester (RME) biodiesel [47]. Within thermochemical conversion, four process options are available: combustion, pyrolysis, gasification, and liquefaction. Biochemical conversion encompasses two process options: digestion (production of biogas, a mixture of mainly methane and carbon dioxide) and fermentation (production of ethanol) [47].

Among the thermochemical processes, pyrolysis has received an increasing attention because the process
conditions may be optimized to produce high energy density pyrolytic oils in addition to the derived char and gas. Gasification – the process of converting carbonaceous materials into gaseous products using media such as air, oxygen, or steam – has been suggested as a cleaner alternative to the combustion of low-density materials such as hulls and straw [48, 49]. The chemical composition of straw feedstocks places specific demands on thermal conversion technologies because alkali, silica, chlorine, and sulfur constituents in straw contribute to slag accumulation and corrosion in many previously tested reactors [50]. The process of biomass liquefaction is very complex, the micellar-like broken down fragments produced by hydrolysis are degraded to smaller compounds by dehydration, dehydrogenation, deoxygenation, and decarboxylation. These compounds once produced, rearrange through condensation, cyclization, and polymerization, leading to new compounds [51].

Ethanol derived from biomass, one of the modern forms of biomass energy, has the potential to be a sustainable transportation fuel, as well as a fuel oxygenate that can replace gasoline [52]. The world ethanol production in 2001 was 31 gigaliters (GL) [53]. The major producers of ethanol are Brazil and the United States, which account for about 62% of the world production. The major feedstock for ethanol in Brazil is sugarcane, whereas corn grain is the main feedstock for ethanol in the United States [54]. However, in recent years, lignocellulosic ethanol production has become attractive because the nonfood portion of the plant can be used to produce ethanol, and there is no competition for feedstock with the food industry. Extensive research and development programs have been initiated worldwide to convert lignocellulosic biomass, such as agricultural residues, forestry wastes, waste paper, and energy crops, which has long been recognized as a potential sustainable source of sugars for biotransformation into biofuels and value-added bio-based products [55, 56].

The global annual potential bioethanol production from the six major crop residues (corn stover, barley straw, oat straw, rice straw, wheat straw, and sorghum straw) and sugarcane bagasse is estimated by Kim and Dale in 2004 (Table 1.1) [54]. Furthermore, lignin-rich fermentation residue, which is the coproduct of bioethanol made from crop residues and sugarcane bagasse, can potentially generate both 458 terawatt-hours (TWh) of electricity (about 3.6% of world electricity production) and 2.6 Exajoule (EJ) of steam.

Unfortunately, lignocellulosic biomass is highly recalcitrant to biotransformation, both microbial and enzymatic, which limits its use and prevents economically viable conversion into value-added products. Himmel et al. [55] emphasized that natural factors such as the following contribute to the recalcitrance of lignocellulosic feedstock to chemicals or enzymes: the degree of lignification [57], the structural heterogeneity and complexity of cell-wall constituents such as microfibrils and matrix polymers [58], the challenges for enzymes acting on an insoluble substrate [59], the inhibitors to subsequent fermentations that exist naturally in cell walls or are generated during conversion processes [60], and the crystalline cellulose core of cell-wall microfibrils [61]. In the context of the biorefinery, these chemical and structural features of biomass affect liquid penetration and/or enzyme accessibility and activity and, thus, conversion costs. The conversion of lignocellulosic materials into biofuels typically includes three steps: (1) pretreatment of lignocellulose to enhance the enzymatic or microbial digestibility of polysaccharide components; (2) hydrolysis of cellulose and hemicellulose to fermentable reducing sugars; and (3) fermentation of the sugars to liquid fuels or other fermentative products [56, 62, 63]. Up to now, hydrolysis of lignocellulose to monosaccharides is usually catalyzed either by enzymes or by acid catalysts under heterogeneous conditions [64], and none of the known methods is yet cost-effective for large-scale applications [65]. As a result, effective pretreatment strategies are

TABLE 1.1 Potential Bioethanol Production from the Crop Residues and Sugarcane Bagasse [54]

<table>
<thead>
<tr>
<th>Potential bioethanol production (GL)</th>
<th>Africa</th>
<th>Asia</th>
<th>Europe</th>
<th>North America</th>
<th>Central America</th>
<th>Oceania</th>
<th>South America</th>
<th>Subtotal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn stover</td>
<td>–</td>
<td>9.75</td>
<td>8.23</td>
<td>38.40</td>
<td>–</td>
<td>0.07</td>
<td>2.07</td>
<td>58.60</td>
</tr>
<tr>
<td>Barley straw</td>
<td>–</td>
<td>0.61</td>
<td>13.70</td>
<td>3.06</td>
<td>0.05</td>
<td>0.60</td>
<td>0.09</td>
<td>18.10</td>
</tr>
<tr>
<td>Oat straw</td>
<td>–</td>
<td>0.07</td>
<td>1.79</td>
<td>0.73</td>
<td>0.009</td>
<td>0.12</td>
<td>0.06</td>
<td>2.78</td>
</tr>
<tr>
<td>Rice straw</td>
<td>5.86</td>
<td>186.8</td>
<td>1.10</td>
<td>3.06</td>
<td>0.77</td>
<td>0.47</td>
<td>6.58</td>
<td>204.60</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>1.57</td>
<td>42.6</td>
<td>38.90</td>
<td>14.70</td>
<td>0.82</td>
<td>2.51</td>
<td>2.87</td>
<td>103.80</td>
</tr>
<tr>
<td>Sorghum straw</td>
<td>–</td>
<td>–</td>
<td>0.10</td>
<td>1.89</td>
<td>0.31</td>
<td>0.09</td>
<td>0.41</td>
<td>2.79</td>
</tr>
<tr>
<td>Bagasse</td>
<td>3.33</td>
<td>21.3</td>
<td>0.004</td>
<td>1.31</td>
<td>5.46</td>
<td>1.84</td>
<td>18.10</td>
<td>51.30</td>
</tr>
<tr>
<td>Subtotal</td>
<td>10.8</td>
<td>261.0</td>
<td>63.8</td>
<td>63.2</td>
<td>7.42</td>
<td>5.70</td>
<td>30.20</td>
<td>442.00</td>
</tr>
</tbody>
</table>
necessary with the purpose of removing lignin and hemi-
cellulosics, reducing cellulose crystallinity, and increasing
the porosity of the materials. Different pretreatment methods
have been investigated for different materials [66], but they
must meet the following requirements: (1) improve the
formation of sugars or the ability to subsequently form sugars
by enzymatic hydrolysis; (2) avoid the degradation or loss of
carbohydrate; (3) avoid the formation of byproducts
inhibitory to the subsequent hydrolysis and fermentation
processes; and (4) be cost-effective [56]. Himmel et al. [55]
mentioned that although biofuel production has been greatly
improved by new technologies, there are still challenges that
need further investigations.

In addition to feed, paper, and energy, other mainly
attractive applications for straw are bio-based products,
such as wood-based materials, biodegradable plastics, and
adsorbents. Since the 1980s, depletion of the world’s forests
has steadily forced up the price of wood and wood-based
materials [67]. In recent years, it has been difficult to obtain
solid woods, and this causes problems for wood-based
industry. Agricultural residues offer a great promise and
new challenges as a replacement for wood and engineered
wood products; rice straw and wheat straw can be easily
crushed to chips or particles, which are similar to wood
particle or fiber, and may be used as substitutes for wood-
based raw materials [68]. Wheat straw, for example, offers
desirable geometric and mechanical attributes for replace-
ment of wood in cement-bonded particleboard [69]. Rice
straw-wood particle composite boards and rice straw-waste
tire particle composite boards are successfully manufactured
as insulation boards, using the method used in the wood-
based panel industry [68, 70].

Recently, because of the growing environmental aware-
ness and ecological concerns and new legislations,
composite industries are seeking more eco-friendly materi-
als for their products [71]. Biodegradable plastics and bio-
based polymer products based on annually renewable
agricultural and biomass feedstock can form the basis for
a portfolio of sustainable, eco-efficient products that can
compete and capture markets currently dominated by
products based exclusively on petroleum feedstock [72].
Worldwide production of biodegradable plastics grew five-
fold between the years 1996 and 2001. There is ample room
for market growth, as global production of biodegradable
plastics in the year 2001 was approximately 8% of that of
petroleum-derived plastics in the same year [3, 73]. It was
found that tensile and flexural properties of the agro-
residue-filled composites showed that they could be used as
an alternative to wood-fiber-filled composites [71].

Water pollution is one of the most serious environmental
problems faced by the modern society [74]. Among various
pollutant sources, the pollution from heavy metals, dyes,
and oil are serious. Toxic heavy metal ions get introduced to
the aquatic streams by means of various industrial activities
such as mining, refining ores, fertilizer industries, tanneries,
batteries, paper industries, and pesticides and posses a
serious threat to environment [75–77]. Effluents discharged
from dyeing industries are highly colored, of low
biochemical oxygen demand (BOD), and of high chemical
oxygen demand (COD). Disposal of this colored water into
receiving waters can be toxic to aquatic life [78, 79]. The
dyes upset the biological activity in water bodies. They also
pose a problem because they may be mutagenic and
carcinogenic [80, 81] and can cause severe damage to
human beings, such as dysfunction of kidney, reproductive
system, liver, brain, and central nervous system [82]. It is
believed that traditional treatment processes of waste
streams contaminated with metals and dye have their own
inherent limitations such as less efficiency, sensitive
operating conditions, and production of secondary sludge,
and further the disposal is a costly affair [83]. Among many
new technologies, utilizing plant residues as adsorbents for
the removal of metal ions and dyes from wastewater is a
prominent technology [84, 85]. The promising agricultural
waste materials are used in the removal of metal ions and
dyes either in their natural form or after some physical or
chemical modification. Another powerful technology is the
adsorption of heavy metals and dyes by activated carbon for
treating wastewater [86–87]. However, the high cost of
activated carbon and its loss during the regeneration restricts
its application. Therefore, there is a need to search for an
effective adsorbent for economical wastewater treatment.
A wide variety of activated carbons have been prepared from
agricultural residues such as corn straw [88], wheat straw [88],
rice straw [89, 90], bagasse [91, 92], cotton stalk [93], coconut
husk [94], and rice husks [95]. Due to their low cost, after
these materials have been expended, they can be disposed of
without expensive regeneration.

Oil is one of the most important energy and raw material
source for synthetic polymers and chemicals. In the recent
years, tremendous increases of accidental and intentional oil
discharges have occurred during production, transportation,
and refining [96]. Spilled oil causes immense environmental
damage unless it is removed as quickly as possible. One of
the most economical and efficient means for the removal of
spilled oil from either land or sea is the use of adsorbents
[97]. Usually, oil-adsorbent materials can be categorized
into three major classes: inorganic mineral products, organic
synthetic products, and organic vegetable products [96].
Mineral products include perlite, vermiculites, sorbent clay,
and diatomite. These materials do not show adequate
buoyancy retention and their oil sorption capacity is
generally low [98]. Synthetic sorbents such as polypropylene
and polyurethane are the most commonly used commercial
sorbents in oil-spill cleanup, due to their oleophilic and
hydrophobic characteristics [97]. A disadvantage of these
materials is that they degrade very slowly as compared to the
mineral or vegetable products. The limitations of the
inorganic mineral products and organic synthetic products
have led to the recent interest in developing alternative
materials, especially biodegradable ones such as natural agro-based products. Sugarcane bagasse, rice straw, wheat straw, barley straw, kenaf, kapok, cotton, and wool fibers have been used as sorbents in oil-spill cleanup [96, 97, 99–106]. It should be noted that acetylation has been the most widely used and successful chemical modification. Because acetyl groups are more hydrophobic than hydroxyl groups, replacing some of the hydroxyl groups with acetyl groups reduces the hydrophilic property of the cell-wall polymers [107].

It is noticeable that all above-mentioned methods to utilize straw were used in the entire form rather than in as separate components. Straw consists mainly of three groups of organic compounds – cellulose, hemicelluloses, and lignin. In addition to these three main constituents, straw contains various other organic compounds including small amounts of protein, small quantities of waxes, sugars and salts, and insoluble ash. If the valuable compounds of straw could be extracted or separated from straw, many chemicals may be used [1, 6, 108]. The application of straw for chemicals or raw materials after the valuable compounds of the straw have been isolated will be discussed in Chapters 3–6. Chapter 2 will detail the recent studies of structure, ultrastructure, and chemical composition of straw, which will continue to provide new insights into biomass conversion. Many potential applications of straw as novel materials for industries will be discussed in Chapter 7.

In a word, before utilizing it well, we should have a good understanding of straw. This book will lead us to reach the goal of knowing the real identity of straw and producing cost-competitive chemicals or raw materials from straw. With the development of plant science and straw chemistry, we could reasonably believe that straw will play an important role in our lives in the future.

REFERENCES

References


