

Cereal Straw as a Resource for Sustainable Biomaterials and Biofuels

Chemistry, Extractives, Lignins, Hemicelluloses and Cellulose



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and Cellulose

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Cereal Straw as a Resource for Sustainable Biomaterials and Biofuels

The use of materials from renewable resources is attaining increased importance, and the world's leading industries and manufacturers are seeking to replace dwindling petrochemical-based feedstocks with products derived from natural biomass such as cereal straws, which consist mainly of three groups of organic compounds – cellulose, hemicelluloses, and lignin – representing an abundant, inexpensive, and readily available source of renewable lignocellulosic biomass. In particular, the whole concept of the chemical aspect of straw utilization was brought sharply into focus late in the 1990s when the world was faced with the issue of oil and material shortage. On the basis of 30 years of work in this area, I am convinced that cereal straw will play an important role in moving society from its petrochemical dependency to a sustainable economy, and I also note that to use straw wisely and judiciously, we need to have a basic knowledge of its composition and the structure of the cell walls. Chemical studies of straw and its components may provide decisive factors not only for its applicability but also for the economic feasibility of many industrial processes involving straw. However, although several excellent books on wood chemistry were published in the past, there is no book devoted specifically to straw chemistry. More importantly, only recently new processes have been developed where straw components are separated and isolated on the pilot scale. All of these reasons provided the inspiration for this book.

This book provides us a thorough overview of straw chemistry. Chapter 1 provides an introduction. Chapter 2 is concerned with the fundamentals of straw structure, ultrastructure, and chemical composition. Chapter 3 covers the extractives, which include isolation and structural characterization. Chapters 4–6 review what is currently

known about the three main components with respect to their discovery, occurrence, chemical and physical properties, analysis, molecular weight, isolation, and application. The last chapter focuses on chemical modifications of straw as novel materials for various industries.

This book summarizes both our knowledge of straw chemistry and gives a comprehensive account of progress and current knowledge in straw chemistry, drawing on an extensive set of references. I sincerely hope that this book will be used as a teaching book and anticipate that it will be particularly useful not only to scientists with research interests in the areas of natural resource management, environmental chemistry, plant chemistry, material science, polysaccharide chemistry, lignin chemistry, etc., but also to academic and industrial scientists/researchers with an interest in using agricultural residues as novel products for industries and/or recycling technologies. I am sure that this book will play an important role in the process of utilization of straw.

All of the contributors, who were carefully selected to cover each particular subject, are active in research. As a result, this book provides, not only a comprehensive picture of the state of the art, but also much unpublished data from recent studies. I sincerely thank all the contributing authors, who come from Beijing Forestry University, South China University of Technology, University of Wisconsin-Madison, and North-West Agriculture and Forestry University, for their excellent collaboration. I also would like to give special thanks to Fachuang Lu and John Ralph for their long-term cooperation; Chapter 6 contains some unpublished data from their recent studies.

*Run-Cang Sun
Beijing, 2009*

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Introduction

Tong-Qi Yuan* and Run-Cang Sun***

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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

NaOH [9, 21]. Advantages of NH_4OH 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 pulpwood 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 giga-liters (GL) [53]. The major producers of ethanol are Brazil and the United State, 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 State [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]

Potential bioethanol production (GL)	Africa	Asia	Europe	North America	Central America	Oceania	South America	Subtotal
Corn stover	–	9.75	8.23	38.40	–	0.07	2.07	58.60
Barley straw	–	0.61	13.70	3.06	0.05	0.60	0.09	18.10
Oat straw	–	0.07	1.79	0.73	0.009	0.12	0.06	2.78
Rice straw	5.86	186.8	1.10	3.06	0.77	0.47	6.58	204.60
Wheat straw	1.57	42.6	38.90	14.70	0.82	2.51	2.87	103.80
Sorghum straw	–	–	0.10	1.89	0.31	0.09	0.41	2.79
Bagasse	3.33	21.3	0.004	1.31	5.46	1.84	18.10	51.30
Subtotal	10.8	261.0	63.8	63.2	7.42	5.70	30.20	442.00

necessary with the purpose of removing lignin and hemicelluloses, 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 replacement 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 awareness and ecological concerns and new legislations, composite industries are seeking more eco-friendly materials 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 pollutions 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 poses 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.

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Structure, Ultrastructure, and Chemical Composition

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This chapter mainly covers the anatomical structure, ultrastructure, lignin and polysaccharides distribution, and chemical composition aspects in relationship to the field of grass lignocelluloses. The intent is to summarize the obtained information and make a potential user aware of the opportunities that cell wall organization and composition distribution have to offer. Although wood is the most widely used raw material for industrial utilization, many other plant fiber as well as nonwood plant fibers are utilized. The most important group of these are grass plant. Cereal straws, sugarcane bagasse, and bamboo are important grass fibers that are being used now and will be used for a long time in utilizations of renewable resources. The cell wall of wood and nonwood is a heterogeneous natural nanocomposite of cellulose, lignin, and hemicelluloses, with content, composition, and distribution varying over a wide range [1–4].

2.1 ANATOMICAL STRUCTURE

A wooden stem has a continuous growth in the diameter due to the cambium, forming secondary wood (xylem-phloem). The xylem of wood species is characterized by different anatomical structure [5–8]. Unlike wood, as a species of monocots, grasses lack cambium. Instead, grasses have a stem structure with numerous vascular bundles scattered in a ground tissue of parenchyma storing cells, which is surrounded by a strong and dense epidermis.

The stem of grass has two principal functions: support and conduction of nutrients and water. The stems of grasses are hollow or less commonly solid cylinder interrupted at intervals by transverse partitions. The units between the partitions represent the internodes and the transverse septa are at the nodes [9]. The vascular bundles are growing vertically, turning off to set leaves at regular intervals. This regular division into nodes and internodes is typical for all grass stems (Fig. 2.1). Typically, the grass stems have the

internodes developed as a hollow cylinder surrounded by a leaf sheath e.g. straw and bamboo [10]. Sugar cane and maize diverge from most species of the grass family by having a solid stem. The stem is made up of essentially the parenchymatous ground tissue with the vascular bundles embedded in it. Vascular bundles are distributed according to two basic plans. One is the vascular bundles that are in two circles near the periphery of the stem, as in cereal straws (Fig. 2.2 left). The other is vascular bundles that are scattered in the ground parenchyma throughout the cross section of the stem, as in corn, sugarcane, bamboo, and palm (Fig. 2.2 right) [10].

Figure 2.3 shows four basic parts (from outside to inside): epidermis, cortex, vascular bundle, and pith of the grass stem [11]. Epidermis cells arranged in parallel rows are closely packed, and it functions to protect the internal parts of the plant. The walls are thickened and covered with a thin waterproof layer that retains water called the cuticle. Wax is deposited in the cutinized layers, and it makes them impermeable to water. The epidermis contains long cells, short cells, cells of stomata, and bulliform cells. Stomata with guard cells are found in the epidermis for gas exchange. Cortex, the zone between epidermis and the vascular bundles, contains collenchyma and parenchyma cells. The pith occupies the central part of the stem and is composed of thin-walled parenchyma cells often with larger intercellular spaces than you would find in the cortex.

The vascular bundles in the stem of the grass plants vary in number and size, but it shows the same basic structure. Each vascular bundle is composed of xylem and phloem. Xylem is a strengthening and conducting tissue transporting water and solutes. The xylem contains the earlier formed protoxylem, and it later differentiated into metaxylem [12]. The phloem contains thin-walled, unlignified sieve tubes with companion cells. The main function of phloem is transport of photosynthetic products. As shown in Fig. 2.4, the phloem and xylem are surrounded by sheaths of