FOOD AND INDUSTRIAL BIOPRODUCTS AND BIOPROCESSING

Edited by
Nurhan Turgut Dunford

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Preface

Petroleum-derived products have dominated the markets for decades because of the ease of production and economies of scale. In recent years diminishing petroleum resources, volatile political environments in some of the major petroleum producing countries and environmental concerns inspired a paradigm shift. Today significant resources have been dedicated to the development of bioproducts from renewable sources. Research and development efforts to harness the unique chemical and physical properties of plants and microorganisms to produce ecologically benign products that outperform their non-renewable counterparts have accelerated. Ever increasing consumer demand for "chemical free", "healthy" and "natural" foods incited the food industry to reevaluate the conventional food ingredients and processing techniques and adapt new and advanced production systems.

This book, which contains 14 chapters, provides a comprehensive review of the latest developments in food and industrial bioproducts and bioprocessing techniques. Although it is an important topic, biofuels are not covered in the book. This book is designed as a reference source for scientists, students, and government and industry personnel who are interested in the recent developments and future opportunities in food and industrial bioproducts and relevant bioprocessing techniques. The contributing authors of the book from Australia, Canada, Denmark, Germany and the USA are internationally renowned experts in their fields and their contributions to the book are invaluable. I would like to express my sincere gratitude to the authors for accepting my invitation to contribute and completing their chapters in a timely manner. The comments received from the external reviewers, James T.C. Yuan, Ibrahim Banat, Sue, Nokes, David Cowan, Randy Berka, Mark R. Marten, B. Dave Oomah, J.L. Willett, Laurent Bazinet, Dan Farkas, Richard Ashby, Thrandur Helgason, Donghai Wang, Cristina Sabliov, Wenqiao (Wayne) Yuan, Michael J. Haas, Sang-Hyun Pyo, Krister Holmberg, Aaron L. Brody, Amos Richmond and Mike Packer, were extremely helpful. I would like to thank all the reviewers for generously spending time to review the chapters. Certainly their contributions enhanced the quality of the book.

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Abbreviations

ADMET	Acyclic diene metathesis polymerization
AOT	Sodium dioctyl sulfosuccinate
CALA	Candida antarctica lipase A
CALB	Candida antarctica lipase B
DAG	Diacylglycerol
DVB	Divinyl benzene
E	Enzyme
EP	Enzyme-product complex
ES	Enzyme-substrate complex
ESBO	Epoxidized Soybean Oil
FA	Fatty acid
FAME	Fatty acid methyl ester
G (or GLY)	Glycerol
HAP	Hazardous air pollutant
hPL	Human pancreatic lipase
IPN	Interpenetrating network
KmS	Michaelis constant
LOI	Limiting oxygen index
LPL	Lysophospholipids
MAG	Monoacylglycerol
METU	Methyl undec-10-enoate
NMMO	N-methylmorpholine-N-oxide
P	Product
PC	Phosphatidylcholine
PG	Partial Acylglycerol
PGA	Poly(glycolic acid)
PHA	Polyhydroxyalkanoate
PHB	Poly(3-hydroxybutyrate)
PHBV	Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PL	Phospholipid
PLA	Poly(lactic acid)
PLA_1	Phospholipase A_1
PLA_2	Phospholipase A_2
PLC	Phospholipase C
PLCD	Phospholipase D
PLLA	Poly(l-lactic acid)
PU	Polyurethane

PVA	Poly(vinyl alcohol)
RM	Rhizomucor meihei
S	Substrate
S*	Micellar substrate
TAG	Triacylglycerol
TLL	Thermomyces lanuginosum
UA	Undec-10-enoic acid
V	Velocity
VOC	Volatile organic compounds

1 Traditional and Emerging Feedstocks for Food and Industrial Bioproduct Manufacturing

Nurhan Turgut Dunford

1.1 INTRODUCTION

Many industrial products, such as dyes, inks, paints and plastics, were made from biomass generated by trees, vegetables or other crops during the early 1900s. By 1970, petroleum-based products had largely replaced bio-based products. The utilization of plant-based materials decreased from about 35% to less than 16% between 1925 and 1989 (Forward, 1994). Waning interest in bio-based products was due to the relative ease and lower cost of manufacturing similar products from petrochemicals.

The petrochemical industry has been very successful in developing new products (more than 100 000 commercial products) (Metzger and Eissen, 2004). About 2.6 million barrels per day of petroleum equivalent are used for production of chemicals and industrial building blocks. More than 95% of the world's petrochemical production is derived from oil or natural gas (Weissermel and Arpe, 1997). Excessive reliance on non-renewable energy and resources is the major problem facing petrochemical industry today. In 2001 it was projected that the global oil reserves would last for about 40 years (Metzger and Eissen, 2004). Oil production is expected to reach its maximum in this decade, at the latest by 2015–2020, and then slowly decrease. According to Gavrilescua and Chisti, the issues that make the petrochemical industry unsustainable in the long run are: (1) utilization of manufacturing techniques that are not environmentally benign or safe, (2) production of toxic by-products and waste, (3) products are not readily recyclable and biodegradable after their useful life, and (4) social benefits of the production are not broadly accessible due to excessive regional concentration of production (Gavrilescua and Chisti, 2005).

Nearly one billion of the current world population (the total is about six billion) live in the industrialized countries. The world population is expected to reach to about nine billion by 2050. It is anticipated that the population growth will mainly soar in the developing countries (Metzger and Eissen, 2004). As the population and the standard of living increase, demand for food and other goods will substantially grow, consequently exerting tremendous pressure on resources. Today it is true that "hunger is a problem of poverty rather than absolute food scarcity" (Koning *et al.*, 2008). Yet, the global demand for food production will more than double by 2050, competing for resources needed to grow biomass for other purposes, including biofuels and bio-based non-food industrial products (Koning *et al.*, 2008). A combination of further increases in crop yields (about 2% per year) and doubling

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or tripling of resource use efficiencies (especially of nitrogen and water productivity in biomass production systems) will be necessary to meet the rapidly growing demand for food, feed and industrial bioproducts over the next 20–30 years (Spiertz and Ewert, 2009).

About 224×10^9 tonnes of dry biomass is generated globally as a result of photosynthesis (Champagne, 2008). Today, forestry products and agricultural crops are the major feedstocks for bioproduct manufacturing. Utilization of agricultural residues, forestry, animal and municipal solid wastes and marine vegetation as feedstock could ease the pressure on agricultural land needed to grow food. However, the effect of excessive biomass removal on ecosystems has to be examined very carefully.

In this chapter, current and potential feedstocks for food and bioproduct manufacturing will be reviewed under three categories: grain, oilseed and lignocellulosic biomass, which will include grasses and trees. Microalgae, emerging as a biomass source, will be covered in another chapter of this book.

1.2 GRAIN CROPS

Grain crops, specifically cereal crops, are major feedstocks for the food and fermentation industry because of their high starch and protein content. Cereal crops are by far the most important crops cultivated globally. In 2009 about 2.5 billion tonnes of cereals were produced worldwide (FAO, 2010). Wheat, corn, barley and sorghum are the common starch sources that have been traditionally used in food and industrial bioproduct manufacturing. Straw and stocks from cereal crops are also important as lignocellulosic feedstock for bioproduct manufacturing.

1.2.1 Wheat

1.2.1.1 *Production*

Wheat is one of the major grain crops produced, consumed and traded worldwide. About 683 million tonnes of wheat is produced globally each year (Table 1.1). China, India, the USA and the Russian Federation are among the largest wheat growers (FAO, 2010).

It is believed that einkorn, which was developed from a wild grass native to western Asia, was the first type of wheat cultivated (Atwell, 2001; Orth and Shellenberger, 1988). Four species, *Tiriticum*: *T. monococcum, T. turgidum, T. timopheevi and T. aestivum*, are the commercially important wheat cultivars today. Among these, *T. turgidum* and *T. aestivum*, which are mainly used for bread and pasta making, respectively, are the most widely grown wheat species (Pomeranz, 1988). Enhancement of nutritional composition and value of wheat through biotechnology is an area that is gaining ever increasing scientific attention. It has been shown that a gene, GPC-B1, found in wild wheat but lost its functionality during domestication has the potential of increasing protein and micronutrient content of cultivated wheat by 10–15% (Uauy *et al.*, 2006). Novel wheat varieties with high amylose content have been developed by using the RNAi gene silencing technique that suppresses the expression of two wheat genes, SBEIIa and SBEIIb (Regina *et al.*, 2006). These genes produce starch branching enzymes and play important role in the starch synthesis pathway. The suppression of these two genes produced a wheat variety with high resistant starch (amylose) content and low glycemic index (GI). This new wheat variety could potentially provide health benefits to people with bowel, diabetes and obesity problems.

Table 1.1 Wheat, corn, sorghum and barley production in 2008 (million metric tons).

Wheat		**Corn**		**Sorghum**		**Barley**	
World	683.4	World	826.3	World	66.8	World	155.1
China	112.5	USA	307.1	USA	12.0	Russian Federation	23.2
India	78.6	China	166.0	Nigeria	9.3	Ukraine	12.6
USA	68.0	Brazil	58.9	India	7.9	France	12.2
Russian Federation	63.8	Mexico	24.3	Sudan	3.9	Germany	12.0

Classification of wheat for commercial purposes is based not on variety but on grain properties such as softness/hardness, winter/spring growth habit, red/white bran and protein content. Hard wheat has a hard kernel and produces high protein content flour suitable for making bread and noodles. Soft wheat has lower protein content than hard wheat and is mainly used for making cakes, biscuits and pastries. Winter wheat is planted in late summer or fall and takes the advantage of fall moisture for germination. It is grown in regions where soil does not completely freeze and kill the crop. As the name implies, spring wheat is sown in spring and harvested in late summer. Yields for winter wheat tend to be higher than that for spring wheat due to the risks associated with summer harvest (Pomeranz, 1988). Color, white or red, refers to the color of the outer layers of grain. Depending on milling extraction rate (bran removal rate), the color of the wheat flour can be quite dark, affecting the appearance of the final product. Major wheat exporting countries have their own wheat grading standards that are based on test weight, protein content, moisture, foreign material content and so on (Bushuk and Rasper, 1994). The US Grain Standards Act is enforced by inspectors under the supervision of the US Department of Agriculture (USDA, 2006).

Although wheat straw production yield depends on variety and agronomic and climatic factors, in general 1.3 kg of straw per kg of grain is produced for the most common varieties (Montane *et al.*, 1998). It is estimated that over 90 million metric tons (tonnes) of wheat straw is produced annually in the United States. Considering that world wheat production was about 683 tonnes in 2008 (Table 1.1), global wheat straw production would be 888 tonnes in the same year. About 500 kg of straw per acre needs to be left on the soil surface during wheat harvest for erosion control of steeply sloped ground (Mckean and Jacobs, 1997). It is apparent from these numbers that a significant amount of wheat straw is available for value-added product development.

1.2.1.2 *Chemical composition*

Chemical composition of wheat fractions varies significantly by variety, agronomic and climatic conditions and separation techniques used. Grain consists of 40–50% of the biomass produced by the crop. Wheat grain structure is very complex and composed of many layers (Godon, 1994). Broadly speaking wheat grain consists of endosperm, bran and germ, which account for 81–84%, 14–16% and 2–3% of the grain, respectively (Atwell, 2001). Whole wheat grain is generally processed by dry milling to obtain flour. Various forms of bran, germ and the "clean-out" of the screen room represent almost 25% of the original wheat grain.

Carbohydrates make up about 60–80% of the dry grain weight. Starch is the main carbohydrate found in endosperm or flour. Other carbohydrates present in wheat include free sugars, glucofructans, cellulose and hemicellulose. Arabinose and xylose are the major free sugars.

Proteins are the second largest group of compounds in endosperm (12–15%). Cereal proteins are classified based on their solubility characteristics; water soluble albumins (5–10%), dilute salt-solution soluble globulins (5–10%), aqueous alcohol soluble prolamins (40–50%) and dilute acid or alkali soluble glutelins (30–40%) (Godon, 1994). Cereal proteins, similar to other plant proteins, are low in some of the essential amino acids, for example lysine. Glutamic acid is the major amino acid in wheat.

Lipids are the minor components of wheat grain (2–3%) and consist of polar and nonpolar components. Triacylglycerides (TAG) make up majority of the nonpolar lipids that are rich in unsaturated fatty acids. Huge variations in linoleic acid content of wheat, 45–75% of total fatty acids, were reported among five market classes of wheat (Davis *et al.*, 1980). Polar lipids include glycolipids and phospholipids (Godon, 1994).

The mineral content of wheat grain varies between 1 and 3%. Even though the mineral content is not very high, wheat could provide significant amount of minerals as it is readily found in most daily diets. Magnesium, phosphorous and potassium are the most abundant minerals. Phosphorous is mostly present in the organic form phytic acid. It has been reported that agronomic condition does not have a significant effect on the mineral composition of wheat grain (Godon, 1994). Wheat grain is rich in vitamins, niacin (about 6 mg/100 mg) and tocopherols (about 20 mg/100 g) (vitamin E).

Wheat bran and germ fractions are rich sources of a number of phytonutrients, including policosanol (PC), phytosterols (PS), α-tocopherol and phenolic acids. A number of studies have shown that PS and PC reduce serum low density lipoprotein (LDL) cholesterol levels (Ostlund, 2002; Hirai *et al.*, 1984; Quilez *et al.*, 2003; Aleman *et al.*, 1994; Castano *et al.*, 2000; Gouni-Berthold and Berthold, 2002). Antioxidant properties of wheat bran and germ extracts are well known (Zhou *et al.*, 2004). It has been reported that dietary wheat bran provides protection against colorectal cancer (Qu *et al.*, 2005). This property is due to the presence of phenolic acids, lignans and flavonoids in wheat bran. Wheat germ contains approximately 11% oil (Dunford and Zhang, 2003; Eisenmenger and Dunford, 2008; Dunford, 2005). The oil contains a number of bioactive compounds, such as tocopherols (Eisenmenger and Dunford, 2008; Dunford and Zhang, 2003), polyunsaturated fatty acids, PS (Chen *et al.*, 2009a), and PC (Chen *et al.*, 2009b; Irmak and Dunford, 2005; Irmak *et al.*, 2005). Wheat germ oil (WGO) is the richest natural source of vitamin E (Kahlon, 1989). It has been reported that wheat germ oil improves human physical fitness; this effect is attributed to its high PC content (Cureton, 1972). There are numerous research studies indicating that 5–20 mg/day of PC consumption is effective in lowering total cholesterol (17–21% reduction) and low density lipoprotein (21–29% reduction) levels and increasing high density lipoprotein (HDL) (8–15% increase) by inhibiting cholesterol synthesis and increasing LDL processing (Menendez *et al.*, 1994, 1999). There is scientific evidence that PC has additional beneficial effects on smooth muscle cell proliferation, platelet aggregation and LDL peroxidation (Taylor *et al.*, 2003). PC formulations are being used as "antifatigue drugs" (Cureton, 1972). Currently, beeswax and sugar cane are the main sources of PC. It is important to note that there have been reports indicating that the cholesterol lowering properties of PC are not reproducible in studies performed in United States (Varady *et al.*, 2003). A better understanding of the effects of PC on disease prevention and treatment requires large scale independent animal and clinical studies involving various ethnic groups and subjects with different health histories.

Wheat straw is a lignocellulosic material containing about 35–40% cellulose, 30–35% hemicellulose and 10–15% lignin (Harper and Lynch, 1981). Wheat straw also contains both lipophilic and hydrophilic extractives, which may be released and/or interfere during pulping and pretreatment of feedstock prior to hydrolysis of carbohydrate polymers to their monomeric sugars prior to microbial fermentation (Sun *et al.*, 2003; Sun and Tomkinson, 2003; Sun and Sun, 2001). Wheat straw contains many bioactive compounds, including PC and PS (Sun and Sun, 2001; Irmak *et al.*, 2005; Dunford and Edwards, 2010). Recovery of these high value bioactive compounds during or prior to bioconversion of wheat straw to bioproducts could improve the feasibility of the conversion process and may improve the efficiency of the hydrolysis of cellulose and hemicellulose and the subsequent fermentation process.

1.2.1.3 *Utilization*

Wheat is a vital component of human diet in many countries. In the United States about 17–18% of total daily calories are acquired from foods derived from wheat. In some other countries wheat-based foods may provide two thirds, even more of the daily caloric intakes (Bushuk and Rasper, 1994). In the United States about 70% of wheat is utilized for human consumption, 24% as animal feed and the remainder for seed or industrial products. The main reason for using a small fraction of wheat in industrial products is due to high demand for wheat for food and feed applications.

Annetts and Audsley (Annetts and Audsley, 2003) defined the term “biorefinery” as “a factory consisting of a collection of processes which takes agricultural inputs from the surrounding area, and produces a wide range of products which are specifically targeted at different market uses and are refined to their specification”. Wheat is an excellent crop to demonstrate the “biorefinery” concept. Current and emerging processing techniques present tremendous opportunities for converting wheat fractions – flour, milling industry by-products (bran, shorts and germ) and straw – in to a broad range of bioproducts. In fact, the economic viability of multiproduct wheat biorefinery systems has been examined by various groups (Dorado *et al.*, 2009; Annetts and Audsley, 2003; Clark, 2007; Dunford, 2007; Koutinas *et al.*, 2004). For example, a process for producing a generic wheat-based fermentation feedstock with two liquid streams, one rich in glucose and one rich in nitrogen, was developed and successfully used for the production of ethanol, lactic acid, pigment and glycerol (Webb and Wang, 1997; Koutinas *et al.*, 2004).

Currently excess straw is baled for use as livestock bedding or low-grade animal feed providing minimal economic return. Straw represents a significant opportunity for fiber substitution. Pulp from straw is already being partially substituted for wood fiber in some paper and paperboard products (Mckean and Jacobs, 1997). Advanced cellulose hydrolysis technologies are being developed for converting straw to biofuels and other industrial bioproducts (Szczodrak, 1988; Ahring *et al.*, 1996; Saha *et al.*, 2005). Recovery and conversion of surface waxes and other bioactive compounds present in wheat straw into high value products, such as insecticides, nutracueticals and cosmeceutical ingredients, may improve the economic feasibility of other commodity or lower value products generated in a biorefinery (Dunford and Edwards, 2010; Irmak *et al.*, 2005; Clark, 2007). Waxes derived from sustainable plant products have a growing market for the replacement of both synthetic (petroleum derived) and animal product derived waxes including lanolin obtained from sheep’s wool (Clark, 2007).

1.2.2 Corn

1.2.2.1 *Production*

Maize or corn (Zea mays) has a long history as a domesticated crop. Today corn is the most widely grown cereal crop in the world. In 2008, world corn production was 826.3 million tonnes (USDA-FAS, 2008). It is estimated the grain yield will reach 1.2 tonnes/ha

(190 bu/acre) by 2030 from the current 940 kg/ha (150 bu/acre), assuming that current 1% annual genetic gain in corn grain yield can be sustained over time (Duvick and Cassman, 1999). In an average year corn is grown on 30–32 million hectares in the United States. Yet, in 2007, 36.5 million hectares (90 million acres) was dedicated to corn because of the high demand for ethanol production. Presuming that production area is maintained at the 2007 level, United States' corn production could reach 430 million tonnes (approximately 17 billion bu/year) accounting for the future yield increases (Dhugga, 2007). Even under these conditions United States would be far short of producing enough corn needed to produce enough ethanol to replace gasoline and meet the increasing demand of grain corn for feed and food (Dhugga, 2007).

1.2.2.2 *Chemical Composition*

Corn is categorized as dent, flint, flour, sweet, pop or pod based on its kernel characteristics.

The majority of corn grown in the United States is yellow dent, yellow referring to the color of endosperm. Chemical composition of corn kernel varies significantly depending on type, variety, environmental conditions and agronomic practices used during crop production (Reynolds *et al.*, 2005). Starch is the most economically important component of corn. Typical starch content of dent type corn is about 60% (NCGA, 2010). Mature kernels of some corn hybrids may contain as high as 75% starch (w/w, dry basis). Morphological, rheological, functional and thermal properties of starches from different corn types vary significantly (Li *et al.*, 1994). Amylopectin and amylose are two structural components of starch. Regular corn starch consists of 75% branched amylopectin and 25% linear amylose while waxy corn hybrids may contain 100% amylopectin. A clear understanding of starch properties in different corn types and lines is vital for selecting corn for breeding purposes and producing starch with specific properties that are required by manufacturing industry.

Sweet corn is primarily grown for fresh consumption. Young sweet corn kernels are succulent because of a mutant recessive sugary-1 gene that retards the conversion of sucrose into starch during endosperm development (Dickerson, 2003). Immature sweet corn contains about 10% sucrose, which is rapidly converted to starch after harvest. Kernels can lose up to 50% of their sucrose at ambient temperature within 24 hours after harvest.

The protein content of corn kernel is about 10%. Zein is the major storage protein and comprises 45–50% of the total protein in corn. Zein cannot be digested efficiently by humans and other non-ruminants. Since corn is an important staple in many countries, its protein quality is important. Corn kernels tend to be low in lysine and tryptophan, two of the eight essential amino acids, requiring corn-based diets to be supplemented with other proteins such as bean proteins. Corn kernels containing the Opaque-2 gene are shown to have lower amounts of zein and higher amounts of lysine and tryptophan in their endosperm than standard dent corn (Paulis *et al.*, 1991). High lysine corn containing increased levels of lysine and tryptophan has been developed. Although high lysine corn has demonstrated nutritional advantage over field corn it still has several disadvantages. It has soft texture, dull appearance and very little hard endosperm, which make high lysine corn difficult to harvest and prone to attack by pests. The value of high lysine corn in poultry rations is limited because of its insufficient methionine content. Furthermore, high lysine corn has lower crop yield and must be segregated from other corn varieties to preserve protein quality (Dickerson, 2003).

Field corn contains 4–6% oil. Corn oil is a healthy energy source for both humans and livestock because of its high polyunsaturated fatty acid, specifically linoleic acid content. High oil corn, which contains 7–8% oil, is preferred by cattle feeders for its high calorie content, which promotes greater animal weight gain per unit of feed. Nevertheless, corn varieties with oil content higher than 6% tend to have lower crop yields.

1.2.2.3 *Utilization*

In 2007, about 98% of the world corn production was consumed as food or feed (USDA-FAS, 2008). The majority of the corn grown in the United States is used as feed. Nearly 43% of the 2009 US corn production was used as feed or left as residue on the field (NCGA, 2010). The same year biofuel, particularly the ethanol production industry, utilized almost 32% of the corn grown in United States. The shares of food/cereal and high fructose corn syrup production in corn consumption were relatively low, 5 and 12 million tonnes, respectively. The high fructose corn syrup production industry takes up about 3–4% of total United States corn production.

Besides its food and feed use, corn has numerous other industrial applications. According to the US National Corn Growers Association, there are more than 4200 different uses for corn products (NCGA, 2010). Although zein, a major storage protein in corn, is not directly used for human consumption it has many potential industrial applications in fiber, adhesive, coating, ceramic, ink, cosmetic, textile, chewing gum and biodegradable plastics production (Shukla and Cheryan, 2001). Biofuels, starch and high value products such as recombinant pharmaceutical proteins and specialty chemicals are some of the economically important corn-based products (Naqvi *et al.*, 2011).

A significant fraction of United States corn is used to produce ethanol. Corn is converted into ethanol primarily by two processes: wet milling and dry grinding. In wet milling, the corn kernel is fractionated into germ, fiber, and starch resulting in several co-products. The starch portion of the corn kernel is converted to ethanol, while the protein, fiber and oil are passed through to the by-products. Only one co-product, distillers' dried grains with solubles (DDGS), is produced when dry milled corn is used for ethanol production. Every bushel of corn (approximately 25 kg) processed for sweeteners, oil, or ethanol generates nearly 7 kg of protein and fiber-rich residues (Leathers, 2003). Currently these by-products are used in low value applications. It has been suggested that ethanol production industry by-products have the potential to be used as inexpensive fermentation media for production of polysaccharides and carotenoids by yeasts or yeast-like fungi (Leathers, 2003). The potential of DDGS for value-added product development has also been explored. Utilization of DDGS as a substrate for biobutanol production by various clostridia species is an area that is drawing attention (Ezeji and Blaschek, 2008).

Today corn is the leading platform to synthesize high value molecules, including pharmaceuticals, through biotechnology. Corn has a number of advantages over other plants for molecular pharming in crops. These advantages include its GRAS (Generally Regarded As Safe) status, well characterized genetic properties, responsiveness to *in vitro* manipulation and gene transfer, well established agricultural infrastructure and efficient biomass production (Ramessar *et al.*, 2008). Initially new traits for herbicide tolerance and pest or disease resistance were introduced into corn. Recent research on metabolic pathways that produce primary and secondary metabolites, specifically the compounds that are beneficial for human health and nutrition, has led to the introduction of novel traits in to corn. In a recent article utilization of advanced biotechnology tools to produce a broad range of high value molecules in corn was reviewed (Naqvi *et al.*, 2011). Some of the compounds successfully produced in transgenic corn include amino acids (Galili and Höfgen, 2002), very long chain polyunsaturated fatty acids (Napier *et al.*, 2006), vitamins (Giuliano *et al.*, 2008; Zhu *et al.*, 2008; Chen *et al.*, 2006; Ishikawa *et al.*, 2006) and minerals (Drakakaki *et al.*, 2005). The emerging regulations that govern how transgenic corn plants and their products are grown, used and traded were also discussed by Naqvi and co-workers (2011).

Utilization of corn stover for bioproducts has advantages over alternative crops that are being examined as feedstock, because corn stover is already produced with grain and does not require dedicated land. The challenge is to determine the sustainable levels of stover that can be collected without adversely affecting ecosystems. Corn fiber is a by-product of the wet-milling process that separates fiber, gluten and germ from starch. Stillage residues from starch fermentation are folded into the corn fiber to produce corn gluten feed and sold as low-value cattle feed. New co-products from corn fiber and gluten feed could also add value to the corn processing industry. For example, it has been shown that corn fiber is a rich source of oryzanol (ferulic acid esters of phytosterols), which has cholesterol lowering properties (Jain *et al.*, 2008). Both corn fiber oil and gum have potential for functional food applications (Yadav *et al.*, 2007).

1.2.3 Barley

1.2.3.1 *Production*

Barley is among the four largest cereal crops (with wheat, maize and rice) grown in the world (Newman and Newman, 2008). In 2008 global barley production was about 155.1 million tonnes (FAO, 2010). The top barley growing countries are the Russian Federation, Ukraine, France and Germany. The United States was ranked as the ninth highest barley grower in the world with 5.3 million tonnes of production in 2008.

Barley is a grass that belongs to the Poaceae family, Triticeae tribe and genus Hordeum (Newman and Newman, 2008). One of the most important mutations associated with the domestication of wild barley to cultivated barley was non-brittle rachis formation, which resulted in efficient harvest without loss of grains (Pourkheirandish and Komatsuda, 2007). Genetic variation in starch structure and composition determine the end uses of barley. Traditionally, barley breeders focused on the improvements that benefit malting and the brewing industries rather than the feed market because malting barley receives premium price (Ullrich and Eslick, 1978). Recently, feed quality of barley has been receiving attention from the breeders, partly because barley is becoming a very important feed crop due to the increasing industrial uses and uncertainty in the availability of corn as feed (Rudi *et al.*, 2006).

The first transgenic barley plants were developed in 1994 (Jähne *et al.*, 1994). Early barley transformation studies aimed at improved grain quality for feed and beverages (Jensen *et al.*, 1996; Horvath *et al.*, 2000) or disease resistance (McGarth *et al.*, 1997; Leckband and Lörz, 1998). These studies have demonstrated that functional recombinant proteins such as enzymes can also be produced in transgenic barley, specifically in grain.

1.2.3.2 *Chemical Composition*

Barley is classified in several ways depending on agronomic properties, chemical composition and end use. The most common barley types are: spring and winter, two- and six-row, hulled and hulless, malting and feed, normal, waxy and high amylose starch, high lysine, high β-glucan, and proanthocyanidin-free barley (Baik and Ullrich, 2008). The chemical composition of barley grain varies significantly with genotype, agronomic practices and environmental conditions (Griffey *et al.*, 2009; Aman *et al.*, 1985; Oscarsson *et al.*, 1996). Barley hull comprises about 13% of the kernel and consists mostly of cellulose, hemicelluloses (xylans), lignin and a small amount of protein (Andersson *et al.*, 1999). Hulls adhere to the caryopsis of the hulled barley while they are not attached or loosely attached to the grain surface of hulless barley. According to Bhatty (1999), hulless barley would ideally have less than 5% adhering hulls. The thickness of the hulls varies. Thick hulls adhere to the caryopsis less firmly than thin hulls. Presence or absence of hulls significantly affects grain composition. Hulless barley generally has lower ash and dietary fiber but higher starch, protein and oil content due to the absence of the hull.

Carbohydrates comprise about 80% of the barley grain. Starch is the major grain component and barley may contain up to 65% starch (Song and Jane, 2000). Starch and protein contents of hulless barley can be as high as those of field corn. A study on the chemical composition of 92 Swedish barley varieties showed that two-rowed barley varieties had slightly higher starch content while six-rowed barleys had higher protein and fiber (Aman *et al.*, 1985). Waxy barley varieties contain 5–8% less starch than that of non-waxy/regular barley varieties (Bhatty, 1999). Starch type and properties have a significant effect on barley end use. Amylopectin comprises 72–78% of the total starch in barley (Bhatty, 1999). Waxy barley varieties contain very high levels of amylopectin. The existence of barley cultivars with 100% amylopectin has been reported (Bhatty, 1997). Zero or waxy, normal and high amylose barley contain 0–5%, 20–30% and up to 45% amylose (based on grain weight), respectively (Baik and Ullrich, 2008). Starch granule size in hulless barley ranges from 2 to 30 μm (Bhatty, 1999; You and Izydorczyk, 2002). Among four types of hulless barley (normal, high, waxy and zero amylose), normal amylose type has the greatest amount of large granules (74.7%). Waxy, zero and high amylose starches consist of 66.4, 43.9 and 19.4% large granules, respectively (You and Izydorczyk, 2002).

The major non-starch carbohydrates in barley comprise (1,3)(1,4)-β-D-glucans and arabinoxylans. β-Glucans, which are mainly present in the endosperm cell walls (Oscarsson *et al.*, 1996), consist of high molecular weight linear chains of β-glucosyl residues polymerized through β-(1-3) and β-(1-4) linkages (Newman and Newman, 2008). The high β-glucan content of barley (2.5–11.3%) is notable (Izydorczyk and Dexter, 2008). High amylose and waxy barley have been reported to contain higher β-glucan than normal amylose type (You and Izydorczyk, 2002). β-Glucan is partially soluble in aqueous solutions due to the molecular, structural and solubility differences of polysaccharides present in its chemical structure (Newman and Newman 2008). The water soluble part of β-glucan produces high viscosity starch slurries that can cause problems during industrial processing. High viscosity mash increases pumping costs and complicates production. Low β-glucan content in the grain leads to low viscosity and little need of expensive enzymes to break it down for efficient processing and fermentation. Cellulose (1,4-β-D-glucan), fructans, arabinoxylans, glucommannan, galactomannan, arabinogalactan and a number of simple sugars and oligosaccharides are also present in barley grain in relatively small quantities.

Although phenolic compounds are minor constituents in barley, they play an important role in the nutritional quality of the grain. Phenolic compounds bind proteins, carbohydrates and minerals, thereby affecting the nutritional and functional value of the bound constituents. The major nutritional concern is the ability of condensed and hydrolysable tannins to bind strongly to large proteins, specifically to proteins high in proline, thereby reducing protein digestibility. Significant differences were found in flavanol and total phenol content among diverse barley genotypes (Griffiths and Welch, 1982). The variations in phenolic content were not correlated with grain size, malting quality and oil and protein contents. Barley grain also contains numerous polyphenolic compounds, including catechin and proanthocyanidin (Aastrup *et al.*, 1984). Proanthocyanidins cause undesirable haze in beer. Fortunately, about 600 proanthocyanidin-free barley mutants have been isolated and used in breeding programs (Jende-Strid, 1993). Oxidation of phenolic compounds to *o*-quinones results in discoloration of the products made with barley after cooking (Sapers, 1993).

1.2.3.3 *Utilization*

It is estimated that about 85% of the world barley production is utilized as feed (Mäkinen and Nuutila, 2004). Malting is the second largest application for barley grain. Only 2% of barley is used for food production in the United States. However, in regions with extreme climates, such as Himalayan nations, Ethiopia and Morocco, barley remains an important food source (Baik and Ullrich, 2008).

Low protein content barley grain is preferred for malting. In general, protein and starch contents are negatively correlated in crops. Higher starch content in barley grain leads to higher extract content in malt. Low protein is ideal for starch production while higher protein content is desirable in feed barley. The health benefits of barley include reduction of blood LDL cholesterol level, glycemic index and body mass, which lead to control of heart disease and type-2 diabetes. Interest in incorporating low tannin barley in human diet is increasing because of its high nutritional value (Newman and Newman, 2008). The beneficial effects of barley are due to the presence of several bioactive compounds, such as β-glucans, tocopherols and tocotrienols in the grain (Baik and Ullrich, 2008). Indeed the US Food and Drug Administration (FDA) approved a health claim verifying that barley contains high levels of β-glucans which help to prevent coronary heart disease when consumed by humans (FDA, 2005). Although today the main source of barley β-glucan in functional foods is oats, barley β-glucan has a potential for new formulations. Co-products from barley milling can be used to recover phenolic compounds and other antioxidants that can be incorporated into functional foods and nutraceuticals, such as high performance sports drinks and dietary supplements, anti-aging cosmetics and sun-screen lotions (Griffey *et al.*, 2009; Newman and Newman, 2008). Barley has the potential as a platform to produce various enzymes, therapeutic proteins and novel high value chemicals through genetic modifications (Jensen *et al.*, 1996; Jende-Strid, 1993; Horvath *et al.*, 2000).

Interest in using barley, particularly winter hulless winter barley, for bioproduct and biofuel production is growing specifically outside the Corn Belt area in the United States (Septiano *et al.*, 2010; Griffey *et al.*, 2009). Ground whole barley grain and flour have been successfully converted to bioethanol (Sohn *et al.*, 2007; Septiano *et al.*, 2010; Gibreel *et al.*, 2009). Production of valuable high protein content DDGS as a by-product improves the feasibility of barley as feedstock for alcohol production for fuel and solvent uses (Ingledew *et al.*, 1995).

1.2.4 Sorghum

1.2.4.1 *Production*

Sorghum is a member of the grass family Poaceae. It is a drought-tolerant crop that grows well with minimal input. In regions with low rainfall, less than 900 mm annual rainfall, sorghum out-performs corn, making it an appealing crop in semiarid regions of the world (Zhan *et al.*, 2003). Total world production of barley was 66.8 million tonnes in 2008 (FAO,