Chapter 1
Waste Biomass: A Prospective Renewable Resource for Development of Bio-Based Economy/Processes

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1.1 Introduction

The sustainable socioeconomic development owing to the continued pace of world economic growth heavily relies upon a secure supply of raw material inputs for agriculture, industry, energy, and related sectors. The development heavily depends on energy, its applications ranging from home appliances, transportation, and industrial processes to supply commodities for our daily needs. To fulfill the energy needs, we consume nearly 500 Quadrillion Btu (QBtu) of energy, and majority of it (92 %) comes from nonrenewable resources, such as petroleum, coal, and nuclear and natural gas (Khanal and Lamsal 2010). Energy demand is expected to escalate by around 44 % by 2030 mostly due to the increasing demand from developing countries, such as India and China. However, today's heavy reliance on nonrenewable resources, especially fossil fuels, is increasingly constrained by economic, political, and

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environmental factors. The dependence on these conventional resources is also accompanied by a heavy reliance on chemical and thermochemical processes. However, due to the continuous and fast depletion of the conventional energy resources and the growing awareness and concern regarding the environmental effects of their utilization, there has been a major challenge in the recent past to identify and develop alternate energy sources. In this regard, the bio-based processes are growing at a faster pace, although currently their role in the global economy is trivial. There are increasing initiatives from both public and private sector interests that support the supply of our energy needs and other industrial products through biological processes and/or biomass resources.

Rapid increase in volume and types of agricultural and industrial waste biomass, as a result of intensive agriculture in the wake of population growth, food processing, and improved living standards, is becoming a burgeoning problem. The waste biomass being rich in carbon and other vital nutrients is highly amenable to biological degradation and emits methane and leachate. Moreover, the open burning of agricultural wastes, such as rice stubble by the farmers to clear the lands, generates CO_2 and other pollutants. Hence, improper management of agricultural and agro-industrial waste biomass is contributing towards climate change, water and soil contamination, and local air pollution which jeopardizes the health of flora and fauna. Furthermore, this waste biomass is of high value with respect to material and energy recovery.

In the context of bio-based economy, the current chapter discusses the different sources, types, and nature of waste biomass. The overview of the different management strategies applied for the value addition of different types of waste biomass is discussed. This chapter also provide insights into the role of biotransformation of waste biomass resources for developing bio-based economy/processes. Finally, the chapter gives a brief summary of directly extractable high-value biochemicals from waste biomass.

1.2 Waste Biomass

Biomass is a renewable resource and refers to any material having recent biological origin, such as plant materials, agricultural crops, and even animal manure. According to National Renewable Energy Laboratory (NREL), biomass can be defined as any plant-derived organic matter. Biomass available for energy on a sustainable basis includes herbaceous and woody energy crops, agricultural food and feed crops, agricultural crop wastes and residues, wood wastes and residues, aquatic plants, and other waste materials including some municipal wastes. Biomass is a very heterogeneous and chemically complex renewable resource. Owing to its natural abundance, sustainability, and often low cost, biomass is a potential alternative to nonrenewable energy sources for production of chemicals. Biomass has a chemical composition comprised of C, H, O, and N, similar to fossil feedstocks which contain C and H. Currently, the annual worldwide production of biomass is estimated to exceed 100 trillion kilograms (Xu et al. 2008). However, presently, only 5 % of chemicals are derived from renewable resources (Lucia et al. 2006). Hence, there is an enormous potential for production of bio-based chemicals to compete with their fossil-derived counterparts.

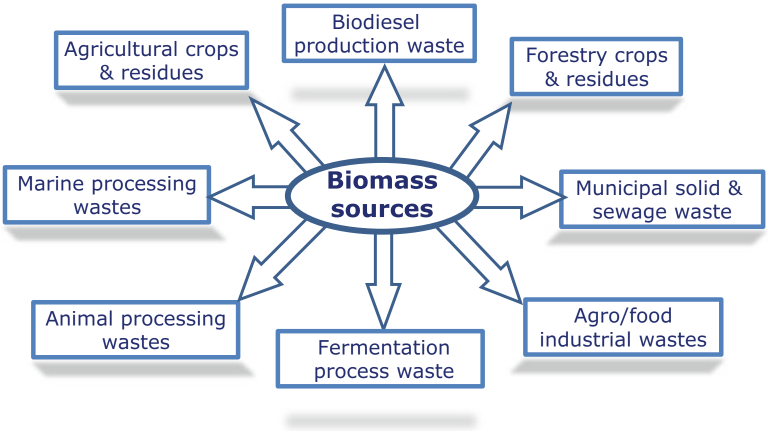

Fig. 1.1 Different types of waste biomass

1.2.1 Types of Waste Biomass/Potential Waste Biomass Resources

Globally, 140 billion metric tons of biomass is generated every year from agriculture. The main sources of biomass waste are given below (Fig. 1.1).

- *Agricultural and agro-industrial wastes*: Agricultural biomass generally comprises of leftovers after grain separation, such as residual stalks, straw, leaves, roots, husk, nut or seed shells, waste wood, and animal husbandry waste. Some common examples are coconut (fronds, husk, shell), coffee (hull, husk, ground), corn (cob, stover, stalks, leaves), cotton (stalks), nuts (hulls), peanuts (shells), rice (hull/husk, straw, stalks), sugarcane (leavings, bagasse, molasses), vegetable wastes, etc.
- *Animal husbandry wastes*: Manure from cattle, poultry, and hogs.
- *Food processing wastes*: Include by-products and leftovers processing, such as fruit pomace wastes (peels, seeds, and pulp) and wastewater sludge, brewery wastes (brewer’s spent grain, spent hops, wastewaters, and surplus yeast), winery wastes (solid by-products include marcs, pomace, and stems and may account on average for almost 30 % (w/w) of the grapes and liquid sludge from organic wastewater treatment plants), starch industry wastes, dairy industry wastes (whey), and meat processing wastes.
- *Forestry residues*: Wood chips, bark, sawdust, timber slash, and mill scrap.
- *Municipal waste*: Solid household wastes, wastewater sludge, waste paper, and yard clippings.
- *Marine processing wastes*: fish industry waste (scales, skin, visceral mass (viscera, air bladder, gonads, and other organs), head, fins, and visceral mass) and crustacean shell and shell fish waste (head and body carapace).

- *Biotechnological industry wastes*: Waste fungal/bacterial/yeast/microalgae biomass.
- *Biodiesel industry wastes*: Crude glycerol from biodiesel production.

This high volume of biomass can be converted to an enormous amount of energy and raw materials. Agricultural waste biomass converted to energy can substantially displace nonrenewable-based fossil fuels, reduce emissions of greenhouse gases (GHG), and provide renewable energy. Biomass is a renewable resource that has a steady and abundant supply, especially those biomass resources that are by-products of agricultural activity. With the increasing global concerns to combat climate change, countries are now looking for alternative sources of energy to minimize GHG emissions. Apart from being carbon neutral, the utilization of biomass for energy decreases reliance on the consumption of fossil fuel, hence, contributing to energy security and climate change mitigation while closing the carbon cycle loop. Currently, as the debate on food versus fuel gets intensified, the biomass can provide extra income to farmers without compromising the production of main food and even nonfood crops.

Although there is an increasing trend on the utilization of biomass for energy and other industrial products, biomass is still largely underutilized and left to rot or openly burned in the fields, especially in developing countries. Mostly, these countries do not have strong regulatory laws to control such environmentally unfriendly practices or either fail to implement them. As a common practice, the burning of agricultural residue (e.g., open field burning of rice stubble) results in air pollution which poses risk to human and ecological health. Biomass is a renewable resource that causes problems when not used. The challenge, therefore, is to convert biomass as a resource for energy and other productive uses.

1.2.2 Nature of Biomass Feedstock

Agricultural crops can be roughly divided according to the composition of their (main) economic products, such as sugar, starch (grains, tubers), oilseed, protein, or fiber crop and crops for specialty products (pharmaceutics, cosmetics, dyes, fragrance, and flowers). Besides the main harvested product, all crop processing systems yield more or less secondary products/by-products and residues. These products may find an application depending on demand and possibilities for economic conversion. Biomass residues can be categorized into three main groups: (1) primary biomass residues, available at the farm; (2) secondary biomass residues, released in the agro-food industry; and (3) tertiary biomass, which is remaining after use of products. The characteristics that influence availability and suitability of the waste biomass as feedstocks are the nature of biomass, moisture content, the density, and the seasonality of supply.

Lignocellulosic biomass comprising forestry, agricultural, and agro-industrial wastes are abundant, renewable, and inexpensive energy sources. Such wastes include a variety of materials, such as sawdust, poplar trees, sugarcane bagasse,

Table 1.1 The main components of different lignocellulose wastes (refs. Nigam et al. 2009; Dhillon et al. 2011b)

Lignocellulose waste	Cellulose (wt %)	Hemicellulose (wt %)	Lignin (wt %)
Sugarcane bagasse	40.0	27.0	10.0
Rice straw	36.2	19.0	9.9
Wheat straw	32.9	24.0	8.9
Barley straw	33.8	21.9	13.8
Rye straw	37.6	30.5	19.0
Oat straw	39.4	27.1	17.5
Corn cobs	33.7	31.9	6.1
Corn stalks	35.0	16.8	7.0
Cotton stalks	58.5	14.4	21.5
Soya stalks	34.5	24.8	19.8
Sunflower stalks	42.1	29.7	13.4
Apple pomace	7.2	–	23.5
Brewer’s spent grain	13.1–25.4	28.4–29.96	11.9–27.8
Citrus waste	8.8	4.4	3.7

waste paper, brewer’s spent grains, coconut coir and shell, fruit pomace and liquid sludge, switch grass, and straws, hull, stems, stalks, leaves, husks, shells, and peels from cereals like rice, wheat, corn, sorghum, and barley, among others. Lignocellulosic biomass is chemically composed of three main fractions: cellulose, hemicellulose, and lignin in varied concentrations (Table 1.1) with smaller amounts of proteins, lipids, and ash (Fig. 1.2). Cellulose is a polymer of glucose (a C6 sugar), which can be used to produce glucose monomers for fermentation to produce a variety of products, such as renewable fuels, platform chemicals, organic acids and biopolymers among others. Hemicellulose is a copolymer of different C5 and C6 sugars including xylose, mannose, and glucose, depending on the type of biomass. Lignin is a branched polymer of aromatic compounds. Both the C5 sugars and the lignin fragments can be used as feedstock for the production of various value-added products including high-value biochemicals in a biorefinery.

These polymers are closely associated with each other constituting the cellular complex of the vegetal biomass. Basically, cellulose forms a skeleton which is surrounded by hemicellulose and lignin (Fig. 1.2). The pretreatment of lignocellulosic biomass helps to disrupt the 3D network structure of lignin, cellulose, and hemicellulose, allowing high yields of fermentable sugars to be produced in subsequent enzymatic hydrolysis. Different pretreatments used for the separation of different polymers in lignocellulosic waste are given in Fig. 1.3. The pretreatments help the enzymes for easy excess for the biomass hydrolysis to simple sugars.

Currently, biomass pretreatment is still a necessary step to establish a cheap sugar platform for bioethanol and other biochemicals. An ideal pretreatment technology should target the three basic requirements: simple process, cost-effective, and high sugar recovery.

Cellulose and hemicellulose are sugar-rich fractions of interest for use in fermentation processes, since microorganisms may use the sugars for growth and

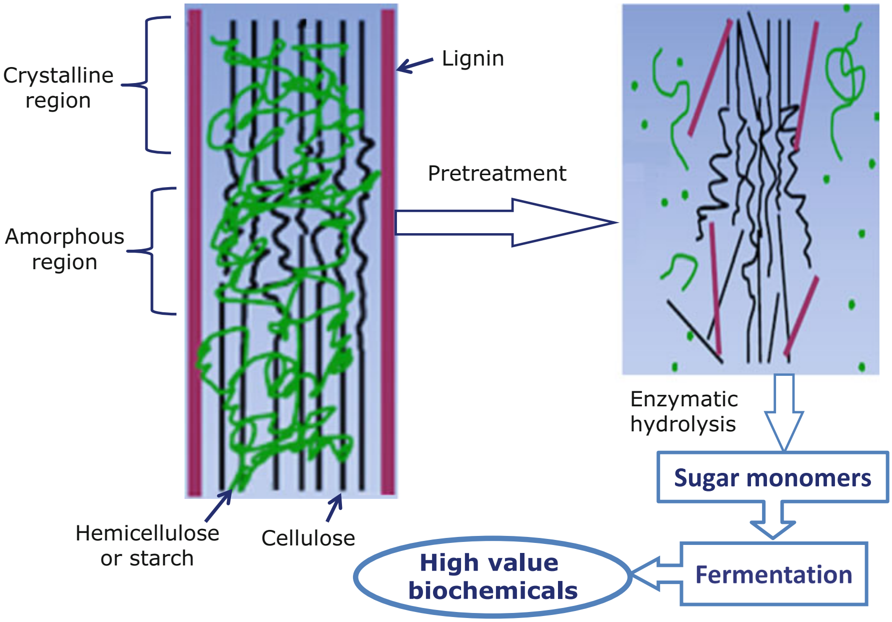

Fig. 1.2 The structure of lignocellulosic material and routes for its biotransformation to high-value biochemicals

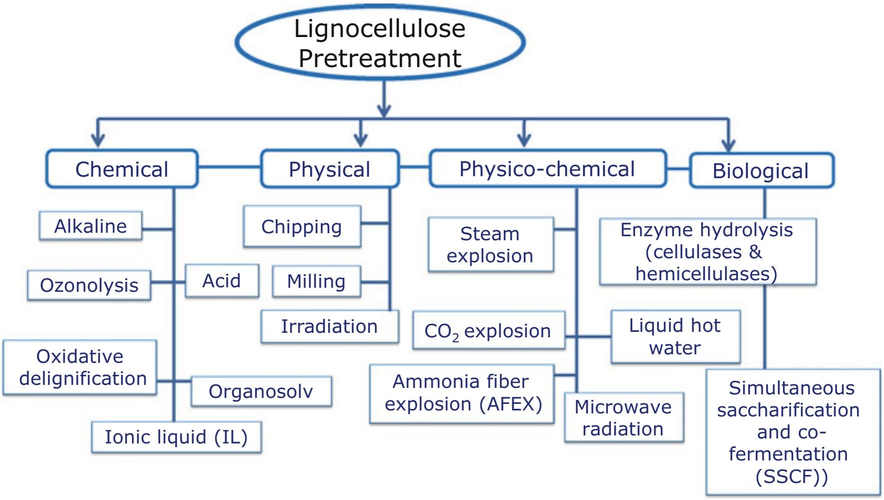

Fig. 1.3 Different pretreatments for the hydrolysis of lignocellulosic biomass

Table 1.2 Examples of biomass residues for different crops

Type of crop	Primary residues	Secondary residues	Residue ratio[a]
Fruits and nuts	Seeds		–
		Fruit pulp, peelings, fruit pomace	0.2–0.4
Vegetables	Leaves, stems, etc.		0.2–0.5
		Peelings, skin	0.1–0.2
Grains (wheat, corn, rice, barley, millet)	Straw (stover)	–	1.0–2.0
	Chaff (hulls, husks)	Bran, cobs	0.2–0.4
Sugarcane	Leaves and tops	–	0.3–0.6
	–	Bagasse	0.3–0.4
		Molasses	–
Tubers, roots (potato, cassava, beet)	Foliage, tops	–	0.2–0.5
		Peels	0.1–0.2
Oil seeds	Hulls		0.2–1.2
		Press cake	0.1–0.2
Sunflower, olive	Foliage, stems		0.2–0.5
Cocos, palm oil	Husks, fronts	Shells	0.3–0.4
Soy, rape, peanut	Foliage	Seed coat, shells	0.3–0.5

Sources: UNDP (2007), Van Dam (2002, Rosillo-Calle et al. (2007)

[a] Residue ratio refers to ratio of dry matter weight to crop produced

production of value-added compounds, such as ethanol, food additives, organic acids, enzymes, among others. Submerged and solid-state fermentation systems have been used to produce compounds of industrial interest from lignocellulosic wastes, as an alternative for valorization of these wastes and also to solve environmental problems caused by their disposal. When submerged fermentation systems are used, a previous stage of hydrolysis for separation of the lignocellulose constituents is required.

Few common primary and secondary residues from agricultural crops are given in Table 1.2. There is significant variation in the quantities available. For instance, in some cases, residues amount to only about 10–20 % of the crop by weight, whereas in other cases, the residues might actually be greater than the original crop. As evident from the Table 1.2, grain crops tend to have the highest overall residue ratio, amounting to as much as double the crop weight. For this reason, utilization of straw from grains should be a much higher priority for utilization of this largely untapped reservoir of biomass resources.

Lignocellulose wastes are accumulated every year in large quantities, causing environmental problems. However, due to their chemical composition based on sugars and other compounds of interest, they could be utilized for the production of a number of value-added products. Therefore, besides the environmental problems caused by their accumulation in the nature, the nonuse of these materials constitutes a loss of potentially valuable sources. .

The underutilized biomass resources from different possible sources, such as primary agricultural production, agro-industries, and municipal waste, are generally available in abundant quantities at negligible costs. Agriculture-based wastes, such

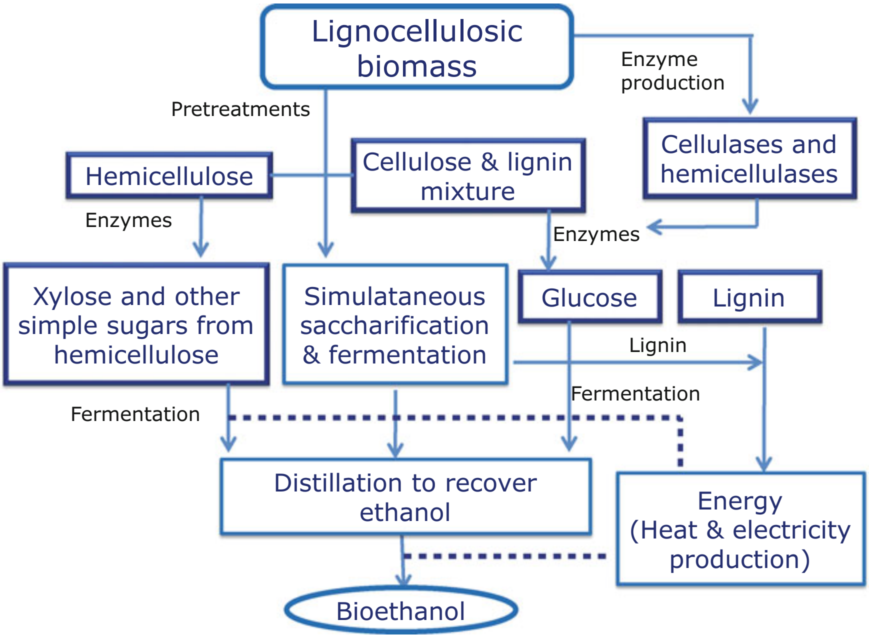

Fig. 1.4 Process showing the pretreatment and enzymatic hydrolysis of lignocellulosic biomass to produce sugar syrups for production of bioethanol

as straws or seed hulls, can be harvested and collected at the farm or at central processing units. Others wastes, such as food industry wastes, are only available in dispersed/diluted forms and need collection systems to be installed at particular industries.

Earlier, agricultural residues were promoted mainly for energy (e.g., bioethanol production) use, often at low efficiency (Fig. 1.4). However, it is now more widely recognized that there are in fact other possible routes that may provide higher-value-added products or could serve as complementary products via coproduction schemes alongside energy applications. The sugar-rich syrups produced after pretreatment and enzymatic hydrolysis of lignocellulosic biomass can be used for the production of high-value products. Currently, such integrated processes are recurring theme in industrial biotechnology development (van Dam et al. 2005). For instance, microalgae/fungal/yeast cultivations involving production of various products result in waste microalgae/fungal/yeast biomass as a by-product. The fungal biomass is rich in chitin which can be extracted and transformed to its deacetylated derivative, chitosan (Dhillon et al. 2012a; Kaur and Dhillon 2013a). Similarly, microalgae biomass resulting after lipid extraction for biodiesel is also rich in carbohydrates, proteins and other products, such as pigments.

Crude glycerol (CG) is a waste by-product of biodiesel production process. For every 100 kg of biodiesel produced by transesterification of vegetable oil/animal fat/microalgae-derived lipids, 10 kg of CG is produced. CG is a carbon-rich source and an emerging and less expensive feedstock for bioprocess technology. CG can be used for the production of a wide range of products, such as ethanol and biohydrogen. More recently, it has been evaluated for the production of high-value biochemical, such as eicosapentaenoic acid, docosahexaenoic acid, glycolipid, biosurfactant, 1,3-propanediol, and antibiotics, such as cephalosporin C (Pyle et al. 2008; Athalye et al. 2009; Liu et al. 2011; Shin et al. 2011; Ferreira et al. 2012).

1.3 Bio-Based Economy/Processes

Recently, a great deal of research is being devoted to the area of sustainable processes (Bruggink et al. 2003). The need for such processes stems from the burgeoning human population and the accompanied required growth in availability of materials and energy (Song 2006). A significant part of the developments is dedicated to bio-based sustainable processes, which make use of renewable feedstocks, such as agro-industrial wastes and industrial by-products, to decrease the use of nonrenewable fossil resources which are depleting very quickly. Owing to the higher efficiency in terms of energy and materials and the reduction of environmentally unfriendly wastes, the bio-based processes are clearly advantageous. In view of bio-based green processes, the identification and assessment of environmentally sound technologies that promote the use of biomass, i.e., conversion of lignocellulosic biomass into energy and raw materials, is highly desired.

The bio-based economy can be defined as consisting of those sectors that derive a majority of their market value from biological processes and/or products derived from natural materials, as compared to products/processes allied with nonrenewable resources and/or purely based on chemical processes. The industrial portion of the bio-economy is somewhat distinct from agricultural, forestry, and other sectors, in the sense that raw materials are utilized to make industrial feedstocks or products or to drive industrial processes. Sustainable feedstock supply is one of the key issues for the evolution towards the bio-based economy. Therefore, the resource base needs to be identified from the perspective of supply and demand. The waste biomass derived from crop residues of food and feed production, forestry residues, fermentation process wastes, food/beverage processing wastes, marine crops and processing wastes, municipal waste, manure and animal products, and biological process-derived wastes are potential candidates/resources towards the realization of a bio-based economy.

The deliberate importance of the bio-economy is linked to those areas in which bio-based products and processes can provide alternative for fossil- or mineral-based products and/or chemical processes. Since the vast majority of industrial products and processes are currently centered on nonrenewable resources and minerals, such substitution has considerable potential to make various industry sectors more sustainable in the long run while also reducing environmental impacts in the near future, especially with regard to the Kyoto protocol aiming towards reducing GHG emissions and land disposal requirements. The utilization of bio-based renewable resources holds great potential value for industries in various sectors, such as energy, platform chemicals, biopolymers, and health/personal care products. In general, a bio-based economy offers many benefits and opportunities:

- New areas of economic growth and development for the many regions especially rural areas that have abundant biomass resources.
- Creation of new innovative business sectors and entrepreneurial skills.
- Improved energy security, by reducing dependence on nonrenewable resources, such as fossil fuels.
- Enhanced economic and environmental linkages between the agricultural sector and a more prosperous and sustainable industrial sector.
- Mitigation of GHG emissions.
- Improved health by alleviating exposure to harmful substances through substitution of natural bio-based materials for chemical and synthetic materials.
- Employment creation and rural development.
- Avoid the competition of land used as raw material for industry with other land uses, especially in relation to food and animal feed (competition for other uses of biomass, especially food, feed, and fiber).

1.4 Value Addition of Waste Biomass

Transformation of waste biomass to various biotechnological products and bioenergy is carried out through different routes. The major routes comprise biological, chemical, and thermal processes and are depicted in Fig. 1.5. The conversion of biomass either can result in final products or may provide building blocks for further processing.

1.4.1 Biotransformation of Biomass

Biological transformation involves the utilization of living organisms or enzymes (biocatalysts) to catalyze the conversion of biomass into specialty and commodity chemicals. Generally, it is considered to be the most flexible mode for conversion of biomass into various industrial products (Dale 2003). Compared to chemical transformations, where high temperatures and pressures are involved, operating conditions for biological transformations are relatively mild. Fermentation is the primogenital and the most fundamental and mature area of biotechnology for biological transformation. For centuries, fermentation was used for preserving and processing food and beverages. Only in the last several decades due to current advancements in biotechnology, it has been used to bring to market a wide variety of fermentation-based products, including platform chemicals, renewable fuels, biopolymers, antibiotics, amino acids, organic acids, and pharmaceuticals using various agro-industrial feedstocks. Some commercial bulk chemicals, such as ethanol, lactic acid, citric acid, acetone, and butanol, have been produced via yeast,

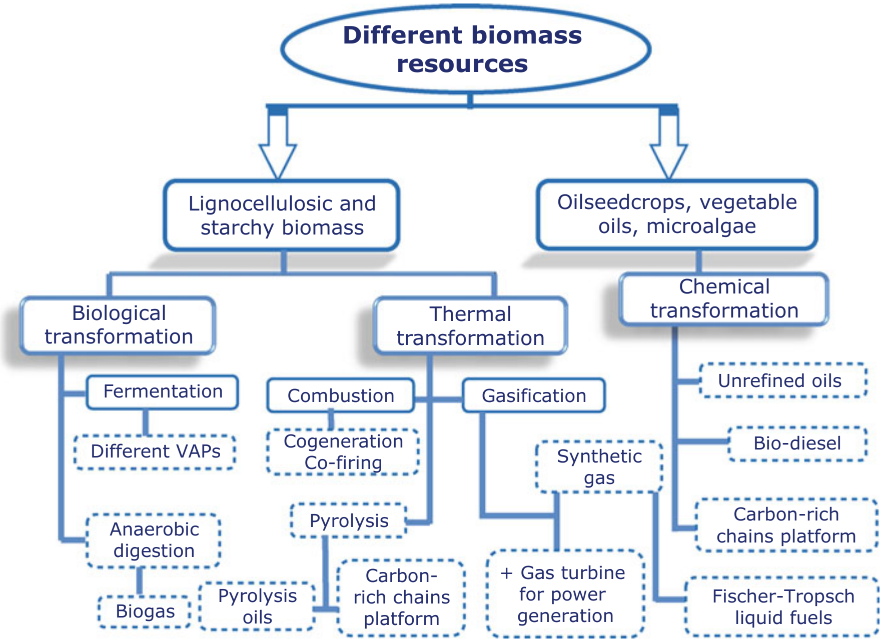

Fig. 1.5 Conversion routes of biomass to bioenergy and other biotechnological products

fungal and bacterial fermentation processes (Atsushi et al. 1996; Huang et al. 2005; Ezeji et al. 2007; Dhillon et al. 2011c).

Recently, there has been increasing interest in the utilization of biocatalysts to transform renewable resources into biochemicals, owing to high yield and selectivity, and fewer by-products as compared to chemical synthesis. Table 1.3 shows the biotransformation of different wastes to high-value biochemicals through different processes. However, due to the metabolic restriction in microorganisms, only a few bulk products currently are produced via fermentation (Danner and Braun 1999). Therefore, development of new technologies to broaden the product range is necessary. Advances in genetic engineering have been viewed as a powerful tool for genetic manipulation of multistep catalytic systems involved in cell metabolism (Zha et al. 2004). Recombinant DNA technology has been used to clone and manipulate gene encoding enzymes in organisms. Recombinant microorganisms, with altered sugar metabolism, are able to ferment sugar to few specialty biochemicals, which cannot be produced by the corresponding wild strain (Danner and Braun 1999). For instance, catechol and adipic acid were produced from glucose using genetically modified *Escherichia coli*. Both glucose and xylose, in cellulosic biomass, have been converted into ethanol by recombinant *Saccharomyces* strains (Anastas and Kirchhoff 2002). Hence, it is imperative that the recombinant strains can be used for the efficient utilization of pentose and hexose sugars from the abundant lignocellulosic biomass. Moreover, immobilized enzyme systems and whole cells have been used to produce various biochemicals from biomass.

Table 1.3 Biotransformation of different wastes to high-value biochemicals through different processes

Waste biomass	High-value product/microorganisms	Remarks	References
Agricultural wastes (vegetable and fruit processing wastes)			
Rice husk and straw	Antibiotic, neomycin by *Streptomyces marinensis*	SSF	Ellaiah et al. (2004)
Sugarcane bagasse/molasses and corn steep waste	Antibiotic, cephalosporin C- by *Acremonium chrysogenum*	SSF	Cuadra et al. (2008)
Wheat bran flour and coconut oil cake	Antibiotic, cyclosporin A by *Tolypocladium inflatum*	SSF	Survase et al. (2009)
Peanut shells, corn pomace/husk/cob, wheat bran, cassava peels, coconut oil cake, groundnut oil cake, groundnut shell, and rice husk	Antibiotics—tetracycline *and* oxytetracycline (*Streptomyces strains*); rifamycin B (*Amycolatopsis sp.*)	SSF	Asagbra et al. (2005a, b); Mahalaxmi et al. (2010); Vastrad and Neelagund (2012)
Apple pomace and sludge	Natural antioxidants, biopolymers, organic acids	SSF and SmF	Dhillon et al. (2011c); Ajila et al. (2011); Gassara et al. (2012)
Apple pomace	*Antibiotic*, mevastatin by *Streptomyces fradiae*	SSF	Vastrad and Neelagund (2011)
Grape pomace	Various antioxidant compounds	Extraction	Knoblich et al. (2005)
Tomato peel and seed by-products	Carotenoids from peel: lycopene, lutein, *β*-carotene, and *cis*-*β*-carotene. Carotenoids from seeds: Lycopene and other carotenoids	Extraction	Strati and Oreopoulou (2011); Spatafora and Tringali (2012)
Date palm juice by-products	Xanthan exopolysaccharides (EPS)—*Xanthomonas campestris*	43.35 g/l	Ben Salah et al. (2010)
Cassava residues	Astaxanthin by *Phaffia rhodozyma* (*yeast*)	0.060 mg/g	Yang et al. (2011)
Cassava bagasse	Polyketide mix (pigment)—*Monascus sp.*	SSF	Carvalho et al. (2007)
Citrus peel, mango kernel, banana peel, litchi pericarp and seeds, olive pomace, pomegranate peels and seeds	Different phenolic compounds	Antimicrobial compounds	Arogba (2000); Puravankara et al. (2000); Someya and Okubo (2002); Obied et al. (2005); Tehranifara et al. (2011); Duan et al. (2007)

Strawberry/blackberry/raspberry pomace	Anthocyanins, tannins, starches, saponins, polypeptides and lectins, polyphenols, lactones, flavones, and phenons	Antimicrobial compounds	Krisch et al. (2009)
Beet root pomace	Phenolic, flavonoid betalaine	Antimicrobial compounds	Canadanovic et al. (2011)
Citrus peels	Flavonoids, saponins, steroids, terpenoids, tannins, and alkaloids	Antimicrobial compounds	Ashok et al. (2011)
Guava bagasse	Epicatechin, quercetin and caffeic	Antimicrobial compounds	Martin et al. (2012)
Beet molasses, sugarcane molasses, waste residue of rice bran oil	2-phenylethanol, acetoin, vanillin	Aroma compounds	Etschmann et al. (2003); Xiao et al. (2007); Zheng et al. (2007)
Food processing industry waste			
Starchy wastewater	Poly(β-hydroxybutyric) (PHB)—*Alcaligenes latus*	55 % (g/g)	Yu (2001)
Potato peels	Gallic acid, caffeic acid, vanillic acid	–	Zeyada et al. (2008)
Carrot peels	Phenols, β-carotene	–	Chantaro et al. (2008)
Cucumber peels	Chlorophyll, pheophytin, phellandrene, caryophyllene	–	Zeyada et al. (2008)
Dairy waste			
Whey	β-carotene by *Blakeslea trispora* (*fungus*)	170 mg/g	Varzakakou et al. (2010)
Reconstituted whey	β-carotene by *Sporobolomyces roseus* (yeast)	0.55 mg/g	Marova et al. (2012)
Whey	Pigment canthaxanthin—*Dietzia natronolimnaea* (bacteria)	0.020 mg/g	Khodaiyan et al. (2008)
Beverage production wastes			
Brewer's spent grain—requires no preliminary detoxification steps and overall production is favored by high initial xylose concentrations	Xylitol (sweetener), a rare sugar that exists in low amounts in nature—used to combat dental caries, diabetes, disorders in lipid metabolism, and parenteral and renal lesions and to prevent lung infection, otitis, and osteoporosis	Acid hydrolysis and yeast fermentation	Mussatto and Roberto (2005, 2008)

(continued)

Table 1.3 (continued)

Waste biomass	High-value product/microorganisms	Remarks	References
Brewer's spent grain	Ferulic acid, hydroxycinnamic acid	(1) alkaline hydrolysis—0.3 % (2) Esterase from *A. niger*—3.3 %	Bartolomè et al. (1997, 2002, 2003)
Brewer's spent grain	Pullulan—an extracellular water-soluble microbial polysaccharide produced by strains of *Aureobasidium pullulans*	Maximum conc. (6.0 g/l) after 72 h of fermentation	Roukas (1999)
Wine industry waste (pomace—grape seeds, skins, stems)	Polyphenolic antioxidants—e.g., gallic acid, anthocyanins, proanthocyanidins, flavanols, and hydroxycinnamates	Extraction	Guendez et al. (2005); Pinelo et al. (2005); Makrisa et al. (2007)
Marine processing wastes			
Fish industry waste	Fish oil	Extraction	
Crustacean shell wastes	Carotenoid pigments—astaxanthin, canthaxanthin, 4-hydroxyechinenone, 3-hydroxycanthaxanthin, echinenone, isocryptoxanthin, β-carotene	Extraction	Pokorny et al. (2001)
Biotechnology industry wastes			
Fungal-based processes waste	Biopolymers—chitin/chitosan, proteins, pigment, and minerals	Extraction	Dhillon et al. (2012a)
Microalgae-based processing waste	Pigments, proteins, antioxidants, polysaccharides, vitamins, triglycerides, polyunsaturated fatty acids	Extraction	Mata et al. (2010)

Currently, research efforts are ongoing to isolate, identify, characterize, and even tailor microorganisms and enzymes in order to better utilize renewable resources to produce structurally diverse and complex chemicals. Biotransformation of biomass to higher-value chemicals provides advantages of high yield and selectivity, as well as minimum waste streams. However, there are still problems with current biological transformation technologies including both upstream and downstream processes. The capital costs related to energy requirements, such as pretreatment, sterilization, production, agitation, aeration, temperature control, and finally recovery of target products from aqueous systems with low product concentration, result in high-cost processes (Danner and Braun 1999). Further, considerable investment is required to make processes highly efficient and continuous (Dodds and Gross 2007). Therefore, there are research opportunities in the development of new economic biological transformation technologies which could effectively transform biomass into high-value biochemicals.

Biological conversion or biotransformation is a well-established process and comprises of fermentation and anaerobic digestion. Sugar and starchy crops provide the main feedstocks for the process of fermentation in which a microorganism converts the sugars into bioethanol. As an economic alternative to costly sugars, lignocellulosic biomass can be used as feedstock after pretreatment which helps to break it down into simple sugars. The pretreatment can be carried out by enzymes or acids. Although acid hydrolysis offers the more mature conversion platform, enzymatic hydrolysis appears to offer the best long-term option in terms of technical efficiency. Besides its recalcitrant structure, the efficient hydrolysis of lignocellulosic wastes and subsequent conversion of sugar syrups to various value-added products also depends upon various other factors, such as crystalline structure of cellulose, amount and nature of lignin present, and production of various inhibitory compounds during acid hydrolysis (Fig. 1.6). Lignocellulosic conversion would greatly increase the supply of raw materials available for production of various high-value products. The lignin residues could be used as fuel for the energy required and even providing surplus energy, resulting in significantly improved energy balances and resulting potential reductions in GHG emissions. The following sections discusses the potential of two underutilized wastes (marine processing and biotechnological process wastes) for the production of high-value biochemicals.

1.4.1.1 Biotransformation of Marine Processing Wastes

Large quantities of marine processing by-products are accumulated as aquaculture waste and shells of crustaceans and shellfish. Generally, the fishery by-products find applications for production of low-economic-value products, such as fish oil, fishmeal, fertilizer, pet food, and fish silage (Choudhury and Gogoi 1995). Currently, studies have identified a number of high-value bioactive compounds from fish wastes, such as fish muscle-derived peptides, collagen and gelatin, fish oil (source of omega-3 fatty acids), fish bone (consists of 60–70 % of inorganic substances, mainly composed of calcium phosphate and hydroxyapatite), and other

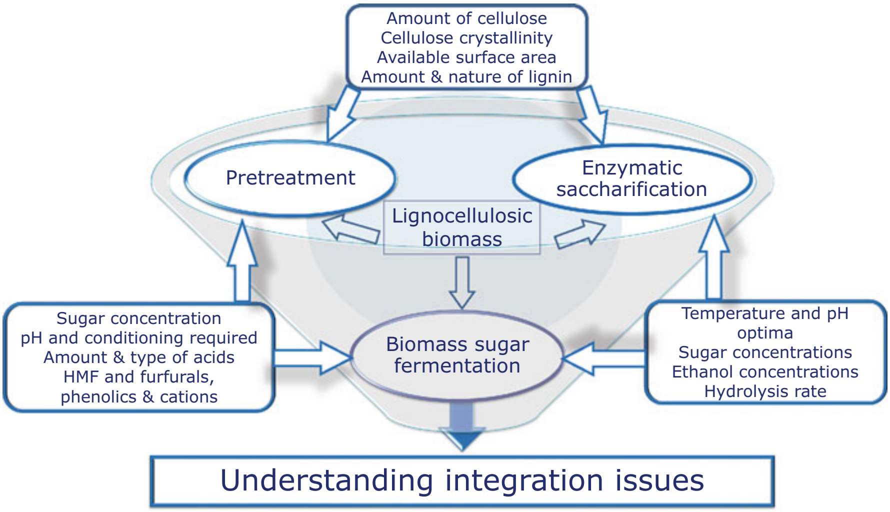

Fig. 1.6 Schematic diagram showing different aspects of lignocellulosic hydrolysis and its value addition

visceral organs (rich in a range of proteolytic enzymes including pepsin, trypsin, chymotrypsin, and collagenases) (Kim et al. 2001; Je et al. 2005). Lipid-based compounds that can be recovered from fish waste include fish oil, omega-3 fatty acids, phospholipids, squalene, vitamins, and cholesterol. Recovery of oil or lipids from fish industry waste offers not only the revenue generation but makes it suitable for other applications, such as spreading on land as a fertilizer or feedstuffs in swine diets to meet the protein requirements and as a substitute for common protein sources (i.e., soybean meal and commercial fishmeal) (Esteban et al. 2006).

Similarly, the other important class of by-products from marine bioprocessing plants includes crustacean shells and shellfish wastes mainly in the form of head and body carapace. These body parts comprise 48–56 % depending on the species. The efficient utilization of shellfish and crustacean shell by-products also becomes an environmental priority due to increased quantity of accumulation from processing plants as well as slow natural degradation of these materials. Shellfish and crustacean shells are a potential source of high-value biochemicals, such as biopolymers (chitin, chitosan), pigments (a carotenoid, astaxanthin), minerals, and proteins (Kaur and Dhillon 2013a, b) (Fig. 1.7). Most crustaceans, such as shrimp, lobsters, and crabs, are important reservoirs of natural carotenoids, such as astaxanthin and its esters (Sachindra et al. 2005).

However, the recovery of shell waste products, such as pigments and proteins, through chemical methods is complicated and the biological value of chemically extracted compounds is low. Additionally, these methods generate large quantities of hazardous chemical wastes. This has led to amplified interest in biotechnology research regarding the identification and extraction of high-grade, low-volume bioactive compounds produced from crustacean shell wastes. Recently, fermentation

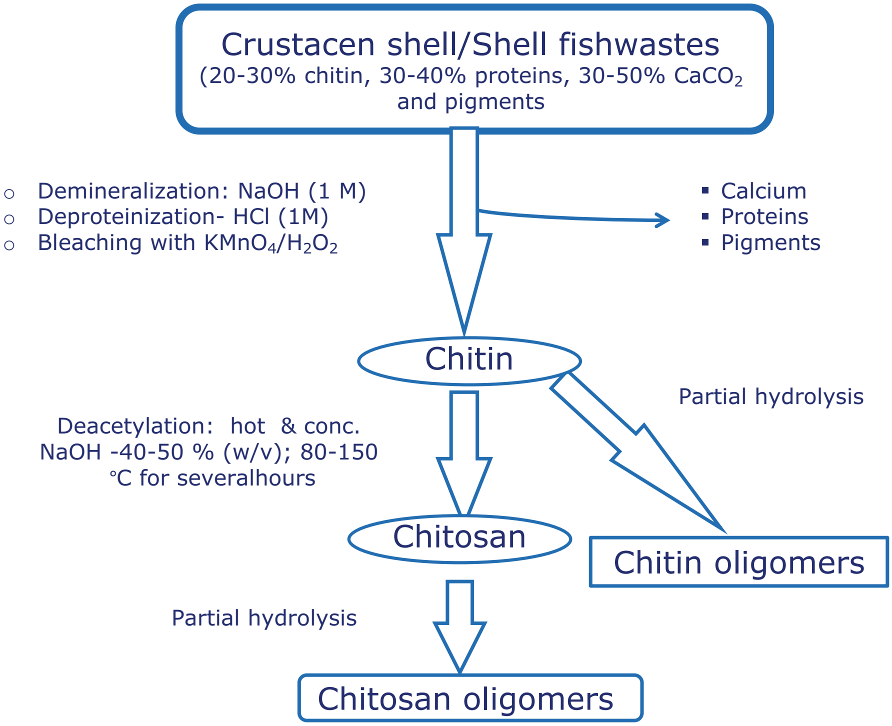

Fig. 1.7 Schematic diagram for preparation of proteins, pigments, chitin, chitosan, and their oligomers from marine wastes

has also been reported as a suitable and economic method to extract carotenoid pigments from crustacean shell wastes. These bioactive compounds can be extracted and purified with technologies varying from simple to complex. Furthermore, some of these bioactive compounds have been identified to possess nutraceutical potentials that are beneficial in human health promotion. Therefore, development of new technologies in exploration of new bioactive compounds from marine processing wastes will alleviate costs associated with its safe disposal. The bioactive compounds from marine processing wastes will add high value to marine waste and represent unique challenges and opportunities for the seafood industry.

The commercial applications of marine fish processing by-products are expanded every year. However, their applicability as bioactive compounds and their nutraceutical properties are not well described. High-value profit can be achieved by identifying bioactive compounds and exploring their nutraceutical properties and pharmaceutical and personal care applications. Identification of nutraceutical potential of natural compounds is a growing field and marine processing by-products represent potential feedstocks for this purpose. To date, only a limited number of bioactivities have been identified from isolated compounds and mandate future research developments to apply them for the human health promotion.

1.4.1.2 Biotransformation of Fermentation/Biotechnological Process Wastes

The advancements in bioprocess technology led to commercialization of various biotechnological/fermentation processes for the production of various bioproducts, such as food and beverages, organic acids, antibodies, pharmaceutical products, and renewable fuels among others. These microorganism-mediated processes result in thousands of tons of waste biomass, such as of yeast, bacteria, fungi, and algae. These waste are rich in various kinds of bioactive compounds, such as biopolymers, proteins, lipids, and pigments, among others.

Chitin and chitosan occur naturally in some fungi (*Mucoraceae*). Fungal cell walls are composed of polysaccharides and glycoproteins. Polysaccharides, such as chitin and glucan, are the structural components, whereas the glycoproteins, namely, mannoproteins, galactoproteins, xylomannoproteins, and glucuronoproteins, form the interstitial components of fungal cell walls (Bowman and Free 2006; Dhillon et al. 2012a). Commercially, chitin and chitosan are mainly derived from the marine processing wastes, such as shrimp, crabs, squids, and lobsters shell by chemical deacetylation, using a hot concentrated base solution (30–50 % w/v) at high temperatures (<100 °C) for a prolonged time (Dhillon et al. 2012a). However, the chitosan obtained by such treatments suffers some inconsistencies, such as protein contamination, inconsistent levels of deacetylation, and high molecular weight (MW), which results in variable physicochemical characteristics (No et al. 2000). There are some additional problems, such as environmental issues, due to the large amount of waste (concentrated alkaline solution), seasonal limitation of seafood shell supply, and high cost (Wu et al. 2005). In this context, production and purification of chitin and chitosan from the cell walls of waste fungal mycelium (Fig. 1.8) offers the advantage of being environmentally friendly and provides greater potential for a consistent product (Dhillon et al. 2012a; Kaur and Dhillon 2013a). Additionally, β-glucan can also be isolated from the mycelia chitosan–glucan complex and has important applications in biomedicine (Pomeroy et al. 2001).

Edible mushrooms are produced and consumed on a large scale. The amount of waste remaining after removing the edible part mainly consists of stalks and mushrooms with irregular dimensions and shapes and accounts for 5–20 % of the total production volume. In the USA alone, mushroom production results in nearly 50,000 metric tons of mushroom waste material per year with no suitable commercial application (Wu et al. 2005). The huge amount of wastes of edible mushrooms, such as *Agaricus bisporus*, *Lentinus edodes*, *Pleurotus* species, and *Volvariella volvacea*, among others, can be potentially used for the extraction of the high-value-added product chitosan, which nowadays finds promising applications in various fields (Dhillon et al. 2012a; Kaur and Dhillon 2013a; Dhillon et al. 2013).

Aspergillus niger strains are extensively used for the bioproduction of citric acid (CA) (Dhillon et al. 2011a, b, c, 2012b, c). The annual worldwide production of CA is estimated to be 1.7 million tons, which results in 0.34 million tons of *A. niger* mycelium waste per year, and furthermore, the industry continues to expand with an annual growth rate of 5 % (Wu et al. 2005; Dhillon et al. 2011c). *A. niger* strains contain approximately 15 % chitin, which can be separated and transformed into chitosan (Dhillon et al. 2012a).

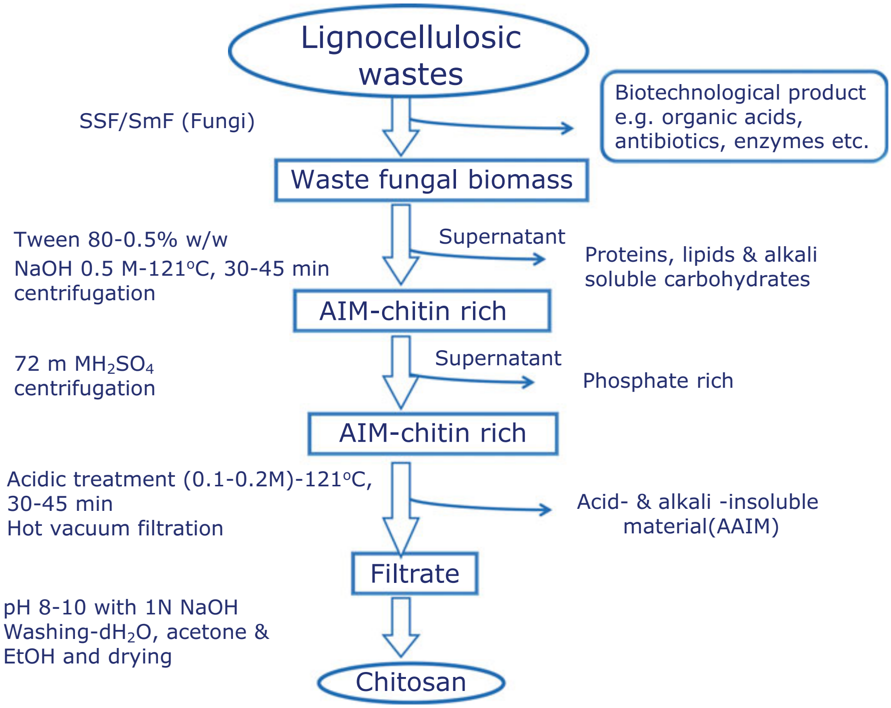

Fig. 1.8 Extraction of chitosan and other products from waste fungal mycelium (*SmF* submerged fermentation, *SSF* solid-state fermentation)

Penicillium chrysogenum is widely used for the large-scale production of antibiotics. As a by-product of the antibiotic industry, a large amount of *P. chrysogenum* mycelia waste is managed by incineration. Only a small percentage is used as an additive for cattle feed and in agriculture as fertilizers. Similarly, another important microbial strain, *Rhizopus oryzae*, is widely used in the food industry. Some yeast strains, such as *Saccharomyces cerevisiae*, find commercial applications in the brewery and bioethanol production. These yeasts strains are rich source of proteins and biopolymers. The development of bio-based economy mandates need to develop some integrative technology to utilize the unlimited waste mycelium resulting from fermentation industries which has not only a commercial advantage but also an ecological benefit.

1.4.2 Direct Extraction of Biochemicals from Biomass

Generally, the waste biomass contains many extractable compounds of high value which can be extracted directly from waste biomass. Fruit industry wastes, such as apple pomace (AP), are rich source of natural antioxidant compounds. Due to health and environmental awareness, sustainable food production and value addition of agro-industrial wastes is the principal issue in the agro- and food processing industry. AP is an excellent source of natural antioxidants, such as catechins, procyanidins, caffeic acid, phloridzin, phloretin glycosides, quercetin glycosides, chlorogenic acid, among others. Apple pomace, including seeds, contains polyphenolics with the strong antioxidant activity of quercetin glycosides, phloridzin, and its oxidative products (Schieber et al. 2003; Sanchez-Rabaneda et al. 2004; Guyot et al. 2007; Cetkovic et al. 2008). Similarly, many other fruit wastes are rich source of various natural oxidants and hence can be viewed as potential sources of bioactive phenolics.

Ferulic acid, a precursor for vanillin, occurs in a relatively high concentration in the form of xylan polysaccharide ester in corn fiber. The ferulic acid was extracted from corn fibers using novel fungal and bacterial feruloyl esterases (Shin et al. 1978). Vanillin is commonly used in the flavor and fragrance industries and it can be recovered by alkaline oxidation of lignin in the presence of a copper catalyst (Azadbakht et al. 2004). Ecket et al. (2007) described a more benign and cost-efficient method to extract vanillin from lignin using a gas-expanded liquid. Arabinogalactan and quercetin dihydrate were isolated from larch wood (Kuznetsova et al. 2008). Direct extraction of high-value biochemicals is a promising pathway for utilizing renewable resources, irrespective of scale. From an economic point of view, the extraction of high-value-added chemicals from biomass can be the most profitable, though the availability and variety of chemicals are limited.

Brewer's spent grains are the by-products of mashing process in brewery which is carried out in order to solubilize the malt and cereal grains to ensure adequate extraction of the wort (water with extracted matter). Following different separation strategies, the amount of BSG generated could be about 85 % of the total by-products (Tang et al. 2009). BSG is a readily available, high-volume, low-cost by-product of brewing and is a potentially valuable resource for industrial exploitation (Dhillon et al. 2012d). According to Stojceska et al. (2008) about 3.4 million tons of BSG from the brewing industry is produced in the EU every year. Ferulic (4-hydroxy-3-methoxy-cinnamic acid) and *p*-coumaric acid (4-hydroxycinnamic acid) are the most abundant phenolic acids in BSG (Bartolomè et al. 1997, 2002, 2003). The extraction of these high-value biochemicals opens up new possibilities for the use of BSG. Ferulic acid exhibits a number of potential applications, such as natural antioxidant, food preservative/antimicrobial agent, anti-inflammatory agent, photoprotectant, and as a food flavor precursor, while *p*-coumaric exhibits chemoprotectant and antioxidant properties (Bartolomè et al. 2002; Mussatto et al. 2007). Similarly, winery waste which is composed of solid pomace is rich in antioxidant polyphenols which can be extracted by various mild hydrolysis methods.

The food processing industry produces large volumes of both solid and liquid wastes. These wastes pose increasing dumping and severe pollution problems and represent a loss of valuable biomass and nutrients. In the past they often have been dumped or utilized without treatment for low-value applications, such as for animal feed or as fertilizers. However, due to the increasing environmental awareness as well as for economic motives and the need to conserve energy and new materials, recently new methods and policies for waste handling and treatment have been introduced in the recovery, bioconversion, and utilization of valuable constituents from these wastes. With the advancement in technology, food processing wastes might have a potential for recycling raw materials or for conversion into useful products of higher value as a by-product, or even as raw material for other industries, or for the use as food or feed/fodder after biological treatment. The biotransformation of food processing residues is receiving increased attention regarding the fact that these residual matters represent a possible and utilizable resource for transformation to high-value products.

1.5 Conclusions and Future Prospects

Interest in waste biomass utilization has increased dramatically over the last few years as a renewable resource alternative for fossil fuels as well as an input into other industrial processes. The environmental impacts of waste biomass utilization for energy and other commodity products are quite significant and are arguably greater in scale and scope than any other class of energy resources, viz., renewable or nonrenewable, due to the intensive use of land, water, and other resources. Developing countries have a vast agricultural resource base for alternatives for bioenergy and industrial biotechnology. The majority of biomass is found in rural areas resulting from agriculture processes. Therefore, the bio-economy has the potential to provide much needed diversification of the rural economy. The biomass has been viewed as an alternative to energy; while it has potential it can also be used as input into various biotechnological processes for production of various consumer products. Production of value-added by-products serves to expand a bio-based economy or sustainable development, offering alternatives for fossil fuel-based products and facilitating a lower overall cost of production. A greater reliance on bio-based resources and biological processes is an inevitable part of an overall sustainability transition, and thus the main questions for technical innovation and policy development relate to how to positively impact the nature and pace of such changes. In many developing countries, biomass is currently a significant source of energy and materials only for local and traditional uses. The biomass is generally used inefficiently with very few higher-value-added product markets. Bio-based renewable resources can provide raw materials for many new and growing biotechnological industries while also stimulating rural development, job creation, and GHG reduction. In assessing the options and strategies of a bio-based economy, economic, environmental, and social issues need to be addressed to ensure that sustainable development objectives can be met.

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