Part I

Introduction

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Introduction

Much has been learnt about the detrimental effects of finite fossil resources on the environment, society and economy, making their current exploitation to satisfy human needs unsustainable. This has renewed the surge of biomass as a low carbon source of energy, combined heat and power (CHP), liquid transportation fuels known as biofuels, gaseous fuels, chemicals (commodity and specialty) and materials (polymers and elements). The complex site configurations arising from integration between biomass feedstocks, processes and products are known as biorefineries. Biorefineries have brought opportunities of using biomass feedstocks in an efficient way to ensure benefits to the environment and society as well as long-term economic viability against fossil based counterparts. The call for cost-effective and sustainable production of energy, chemical and material products from biomass gives light for the conception of biorefineries. In the most advanced sense, a biorefinery is a facility with integrated, efficient and flexible conversion of biomass feedstocks, through a combination of physical, chemical, biochemical and thermochemical processes, into multiple products. The concept was developed by analogy to the complex crude oil refineries adopting the process engineering principles applied in their designs, such as feedstock fractionation, multiple value-added productions, process flexibility and integration. For sustainable biorefinery design, the nature and range of alternatives for feedstocks, process technologies, intermediate platforms and products are important to know. In this chapter, the fundamental features and principles of biorefinery configurations are introduced alongside some research problems, concepts and tools to assess the sustainability of biorefineries.

1.1 Fundamentals of the Biorefinery Concept

1.1.1 Biorefinery Principles

The generation of products from biomass is not new. Biorefinery is a concept created for efficient processing of biomass coming from plant, animal and food wastes into energy, fuels, chemicals, polymers, food additives, etc. There are several definitions for biorefineries emphasizing the key elements of sustainability, integration and multiple value-added productions. The biorefinery concept has been developed by analogy to crude oil refineries. Biorefining must embrace the process engineering principles applied to crude oil refining for their successful development.

Table 1.1 shows the processing principles used in modern crude oil refineries and their adoption in the concept of biorefineries. As in petroleum refineries, biorefineries must follow the strategy of feedstock separation into more useful and treatable fractions, known as *platforms* or *precursors*. Then each fraction must create a production line to diversify their product slate and to increase profit and adaptability for low carbon pathways. A combination of various high throughput technologies allows conversion of the whole ton of biomass into commodity (e.g., biofuels, electricity) and specialty products (e.g., chemical building blocks replacing petrochemicals). These combinations create a complex system

Biorefineries and Chemical Processes: Design, Integration and Sustainability Analysis, First Edition.
Jhuma Sadhukhan, Kok Siew Ng and Elias Martinez Hernandez.

Companion Website: http://www.wiley.com/go/sadhukhan/biorefineries

Table 1.1 Principles adopted in biorefinery from its analogy to a crude oil refinery.

Oil Refinery	Biorefinery
Mature process technology (e.g., thermal and catalytic cracking, reforming, hydrotreatment)	Mature and innovative process technology (e.g., biomass gasification, pyrolysis, fermentation, anaerobic digestion, hydrocracking and bioseparations)
Use of every crude oil fraction	Use of every biomass fraction and components
Process flexibility and product diversification	Process flexibility and product diversification
Coproduction of valuable chemical building blocks	Coproduction of valuable and highly functionalized chemical building blocks
Cogeneration of heat and power	Cogeneration of heat and power
Process integration	Process integration and design for sustainability
Economy of scale	Scale according to biomass logistics but must be maximized to benefit from economy of scale

able to exchange material (waste streams, platforms and products) and energy streams to supply their requirements and achieve self-sufficiency. The complexity gives opportunities for process integration to increase energy efficiency, save water and reduce wastes and emissions that will contribute to the overall economic and environmental sustainability of the biorefinery. Thus, biorefinery design must be carried out by adopting process integration strategies and sustainability concepts in every stage.

The learning experience of the processing technologies, capability of processing various feedstocks, diversification of product portfolio, and application of process integration will make biorefineries into highly integrated, resource efficient, and flexible facilities. Although this is the final goal of the biorefinery concept for biomass processing, there is still a long way to go for biorefineries to reach such an advanced stage of development. New processing technologies and process engineering concepts are to be developed; there are barriers to overcome and lessons to learn in order to make the full biorefinery concept a reality.

1.1.2 Biorefinery Types and Development

The biorefinery principles have been practised to some degree in corn wet mill, pulp and paper and, more recently, biofuel plants by introducing additional production lines and process flexibility in the search for improved process economics. These facilities are considered as the precursors to biorefineries. Three types of biorefineries can be identified according to their phases of development defined by their degrees of complexity and flexibility, shown in Figure 1.1[1].

I. Single feedstock, fixed process and no product diversification. Examples include dry-milling bioethanol plants using wheat or corn, and biodiesel plants using vegetable oils, which have no process flexibility and produce fixed amounts of fuels and coproducts.
II. Single feedstock, multiple, and flexible processes and product diversification. An example is a wet-milling plant using corn and various processes with the capability to adapt multiple productions depending on product demands and market prices.
III. Multiple, highly integrated and flexible processes allowing conversion of multiple feedstocks of a different or the same nature into a highly diverse portfolio of products. Flexible biorefineries will allow switching between feedstocks and blending of feedstocks for conversion into products.

The biorefinery Type III corresponds to the biorefinery concept in its broader extension. Various schemes for this type of biorefinery are under extensive research and development. The most workable one is the *lignocellulosic* feedstock based biorefinery for the processing of *agricultural residues*, *straw*, *wood*; *wastes such as sewage sludge and municipal solid wastes or refuse-derived fuels*, etc. Other developments include the two-platform biorefinery which combines biochemical with thermochemical processes and, more recently, the algae biorefinery. Materials and tools involved for sustainable designs of these processes are discussed in this book.

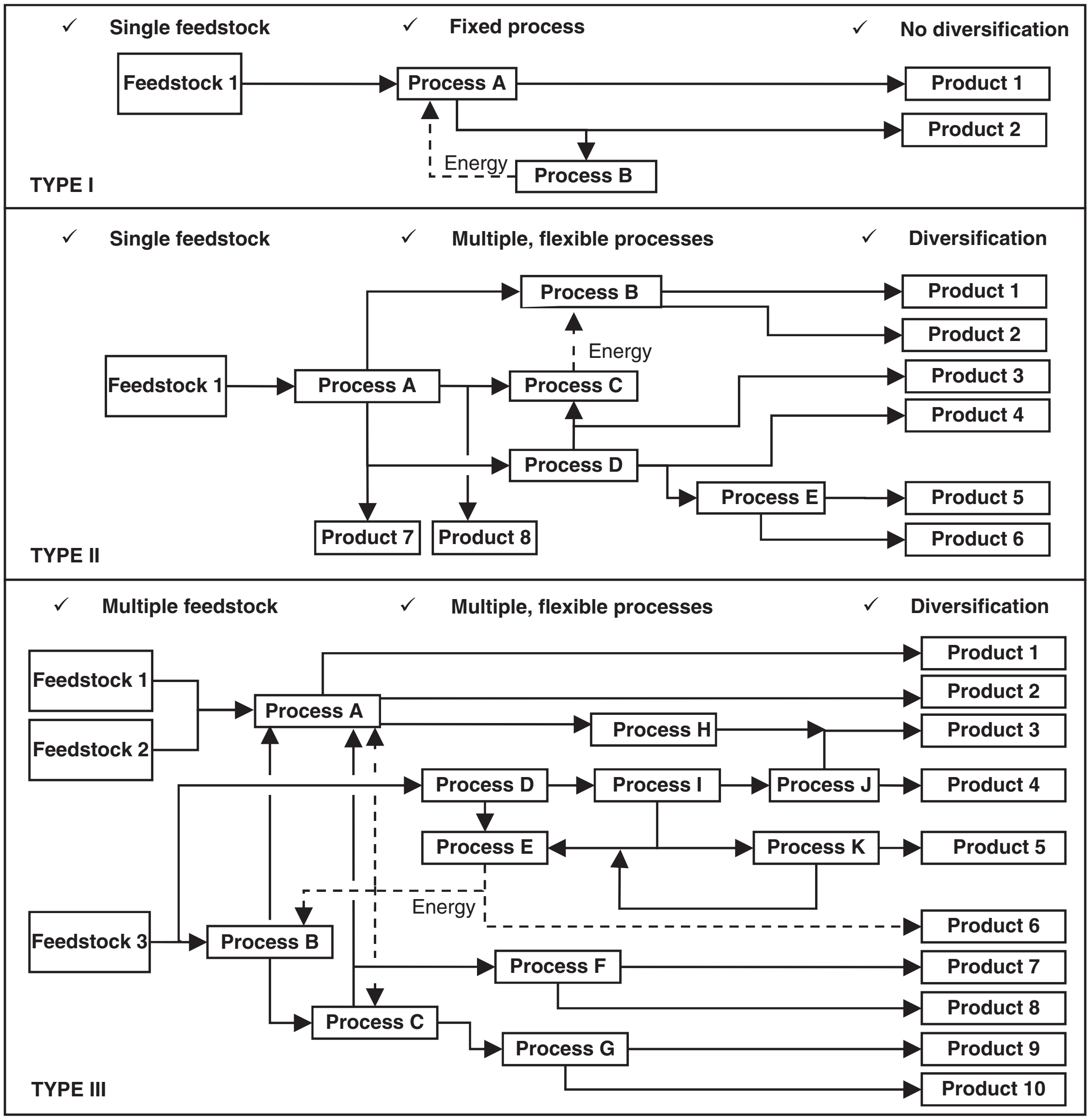

Figure 1.1 *Biorefinery types according to the phase of development. (Reproduced with permission from Kamm, Gruber, and Kamm (2006)*[1]*. Copyright © 2006 WILEY-VCH Verlag GmbH & Co. KGaA.)*

1.2 Biorefinery Features and Nomenclature

The basic features of a biorefinery can be grouped into *feedstock(s), processing technologies, platforms* and *products*, discussed in Sections 1.3 to 1.5. A biorefinery configuration is formed by a combination of at least one of each of those features. Thus, in a biorefinery, the biomass feedstock is first fractionated into *intermediate components* or *platforms*, which are further processed to produce a set of end products.

A systematic nomenclature would help to identify different biorefinery configurations. Attempts have been presented in the literature to name and classify biorefineries according to one of their features, that is, feedstock, platform or product. However, the lack of consistency in criteria can lead to ambiguity. A nomenclature system based on the four biorefinery basic features, accepted by the International Energy Agency (IEA) within the Bioenergy Task 42 "Biorefinery," is explained[2]. The features in a biorefinery configuration are identified and classified according to groups and subgroups in feedstocks, processes, platforms, and products. Then, the biorefinery is named following the structure:

$$\text{Number of platforms (name(s))} + \text{biorefinery for} + \text{products} + \text{from} + \text{feedstock (name(s))}$$

In an example shown in Figure 1.2, the biorefinery has the following features: wheat as feedstock which is a starch crop, C6 is the platform followed in this case, and the products are bioethanol and animal feed (dried distillers grains with solubles, DDGS). This biorefinery system is then named as: one platform (C6 sugar) biorefinery for bioethanol and

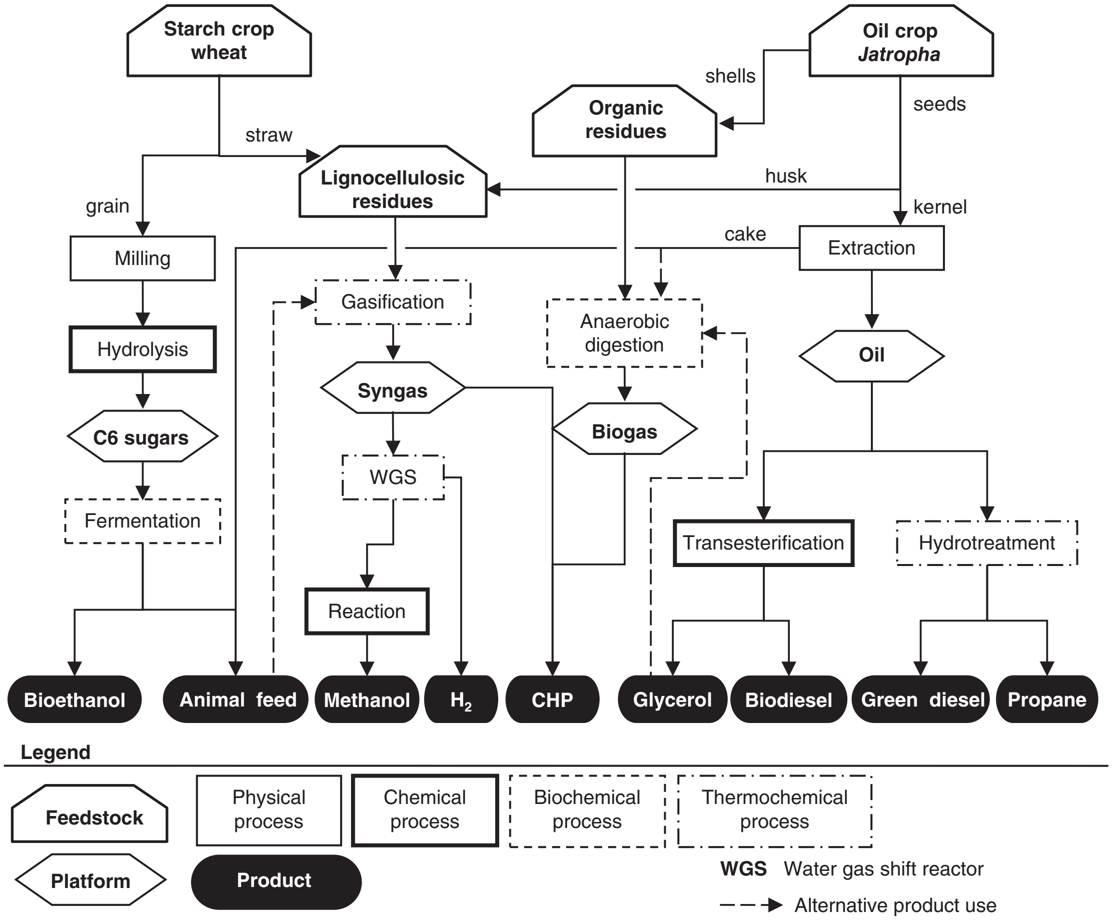

Figure 1.2 *Example of two biorefinery configurations. One platform (C6 sugar) biorefinery for bioethanol and animal feed from starch crops (wheat). One platform (oil) biorefinery for biodiesel, glycerol and animal feed from oil crops (*Jatropha*). Note that a syngas or biogas platform can also be integrated for the use of residues or cake.*

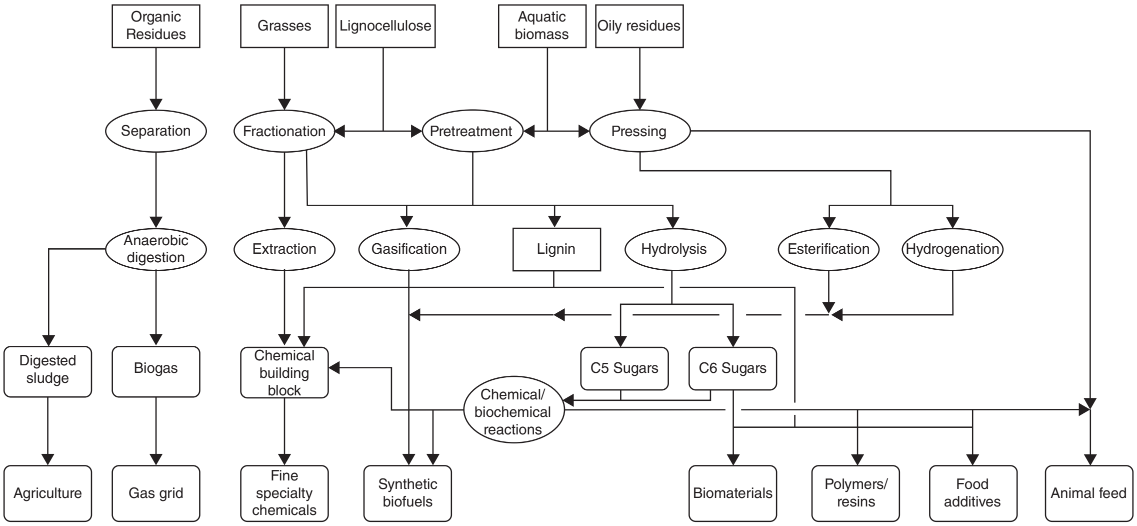

Figure 1.3 *Network of interlinked biorefinery configurations. (Reproduced with permission from Cherubini et al. (2009)*[2]*. Copyright © 2009 Society of Chemical Industry and John Wiley & Sons, Ltd.)*

animal feed from starch crops (wheat). For classification purposes, the biorefinery type corresponds to the description without the names between brackets, that is, “C6 sugar platform biorefinery for bioethanol and animal feed from starch crops.” A biorefinery with the same process and products but using corn instead of wheat falls within this classification. As shown in Figure 1.2, a syngas or biogas platform can also be integrated for the use of residues or cake.

The various options for the biorefinery features forming alternative configurations can be combined into a major *superstructure* network for optimization. A network structure including all possible inter- and intraprocess connections is called a superstructure. A superstructure poses a great engineering and mathematical challenge to solve for optimal network configurations. Figure 1.3 shows a network including some possible configurations mentioned and their combinations for biorefineries[2]. It can be seen from this network that feedstocks can be converted to almost any platform in one or several steps. In addition, one particular product can be produced from different combinations of feedstocks and using different processing pathways. This facility can be integrated with utility systems to create a biorefinery design. The biorefinery system needs to be colocated with feedstock supply systems and synergistically integrated with product distribution systems to form a complete value chain.

Much research will have to go into the creation of a renewable future. It will be a shifting from a fossil energy era into a renewable energy era and into a biomass era – mainly for chemical and material production. Biomass is going to be the only renewable source of carbon. A timeline for the displacement of fossil fuel energy by biomass is shown in Figure 1.4. Current biofuel technologies include biodiesel and bioethanol production (known as *first generation biofuel*) from food crops. *Second generation biofuels* include lignocellulosic ethanol and biomass-to-liquid (BTL) fuels, which use the lignocellulosic crops such as miscanthus, wood, etc., rather than food crops as the feedstock. Advanced biorefineries can be lignocellulosic, green and multiplatform biorefineries. It is expected that renewable energy would widely and commercially be available on a large scale within the next few decades. The motivations and the rationale for this book are to help renewable energy deployment of substituting fossil resources, by training engineers in multidisciplinary areas.

1.3 Biorefinery Feedstock: Biomass

The biorefinery concept relies on the availability of lignocellulosic biomass as feedstock. The biomass feedstock is the starting point for planning and design of biorefineries. Its current and potential availability influences the scale and

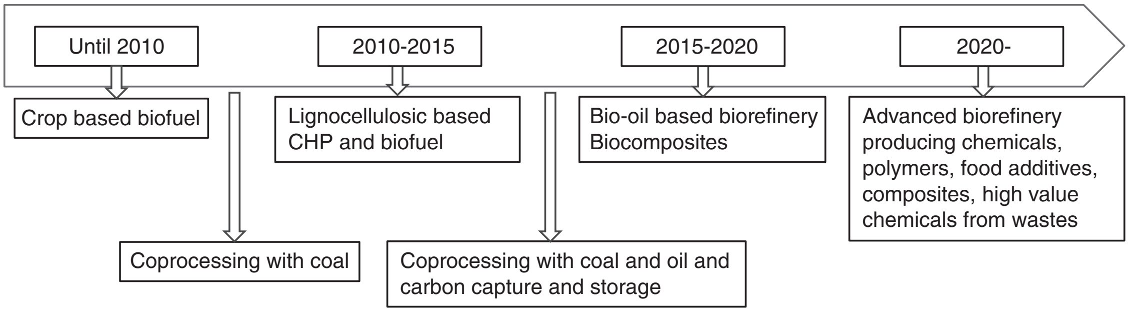

Figure 1.4 *Estimated timeline for biorefinery deployment.*

location of a biorefinery, whilst its nature decides the processes that can be used and the platforms and products that can be generated from it.

A comprehensive definition of *biomass*, including all the potential biomass as renewable feedstock, is: "*any organic matter that is available on a renewable or recurring basis, including dedicated energy crops and trees, agricultural residues, algae and aquatic plants, wood and wood residues, animal wastes, wastes from food and feed processing and other waste materials usable for the production of energy, fuels, chemicals, materials*."[1] The biodegradable fraction of industrial and municipal waste is also included.

The biomass production phase reduces the global warming potential impact of the biorefinery products. Biomass from plants or algae or marine biomass is advantageous over fossil resources since they naturally capture CO_2 from the atmosphere during photosynthesis. For this reason, biomass is considered as carbon neutral or balanced feedstock and biorefinery is an effective way to alleviate climate change. However, food crops, i.e., corn, wheat, sugarcane, oil seeds, etc., to produce bioethanol and biodiesel have generated a sensible debate about deviating food and feed for biofuels and thus its socioeconomic consequences. As a response, alternative feedstocks are being explored, including lignocellulosic residues, *Jatropha curcas*, algae, etc. Lignocellulosic feedstocks are seen as promising options if the technological barriers for the breaking of their complex structure into functional products are overcome. Crop residues have the advantage to be cheap and do not need added land for production. However, lignocellulose processing pathways are yet to be fully developed to reduce the environmental footprint, by learning from the successes and failures with the first generation crops and fossil resources.

As the biorefinery processes and technologies reach a mature state of development and efficiency, the cost of biomass will dominate the economics of biorefineries. Cheap waste feedstocks, municipal waste, sludge and algae, etc., are essential to make the processes profitable and to deliver products that can be competitive with fossil based products. If the high crude oil prices trend remains, biomass processing may become economically attractive. A list of dedicated biomass feedstocks for biorefining is shown as follows.

1. Agricultural and forestry residues and energy crops: wood, short rotation coppice, poplar, switchgrass and miscanthus.
2. Grass: leaves, green plant materials, grass silage, empty fruit bunch, immature cereals.
3. Oily crops and *Jatropha*.
4. Oily residues: waste cooking oils and animal fat.
5. Aquatic: algae and seaweed.
6. Organic residues: municipal waste, manure, and sewage.

1.3.1 Chemical Nature of Biorefinery Feedstocks

In order to develop conversion processes for a biomass feedstock, it is important to understand its chemical nature. Biomass is composed of *cellulose*, *hemicellulose*, *lignin*, ash and a small amount of extractives with a wide range of chemical structures. The components of interest for biorefining are discussed as follows.

Table 1.2 *Chemical compositions of some lignocellulosic feedstocks*[3].

Feedstock	Cellulose	Hemicellulose	Lignin	Protein	Ash
Corn stover	26	38	23	5	6
Soybean straw	14	33	14	5	6
Wheat straw	29	38	24	5	6
Switchgrass	29	37	25	4	6
Miscanthus	24	43	19	3	6
Alfalfa	12	27	8	3	2
Sweet sorghum	14	23	11	17	9
Willow	49	14	20	–	5

Sugars. Sugar crops, for example, sugarcane and sugar beet, convert CO_2 and solar energy into the readily fermentable sugars: glucose and fructose ($C_6H_{12}O_6$, known as C6 sugars) mainly forming the disaccharide sucrose ($C_{12}H_{22}O_{11}$). Sugarcane in Brazil and sugar beet in the EU are used for bioethanol production.

Starch. Cereals, for example, corn, wheat, sorghum; roots and tubers, for example, cassava and sweet potato; store energy in the form of minute granules of starch ($(C_6H_{10}O_5)_n$). Starch is a polymer of glucose and consists of amylose and amylopectin as the main structural components, which can be easily broken down to fermentable C6 sugars by enzymatic hydrolysis. Wheat and corn are used as feedstock for bioethanol production in the EU and US, respectively. These cereals also contain protein, oil, and fibers that are recoverable as value-added products.

Lignocellulose. Lignocellulosic feedstocks include wood, grasses, and agricultural and forestry residues composed mainly of cellulose, hemicellulose and lignin forming a three-dimensional polymeric composite called lignocellulose. Table 1.2 provides typical chemical compositions for some lignocellulosic feedstocks. Cellulose is a polysaccharide having the generic formula $(C_6H_{10}O_6)_n$ yielding individual glucose monomers on hydrolysis. Hemicellulose is a macromolecular polysaccharide forming a mixture of straight and highly branched chains of both C5 and C6 sugars. Their hydrolysis produces the C6 sugars: glucose, mannose and galactose and the C5 sugars: xylose and arabinose. C5 hemicelluloses ($(C_5H_8O_4)_n$) include xylan, arabinan and mannan, and they can occur in large amounts (20 to 40%) in corncobs and corn stalks, straws and brans. The lignin fraction ($C_9H_{10}O_2(OCH_3)_n$) consists of complex phenolic polymers. The dominant monomeric units in the lignin polymers are benzene rings bearing methoxyl, hydroxyl and propyl groups that can be attached to other units. Lignin poses an obstacle to microbial digestion of structural carbohydrates because of its physical barrier and the depressing effect on microbial activity due to its content of phenolic compounds. Lignin has the potential to unlock the market for high functional material and chemical production, thus making biorefinery commercially practical.

Lipids. Most lipids in biomass are esters formed between one molecule of glycerol and one, two or three of fatty acids called monoglycerides, diglycerides and triglycerides, respectively. These water-insoluble esters are the main fraction of interest in the oily feedstocks including oil seeds, algae, animal fat, waste cooking oil and other food residues. Common triglycerides having the same saturated fatty acid in their structure include trilaurin ($C_{39}H_{74}O_6$), trimyristin ($C_{45}H_{86}O_6$) and tripalmitin ($C_{51}H_{98}O_6$). Triolein ($C_{57}H_{104}O_6$) and trilinolein ($C_{57}H_{98}O_6$) are triglycerides of the unsaturated oleic (one unsaturated bond) and linoleic acid (two unsaturated bonds), respectively. The content of free fatty acids, that is, not esterified, is critical especially in biodiesel production. The content of saturated and unsaturated fatty acids and triglycerides affects the properties of the biodiesel produced (via esterification and transesterification) and the amounts of auxiliary raw materials required for their processing.

Proteins and other components. Proteins are polymers of natural amino acids bonded by peptide linkages. Proteins are found in most biomass, but are particularly abundant in cereals and herbaceous, perennial species. They do not represent a viable feedstock for fuels, but may be useful for production of amino acids and other nutraceutical products. Protein can be extracted from feedstock or by-products as a food and feed additive. Other valuable biomass components include vitamins, dyes, flavoring, pesticides and pharmaceuticals, which can be extracted as value-added products before conversion.

Organic residues. Some residues such as fruit shells, plant pruning, food processing wastewater, animal manure, domestic food waste, etc., are rich in organic matter and nutrients. They may contain high amounts of water and can be exploited as substrate for anaerobic digestion to generate biogas or hydrogen.

1.3.2 Feedstock Characterization

Information about the composition and properties of a biomass feedstock is helpful to evaluate its suitability for a process technology. Chemical analyses and physical properties characterizing a biomass feedstock are described as follows.

Chemical composition. Chemical composition plays a major role in defining the processes for pretreatment and further processing of biomass. Feedstocks rich in sugars can be readily fermented, whilst starch rich feedstocks need an enzymatic pretreatment to release the sugars for fermentation. High protein content can be a negative factor for bioethanol production from wheat, thus needing pre-extraction by mechanical processes such as pearling before the saccharification and fermentation to bioethanol production. The processes of arabinoxylan extraction from wheat bran before fermentation to bioethanol production are shown in detail in the literature[4–6]. For oily feedstocks, free fatty acid content determines whether a feedstock needs to be treated by esterification using acid catalyst before transesterification to biodiesel production. The processes including mechanistic studies are shown in detail in later literature[7–9].

Compositional analysis is useful in biochemical processing of lignocellulosic feedstocks. For bioethanol production, a biomass feedstock with a high ratio of [(cellulose+hemicellulose)/lignin] is desirable for high yields. Other relevant analyses include fatty acid profile analysis in oil and fat processing, type and content of nutrients in biochemical processing of organic residues, proximate and ultimate analyses in thermochemical processing, etc.

Proximate and ultimate analyses. These analyses are relevant to combustion and other thermochemical processes. Proximate analysis shows the volatile matter and fixed carbon fractions. The volatile matter is the fraction (mainly organic matter) released in the form of gas when a biomass is heated to high temperature (950 °C) and indicates how easily the biomass can be combusted, gasified or partially oxidized. The remaining fraction is the fixed carbon, generally determined by the difference between the results of volatile matter, moisture and ash contents. Ultimate analysis shows the elemental composition (C, H, O, N, S and, sometimes, Cl) of biomass. Table 1.3 shows the proximate and ultimate analyses including higher heating values (HHV) of some biomass feedstocks. The main compositional difference between biomass and crude oil is the amount of oxygen, which can be up to 45% by mass in biomass, whilst oxygen is practically absent in crude oil. Biomass also has a lower carbon content than crude oil. As a result, biomass has a lower calorific value than fossil resources and produces unstable bio-oil upon pyrolysis due to the presence of oxygen in biomass. Bio-oil can be stabilized and can become an important platform compound for advanced biorefinery design (Figure 1.4), giving rise to transportation fuels, commodity chemicals and CHP[10–13]. The configurations are ready to capture carbon dioxide for an overall negative carbon footprint[13–16].

Ultimate analysis provides insights into the biomass quality as fuel. For example, high O/C and H/C ratios reduce the energy value of a fuel due to the lower energy contained in carbon–oxygen and carbon–hydrogen bonds than in carbon–carbon bonds[22]. Ultimate analysis can also be useful in identifying potential processing problems such as

Table 1.3 *Proximate and ultimate analyses of some biomass feedstocks.*

Component	Corn Stover[a]	Wheat Straw[b]	Rice Husk[c]	Rice Straw[c]	Switchgrass[d]
Proximate analysis (% *weight*)					
Moisture	11.75	4.10	8.20	10	8.38
Ash	4.63	6.04	13.17	10.40	7.33
Volatile matter	69.72	73.27	58.93	60.71	69.63
Fixed carbon	13.90	16.59	19.70	18.90	14.66
HHV (MJ kg^{-1})	18.6	18.9	16.6	17.2	18.3
Ultimate analysis (% *weight*)					
Carbon	42.37	45.36	39.05	39.13	42.6
Hydrogen	4.83	6.52	4.58	5.15	4.9
Nitrogen	1.93	0.77	0.18	0.60	0.6
Oxygen	34.40	36.92	34.75	36.24	36.11
Sulfur	0.09	0.29	0.04	0.09	0.08

[a] Sebesta Blomberg, 2002[17].
[b] Bridgeman *et al.*, 2008[18].
[c] Jangsawang, *et al.*, 2007[19], HHV calculated after Gaur and Reed, 1998[20].
[d] Carpenter *et al.*, 2010[21], HHV calculated after Gaur and Reed, 1998[20].

NO_x, SO_x and H_2S emissions and corrosion. In general, sulfur concentrations are much lower in biomass than in fossil resources, decreasing the potential for SO_2 emissions. Generation of H_2S, however, can be a problem in gasification, anaerobic digestion and in particular downstream energy generation processes: fuel cell, Fischer–Tropsch, gas turbine and methanol synthesis, etc. Hence, sulfur components are removed using scrubbing and Claus processes from the gas produced.

Moisture content. For thermochemical processes, high moisture content in biomass feedstock indicates poor quality because energy is required for heating and evaporating the water, hence lowering the efficiency. Crop residues have the lowest moisture content with 4−18% on a weight basis, while aquatic biomass can have up to 85−97% on a weight basis. High moisture feedstock (e.g., sugarcane, marine biomass, manure, wet organic residues) can be better for biochemical processes that are carried out in the aqueous phase. However, moisture can affect feedstock during storage, degrading its quality, even for biochemical processing. Moisture is also an issue for biomass logistics since biorefineries will need a consistent supply of feedstock.

Ash content. The solid residue formed from the inorganic mineral matter in biomass after high temperature treatment is called *ash*. In comparison to carbon and crude oil, biomass has a low ash content. However, an ash chemistry leading to low melting point solids called *tar* represents operational challenges to thermochemical processing. Ash can be recovered as fertilizer or for mineral extraction after, for example, rotating cone filtration.

Heating value. The energy content of biomass is a crucial parameter for thermochemical processes producing heat and power. The heating value (HV) indicates the energy content of a substance and refers to the heat released when the substance is combusted. The *higher heating value* (*HHV*) includes the latent heat contained in the water vapor recoverable by condensation. The *lower heating value* (*LHV*) indicates the heat available excluding that heat. The form and the actual amount of energy recovered from a feedstock will depend on the conversion process applied. Energy efficiency of conversion is often reported on an HHV or LHV basis. The heating value is also affected by the nature and content of the biomass components, that is, cellulose, lignin, etc.

Density and particle size. The bulk density of biomass feedstock is an important characteristic with regard to transportation. The particle size and density also impact on the handling, feeding and storage system requirements. Particle size and size distribution may affect the fluid dynamics in biochemical and thermochemical processing.

Digestibility parameters. Parameters indicating the digestibility or biodegradability properties of organic wastes are relevant in biochemical processing, particularly in anaerobic digestion for biogas production. These parameters include the dry matter content as total solids (TSs), the biodegradable fraction or volatile solids (VSs) as a percentage of TS, the nutrient ratio C:N and chemical composition. Water content is also important in terms of equipment sizing and fluid dynamics of the mixture. Compositional analysis is required to identify likely inhibitory problems due to high ammonia content or the presence of toxic components like antibiotics, pesticides, heavy metals, etc. Carbohydrates and proteins are beneficial due to fast conversion rates. All the factors above affect the yield and methane content of the biogas produced.

Feedstock characterization is also useful to track quality variations and respond accordingly by manipulating process conditions. In addition, composition and properties of biomass components are essential input to perform process simulations under different scenarios. Wooley and Putsche (1996) developed a database for biomass components present in lignocellulosic feedstock and bioethanol production[23]. Chang and Liu (2010) developed models for property prediction of triglycerides and other components involved in biodiesel production[24]. Information on composition, energy content, and other properties for a wide range of biomass can be found in the following databases:

- IEA Task 32 biomass database (www.ieabcc.nl)
- Phyllis biomass database (www.ecn.nl/phyllis/)
- University of Technology of Vienna biomass database (www.vt.tuwien.ac.at/biobib)
- US Department of Energy (DOE) biomass feedstock composition and property database (http://www1.eere.energy.gov/biomass/printable_versions/feedstock_databases.html)

Table 1.4 shows the main feedstock characteristics and their relevance to different process types. Both biomass properties and process requirements must be evaluated simultaneously to develop a technically and economically feasible and environmentally sustainable biorefinery design.

Table 1.4 *Feedstock characteristics and their relevance to different process types. (Reproduced with permission from Klass (1998)[25]. Copyright © 1998, Elsevier.)*

Characteristic	Physical	Thermochemical	Biochemical	Chemical
Chemical composition		×	×	×
Proximate and ultimate analyses		×		
Moisture content	×	×	×	×
Ash content	×	×	×	
Energy content	×	×		×
Density	×			
Particle size/size distribution	×	×	×	×
Digestibility/biodegradability			×	
Nutrient type and content			×	

1.4 Processes and Platforms

Biomass refining through fractionation and upgrading allows an efficient use of biomass feedstock and generation of value-added products through valorization. As discussed in the earlier section, biomass is a complex feedstock made up of carbohydrate and phenolic polymers that need to be broken down to access to more treatable and versatile components. Biomass components need to be modified according to the type of products desired. For example, oxygen content needs to be reduced for biofuels since oxygen reduces their energy content and makes them polar, hydrophilic and unstable, which are problematic for storage, transportation and blending. On the other hand, oxygen provides functionality for chemical building blocks. Thus, various processes are necessary to extract, depolymerize, deoxygenate or modify functionality of biomass components to produce useful and valuable chemical and material products. Biorefinery processes can be classified as follows.

- *Mechanical/physical.* These processes are mainly used to perform size reduction (e.g., chopping, milling) and densification of feedstock (e.g., chipping, briquetting) or physical separation (e.g., mechanical fractionation, pressing, distillation, centrifugation, filtration, decantation, extraction, etc.) of components and products.
- *Biochemical*. These processes include anaerobic digestion, fermentation and other enzymatic conversions using microorganisms. Biochemical processes have the potential to convert substrates into final products in one or few steps and using mild reaction conditions (e.g., fermentation at 20−32 °C), which can lead to a more sustainable production due to less energy requirements and less waste generation.
- *Chemical*. These processes (e.g., hydrolysis, esterification and transesterification, deoxygenation, hydrodeoxygenation and decarboxylation, steam reforming, electrochemistry, Fischer–Tropsch and methanol synthesis, etc.) are used to change the chemical structure of a substrate. They may need high temperature and pressure. They need catalysts to keep the operating temperature and pressure at moderate levels and increase reaction conversion and desired product yield and purity.
- *Thermochemical*. Thermochemical processing is a special case of chemical processing, involving thermal decomposition, thermal oxidation, etc. In these processes (e.g., pyrolysis, gasification, combustion, and supercritical processing) feedstock is treated under medium to high temperature (350−1300 °C) and/or pressure with or without a catalyst.

The processes are able to generate products via a building block called *platform*. The following platforms deduced from biomass are established.

1. Syngas (using gasification)
2. Biogas (using anaerobic digestion)
3. Bio-oil (using pyrolysis)
4. C5 sugars (using fractionation into hemicellulose)
5. C6 sugars (using fractionation into cellulose)

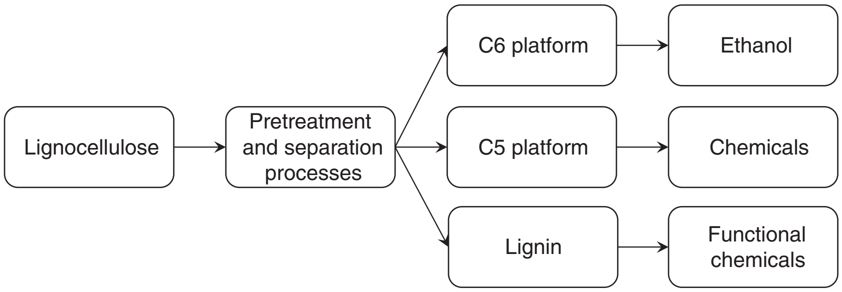

Figure 1.5 *Conceptual block diagram for various productions upon lignocellulose fractionation into cellulose, hemicellulose, and lignin.*

6. Lignin (using fractionation of lignocellulose)
7. Oils (using extraction)
8. Hydrogen (using chemical, thermochemical routes)

Biomass is best utilized for value-added chemical production (medium-to long-term solution) and has the least value-added from energy production (short-term solution). Biomass being the only alternative renewable carbon source, naturally occurring polymers from biomass and chemicals upon conversion of biomass can be extracted in various ways to replace a fossil resource.

Biomass-derived products broadly fall into the following categories: (1) energy and low molecular weight chemicals, (2) natural polymers, (3) monomers and aromatics. Their optimal production relies on how effectively functionalities, conversion, separation and purification steps are coupled. Thus, process integration inspired heuristics are needed to find synergies in driving forces to couple functionalities (e.g., reaction chemistry, electrochemistry and physical chemistry) to perform within one vessel. By this, the incentive is to save energy and capital costs as well as to increase productivity and selectivity. Furthermore, heuristics may be generated by applying the concepts of industrial symbiosis, where waste from one process becomes an essential feedstock to another. Once a conceptual process configuration is generated by applying such process synthesis heuristics, optimization is needed to find the best configuration (e.g., least cost and least environmental impacts) for desired products.

The most exploitable route is the depolymerization and conversion into chemicals. There are two ends of the product type from biomass: (1) energy and low molecular weight chemicals and (2) natural polymers. Figure 1.5 shows the conceptual block diagram for various productions from three major components of lignocellulose: C5 and C6 platforms and lignin. Figure 1.6 shows the essential difference between the hydrolysis process for decomposition of lignocellulose

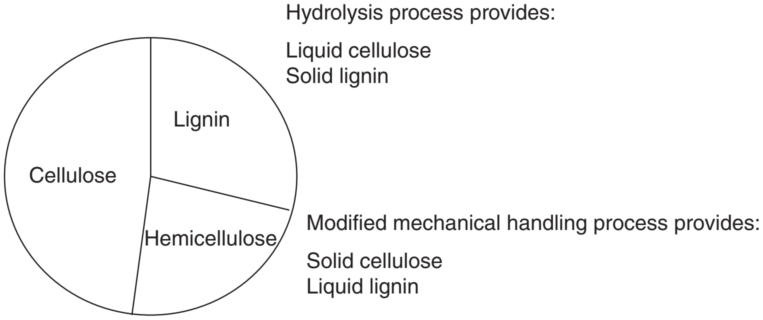

Figure 1.6 *Difference between hydrolysis process for decomposition into liquid cellulose and eventually sugar monomers and modified pulping process for recovery of lignin compounds.*

into liquid cellulose and eventually sugar monomers and solid lignin; and a modified pulping process for recovery of liquid lignin compounds and solid cellulose for production of energy commodities, respectively. Soft wood performs the best (ease of separation in the modified pulping process and greater recovery of the original hemicellulose and lignin present in the biomass) in Borregaard's process, synthesizing ethanol, C5 chemicals and vanillin (from lignin).

In conventional kraft pulping processes, most of the hemicelluloses from wood are degraded into oligomers or mono sugars and dissolved in black liquor along with dissolved lignin and the pulping chemicals (inorganic substances). The black liquor, even though with low calorific value, is usually combusted for steam and electricity generation, due to lack of other uses. However, with optimized pretreatment and separation process schemes, C6 compounds of cellulose and hemicellulose fractions can be converted into ethanol upon fermentation; hemicellulose is a platform for C5 chemicals production (xylose, arabinose and mannose); lignin can be a platform for functional chemicals (functional phenolics). For the production of ethanol, the removal of lignin and hemicelluloses is desired to improve the accessibility of cellulosic material to hydrolytic enzymes for high ethanol yield.

Biomass components can be transformed into intermediate *platforms* to offer processing flexibility to a biorefinery. As shown in Figure 1.3, a platform can be generated from a variety of feedstocks. At the same time, a platform allows shifting between processing pathways according to a desired product. Platforms are generated from biomass fractionation, pretreatment or conditioning, depending on the nature of the feedstock and the type of products to be produced. More than one platform can be present in a biorefinery configuration and the number of platforms is a sign of biorefinery complexity. The primary biorefinery platforms as shown before are discussed as follows.

- *Biogas* (mainly CH_4 and CO_2 and impurities such as H_2S) is produced from anaerobic digestion of organic residues. This biofuel after purification can be utilized for lighting, cooking and heat and power generation. Biogas has 50−70% methane but can be upgraded to 97% purity to be used as a natural gas substitute.
- *Syngas* (CO, CO_2, CH_4 and H_2 and other gases) is produced from biomass gasification. After cleaning, syngas can be used as fuel and for heat and power generation. Depending on the gasification conditions, the syngas produced can also be conditioned to undergo either thermochemical or biochemical processing for production of liquid biofuels and chemicals such as Fischer–Tropsch fuels, methanol, ethanol, dimethyl ether, isobutene, organic acids, ammonia, etc.
- *Hydrogen* (H_2) can be generated from the water gas shift reaction, steam reforming, water electrolysis and fermentation. H_2 can be used as fuel and as a chemical reactant for hydrotreatment of oils, hydrogenation of sugars, ammonia production, etc.
- *C6 sugars* (e.g., glucose, fructose, galactose: $C_6H_{12}O_6$) are released from hydrolysis of sucrose, starch, cellulose and hemicellulose. This platform is mainly used for the production of bioethanol and other chemicals with diverse functionality such as furfural, acetic acid, formic acid, etc.
- *C5 sugars* (e.g., xylose, arabinose: $C_5H_{10}O_5$) are released from hydrolysis of hemicellulose and food and feed side streams. These sugars can also be used for the production of biofuels and chemicals.
- *Lignin* is produced from the fractionation of lignocellulosic biomass. It can be applied as fuels or composite material. Further valorization of lignin includes the production of chemicals such as vanillin and phenolic based aromatic compounds.
- *Pyrolysis liquid* or *bio-oil,* a multicomponent mixture of oxygenated hydrocarbons, is produced from fast pyrolysis of biomass. Bio-oils can be separated into heavy (suitable for cocombustion in coal power stations) and light fractions, which can be upgraded via hydrodeoxygenation to liquid biofuels and chemicals (phenolic based aromatic compounds).
- *Oil and fat* (mainly containing lipids or triglycerides) can be present in oilseed crops, algae and oil based residues, and animal fat. These can be converted into fuels such as biodiesel, green diesel and jet fuel, etc. Due to their chemical functionalities, these can also serve as reactants for the production of surfactants or biodegradable lubricants.
- *Organic juice* is a liquid mixture of different biomass components produced after the pressing of wet biomass (e.g., grass juice, sugarcane bagasse).
- *Electricity and heat* can be internally produced and used to meet the energy needs of the biorefinery and any excess can be sold to the grid.

1.5 Biorefinery Products

Biorefinery products can be grouped into those used as energy carriers (biofuels, heat and electricity) and those used as materials for different industries or human needs including chemicals, nutraceuticals and food ingredients, pharmaceuticals, fertilizers, biodegradable plastics, surfactants, fibers, adhesives, enzymes, etc. Defining the product portfolio will depend on their potential to generate revenues and potential for avoided emission by replacing similar functionality fossil-derived products.

Biofuels, heat and power as renewable energy, or *bioenergy,* have been the most prominent products from biomass. Biofuels for transportation have received special attention due to the importance of such a sector in future energy demands and the avoidance of greenhouse gas emissions. Biofuels have been classified according to the type of feedstock used for their production as *first generation*, *second generation* and *advanced biofuels*. *First generation biofuels* are those produced from food crops and using well-established technologies, mainly ethanol from wheat, corn and sugarcane and biodiesel from edible vegetable oils. *Second generation biofuels* include biogas, methanol, dimethyl ether, ethyl *tert*-butyl ether, methyl *tert*-butyl ether, synthetic and green diesel, gasoline, jet fuel, biobutanol, biohydrogen, and Fischer–Tropsch liquids produced from alternative feedstocks including lignocellulosic materials, organic residues, algae and *Jatropha*. Production of these biofuels uses more advanced technologies including the Fischer–Tropsch process, gasification, hydrotreatment of oils, pyrolysis, etc.

Following the strategy from the crude oil and petrochemical industries, biorefineries aim to produce the chemical *building blocks* for industrial applications. Building blocks are simple but highly functionalized molecules using which further product diversification is possible by organic synthesis. An example of a building block, attracting research and industrial attention, is succinic acid, shown in Figure 1.7. Succinic acid can be produced by fermentation of glycerol coproduced with biodiesel. In fact, several derivatives can be produced from glycerol, making glycerol a building block itself[26].

The presence of oxygen, various functional groups, and bond types makes it possible to produce building blocks of a much wider range of chemicals from biomass than from the crude oil. Two attempts to find the more promising building block products in terms of economics and functionality are the study by Werpy and Petersen (2004) for the US National Renewable Laboratory (NREL) and Patel *et al*. (2006) for the EU BREW project[26,27]. The NREL study is based on the potential market and economic value of building blocks (both specialty and commodity chemicals). The BREW project focuses on the production of bio based bulk chemicals mainly as replacement or substitute products for fossil based products. Results of BREW project screening are summarized and compared to NREL study results in Table 1.5.

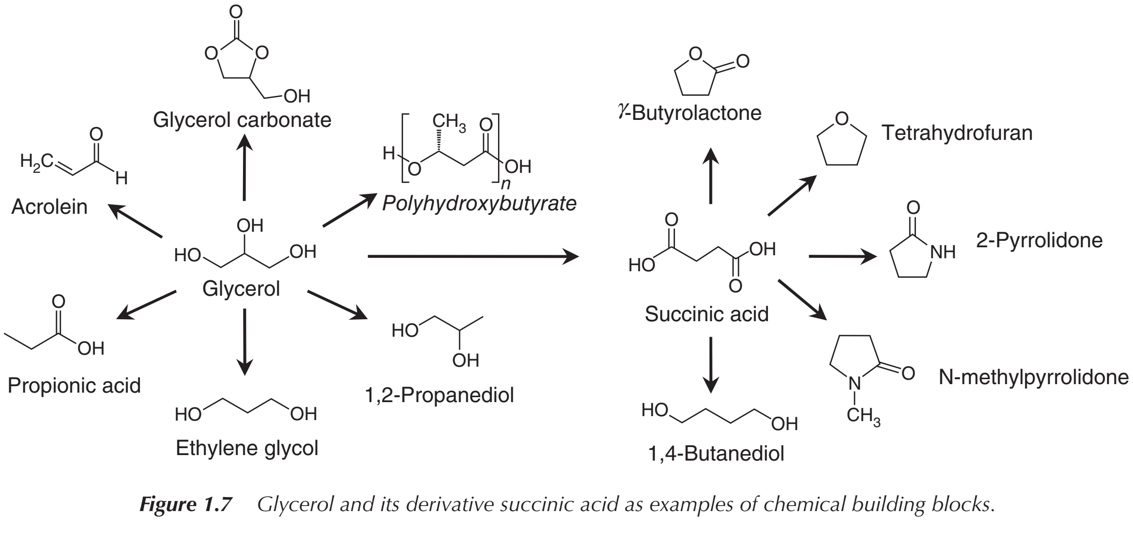

Figure 1.7 *Glycerol and its derivative succinic acid as examples of chemical building blocks.*

Table 1.5 *Promising chemical building blocks*[26,27].

Building Block	C No.	NREL	BREW	Building Block	C No.	NREL	BREW
Syngas ($H_2 + CO$)	C1	×	×	Aspartic acid	C4	×	
Ethanol	C2	×	×	Arabinitol	C5	×	
Acetic acid	C2	×	×	Furfural	C5	×	
Lactic acid	C3	×	×	Glutamic acid	C5	×	
Glycerol	C3	×		Itaconic acid	C5	×	
Malonic acid	C3	×		Levulonic acid	C5	×	
Serine	C3	×		Xylitol	C5	×	
Propionic acid	C3	×		Xylonic acid	C5	×	
3-Hydroxypropionic acid	C3	×		Glucaric and gluconic acid	C6	×	
1,3-Propanediol	C3		×	1-Butanol	C6	×	×
Acrylic acid	C3		×	1,4-Butanediol	C6	×	
Acrylamide	C4		×	Sorbitol	C6	×	×
Acetoin	C4	×		Adipic acid	C6	×	×
3-Hydroxybutryolactone	C4	×		Citric acid	C6	×	×
Malic acid	C4	×		Caprolactam	C6		×
Theonine	C4	×		Lysine	C6	×	×
Succinic acid	C4	×	×	Fat and oil derivatives	>C6		×
Fumaric acid	C4	×		Polyhydroxyalkanoates (PHA)	>C6		×

Further, US Department of Energy (DOE) studies suggest a list of organics from cellulose conversion, as follows[26,28].

Succinic, fumaric, and malic acids
2,5-Furandicarboxylic acid
3-Hydroxypropionic acid
Aspartic acid
Glucaric acid
Glutamic acid
Itaconic acid
Levulinic acid
3-Hydroxybutyrolactone
Glycerol
Sorbitol
Xylitol/arabinitol

The report embraced these screened products as a guide for research. The methodology for screening included factors such as known processes, economics, industrial viability, size of markets and the ability of a compound to serve as a platform for the production of derivatives. The list retains 2,5-furandicarboxylic acid and hydroxymethylfurfural in recent investigations because of their most efficient process and one-pot process development, while glutamic acid remained as an end product and not a building block, and has been dropped from the list.

Of highest importance is the need to extract lignin early from lignocellulose. Unless lignin fraction is routed to value-added chemical production, a biorefinery is unlikely to be economically and environmentally sustainable. Lignin value addition is an important stumbling block, unveiling of which can unlock the sustainability of biorefineries. The potential applications of lignin go from simple combustion for heat and power production to the production of aromatics typically produced from crude oil (phenols; benzene, toluene and xylene: BTX chemicals) or other highly functional chemicals used in the food and flavoring industry (e.g., vanillin). A study by PNNL shows the choices of priority chemicals, as in Figure 1.8[29]. The chemistries and markets are yet to be fully known for the blocks and arrows shown in dotted lines,

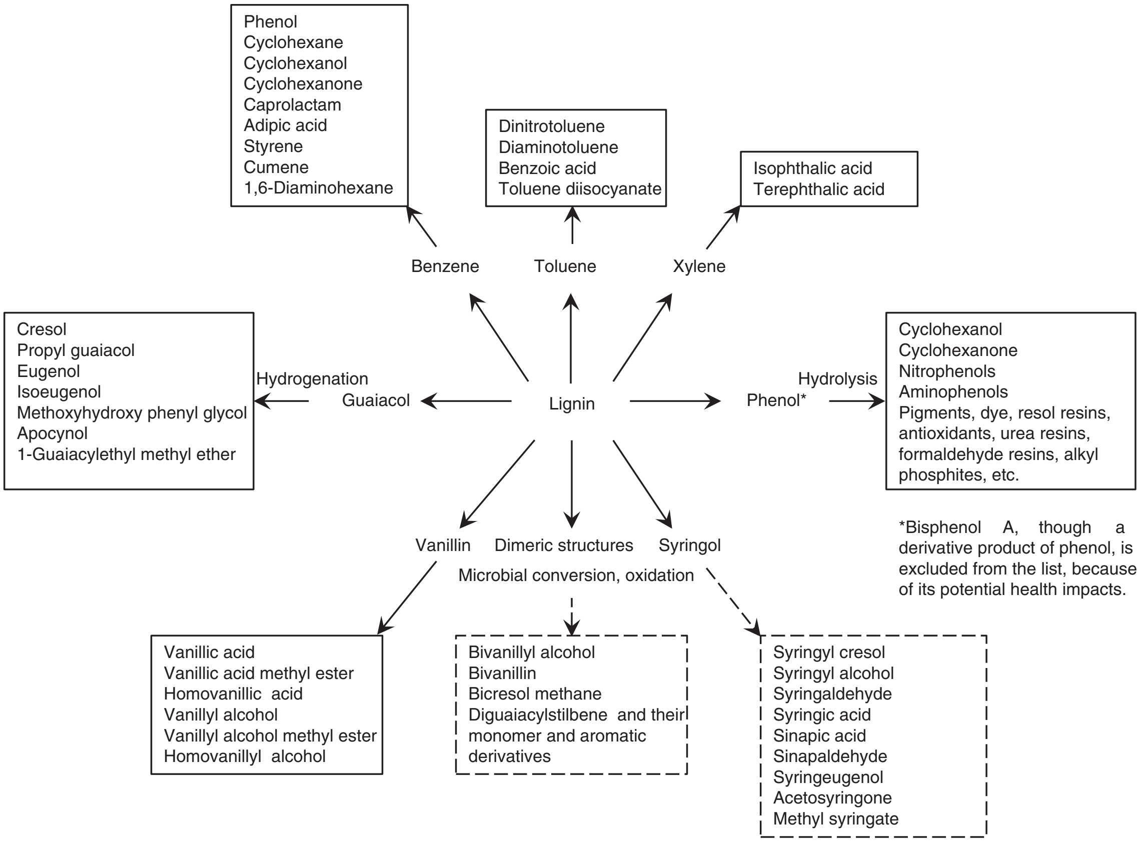

Figure 1.8 *Chemicals from lignin. The chemistries and markets are yet to be fully known for the blocks and arrows shown in dotted lines.*

whilst the productions of BTX derivatives are well established from the petrochemical industry. The sequence from the most mature technology to the furthest-from-market technology utilizing lignin is as follows:

BTX derivatives > phenol and guaiacol derivatives > vanillin derivatives > dimer and syringol derivatives

The revenue potentials have been estimated as US$ 80 billion for biofuels, US$ 10–15 billion for bio based bulk chemicals and polymers, and US$ 65 billion for heat and power by 2020 (King, 2010)[30]. The revenue potential from biofuel and heat and power production is higher compared to chemical production; the higher revenue potential is because of the volume produced, but not the market price of products. A biorefinery is most beneficial by producing one or several specialty chemicals to enhance profitability and a commodity product such as biofuel to ensure market penetration at present. Decision making attending the trade-off between low value–high volume and high value–low volume productions requires a market analysis, while also taking into account the technical feasibility of the processes needed to deliver a particular set of products.

A summary of biorefinery product categories and their market drivers are shown in Figure 1.9. The lowest value products are the energy products (however, due to high volume production, the overall revenue from their production may be higher compared to chemical production), followed by biofuel. This is followed by chemical (methanol and equivalent to primary petrochemical) and hydrogen production. Polymer, composites and food and pharmaceuticals are

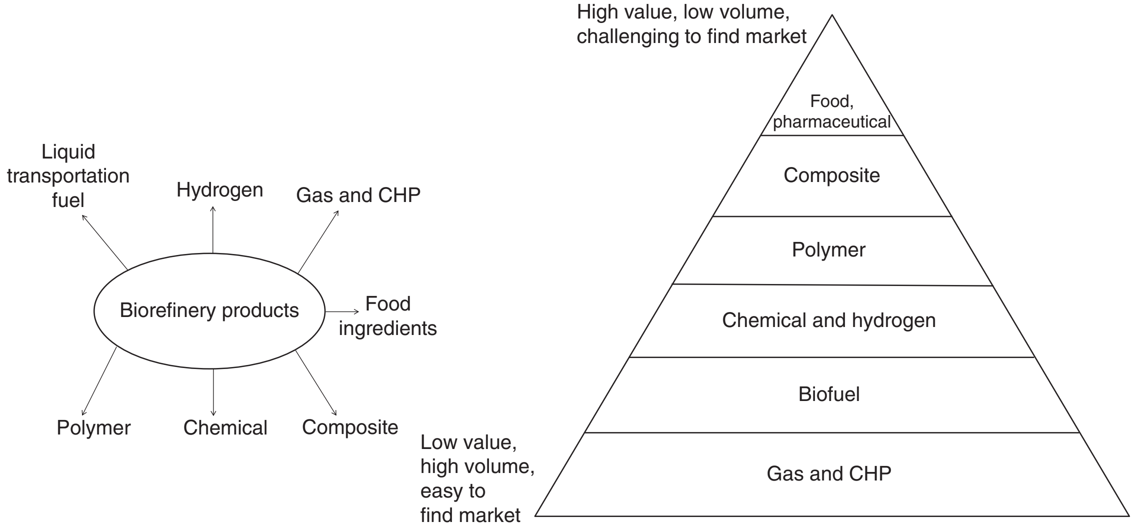

Figure 1.9 *Biorefinery products and their market drivers.*

consecutively the most value-added products. However, with lower extractable volumes in different or new molecular forms (with equal functionality), higher challenges are faced to find a market.

1.6 Optimization of Preprocessing and Fractionation for Bio Based Manufacturing

Biomass based manufacturing is urgently needed to replace fossil based manufacturing of carbon containing products: chemicals, polymers and materials. Electricity and heat though has a large market, but renewable energy resources are practical to fill the needs. Biomass CHP can be brought into action in place of fossil based power plants, to meet peak energy demands. However, biomass is the only carbon source. Amongst the biomass feedstock options, lignocellulosic biomass is the only workable biomass to replace crop based manufacturing causing depletion of land and water resources. The lignocellulose based manufacturing needs to be investigated from more fundamental perspectives: structural integrity and carbon balance of lignocellulose throughout the life cycle, process synthesis for least cost and environmental impacts and highest value generation. Sustainable biomanufacturing thus requires a “whole” systems optimization study.

Lignin encasing cellulose in cell walls provides cell wall rigidity, while encased cellulose microfibrils give tensile strength of cell walls. Extraction of hemicellulose and lignin reduces the cost of production of cellulosic products. This stage is called preprocessing, after which cellulose microfibrils can be easily converted into glucose by enzymatic hydrolysis, followed by ethanol and chemical productions. Alternatively, cellulose microfibrils can be used to form continuous phase (matrix) of composite materials. The discontinuous phase, also known as reinforcement, may consist of glass, carbon or Kevlar fibers. Together, these can form thin films with applications in electronics, for example, moulding transistors or printed circuit boards, construction, automotive as laminates, and marine construction industries.

The preprocessing of biomass at a broad level includes the physical (e.g., kraft processes), chemical (acid hydrolysis, alkali treatment) and biochemical (enzymatic hydrolysis) processes and fractionation to recover products. The concept avoids “end-of-pipe cleaning” of impurities from the main products, by separating the cellulose, hemicellulose and lignin materials upfront and diverting them to desired products, leading to environmentally benign process designs. The screening of lignocellulose preprocessing technologies and products (Figure 1.10) describes a more complex and challenging task than the development of sugar based bioethanol plant. However, to achieve the full potential of biorefineries, extensive extraction is needed for every component, to produce value-added products.

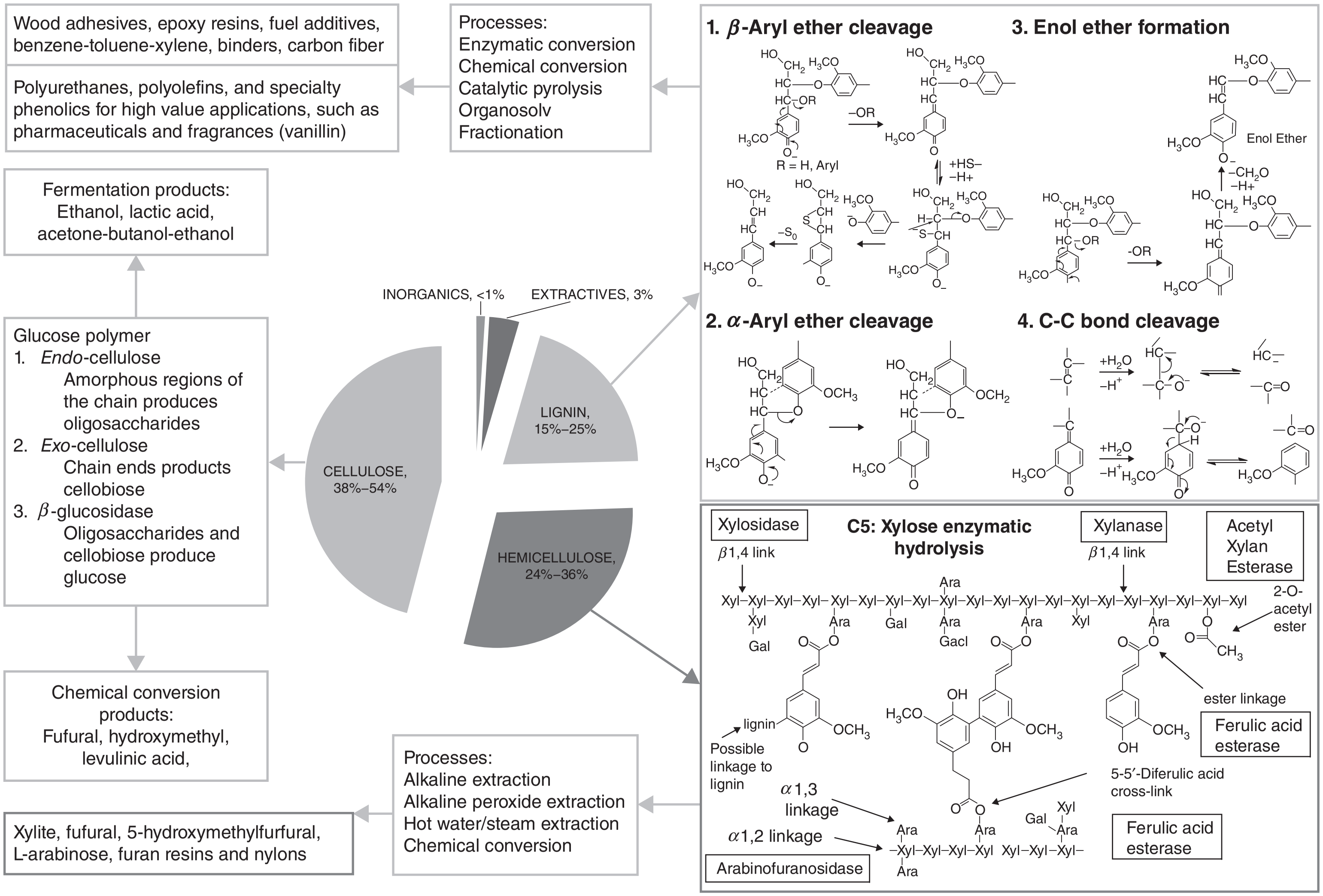

Figure 1.10 *Preprocessing technologies, mechanisms and products.*

On the right hand bottom corner in Figure 1.10, the hemicellulose bond cleavage mechanisms by enzymes are shown (Peng *et al.*, 2012; Reith *et al.*, 2009)[31,32]. The following enzymes are noted to act on the following cleavages. α-L-Arabinofuranosidase liberates the L-arabinose from positions 2 and 3 of the backbone xylan. Ferulic acid esterase hydrolyses the position 5 of arabinofuranoside residues, producing ferulic acid. Acetyl xylan esterase releases the *o*-acetyl of acetyl xylan. Xylanase randomly cleaves the main chain of xylan, producing a mixture of xylo-oligosaccharides. There are two types of Xylanase, *endo*-xylanase randomly breaks the xylan chain, while β-xylosidase releases monosaccharides and xylose from the nonreducing end of the short oligosaccharides.

Similarly, for galactoglucoglucomannans, β-mannosidases and *endo*-1,4-β-mannanses are used to break down into corresponding mono- and oligosaccharides. In order to produce products of desired properties, coordinated activities of cleavage of bonds are required, which must be assisted by genetic engineering and enzymatic pathway analysis.

The established processes for the above enzymatic treatments are as follows:

α-L-Arabinofuranosidase. Ultrafiltration and anion exchange chromatographic columns; pH: 5.8; temperature 45 °C; molecular weight: 160–210.

Ferulic acid esterase. Diethylaminoethyl cellulose chromatography and ammonium sulfate precipitation; pH: 7.5; temperature 45 °C; molecular weight: 20.

Acetyl xylan esterase. Ammonium sulfate precipitation, diethylaminoethyl cellulose chromatography, tertiary butyl hydrophobic interaction and hydroxyapatite chromatography, and Ni^{2+}–NTA agarose column chromatography; pH: 6.5–7; temperature 37–50 °C; molecular weight: 30–34.

Xylanase. Ultrafiltration, anion exchange chromatography, metal affinity resin and precipitation by gravity flow column, ultrafiltration and diethylaminoethyl cellulose chromatography, and a ammonium sulfate precipitation, ion exchange, and gel filtration chromatography; pH: 6–7; temperature 37–60 °C; molecular weight: 22–45.

β-Mannosidases. Diethylaminoethyl cellulose chromatography, anion exchange chromatography, and gel chromatography; pH: 3.5–7; temperature 30–53 °C; Molecular weight: 72–94.

Endo-1,4-β-mannanses. Ultrafiltration and chromatographic columns; pH: 6; temperature 60–65 °C; molecular weight: 38–40.

The main mechanism for cleavage of lignin bonds shown on the right hand top corner of Figure 1.10 includes β-aryl and α-aryl ether cleavages, enol ether formation and C—C bond breakage. Cellulose depolymerization mechanisms are well known, as shown in Figure 1.10. Each fraction, cellulose, hemicellulose and lignin can then be converted into a range of products.

Compositions of lignocellulosic feedstocks are often unpredictable when they are accumulated within a system boundary, maybe an urban system. Hence, which products can be generated and what are those flexible processes that can uptake the mixture of feedstocks and still achieve the desired product slate pose a huge challenge to solve. Unoptimized schemes would suffer from waste formation of low values that will ultimately be released to the atmosphere after combustion or cogeneration or to land from disposal to landfills or to an aquatic body by leaching. Most routes produce low value lignin residues. The lignin and hemicellulose fractions are increasingly recognized as a valuable source of value-added productions in the top of the pyramid shown in Figure 1.9. There are numerous possibilities, amongst which the niche areas need to be carefully selected based on market drives within a geographical region and policy context. The application principles encompass integrated feedstock management, conversion, use of end products, and reuse in cyclical and synergistic loops. Renewable feedstocks from a range of local activities can be converted into products to fulfill local needs and can reversely help produce biomass via anthropogenic activities to meet demands. With co-optimization of anthropogenic activities (agricultural, forestry, residential, industrial and commercial) and demand management, the impacts on land, soil, water and atmosphere will be reduced. A true sustainable biorefinery design calls for such a challenging solution for "whole systems." However, the complete fusion of an industrial symbiosis framework is a gradual process and requires years to stabilize from one state to another, for example, from a fossil based era to a renewable era.

Several routes are commercially established or under development. Table 1.6 shows the physical description and specifications of processes and associated challenges for research.

The economic performance of a biorefinery depends on adding value to the lignin and hemicellulose fractions. The most promising route for exploiting the hemicellulose fraction appears to be by extracting functional oligosaccharides, such as xylo-oligosaccharides, with a potential market as pharmacological supplements and food ingredients. Lignin

Table 1.6 *Preprocessing technologies for separation of cellulose, hemicellulose and lignin fractions and downstream purification technologies.*

Process	Physical Description and Specifications	Challenges
Preprocessing for separation of cellulose, hemicellulose and lignin fractions		
Alkali treatment	Alkali treatment is the most established method, amongst all, for lignocellulose separation into basic components: cellulose, hemicellulose and lignin. The process uses hazardous and expensive $NaClO_2$ for delignifying the lignocellulose. Replacing this with environmentally more benign aqueous alcohol treatment is desirable. Alkali type, concentration, time and temperature have an effect on product yields and qualities. Aqueous solutions of sodium, potassium, lithium, barium, calcium and ammonia (ammonium hydroxide) are commonly used. Some of the elements are abundant, sodium and potassium, compared to which lithium availability may be constrained, especially due to increased demand for lithium ion battery for the transport sector. Sodium hydroxide is more effective in terms of yield compared to potassium hydroxide, while the latter is more effective in terms of purity of products. The experimental conditions are generally within the following range: 1.0 M NaOH at 30 °C for 18 hours, to result > 80% recovery of the original amounts of lignin and hemicellulose present in agricultural residues[33]. Barium hydroxide has shown higher affinity for arabinoxylans extraction, from wheat bran fraction, for example. Alkaline peroxide has shown higher effectiveness in terms of delignification as well as solubilization of hemicellulose than alkaline solutions. Hydrogen peroxide (H_2O_2) in the presence of transition metal, such as iron, manganese and copper, readily decomposes into hydroxyl radicals (OH^-) and oxide anion radicals (O^{2-}). These radicals are thought to oxidize lignin, release carboxyl groups by the cleavage of bonds and eventually decompose lignin and hemicelluloses (by the cleavage of covalent bonds between lignin and hemicellulose and ester bonds) into C5 and phenolic compounds. 2% H_2O_2 at 48 °C for 16 hours at pH 12–12.5 proved to be more effective than alkaline solutions, resulting in almost pure activated lignin and hemicellulose products from agricultural residues[34]. The H_2O_2 stream can be recovered from cellulose fraction, yielding a cellulose rich insoluble residue that can be enzymatically converted into glucose and further to ethanol and chemicals.	Optimize operating conditions. Optimize alkali aqueous mixture not only for better yield and purity of products but also for the recovery of alkali solvent and to minimize make-up solvent requirement. It is essential to optimize solvent recirculation columns with heat integration. Further, microwave assisted columns can be designed for high efficiency and environmentally more friendly performance. Catalyst such as acid catalysts can also be introduced for further improvement. It is essential to analyze life cycle impacts and costs for the choice of raw materials, process configurations and production options.

(*Continued*)

Table 1.6 *(Continued)*

Process	Physical Description and Specifications	Challenges
Organosolv with DMSO	Uses organic solvent for pretreatment of lignocellulose and extraction of hemicellulose and lignin. It is possible to design a multistage extraction process by solvent in aqueous media with various concentrations. Most commonly used solvent is the dimethyl sulfoxide (DMSO). The solvent is more effective for low-branched heteroxylans, because the extraction mechanism does not include cleavage of acetyl ester and glycosidic linkages. This helps to carry out a hemicellulose and lignin structural study and pretreatment and access of wood polymers. However, the main problem is the cost and potential hazard in handling a large quantity.	Design of multistage extraction column. Minimize solvent to biomass ratio. Reduce energy cost. Reduce environmental impacts.
Organosolv with lower molecular weight solvent	The process has the advantage of energy efficient recovery of solvent and low environmental impact, when using low molecular weight organic solvents, such as ethanol, methanol, acetic acid and formic acid, etc. Various solvent mixes are possible. Hence, rigorous investigations must be made for an optimal mixture of solvent for highest value-added generation. The mixtures are methanol–water, ethanol–water, methanol–ethanol–water, acetic acid–water, formic acid–water, acetic acid–formic acid–water, etc. Lower molecular weight solvents are easy to recover, but the degree of recovery is affected and decomposition of hemicellulose and lignin polymers occurs.	Optimize solvent mix. Design of multistage extraction column. Minimize solvent to biomass ratio. Reduce energy cost. Reduce environmental impacts.
Organosolv with catalyst	Acid catalysts are used to increase the yield of hemicellulose and lignin, e.g., 0.1% HCl as catalyst, together with DMSO and aqueous KOH as solvent. To prevent depolymerization, neutral solvents, e.g., 90% dioxane and DMSO, can be used. To facilitate cleavage of acetyl ester and glycosidic bonds and saponification of the ester groups in the polymers, acidic dioxane or medium can be used. Sequential treatments with 80% acidic dioxane, DMSO and 8% KOH primarily give rise to arabinoxylans, especially effectively from crop residues, due to the absence of lignin.	Rigorous simulation for analyses of process configuration, costs and thermodynamic properties. Fully integrated and instrumented one-apparatus system. Saponification and downstream separation for homogeneous systems.

Table 1.6 *(Continued)*

Process	Physical Description and Specifications	Challenges
Organosolv with heterogeneous catalyst	Heterogeneous catalysts, such as solid acids (zeolites, clays, metal oxides, etc.), can give high conversion of hemicellulose into xylose, arabinose and furfural. The reaction conditions are varied by temperature, reaction time and solvent addition and phase separation. When solvent and heterogeneous solid catalysts are optimized for furfural production, the greatest carbon balance can be observed. *The heterogeneous reactive extraction process results in selective conversion into cellulose, hemicellulose and lignin.* The catalysts can be characterized by X-ray diffraction, temperature-programmed desorption of NH_3, inductively coupled plasma spectroscopy, elemental analysis and solid-state nuclear magnetic resonance (NMR) spectroscopy techniques.	Catalyst characterization and meso–nano porous structure. Reactor arrangement and configuration. Continuous reaction. Scaling up of the processes. Physicochemical properties of reaction mixture at various stages of reactive extraction.
Extrusion	The process combines mechanical and physical separation and reaction process using an extruder type twin screw reactor equipped with a filtration system. Functionalities integrated within one apparatus are the extrusion, cooking, liquid–solid extraction and liquid–solid separation (by filtration). Sodium hydroxide can be used as solvent. The sequential treatment with 80% aqueous dioxane containing 0.05 M HCl and DMSO at 85 °C for 4 hours and 8% NaOH at 50 °C for 3 hours results in over 85% recovery of each of the original hemicellulose and lignin present in crop residues.	Fully integrated, optimized and instrumented system. Scale-up risk. Flexible feedstock and process conditions. Catalyst deactivation. Solvent minimization. Solvent and catalyst optimization.
Steam explosion	This is one of the oldest technologies, still effective to fractionate lignocellulose into three major components: cellulose increasing its susceptibility to enzymes; hemicellulose easy to hydrolyze; depolymerized lignin. The basic principle is that biomass is first treated with high pressure steam, the pressure of which is suddenly reduced by expansion to decompose biomass extensively. The Mason process by flash decomposition was developed in 1928. Sequential extraction using steam followed by alcohol solvent (ethanol is often used) is carried out first to separate hemicellulose and then lignin. The controlling parameters are residence time, temperature and feedstock particulate size. The optimal conditions need to be determined to achieve ease of hemicellulose hydrolysis and separation from cellulose. Steam explosion, followed by alkaline peroxide solvent extraction are very effective. Though the processes are environmentally friendly, controlling the degradation of hemicellulose and lignin poses the biggest challenge.	Avoid gas production, but control operating conditions for functional chemical and material production. Controlling degradation of hemicellulose and lignin. Process sequencing and optimization.

(*Continued*)

Table 1.6 *(Continued)*

Process	Physical Description and Specifications	Challenges
Microwave irradiation	Comparatively newer efficient and environmentally friendly technique, this technique applies electromagnetic radiation to decompose lignocellulose. The process is more environmentally friendly, because less or no solvent is required, higher efficiency and better quality products are obtained. The characterization properties include molar mass and its distribution, degree of polymerization and degree of substitution. *The technology can be used in combination with steam explosion to produce external chemical (solvent) free or impurity free products.* Many studies have shown microwave irradiation as an effective technology for mannan production. Also, the technology enables design of microwave assisted alkali or acid pretreatment.	Controllability. Controlling the heat. Adjustment of electromagnetic waves to supply heat of absorption by materials. Good yield without extensive decomposition. Flexibility to change rate according to feedstocks to process and products to produce.
Ultrasonication	*Ultrasonication using sound waves to prefractionate lignocellulose is now showing promise in terms of energy effectiveness amongst all.* The technologies are mostly proprietary to biomass fractionation industries.	Yet to be proven.
Purification processes: the isolated fractions of hemicellulose and lignin contain numerous polymers need to be characterized and purified into functional products.		
Membrane	Purification process involves multisteps such as filtration, ethanol precipitation, centrifuge, etc. Microfiltration, ultrafiltration, nanofiltration using forward, reverse and modified osmosis processes (uses reverse osmosis for purification followed by forward process for membrane clean-up and energy recovery) are effective for purification of lignocellulose products. Membrane processes can also be effectively integrated to other processes, catalytic and solvent treatment, twin screw extrusion and chromatographic separation, etc. Ultrafiltration can be applied to separate high purity arabinoxylans, glucuronoxylans and acetyl-galactoglucomannans of hemicellulose fraction using various cut-off ranges. 150–1000 g mol^{-1} cut-off ranges economic options. Further, nanofiltration can also purify xylo-oligosaccharides from monosaccharide and low molar mass materials such as salts and lignin polymers from functional phenolics, both in high purity forms. The processes can be a good substitute for chromatographic separation for purification. Molar mass cut-off yields, degree of polymerization and degree of substitution are the key design parameters.	Energy recovery across membrane. Forward osmosis to recover energy and clean-up of membranes. Optimize membrane pore sizes. Optimize membrane modular arrangements. Optimize membrane and other pre-processing modular configurations. Cost, operability, controllability and yield optimization.

(*Continued*)

Table 1.6 *(Continued)*

Process	Physical Description and Specifications	Challenges
Chromatographic separation	The chromatographic or adsorption based separation technique is used to characterize materials as well as purify materials by precipitation and ion exchange. The ion exchange technique is more effective in terms of high purity fractions recovery. Diethylaminoethyl (DEAE) is a common chromatography agent to directly recover and fractionate hemicelluloses (e.g., into arabinose, xylose, fractions) from the plant materials. The main strength of the chromatographic method lies in the separation of activated lignin. While these techniques are quite common for crop based lignocellulose, they are less established for wood. The size based elution was applied to separate oligomers from monomers and low molecular weight salts, followed by steam explosion. The lignin is also recovered but to a lesser extent. The technique can find the molecular weight of polysaccharides.	Many columns are used; requires innovative techniques for cost-effective recovery. Generally accompanied by other recovery processes, such as alkali treatment, steam explosion upstream, for effective purity, especially for complex lignocellulose structures, such as wood. Simulated moving bed columns and other innovative sorption–reaction columns are needed.

recovery for specialty phenolics production for high value applications, such as pharmaceuticals and fragrances, is also promising. Within the context of an integrated biorefinery, xylo-oligosaccharides and function phenolics could be extracted economically to enhance the overall biorefinery economics.

Finding a niche market for hemicellulose and lignin based products will be the key to sustainable biorefinery development. The case of vanillin can be shown[35]. Rhodia SA dominates the vanillin market using the catechol-guaiacol process. Borregaard (Norway), the second largest vanillin producer, is one of the remaining producers of lignin based vanillin. Essentially, Borregaard supplies the European market and its vanillin production is almost exclusively for large-scale customers under long-term contracts. Since vanillin is mostly produced from guaiacol, vanillin prices are sensitive to the world oil market. However, lignin based vanillin is in high demand for certain market sectors, particularly for the perfume industry, European chocolate manufacturers, and Japanese market, and as such tends to command a price premium. The price of lignin based vanillin has been consistently maintained at about \$100–200 kg^{-1} above that of guaiacol based vanillin. Systematic process integration and sustainability analysis will allow lignocellulose biorefineries to be a commercial success. Processes can be optimized for one or more of the following particular production objectives.

1. Enzymatic extraction of cellulose into ethanol, acetone–butanol–ethanol (ABE), xylonic acid, lactic acid, 5-hydroxymethylfurfural (HMF), levulinic acid, etc. Cellulosic polymers are the most abundant renewable polymers.
2. Hemicellulose hydrolysis for further processing of C5 into xylite, furfural, HMF, L-arabinose, etc. Hemicellulose is the second most abundant source of biopolymers, consisting of heteropolysaccharides, linked with cellulose and lignin, in cell walls by covalent and hydrogen bonds and by ionic and hydrophobic interactions. After the kraft pulping process, hemicelluloses are obtained along with dissolved lignin, as black liquor. Hemicelluloses in this mixture consist of oligomers or monosugars of C5 and C6: glucose, xylose, mannose, galactose, arabinose, rhamnose, glucuronic acid and galacturonic acid in various amounts depending upon the source.
3. High quality lignin stream recovery wood adhesives and resins, fuel additives, BTX, binders, carbon fiber, etc. Lignin is the third most abundant source of biopolymers and materials after cellulose and hemicellulose.
4. Lignin recovery for phenolic products, activated lignin, epoxy resins, polyurethanes, polyolefins and specialty phenolics for high value applications, such as pharmaceuticals and fragrances.

A biorefinery converting lignin and hemicellulose into functional products would only be economic if the commercial potential of all three fractions, cellulose, hemicellulose and lignin, is fully exploited. Now, it is clear how to add value

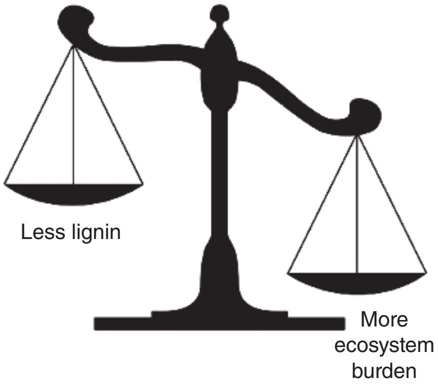

Figure 1.11 *Lignin value generation becomes threshold to sustainable manufacturing.*

to the starch fraction (e.g., through fermentation), but in particular the lignin fraction still needs to be investigated from fundamental synthesis perspectives.

1.6.1 Background of Lignin

Until the late 1990s research has been focused to repress the lignin content in transgenic trees, considering the postharvesting problems to separate it from cellulose. Lignin appears to be inhibiting the use of cellulose to produce biofuels. Lignin is problematic for the pulp and paper industry. Not only had the lignin separation technologies begun to evolve to ease cellulose conversion in these industries but suppression of lignin also became another main line of research in bioengineering.

On the other hand, lignin's resistance to microbial degradation increases plants' persistence to soil, while also retaining approximately 30% of the biogenic carbon captured. Retaining high quality and quantity of lignin in plants directly helps in enhancing plants' structural integrity, strength, rigidity, prolonged capture of biogenic carbon and enhanced ecosystem balance. Reduction of lignin on the contrary reduces the biogenic carbon capture and increases the overall biogenic carbon release to the atmosphere. Thus, lignin quality and quantity becomes a pivot for carbon balancing across the biomanufacturing sector. Figure 1.11 shows that less lignin in plants implies more ecosystem burden.

Lignin fractions are increasingly recognized as a valuable source for functional chemical and material production. A high quality lignin stream can be manufactured, such as vanillin, vanillic acid, dispersing agents, synthetic tannins, polymer filter sand, binding agents, activated carbon, ion-exchanger subtract, etc.

The main lignin compounds are polymers of *para*-hydroxyphenyl (H lignin), guaiacyl (G lignin) and syringyl (S lignin) alcohol, involving many pathways, enzymes, and cofactors (Figure 1.12)[36]. By suppressing some genes, by reducing particular enzymes, the quality and quantity of lignin can be controlled. For example, reduction of CAD enzyme leads to S lignin production provided there is up-regulation of F5H and COMT enzymes. Hence, down-regulation of F5H and COMT enzymes decreases S lignin content. Absence of HCT and C3H enzymes leads to H lignin prominence. It is seen that the structural strength of cell walls depends more prominently on the presence of H lignin. Up-regulating HCT, C3H and CAD enzymes leads to G lignin, a platform for vanillin production. However, studies have shown that perturbation of pathways affects all other pathways and expression of genes apparently seems to be unrelated. This means that research needs to address beyond genetic engineering to uncover molecular mechanisms that accompany lignin modifications, such that carbon can be preserved and lignocellulose cells can act as a bioreactor.

The lignin biosynthetic enzymes are:

PAL: phenylalanine ammonia-lyase
C4H: cinnamate 4-hydroxylase
4CL: 4-coumarate:CoA-ligase
C3H: *p*-coumarate 3-hydroxylase

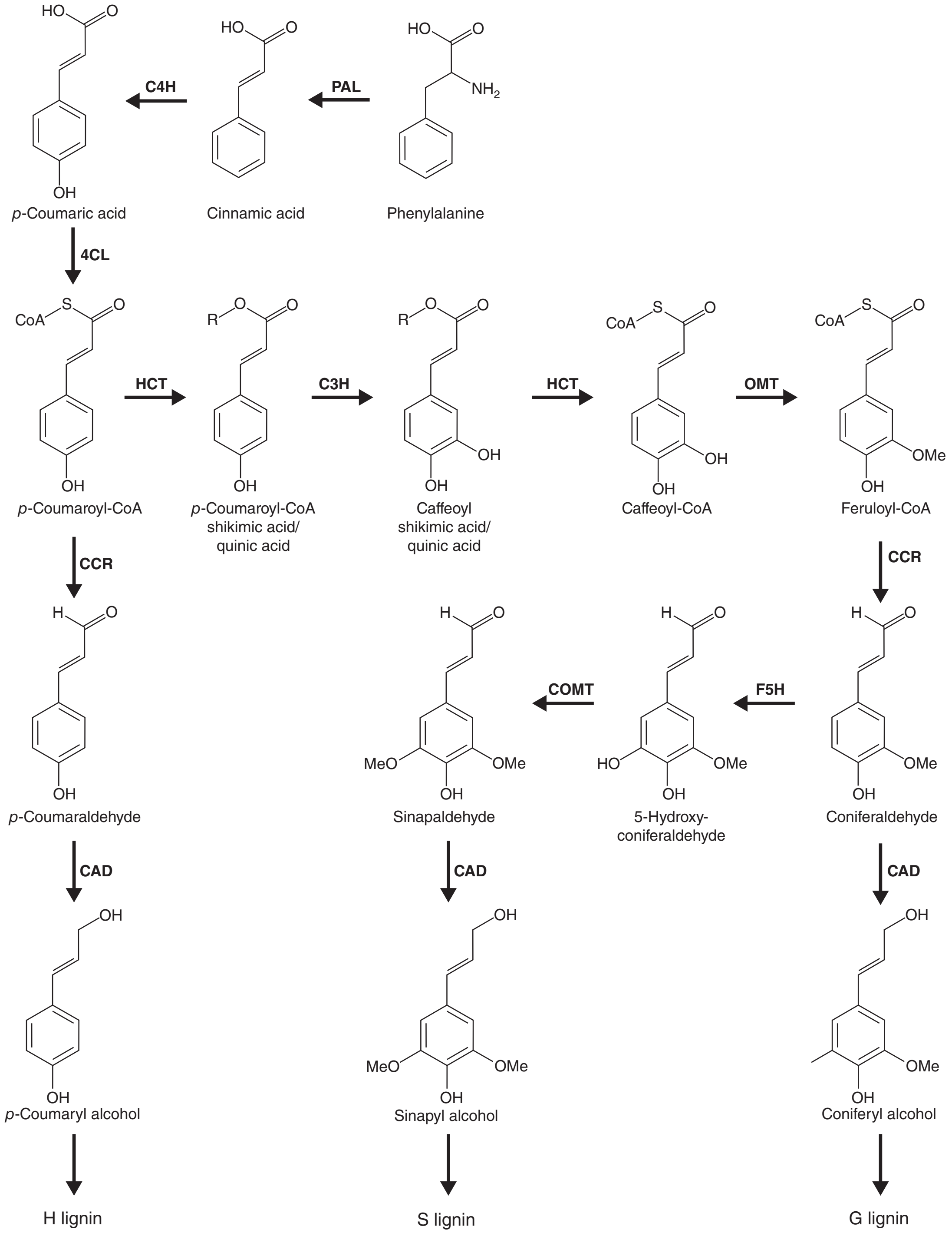

Figure 1.12 *Lignin biosynthetic pathways.*

OMT: *S*-adenosylmethione:caffeate/5-hydroxyferulate-O-methyltransferase
F5H: ferulate 5-hydroxylase
HCT: 4-hydroxycinnamoyl-CoA 3-hydroxylase
COMT: sadenosyl-methionine:caffeoyl-CoA/5-hydroxyferuloyl-CoA-O-methyltransferase
CCR: hydroxycinnamoyl-CoA:NADPH oxidoreductase
CAD: hydroxycinnamyl alcohol dehydrogenase; glucosyltransferase
UDP-G1c: coniferyl alcohol 4-O-glucosyltransferase; glucosidase, coniferin-specific 4-O-glucosidase.

The lignin chemical constituents vary greatly depending on the source of biomass and age, morphological location and growth environment (for agricultural and forestry residues). Lignin from softwoods is predominantly based on guaiacyl as the structural unit. Guaiacyl units are the precursors to vanillin based products. Hardwood lignin consists of syringil:guaiacyl with weight ratios in the range of 1.8–2.3.

Lignin extraction from lignocellulosic materials is the most basic step practiced over hundreds of years in the pulp making process and paper industry. The composition, property and quantity of lignin are highly influenced by the chosen extraction method. Sulfite, kraft and soda processes are most commonly used in the pulp and paper industry. The sulfite process uses salts (sodium, magnesium and ammonium) of sulfurous acid to perform three reaction steps to separate lignin: lignin and free sulfurous acid form lignosulfonic acid; lignosulfonates are formed by the reaction between lignin and cations; fragmentation of the lignosulfonates. The reaction operating conditions are as follows: 140–160 °C and pH: 1.5–2 for acidic and 4–5 for basic media respectively.

The kraft process uses sodium hydroxide and sodium sulfide under alkaline conditions to cleave the ether bonds in lignin in two main stages: lower temperature preheating and premixing at 150 °C and reaction at 170 °C. The reaction is mostly complete in the final stage. In the kraft process, β-1,4 links in cellulose are cleaved, extracting the lignin components. However, the lignin itself is also susceptible to alkali: ethers in lignin readily undergo base-induced hydrolysis under relatively mild conditions. Cleavage of α-aryl ether then takes place before β-aryl ether cleavage, particularly when free phenolic hydroxyl group is available in the para position. The black liquor is separated by light acid treatment, such as using sulfuric acid (more recently carbon dioxide) also to increase pH to 5–7.5 of the kraft lignin, which has a market value. Most of the process development has occurred for kraft lignin.

Most of the lignin separated from wood in the sulfite pulping and the kraft pulping processes is burned to avoid volatile organic matter emissions that could be toxic. With no carbon taxation or financial burden due to carbon dioxide emissions on these industries, burning the volatile matter for energy recovery seems to be an easy way. The remaining amount is isolated from the spent pulping liquors and sold for specialty applications, normally around 1 million tons per year worldwide. Lignin is a sticky material causing numerous operational problems in downstream processes. Lignin also gives rise to phenolic compound emissions with some of these being toxic. Preprocessing to extract lignin and any capture of organic vapor during processing of lignocellulose is highly desirable. The natural use of lignin is as binders in panels and boards. Phenol formaldehyde resins are used globally with a demand over 1 million tonnes per year for this purpose. Lignin can be extracted mechanically by modified kraft processes. The resulting products can be furan resins or modified lignin. These materials have 45% higher mechanical strength (e.g., 2.7 N mm^{-2} for modified lignin) than phenol formaldehyde (e.g., 1.6 N mm^{-2}). Hence, direct substitution of fossil-derived phenol formaldehyde by lignocellulose-derived modified karft lignin is possible.

The soda process being the first chemical extraction method for lignin was commercialized after patenting in 1845. The soda process using aqueous solution of sodium hydroxide (13–16 weight %) is used for lignin extraction from non-wood biomass: wheat straw, help, bagasse, etc. Amongst the three processes, sulfite, kraft and soda processes, the soda process is technically and environmentally more sustainable because there is no sulfur residual from the chemical reagents used in the resulting aqueous (cellulose) and organic (lignin) fractions. The presence of sulfur and its hydrophobic nature makes the lignin from sulfite and kraft processes very difficult to be accessible for value-added production. Therefore the main use of lignin is in energy production, still a usual feature in the pulp and paper industry.

With the push to produce cellulose for bioethanol or platform chemical production, the lignin fraction may as well be recovered at high quality so as to produce functional chemicals and materials from it. Such processes have not been semantically evolved but to link with lignocellulose production and product value chain. Organosolv with lower molecular weight solvents and a heterogeneous catalyst can be used, while keeping both the pulp and the liquid quality controlled at desired levels.

Supercritical carbon dioxide as an antisolvent agent can be used to precipitate a range of chemicals from nano- to microstructures, when used together with a chromatographic separation material (such as dimethyl sulfoxide in water). Carbon dioxide can be easily separated from the product at high purity and recirculated.

Ionic liquids have recently been researched to fractionate lignocellulosic materials. Ionic liquids having a large asymmetric organic cation and a small anion are an excellent solvent to depolymerize lignin for value-added productions. The arrangement is a special type of organosolv using ionic liquid to cleave the linkages between ether and alkyl, to yield monomeric methoxy phenols. Once depolymerized, the organosolv lignin can be catalytically converted into fuels or chemicals. Lewis–Brønsted acid zeolites and supported metal catalysts can be used alongside the ionic liquids as a solvent in organosolv to produce a high yield of propylguaiacol[37]. The stem woody tissue has shown a consistent mass ratio of syringyl to guaiacyl of 1.8–2.3. Depolymerization of these polymers for high value product generation loses the trapped bond energy, while direct extraction of biopolymers for functional materials, such as epoxy resins and composites, can retain the inherent properties of lignin, such as strength and rigidity. The process involves lignin polymer blending and reinforcement with cellulose based microfibrils.

Catalytic transfer hydrogenation is another concept applied to bio-oil hydrocracking that can be applied for lignin value-added chemical extraction. It is potentially attractive as it may not require a source of high pressure, high purity hydrogen gas and can be employed in relatively low pressure equipment whose capital costs are low. The expected outcome of this activity was selection of a process and catalyst that would result in lignin based products after decarboxylation with minimal oxygen removal, with no phase separation, with properties of functional phenolics, and also with a possibility of deriving guaiacol as the primary chemical to many products, shown in Figure 1.13. High throughput screening tests can be employed with a variety of conditions, donors and catalysts to select elementary reactions or reaction pathways to lead to effective product alternative evaluations. The final product can be anything in the product chain shown in Figure 1.13, but can be closely controlled by operating conditions and selective *in situ* removal.

Another alternative route is the hydrogenation to treat lignin with high pressure hydrogen in the presence of nickel-molybdenum or chromium oxide catalysts at 400 °C. The process produces monocyclic aromatics breaking down the lignin polymers. In terms of exergy loss in each conversion route of lignin into functional phenolic products, from the highest to the lowest, the following sequence is obtained:

Hydrogenation > Catalytic transfer hydrogenation > Ionic liquid catalytic organosolv > Mechanical/thermal/chemical blending and reinforcement of natural polymers. Hence, the mechanical/thermal/chemical blending and reinforcement of natural polymers is the most sustainable lignin conversion route.

Figure 1.14 shows the products from the various lignin conversion routes and their place in the market. World demand for phenolic derivatives is 8 million tonnes per year with a price of 1200 euros t^{-1}. In 2009, it was utilized as feedstock to produce bisphenol-A (48% of the world's phenol production), phenolic resin (25%), caprolactam (11%), alkyl phenols

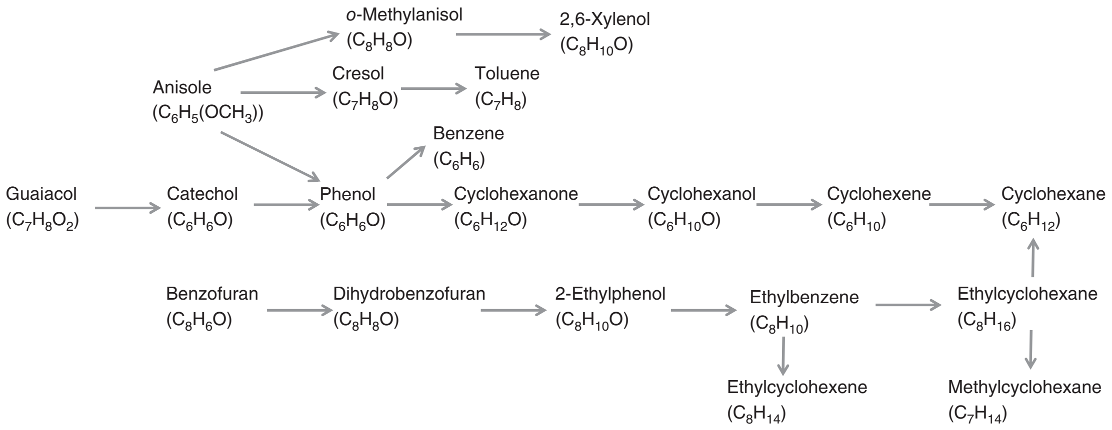

Figure 1.13 *Guaiacol derivatives.*

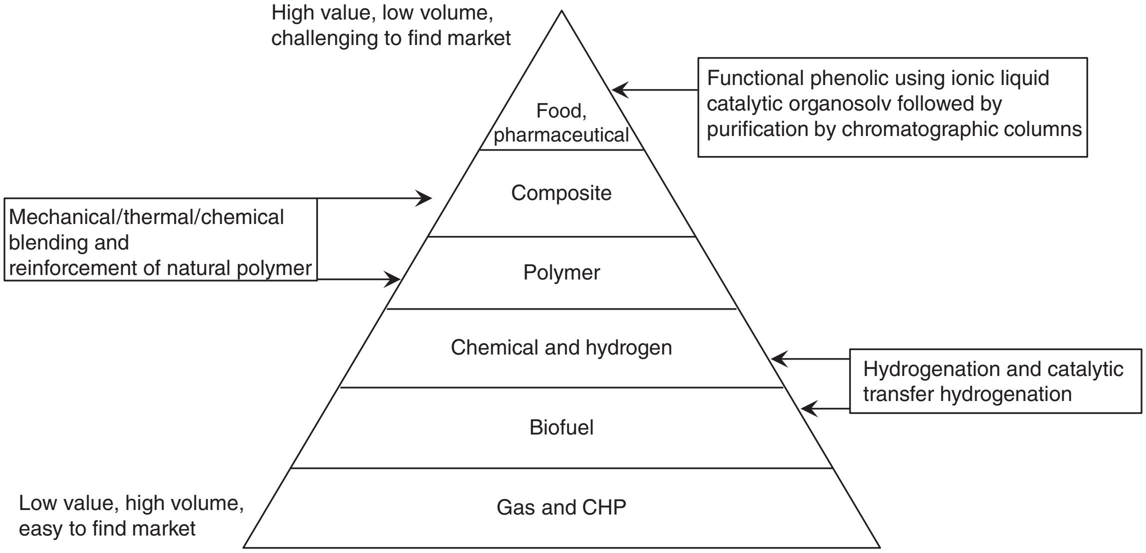

Figure 1.14 *Products from various lignin conversion routes and their place in the market.*

(4%), xylenols (4%), aniline (2%) and others. However, soon after, the United States Food and Drug Administration (FDA) found out about possible hazards of bisphenol-A to fetuses, infants, and young children. In September 2010, Canada for the first time declared bisphenol-A as a toxic substance. The European Union and the United States afterwards have also banned bisphenol-A use in baby bottles. Epoxy resins, as long as they contain no polycarbonate, are a substitute for bisphenol-A in the application of water bottles, dental fillings sealants, eyeglass lenses, sports equipment, CDs, DVDs and lining for water pipes, etc. Another possible route for lignin value addition is the production of renewable carbon fiber, used in lightweight vehicle bodies, lithium ion batteries and semiconductors. The conversion process involved is the multiphase rotating disc contactor organosolv, commercially available for carbon pitch fiber, adaptable for bio based fiber production.

As shown in Figure 1.14, functional phenolics as high value chemicals with moderate thermodynamic performance can be produced using ionic liquid catalytic organosolv. The normal purification process with chromatographic columns and ultra- and nanofiltration membranes can be followed thereafter.

The most commonly used ionic liquid solvent is alkylmidazolium for dissolving cellulose, while 1-ethyl-3-methylimidazolium triflate and chloride (EMIM-TF and EMIM-Cl), butyl and octyl of methylimidazolium triflate and chloride (BMIM and OMIM) and EMIM with a mixture of alkylbenzenesulfonates and xylenesulfonate are the known ionic liquid solvents for lignin, respectively. In general, dialkylimidazolium ionic liquid solvents are known for lignin separation. In addition, a wide range of Lewis and Brønsted acid catalyst can be used. Their effects on the lignin conversion, product yields and composition vary by a wide range, as low as no reaction happening to about 75% by weight of product yield. The main products characterized by gas chromatography are 4-propylguaiacol (highest quantity) > isoeugenol > guaiacol (lowest quantity).

The mechanism for cellulose dissolution is the intramolecular hydrogen bond breakage within cellulose fibers, due to ionic bonds between the anions (e.g., chlorides) of the ionic liquid and the hydroxy groups of the cellulose. The mechanism for lignin breakage is much more complex than cellulose as lignin is structurally more complex. Lignin model compounds have been studied for the dealkylation reaction mechanism. However, the unknown functionality of alkyl substituents and the unknown mechanism of cleavage of ether linkages in lignin are a major stumbling block to design the solvent, catalyst, and experiments. Previously experimented dealkylation conditions for other systems are still used. There is a real risk that the experimental efforts may not reveal anything useful to carry forward. High throughput experimentation is a good strategy, though expensive, but is only practical to apply once the fundamental mechanism is modeled and optimal solvents and experimental conditions are determined by modeling.

Lignin completely dissolves in ionic liquid solvent that is good for separating the lignin from cellulose. However, no identifiable product was formed using gas chromatography of Agilent 6890 DB-column[37]. However, ionic liquids are difficult to separate from lignin for reuse. The potential processes yet to be investigated are precipitation of polymeric lignin based by-products by water and by ultrafiltration membrane. Bioseparation routes are yet to be engineered. Nevertheless, none of the routes discussed has been optimized from bio-origins to reuse, pointing to a promising area for research.

The addition of acid catalysts helps the lignin conversion. Amongst them, some have shown no effect or recoverable production. The failed acid catalysts are shown as follows. However, it must be remembered that the reaction conditions were not optimized and were maintained at the dealkylation conditions studied for other systems[37].

High surface area titania (Ti-0720 T)
Nb_2O_5 hydrate (6518–43–11)
Silica/alumina T-869
Montmorillonite K10
Sulfated ZrO_2
$CoCl_2$
$NiCl_2$
$CuCl_2$
$ZnCl_2$
$InCl_3$
$SnCl_4$
$CeCl_3$
$SmCl_3$
$InCl_3$
etc.

4-Propylguaiacol product was produced in a recoverable quantity (>75% by weight in the product mixture) by the following catalyst: 0.5%Pd/alumina (C3677); $RhCl_3$, in EMIM-TF and EMIM-Cl ionic liquids. The reaction temperature was 180 °C. With increasing temperature, completion to 4-propylguaiacol production may be seen, but with more difficulty in ionic liquid solvent recovery and reuse. With increasing temperature the problem of acid hydrolysis reoccurring may be overcome. Also, using heterogeneous acid catalyst is a promising way to separate the functional phenolic products from the reaction mixture by in situ adsorption or by membrane, as soon as the products form. Further, the top ten chemical productions from lignin can be found in DOE documentation[29]. However, the engineered process designs are yet to be developed.

The screening of products and processing technologies describes a complex task more challenging than the development of fossil based refineries that feature fixed feedstocks (oil or gas) and an established portfolio of products. Considering the importance to scope for alternative feedstocks, processes and products, the biorefinery design requires models with strong *synthesis capabilities* and with functions to optimize degrees of freedom. Multiple chemistries should be screened to produce the most profitable products in the most resource efficient and integrated manner. This book discusses the essential and most important tools to design sustainable biorefinery systems.

1.7 Electrochemistry Application in Biorefineries

The application of electrochemistry powered by electron harvesting from organic wastes and transfer via the electrodes and electrolyte can greatly enhance the sustainability of energy production from biomass. Such technologies discussed in this book include the *proton exchange membrane fuel cell* (PEMFC) processing biogas for electricity and heat generation; *allothermal gasification* (combustion of char and steam gasification of the remaining biomass are carried out in separate, but heat integrated vessels, through which heat is circulated) and *solid oxide fuel cell* (SOFC) integration for efficient energy production, *mixed ionic electronic conducting hollow fiber membrane*, *microbial fuel cell* (MFC) and *bio fuel cell*, etc. Figure 1.15 shows the various types of fuel cells named after the electrolytes used.

Design, integration and sustainability analysis and modeling of SOFC in particular are discussed in this book. Life cycle assessment (LCA) and energy analysis data are provided for a range microgeneration options using fuel cells.

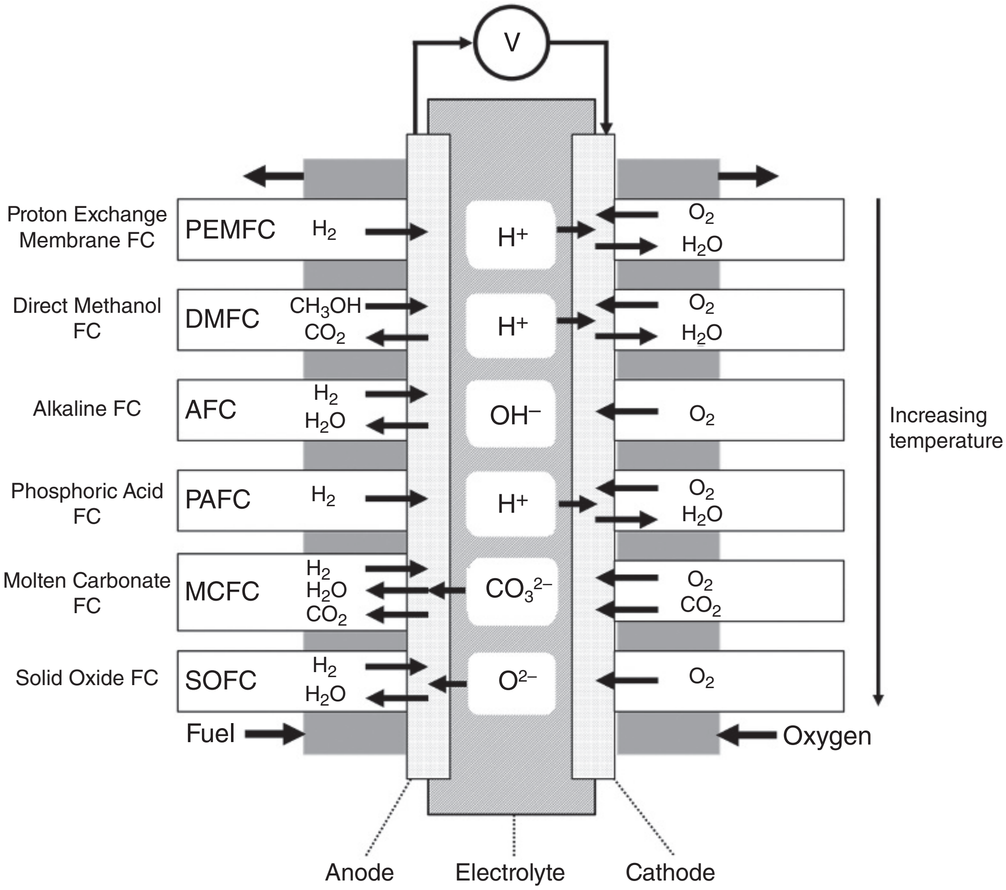

Figure 1.15 *Fuel cell types and reactions.*

MFC and bio fuel cells highlighted also hold promises. Bio fuel cells using glucose as substrate have the potential in the field of biomedical engineering, for example, as a pacemaker for the heart. There is great potential for organic waste disposal (including wastewater treatment) into electricity generation and metal recovery through MFC technology. A major challenge is the low power density compared to other types of fuel cells, as shown in Table 1.7. Though the amount of electric power generation is relatively low at present, future research is expected to improve the efficiency of these unique systems. These systems are a sustainable way to directly convert lignocellulosic biomass or wastewaters into useful energy and water using oxygen from air and hydrogen sourced from the biomass. An MFC can be single or double chambered. In MFC, microorganisms oxidize organic matter in the anode chamber (anaerobic conditions), producing electrons and protons. Electrons transfer via the external circuit to the cathode chamber, while protons transfer through the electrolyte. A solid proton exchange membrane electrolyte can be used to transfer protons from the anode to the cathode chamber. In the cathode chamber, electrons, protons and electron acceptor–oxygen–react together to produce water. Thus, if wastewater is the substrate used as a source of proton in the anode chamber, clean water can be produced from the cathode chamber by oxidizing protons. In a two-chamber setup, the anode and cathode compartments are separated by a proton selective membrane, allowing proton transfer from the anode to the cathode and preventing oxygen diffusion from the cathode to the anode. In a single-chamber MFC, the cathode is exposed directly to the air. Besides these two common designs, several adaptations can be made in MFC designs. The most common anode material is activated carbon cloth (wound or knitted) and brushes. Increasing the surface area per unit volume of anode helps in transferring proton

Table 1.7 *MFC systems research profile. (Reproduced with permission from Catal et al. (2008)*[38]*. Copyright © 2008, Elsevier.)*

Source Inoculum	Substrate and Concentration (g L^{-1})	MFC Anode Specification	MFC Cathode Specification	Power Density (A m^{-2})
Pre-acclaimed bacteria from MFC	Arabitol: 1.22	Non-wet proofed carbon cloth (2 cm^2 per 12 ml)	Wet proofed carbon cloth (7 cm^2 per 12 ml)	6.8
	Galactitol: 1.22	Non-wet proofed carbon cloth (2 cm^2 per 12 ml)	Wet proofed carbon cloth (7 cm^2 per 12 ml)	7.8
	Mannitol: 1.22	Non-wet proofed carbon cloth (2 cm^2 per 12 ml)	Wet proofed carbon cloth (7 cm^2 per 12 ml)	5.8
	Ribitol: 1.22	Non-wet proofed carbon cloth (2 cm^2 per 12 ml)	Wet proofed carbon cloth (7 cm^2 per 12 ml)	7.3
	Sorbitol: 1.22	Non-wet proofed carbon cloth (2 cm^2 per 12 ml)	Wet proofed carbon cloth (7 cm^2 per 12 ml)	6.2
	Xylitol: 1.22	Non-wet proofed carbon cloth (2 cm^2 per 12 ml)	Wet proofed carbon cloth (7 cm^2 per 12 ml)	7.1
Mixed bacterial culture maintained on sodium acetate (*Rhodococcus* and *Paracoccus*)	Glucose: 6.7 mmol	Non-wet proofed carbon cloth (2 cm^2 per 12 ml)	Wet proofed carbon cloth (7 cm^2 per 12 ml)	7
Mixed bacterial culture	Glucuronic acid: 6.7 mmol	Non-wet proofed carbon cloth (2 cm^2 per 12 ml)	Wet proofed carbon cloth (7 cm^2 per 12 ml)	11.8
Pure culture of *Geobacter sulfurreducens*	Sodium fumarate: 25 mmol	Ag/AgCl	Stainless steel (2.5 cm^2)	20.5

to the cathode that is also made up of activated carbon cloth, but with an embedded catalyst, for example, platinum. Reducing platinum quantity has the cost and environmental incentive, indicating that the surface area per unit volume of the anode must be increased with the anode brought closer to the cathode chamber to reduce the distance for proton transport. At the same time, oxygen must be prevented from penetrating through the cathode to the anode to increase the electron transfer rate externally generating power. Hence, proton exchange membrane material such as nafion (sulfonated tetrafluoroethylene based fluoropolymer–copolymer) is commonly used to facilitate proton transfer and a membrane is added on the oxygen side of the cathode chamber to prevent oxygen transport through the cathode.

The demand for water, mineral and energy resources is rapidly increasing due to the growing world population and rising economies. Currently mineral and energy resources are primarily obtained from nonrenewable geological deposits. These extraction processes need water. Though water is considered as a renewable resource, water will inevitably be depleted, beyond recovery, generating wastewater. The development of more sustainable routes to recover resources is paramount. Wastewater generating from agricultural, municipal, industrial and commercial sectors can be potential sources of metals that can be recovered using MFC. Their recovery is otherwise not possible using chemical processes, for example, precipitation, filtration and solvent extraction, etc., due to low metal selectivity and because of their low concentrations in a highly complex mixture. They can also cause secondary pollution from metal enriched sludge, from which it is not technically feasible to recover metals. MFC using bioelectrochemical technology to recover energy and minerals from wastewater offers the potential to overcome these problems. Elemental recovery from wastewaters can add economic and environmental value to the existing MFC technologies. The various electrochemical methods, such as electrodeposition, electrodialysis and electroprecipitation, can be used to recover Cu, Co, Ni, Pb, Cr, Sn and salt from scrap printed circuit boards and dilute wastewater streams.

Water electrolysis and microbial electrolysis cells (MECs) use electrical voltage (and work on the reverse of fuel cell principles) to produce hydrogen. Hydrogen production is an energy intensive process. Natural gas steam reforming (that is a highly endothermic chemical reaction) is the most common hydrogen production method. Renewable electrical energy (e.g., solar, wind, hydro, etc.) can be supplied in MEC to produce hydrogen, renewably. Electrohydrogenesis is an MEC process that requires application of voltage to produce hydrogen using acetate or glucose as a substrate in the anode. The cathode is sealed to keep the oxygen source away to produce hydrogen from a single chamber MEC without a membrane. The process delivers a higher hydrogen yield than fermentation of acetate and a higher energy efficiency than water electrolysis. However, hydrogen produced needs to be compressed and stored before further use as an energy vector. This adds to the economic and environmental life cycle costs. Also, more than a third of the cost is incurred from expensive platinum catalyst used on the cathode; in some cases its loading is as high as 0.5 mg cm^{-2}. To reduce the cost, alternative catalysts have been explored, but these resulted in high loading to achieve the same performance as Pt. A more cost-effective and environmentally sustainable route is to use hydrogen to produce products in the cathode chamber within the same electrochemical apparatus, generally MEC. Electromethanogenesis is a process to produce methane in the cathode chamber combining carbon dioxide, proton, and electron evolved from the anode chamber in a two-chamber MEC, by applying a slightly different electrical voltage needed for electrohydrogenesis. Based on thermodynamic calculations, methane could be produced electrochemically through carbon dioxide reduction at a voltage of 0.169 V under standard conditions, or −0.244 V under more biologically relevant conditions at a pH of 7[39], by primarily using Sabatier's reaction[13]. This has opened up a whole range of opportunities for carrying out environmentally friendly biorefining productions in bioelectrochemical systems (BESs) from organic wastes.

1.8 Introduction to Energy and Water Systems

While most chapters in this book discuss the subject of biorefineries and chemical processes, some features of energy and water systems modeling have been discussed in Web Chapters 2 and 3, because these systems are interacting systems of biorefineries and call for overall integration and analysis for sustainability. Web Chapter 1 includes waste and emission mitigation technologies relevant for biorefineries.

The main use of lignocellulose is for chemical and material productions, because there is no other alternative source of renewable carbon. There are options for renewable energy generation, other than biomass, such as wind, solar, tidal, geothermal and hydropower. Depending upon the availability of these resources, choices of local level renewable energy supplies can be made. The main stress should be on local availability of natural resources and how to make sustainable use of them, not only for technoeconomic viability but also to help grow an economy through education and job creation. Biorefinery engineering is just not about effective use of biomass, but also how whole supply chain systems can be synergistically designed using local resources delivering products of need, for socioeconomic welfare and ecosystem balance.

Renewable technologies need to be developed to mitigate global warming potential resulting from fossil based energy generation systems. However, a renewable energy supply is intermittent in nature. This intermittency has to be resolved by energy storage systems. Energy storage systems can be of various forms, including chemical, such as hydrogen and methanol. Biomass is a form to entrap renewable carbon and hydrogen and thus energy. Hence, to resolve supply intermittency of renewable energy systems listed above, biomass CHP systems can be operated when required. Largely, the renewable energy supply intermittency is addressed by fossil (coal, crude oil) based power plants, even today. However, the world is approaching an era of a lack of or prohibitively expensive fossil resources.

The other ways of energy storage are through the design of functional materials: physical, thermochemical, and electrochemical storage systems. The storage systems can be effectively designed to store water and heat (thermochemical: absorption and adsorption based) as well as water and electricity (fuel cells) simultaneously. Therefore, there are two ways to address the renewable energy resource intermittencies.

1. Biomass CHP generation. (However, remember that the best use of biomass is to produce products containing carbon as there is no other renewable carbon resource available. Excess biomass can be used for energy generation.)
2. Energy storage.

Under these broad levels of groupings, some options for energy supply and storage exist. Technologies need to be developed using abundant, cheap and environmentally friendly material in a scalable and reproducible process. Graphene (the lowest assembly of carbon atoms with one atom thickness) is an important material for energy storage and generation processes. Graphene has been discussed with novel applications in Web Chapter 2, because many fundamental theories in physics, electrochemistry and chemical physics can be generated investigating graphene.

The energy transfer model is at the core of design of materials and systems for energy storage and renewable energy generation; hence, it is the key focus of Web Chapter 2. Two strategies can be adopted to control energy transfer of a system.

1. Active thermal control strategy. An active thermal control strategy is based on process control theory. Processes are associated with unsteady state operations, in which the various properties of process streams and operating conditions change. In order to ensure safe operation of processes and achieve the greatest productivity and purity and least cost, etc., the processes need to operate at optimal operating conditions. Process control is needed to achieve optimal operating conditions during process operation. Hence, the subject of process control has been discussed with sufficient depth for biorefinery engineers in Web Chapter 2.
2. Passive thermal control strategy. A passive thermal control strategy deals with the design of materials to optimize physical properties so as to minimize external heat and power requirements or to maximize net heat and power generations from a system to the surrounding, without incorporation of any external fuel. This is the general philosophy for biorefinery design and is specifically addressed in Web Chapter 2.

Global greenhouse gas emissions result from direct consumption of fossil fuels by 58% and the balance from indirect electricity consumption. Figure 1.16 shows a generic trend of greenhouse gas emissions in percentage weight from end use sectors. The majority is contributed by the transport sector (33%), which can be decarbonized by biofuel production together with carbon capture and storage, followed by the industrial sector (28%) consisting of energy use by the sector, chemical and material production and extraction of metals, residential building (21%) and commercial building (18%). Decarbonization of the industrial sector will depend on how effectively biomass is utilized. Biomass is the only alternative source to chemical and material production, whilst renewable energy systems and energy storage systems can share some portions of the industrial energy use and energy required for metal extraction. Thus, only co-optimization of biorefinery, renewable energy and energy storage systems can fully decarbonize the industrial sector.

More than half of the industrial greenhouse gas emissions is caused by direct fossil resource consumption that must be avoided. At the point of use, a significant fraction of energy use is for heating water for domestic and industrial purposes. This water–energy nexus is the relationship between how energy is used to abstract, treat and transport water to users and water used in many energy conversion processes, waste heat recovery and cooling cycles. With increased insurgence

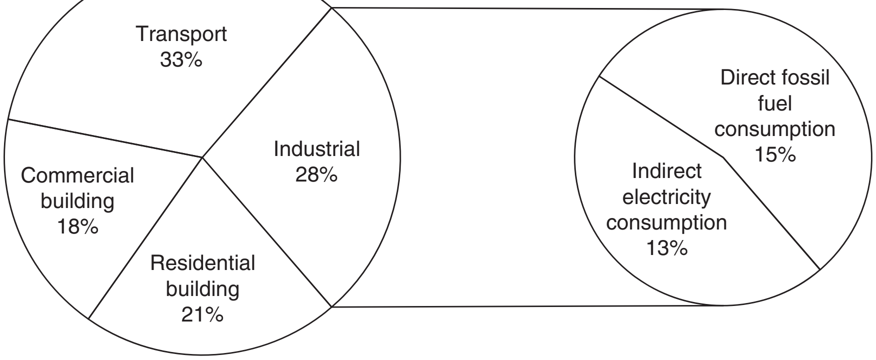

Figure 1.16 *Greenhouse gas emissions in weight percentages from end use sectors.*

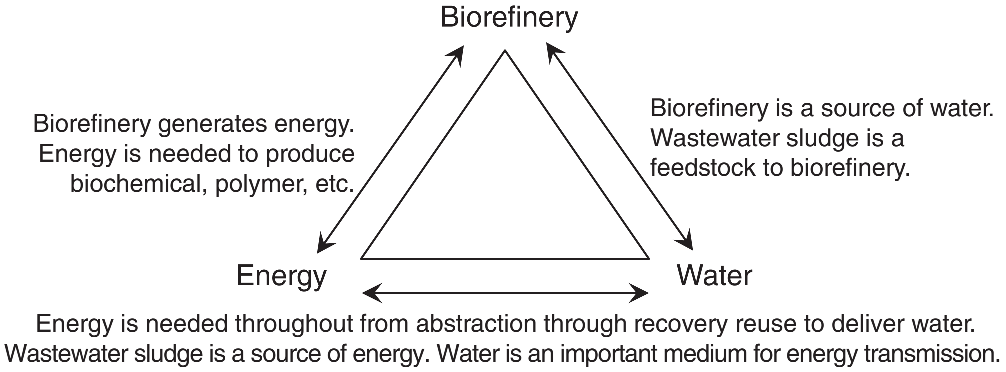

Figure 1.17 *Biorefinery–energy–water nexus.*

of biorefineries, water footprint and thereby energy use is going to increase as biomass has more water content per unit of energy delivered compared to fossil resources. Energy is required to recover this water from biomass. In the biomass gasification route, the wet product gas is cooled to just below its dew point to separate noncondensable gas from water. While biomass is a source of water and energy, wastewater sludge is an important feedstock for a biorefinery. Thus, there are three-way interactions or nexus between the biorefinery, energy and water (Figure 1.17). Hence, the three systems must be designed synergistically for an urban system. Thus, in this book, the latter two are also addressed alongside in-depth learning materials for biorefinery systems. Clearly, engineers need to be aware of such cross-disciplinary nexus areas.

1.9 Evaluating Biorefinery Performances

1.9.1 Performance Indicators

The promise of biorefineries as contributors to sustainable development makes necessary the introduction of sustainability metrics for biorefinery planning and design. The complexity and multifaceted nature of the concept has led to the derivation of various indicators for the economic, environmental and social components. Indicators derived from concepts such as green chemistry and engineering, cleaner production, ecoefficiency, industrial ecology, ecodesign and life cycle analysis are used by industry and institutions such as the Center for Waste Reduction Technologies, the Institution of Chemical Engineers, among others. The various sets of indicators proposed often have similarities and discrepancies, but they can be useful if applied as complementary measures. Indicators continue evolving and new concepts and methodologies are proposed. The various indicators used to analyze sustainability must allow their evaluation from a life cycle approach and must be useful for the identification of hot spots and trade-offs. Environmental impacts of biorefineries have become important, such as climate change, eutrophication, water depletion, land use, depletion of energy and material resources and aquatic toxicity. Several aspects can be categorized according to the particularities of biorefineries.

Considering the significance of indicators for assessing biorefinery sustainability, the most prominent set of parameters are shown in Table 1.8. The metrics are grouped according to their relation to resources use, process efficiency, advantage over fossil-based products and economic performances, etc. The indicators are appropriate for comparison of biorefinery configuration alternatives and for identification of processing pathways for process integration. Not all the indicators are necessary at the same time because they may not differ from one configuration to another and they may be comparable with fossil based equivalent systems.

In addition, local versus global consequences are considered to adopt a biorefinery design configuration. Amongst the indicators shown in Table 1.8, the resource depletion, climate change impacts and aquatic toxicities have global consequences, whilst the acidification potential has regional consequences and the photochemical oxidant creation potential has local level consequences.

Table 1.8 *Indicators used throughout the present work to evaluate biorefinery performances*[40–42].

Indicators	Definition	Measured as: Better or Worse than Fossil Based Equivalents?
Process performance		
Energy conversion efficiency	Ratio between net energy output (as valuable products, including electricity, steam, fuels and other streams contributing to energy generation) to energy input (e.g., total biomass calorific value).	Fraction or percentage. Worse than fossil based equivalents.
Primary resources use		
Cumulative primary energy (CPE)	Primary energy resources (crude oil, natural gas, coal, etc.) consumed throughout the life cycle of a system, process or product.	Energy units. Saves fossil resource.
Abiotic resources use	Depletion of nonrenewable resources.	Mass of Sb equivalent. Saves abiotic resource.
Land use	Amount of land used per unit biomass feedstock production. Lignocellulosic feedstocks are chosen to reduce land use.	ha (hectare) Worse than fossil based equivalents. Lignocellulosic feedstocks are thus urgently sought.
Water use	Amount of freshwater depletion, beyond recovery.	m^3 Worse than fossil based equivalents.
Environment		
Greenhouse gases or global warming or climate change	Gases causing greenhouse effect, i.e., with global warming potential.	Mass of CO_2 equivalent. Avoid GHG emissions.
Eutrophication	Overenrichment of water by nutrients such as nitrogen and phosphorus which, among other effects, can destroy aquatic life in affected areas.	Mass of PO_4^{3-} equivalent. Worse than fossil based equivalents.
Acidification	Emissions of sulfur and nitrogen oxides cause acid rains that destroy vegetation.	Mass of SO_2 equivalent. Better than fossil based equivalents.
Photochemical oxidant creation potential	The volatile organic compounds and ozone in the lower atmosphere are responsible for urban smog and ground level ozone formation and are classified under photochemical oxidant creation potential.	Mass of ethylene equivalent. Worse than fossil based equivalents.
Aquatic toxicity	Toxic substance emissions to water bodies.	Mass of 1,4-dichlorobenzene equivalent. Worse than fossil based equivalents.
Economic performance		
Economic margin	Revenue potential of a biorefinery.	Currency units. Worse than fossil based equivalents.

1.9.2 Life Cycle Analysis

The metrics and tools for evaluating biorefinery sustainability are still evolving as the sustainability concept itself. There is a need for extensive quantitative tools to support decision making in biorefinery design from cradle to grave, that is, focusing not only on a product or process but the entire biorefinery system. Several tools have been developed for this purpose including LCA, the energy-based sustainability index (ESI), material flow analysis (MFA), ecological input/output analysis (EIOA), among others. LCA is the most suitable tool for comprehensive and quantitative assessments capturing the direct and indirect environmental impacts associated with a given product or process design. This tool standardized by the ISO 14040, 14041 and 14044 has been internationally accepted. LCA is playing a leading role for the sustainability analysis of biorefinery systems.

LCA is used to find the environmental burdens associated with a product, process, or activity by identifying and quantifying energy and material resources used and wastes and emissions released to the environment. The life cycle of a system or product includes extraction and processing of raw materials, manufacturing, transportation, distribution, and use of products, and reuse, maintenance and recycling of material of construction. The holistic approach of LCA is needed for sustainable biorefinery design and screening of options, discussed in detail with practical applications to biorefinery and energy systems in this book.

1.10 Chapters

Opening with an introduction on the concept and development of biorefinery, the book is then split into four parts:

Tools. Detailed analysis of economic, environmental and whole system impact, as well as combined economic value and environmental impact (EVEI) analysis. Life cycle assessment and heat integration and utility system design. Mathematical programming based optimization and genetic algorithms.

Process synthesis and design. Focuses on modern unit operations and innovative process flowsheets: reactors; electrochemical, membrane and combined reaction and separation processes with multifunctionalities. Production of chemicals and polymers from biomass. Thermochemical processing of biomass and biochemical processing of biomass. Processes for carbon dioxide capture.

Biorefinery systems. Biorefinery process synthesis examples using design, integration and sustainability analysis tools as appropriate. Bio-oil and algae biorefineries, integrated fuel cells and renewables, multiscale modeling of heterogeneously catalyzed reactions using the example of biodiesel.

Interacting systems of biorefineries. Looks at minimalizing waste and emissions, storing energy and the optimization and reuse of water.

Additional exercises and examples referred to within each chapter of the book can be found on a companion website. Four case studies are given on the companion website: LCA based problem solving approaches on biomass CHP plant design problems, epoxy resin production from biomass, wastewater sludge based CHP and the LCA approach for solar organic photovoltaic cells manufacturing. Figure 1.18 shows the structure of the book for lecture planning.

1.11 Summary

The introduction chapter provides overviews of biorefinery design options, including feedstock, product and platform chemical and process choices. Lignocellulosic biomass has been specifically covered for sustainable biorefinery systems. Lignin value addition holds the key to the commercial success of biorefineries. The background of lignin including process design options has been shown in great detail. The future biorefinery designs will feature electrochemical and bio-oil platforms to produce a range of products in a compact and efficient way. Co-design of lignocellulosic biorefineries, renewable energy systems and energy storage systems is necessary for overall sustainable development in a world without fossil resources. Economics, LCA and multicriteria indicators are applied for biorefinery design, integration and sustainability analysis.

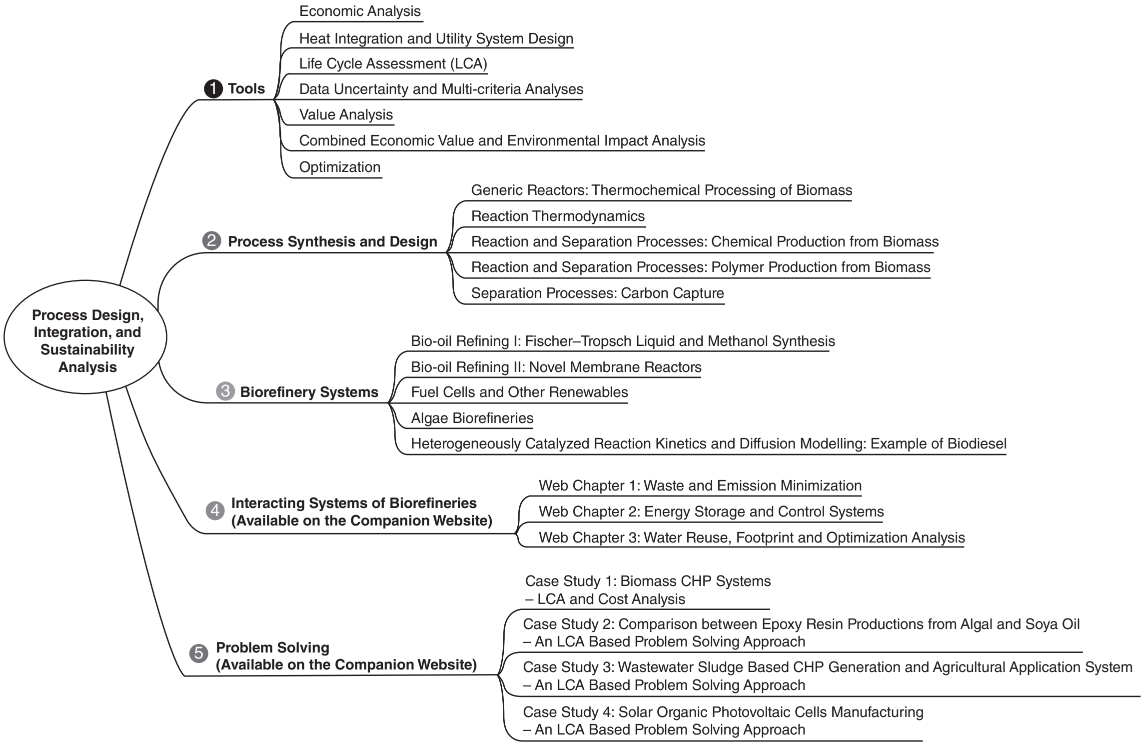

Figure 1.18 *Structure for lecture planning.*

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