Introduction of Biomass and Biorefineries*

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The development of biorefineries represents the key to access the integrated production of food, feed, chemicals, materials, goods, fuels, and energy in the future. Biorefineries combine the required technologies for biogenic raw materials from agriculture and forestry with those of intermediate and final products. The specific focus of this chapter is the combination of green agriculture with physical and biotechnological processes for the production of proteins as well as the platform chemicals lactic acid and lysine. The mass and energy flows (steam and electricity) of the biorefining of green biomass into these platform chemicals, proteins, and feed as well as biogas from residues are given. The economic and ecologic aspects for the cultivation of green biomass and the production of platform chemicals are described.

1.1 INTRODUCTION

One hundred and fifty years after the beginning of coal-based chemistry and 50 years after the beginning of petroleum-based chemistry, industrial chemistry is now entering a new era. An essential part of the sustainable future will be based on the appropriate and innovative use of our biologically based feedstocks. It will be particularly necessary to have a substantial conversion industry in addition to research and development investigating the efficiency of producing raw materials and product lines, as well as sustainability.

Whereas the most notable successes in research and development in the field of biorefinery system research have been in Europe and Germany, the first significant

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industrial developments were promoted in the United States of America by the President and Congress [1–5]. In the United States, it is expected that by 2020 at least 25% (compared to 1995) of organic carbon-based industrial feedstock chemicals and 10% of liquid fuels will be obtained from a biobased product industry [6]. This would mean that more than 90% of the consumption of organic chemicals and up to 50% of liquid fuel requirements in the United States would be supplied by biobased products [7]. The US Biomass Technical Advisory Committee (BTAC)—in which leading representatives of industrial companies such as Dow Chemical, E.I. du Pont de Nemours, Cargill, Dow LLC, and Genecor International Inc., as well as corn growers' associations and the Natural Resources Defence Council are involved, and which acts as an advisor to the US government—has made a detailed step-by-step plan of the targets for 2030 with regard to bioenergy, biofuels, and bioproducts [8–10].

Research and development are necessary to

(1) increase the scientific understanding of biomass resources and improve the tailoring of those resources;

(2) improve sustainable systems to develop, harvest, and process biomass resources;

(3) improve the efficiency and performance in conversion and distribution processes and technologies for a multitude of product developments from biobased products; and

(4) create the regulatory and market environment necessary for the increased development and use of biobased products.

BTAC has established specific research and development objectives for feedstock production research. Target crops should include oil- and cellulose-producing crops that can provide optimal energy content and usable plant components. Currently, however, there is a lack of understanding of plant biochemistry as well as inadequate genomic and metabolic information on many potential crops. In particular, research to produce enhanced enzymes and chemical catalysts could advance biotechnological capabilities.

In Europe, there are existing regulations regarding the substitution of nonrenewable resources by biomass in the field of using biofuels for transportation as well as the "Renewable energy law" [11, 12]. According to the EC Directive "On the promotion of the use of biofuels," the following products are considered as "biofuels": (a) "bioethanol," (b) "biodiesel," (c) "biogas," (d) "biomethanol," (e) "bio-dimethylether," (f) "bio-ETBE (ethyl-*tert*-butylether)" based on bioethanol, (g) "bio-MTBE (methyl-*tert*-butylether)" based on biomethanol, (h) "synthetic biofuels," (i) "biohydrogen," and (j) pure vegetable oil.

Member states of the EU have been asked to define national guidelines for the minimum usage quantities of biofuels and other renewable fuels (with a reference value of 2% by 2005 and 5.75% by 2010, calculated on the basis of the energy content of all petrol and diesel fuels for transport purposes). Currently, there are no guidelines for biobased products in the EU or in Germany. However, after passing directives for bioenergy and biofuels, such activities are on the political agenda.

Recently, the German Government has announced the biomass action plan for substantial use of renewable resources, and the German Chemical Societies have published the position paper "Raw material change," including nonfood biomass as raw material for the chemical industry [13, 14]. The European Technology Platform for Sustainable Chemistry has created the EU Lead Market initiative [15]. The directive for biofuels already includes ethanol, methanol, dimethylether, hydrogen, and biomass pyrolysis, which are fundamental product lines of the future biobased chemical industry. A recent paper looking at future developments, published by the Industrial Biotechnology section of the European Technology platform for Sustainable Chemistry, foresaw up to 30% of raw materials for the chemical industry coming from renewable sources by 2025 [16]. The ETPSC has created the EU Lead Market initiative [15].

The European Commission and the US Department of Energy have come to an agreement for cooperation in this field [17]. Based on the European biomass action plan of 2006, both strategic EU-projects (1) BIOPOL, European Biorefineries: Concepts, Status and Policy Implications and (2) Biorefinery Euroview: Current situation and potential of the biorefinery concept in the EU: strategic framework and guidelines for its development, began preparation for the 7th EU framework [18–20].

In order to minimize food–feed–fuel conflicts and to use biomass most efficiently, it is necessary to develop strategies and ideas for how to use biomass fractions, in particular, green biomass and agricultural residues such as straw, more efficiently. Such an overall utilization approach is described in Section 1.2. In future developments, food- and feed-processing residues should therefore also become part of biorefinery strategies, since either specific waste fractions may be too small for a cost-efficient specific valorization (capitalize on nature's resources) treatment *in situ* or the diverse technologies necessary are not available. Fiber-containing food-processing residues may then be pretreated and processed with other cellulosic material from other sources in order to produce ethanol or other platform chemicals. Food-processing residues have, however, a particular feature one has to be aware of. Due to their high water content and endogenous enzymatic activity, food-processing residues have a comparatively low biological stability and are prone to uncontrolled degradation and spoilage including rapid autoxidation. To avoid extra costs for transportation and conservation, the use of food-processing residues should also become part of a regional biomass utilization network [21].

1.2 BIOREFINERY TECHNOLOGIES AND BIOREFINERY SYSTEMS

1.2.1 Background

Biobased products are prepared for economically viable use by a suitable combination of different methods and processes (physical, chemical, biological, and thermal). To this end, base biorefinery technologies need to be developed. For this reason, it is inevitable that there must be profound interdisciplinary cooperation among the individual disciplines involved in research and development. Therefore, it is appropriate to use the term "biorefinery design," which implies that well-founded

scientific and technological principles are combined with technologies, products, and product lines inside biorefineries that are close to practice. The basic conversions of each biorefinery can be summarized as follows.
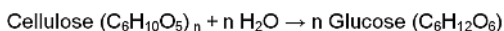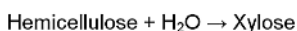
In the first step, the precursor-containing biomass is separated by physical methods. The main products (M1–Mn) and by-products (B1–Bn) will subsequently be subjected to further processing by microbiological or chemical methods. The subsequent products (F1–Fn) obtained from the main products and by-products can be further converted or used in a conventional refinery. Four complex biorefinery systems are currently under testing at the research and development stage:

(1) Lignocellulosic feedstock biorefinery using naturally dry raw materials such as cellulose-containing biomass and wastes.
(2) Whole-crop biorefinery using raw material such as cereals or maize (whole plants).
(3) Green biorefineries using naturally wet biomasses such as green grass, alfalfa, clover, or immature cereal [22, 23].
(4) The two-platforms biorefinery concept, which includes the sugar platform and the syngas platform [24].
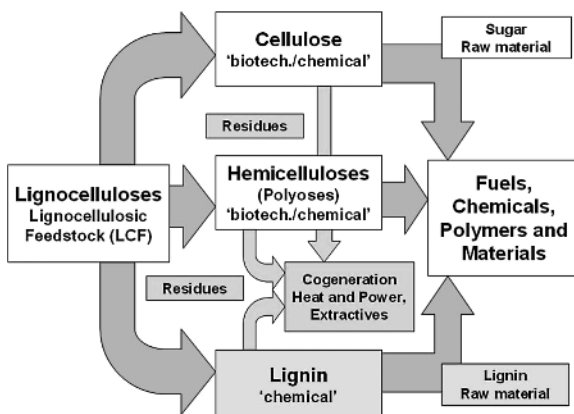
1.2.2 Lignocellulosic Feedstock Biorefinery

Among the potential large-scale industrial biorefineries, the lignocellulosic feed-stock (LCF) biorefinery will most probably be the most successful. First, there is optimum availability of raw materials (straw, reed, grass, wood, paper waste, etc.), and second, the conversion products are well-placed on the traditional petrochemical as well as on the future biobased product market. An important factor in the utilization of biomass as a chemical raw material is its cost. Currently, the cost for corn stover or straw is US $50/metric ton, and for corn US $80/metric ton [25].

Lignocellulose materials consist of three primary chemical fractions or precursors: (1) hemicellulose/polyoses—a sugar polymer predominantly having pentoses; (2) cellulose—a glucose polymer; and (3) lignin—a polymer of phenols (Fig. 1.1). The lignocellulosic biorefinery system has a distinct ability to create genealogical trees. The main advantages of this method are that the natural structures and structure elements are preserved, the raw materials are cheap, and many product varieties are possible (Fig. 1.2). Nevertheless, there is still a requirement for development and

$$\text{Lignocellulose} + H_2O \rightarrow \text{Lignin} + \text{Cellulose} + \text{Hemicellulose}$$

$$\text{Hemicellulose} + H_2O \rightarrow \text{Xylose}$$

$$\text{Xylose } (C_5H_{10}O_5) + \text{Acid Catalyst} \rightarrow \text{Furfural } (C_5H_4O_2) + 3H_2O$$

$$\text{Cellulose } (C_6H_{10}O_5)_n + n\, H_2O \rightarrow n\, \text{Glucose } (C_6H_{12}O_6)$$

FIGURE 1.1 A possible general equation of conversion at the lignocellulosic feedstock (LCF) biorefinery [26].

FIGURE 1.2 Lignocellulosic feedstock biorefinery [26].

optimization of these technologies, for example, in the field of separating cellulose, hemicellulose, and lignin, as well as in the use of lignin in the chemical industry.

Furfural and hydroxymethylfurfural, in particular, are interesting products. Furfural is the starting material for the production of Nylon 6,6 and Nylon 6 [27]. The original process for the production of Nylon 6,6 was based on furfural. The last of these production plants in the United States was closed in 1961 for economic reasons (the artificially low price of petroleum). Nevertheless, the market for Nylon 6 is still very large.

However, some aspects of the LCF system, such as the utilization of lignin as a fuel, adhesive, or binder, remain unsatisfactory because the lignin scaffold contains considerable amounts of monoaromatic hydrocarbons which, if isolated in an economically efficient way, could add significant value to the primary process. It should be noted that there are no obvious natural enzymes to split the naturally formed lignin into basic monomers as easily as polymeric carbohydrates or proteins, which are also naturally formed [28].

An attractive accompanying process to the biomass-nylon process is the previously mentioned hydrolysis of cellulose to glucose and the production of ethanol. Certain yeasts produce a disproportionate amount of the glucose molecule while generating glucose out of ethanol. This process effectively shifts the entire reduction ability into the ethanol and makes the latter obtain a 90% yield (w/w; with regard to the formula turnover). Based on recent technologies, a plant was designed for the production of the main products furfural and ethanol from LC-feedstock in West Central Missouri. Optimal profitability can be reached with a daily consumption of about 4360 ton feedstock. Annually, the plant produces 47.5 million gallons ethanol and 323,000 ton furfural [29].

Ethanol may be used as a fuel additive. Ethanol is also a connecting product for a petrochemical refinery, and can be converted into ethylene by chemical methods.

As is well-known from the use of petrochemically produced ethylene, nowadays ethanol is the raw material for a whole series of large-scale technical

chemical syntheses for the production of important commodities, such as polyethylene or polyvinylacetate. Other petrochemically produced substances, such as hydrogen, methane, propanol, acetone, butanol, butandiol, itaconic acid, and succinic acid, can similarly be manufactured by substantial microbial conversion of glucose [30–32]. DuPont has entered into a 6-year alliance with Diversa to produce sugar from husks, straw, and stovers in a biorefinery, and to develop processes to coproduce bioethanol and value-added chemicals such as 1,3-propandiol. Through metabolic engineering, the microorganism *Escherichia coli* K12 produces 1,3-propandiol in a simple glucose fermentation process developed by DuPont and Genencor. In a pilot plant operated by Tate and Lyle, the 1,3-propandiol yield reaches $135\,g\,L^{-1}$ at a rate of $4\,g\,L^{-1}\,h^{-1}$ [33]. 1,3-Propandiol is used for the production of polytrimethylene-terephthalate (PTT), a new polymer used in the production of high-quality fibers with the brand name Sorona [33]. Production was predicted to reach $500\,kt\,year^{-1}$ in 2010.

1.2.3 Whole-Crop Biorefinery

Raw materials for whole-crop biorefineries are cereals such as rye, wheat, triticale, and maize (Fig. 1.3). The first step is their mechanical separation into grain and straw, where the portion of grain is approximately 1 and the portion of straw is 1.1–1.3 (straw is a mixture of chaff, stems, nodes, ears, and leaves). The straw represents an LCF and may be processed further in an LCF biorefinery system. Initial separation into cellulose, hemicellulose, and lignin is possible, with their further conversion within separate product lines, as described above for LCF biorefineries. Furthermore, straw is a raw material for the production of syngas via pyrolysis technologies. Syngas is the base material for the synthesis of fuels and methanol (Figs. 1.3 and 1.4).

The corn may either be converted into starch or used directly after grinding into meal. Further processing can take one of the four routes: (1) breaking up, (2) plasticization,
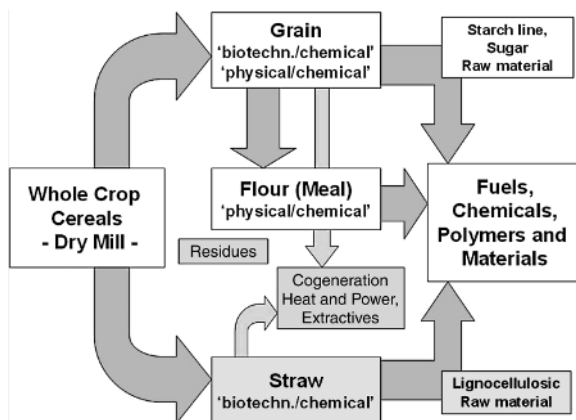

FIGURE 1.3   Whole-crop biorefinery—based on dry milling [26].
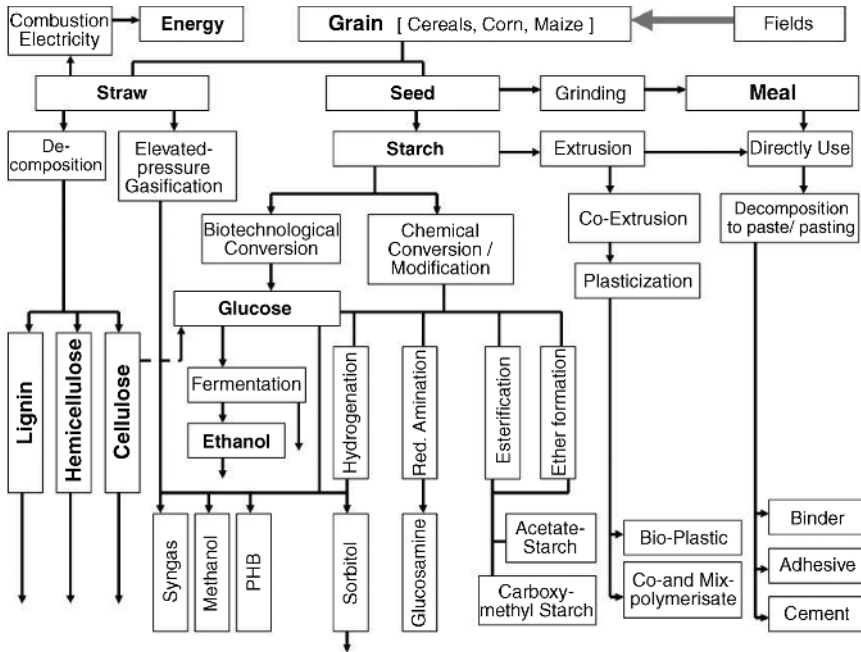
FIGURE 1.4   Products from the whole-crop biorefinery [22, 23].

(3) chemical modification, or (4) biotechnological conversion via glucose. The meal can be treated and finished by extrusion into binder, adhesives, or filler. Starch can be finished via plasticization (co- and mix-polymerization, compounding with other polymers), chemical modification (etherification into carboxy-methyl starch; esterification and re-esterification into fatty acid esters via acetic starch; splitting reductive amination into ethylene diamine), and hydrogenative splitting into sorbitol, ethylene glycol, propylene glycol, and glycerine [34–36]. In addition, starch can be converted by a biotechnological method into poly-3-hydroxybutyric acid in combination with the production of sugar and ethanol [37, 38]. Biopol, the copolymer poly-3-hydroxybutyrate/3-hydroxyvalerate, developed by ICI is produced from wheat carbohydrates by fermentation using *Alcaligenes eutropius* [39].

An alternative to the traditional dry fractionation of mature cereals into sole grains and straw has been developed by Kockums Construction Ltd (Sweden), now called Scandinavian Farming Ltd. In this whole-crop harvest system, whole immature cereal plants are harvested and all the harvested biomass is conserved or dried for long-term storage. When convenient, it can be processed and fractionated into kernels, straw chips of internodes, and straw meal, including leaves, ears, chaff, and nodes (see also Section 1.2.4).

Fractions are suitable as raw materials for the starch polymer industry, the feed industry, the cellulose industry and particle-board producers, as gluten for the chemical industry, and as a solid fuel. This kind of dry fractionation of the whole crop to
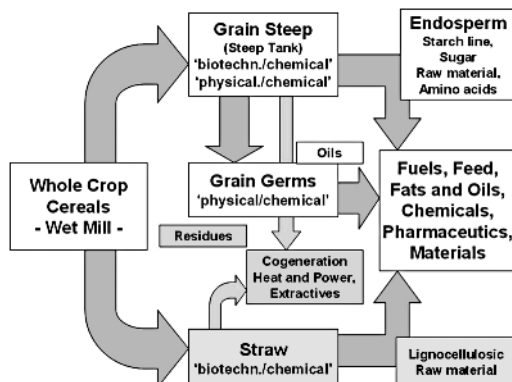
FIGURE 1.5 Whole-crop biorefinery, wet-milling [26].

optimize the utilization of all botanical components of the biomass has been described in Rexen (1986) and Coombs and Hall (1997) [40, 41]. An example of such a biorefinery and its profitability is described in Audsley and Sells (1997) [42]. The whole-crop wet-mill-based biorefinery expands the product lines into grain processing. The grain is swelled and the grain germs are pressed, generating highly valuable oils.

The advantages of the whole-crop biorefinery based on wet milling are that the natural structures and structure elements such as starch, cellulose, oil, and amino acids (proteins) are retained to a great extent, and well-known base technologies and processing lines can still be used. The disadvantages are the high raw material costs and costly source technologies required for industrial utilization. On the other hand, many of the products generate high prices, for example, in pharmacy and cosmetics (Figs. 1.5 and 1.6).

The wet milling of corn yields corn oil, corn fiber, and corn starch. The starch products obtained from the US corn wet-milling industry are fuel alcohol (31%), high-fructose corn syrup (36%), starch (16%), and dextrose (17%). Corn wet milling also generates other products (e.g., gluten meal, gluten feed, oil) [43]. An overview of the product range is shown in Figure 1.6.

1.2.4 Green Biorefinery

Often, it is the economics of bioprocesses that are the main problem because the price of bulk products is affected greatly by raw material costs [44]. The advantages of green biorefineries are a high biomass profit per hectare and a good coupling with agricultural production, combined with low prices for raw materials. On the one hand, simple base technologies can be used, with good biotechnical and chemical potential for further conversions (Fig. 1.7). On the other hand, either fast primary processing or the use of preservation methods such as silage or drying is necessary for both the raw materials and the primary products. However, each preservation method changes the content of the materials.
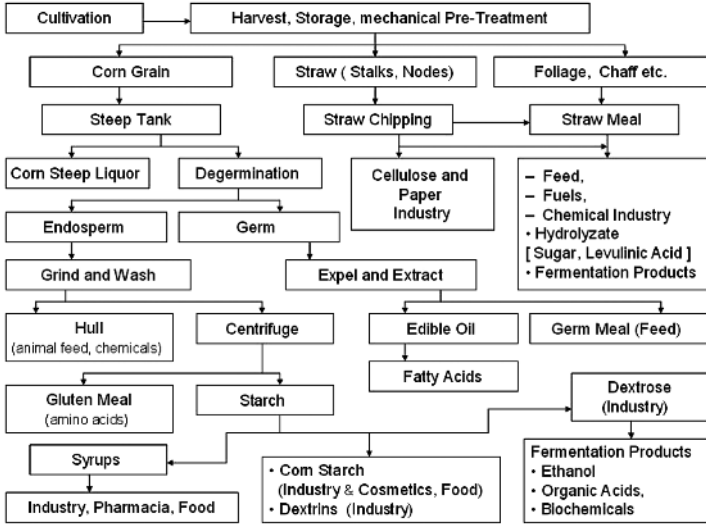
FIGURE 1.6 Products from the whole crop wet mill based biorefinery [26].

Green biorefineries are also multiproduct systems and operate with regard to their refinery cuts, fractions, and products in accordance with the physiology of the corresponding plant material; in other words, maintaining and utilizing the diversity of syntheses achieved by nature. Green biomass consists of, for example, grass from the cultivation of permanent grassland, closed fields, nature preserves, or green crops such as lucerne (alfalfa), clover, and immature cereals from extensive land cultivation.
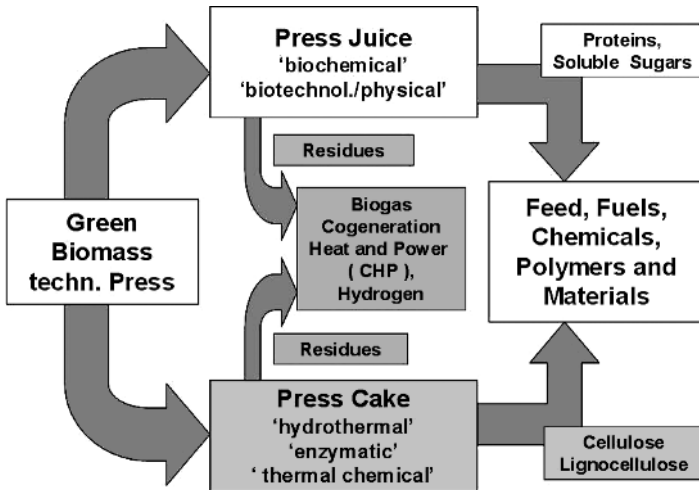

FIGURE 1.7 A green biorefinery system [26].

Today, green crops are used primarily as forage and a source of leafy vegetables. In a process called wet-fractionation of green biomass, green crop fractionation can be used for the simultaneous manufacture of both food and nonfood items [45]. Thus, green crops represent a natural chemical factory and food plant.

Scientists in several countries in Europe and elsewhere have developed green crop fractionation; indeed, green crop fractionation is now studied in about 80 countries [45–48]. Several hundred temperate and tropical plant species have been investigated for green-crop fractionation [48–50]. However, more than 300,000 higher plant species remain to be investigated (for reviews, see Refs. [1, 46, 47, 51–54]).

By fractionation of green plants, green biorefineries can process from a few tonnes of green crops per hour (farm-scale process) to more than $100\,t\,h^{-1}$ (industrial-scale commercial process). Wet-fractionation technology is used as the first step (primary refinery) to carefully isolate the contained substances in their natural form. Thus, the green crop goods (or humid organic waste goods) are separated into a fiber-rich press cake (PC) and a nutrient-rich green juice (GJ).

Besides cellulose and starch, PC contains valuable dyes and pigments, crude drugs, and other organics. The GJ contains proteins, free amino acids, organic acids, dyes, enzymes, hormones, other organic substances, and minerals. In particular, the application of biotechnological methods is ideally suited for conversions because the plant water can simultaneously be used for further treatments. When water is added, the lignin–cellulose composite bonds are not as strong as they are in dry lignocellulose feedstock materials. Starting from GJ, the main focus is directed to producing products such as lactic acid and corresponding derivatives, amino acids, ethanol, and proteins. The PC can be used for the production of green feed pellets and as a raw material for the production of chemicals such as levulinic acid, as well as for conversion to syngas and hydrocarbons (synthetic biofuels). The residues left when substantial conversions are processed are suitable for the production of biogas combined with the generation of heat and electricity (Fig. 1.8). Reviews of green biorefinery concepts, contents, and goals have been published [13, 26, 55].

1.2.5 The Two-Platforms Biorefinery Concept

The "two-platform concept" means that first biomass consists on average of 75% carbohydrates, which can be standardized over an intermediate sugar platform as a basis for further conversions, and second that the biomass is converted thermochemically into synthesis gas and further products.

- The "sugar platform" is based on biochemical conversion processes and focuses on the fermentation of sugars extracted from biomass feedstocks.
- The "syngas platform" is based on thermochemical conversion processes and focuses on the gasification of biomass feedstocks and by-products from conversion processes.[24, 46, 56]. In addition to gasification, other thermal and thermochemical biomass conversion methods have also been described: hydrothermolysis, pyrolysis, thermolysis, and burning. The application used depends on the water content of the biomass [57].
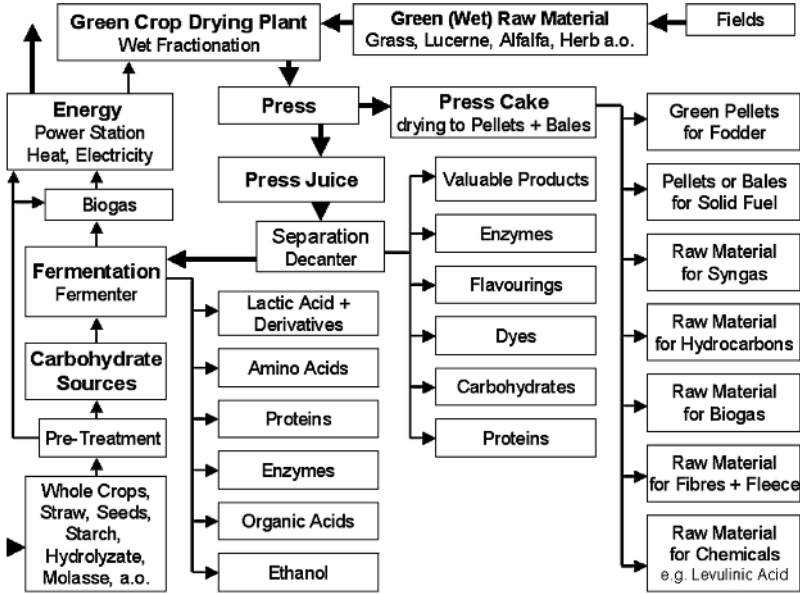
FIGURE 1.8   Products from a green biorefinery system, combined with a green crop drying plant [22, 23].

Gasification and all the thermochemical methods concentrate on the utilization of the precursor carbohydrates as well as their inherent carbon and hydrogen content. The proteins, lignin, oils and lipids, amino acids and general ingredients, as well as the N- and S-compounds occurring in all biomass, are not taken into account in this case (Fig. 1.9).
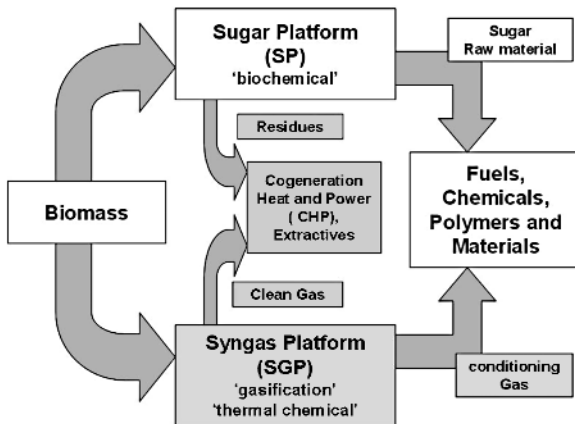

FIGURE 1.9   Sugar platform and Syngas platform [26, 58].

1.3 PLATFORM CHEMICALS

1.3.1 Background

A team from the Pacific Northwest National Laboratory (PNNL) and the National Renewable Energy Laboratory (NREL) submitted a list of 12 potential biobased chemicals [24]. The key areas of the investigation were biomass precursors, platforms, building blocks, secondary chemicals, intermediates, products, and uses (Fig. 1.10).

The final selection of 12 building blocks began with a list of more than 300 candidates. A shorter list of 30 potential candidates was selected using an iterative review process based on the petrochemical model of building blocks, chemical data, known market data, properties, performance of the potential candidates, and the prior industry experience of the team at PNNL and NREL. This list of 30 was ultimately reduced to 12 by examining the potential markets for the building blocks and their derivatives, and the technical complexity of the synthesis pathways.

The selected building-block chemicals can be produced from sugar via biological and chemical conversions. The building blocks can subsequently be converted to a number of high-value biobased chemicals or materials. Building block chemicals, as considered for this analysis, are molecules with multiple functional groups that possess the potential to be transformed into new families of useful molecules. The 12 sugar-based building blocks (Fig. 1.10) are 1,4-diacids (succinic, fumaric, and malic); 2,5-furan dicarboxylic acid; 3-hydroxy propionic acid; aspartic acid; glucaric acid; glutamic acid; itaconic acid; levulinic acid; 3-hydroxybutyrolactone; glycerol; sorbitol; and xylitol/arabinitol [24].

A second-tier group of building blocks was also identified as viable candidates. This group included gluconic acid; lactic acid; malonic acid; propionic acid;
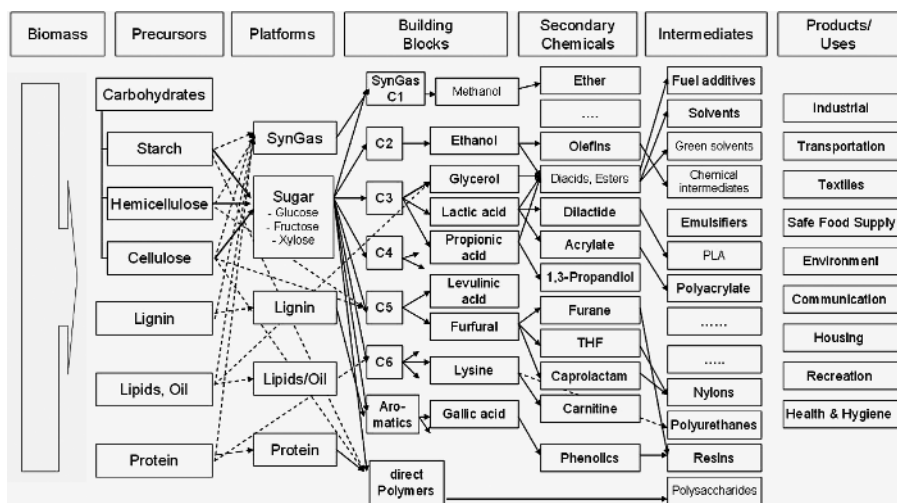

FIGURE 1.10 Model of a biobased product flowchart for biomass feedstock [26].

thetriacids, citric and aconitic acids; xylonic acid; acetoin; furfural; levuglucosan; lysine; serine; and threonine. Recommendations for moving forward include examining top-value products from biomass components such as aromatics, polysaccharides, and oils; evaluating technical challenges related to chemical and biological conversions in more detail; and increasing the number of potential pathways to these candidates. No further products obtained from syngas were selected. For the purposes of this study, hydrogen and methanol are the best short-term prospects for biobased commodity chemical production because obtaining simple alcohols, aldehydes, mixed alcohols, and Fischer–Tropsch liquids from biomass is not economically viable and requires additional development [24].

1.3.2 The Role of Biotechnology in Production of Platform Chemicals

The application of biotechnological methods will be of great importance, and will involve the development of biorefineries for the production of base chemicals, intermediate chemicals, and polymers [59, 60]. The integration of biotechnological methods must be managed intelligently with respect to the physical and chemical conversions of the biomass. Therefore biotechnology cannot continue to be restricted to glucose from sugar plants and starch from starch-producing plants (Fig. 1.11).

One of the main goals is the economical processing of biomass containing lignocellulose and the provision of glucose in the family-tree system. Glucose is a key chemical for microbial processes. The preparation of a large number of family-tree-capable base chemicals is described in the following sections. Among the variety of possible product family trees that can be developed from glucose accessible microbial and chemical sequence products are the C-1 chemicals methane, carbon dioxide, and methanol; C-2 chemicals ethanol, acetic acid, acetaldehyde, and ethylene; C-3 chemicals lactic acid, propandiol, propylene, propylene oxide, acetone, acrylic acid; C-4 chemicals diethylether, acetic acid anhydride, malic acid, vinyl acetate, n-butanol, crotone aldehyde, butadiene, and 2,3-butandiol; C-5 chemicals itaconic acid, 2,3-pentane dione, and ethyl lactate; C-6 chemicals sorbic acid, parasorbic acid, citric acid, aconitic acid, isoascorbinic acid, kojic acid, maltol, and dilactide; and the C-8-chemical 2-ethyl hexanol (Fig. 1.12).
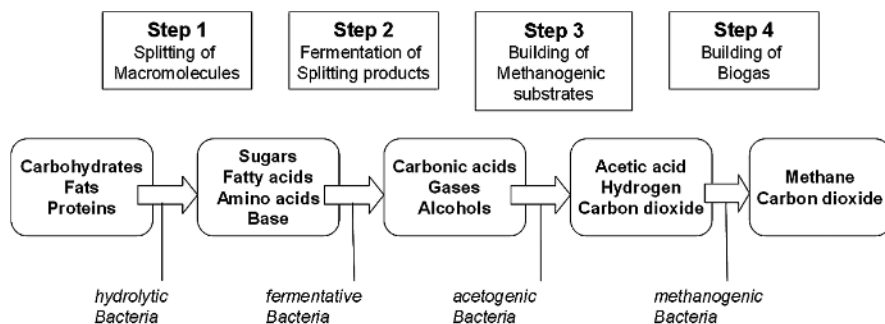

FIGURE 1.11 Simplified presentation of a microbial biomass-breakdown regime [22].
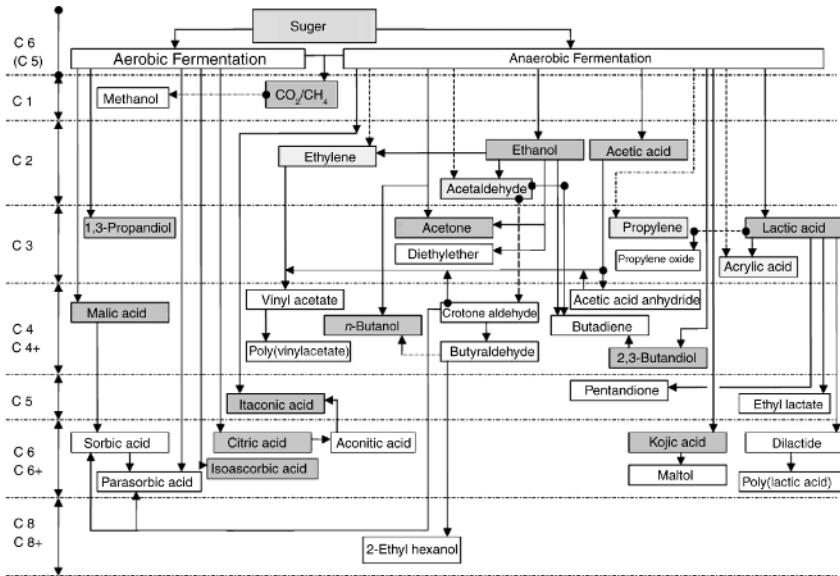
FIGURE 1.12   Biotechnological sugar-based product family tree.

Currently, guidelines are being developed for the fermentation section of a biorefinery. An answer needs to be found to the question of how to produce an efficient technological design for the production of bulk chemicals. The basic technological operations for the manufacture of lactic acid and ethanol are very similar. The selection of biotechnology-based products from biorefineries should be done in a way that they can be produced from the substrates glucose or pentoses. Furthermore, the fermentation products should be extracellular. Fermentors should have a batch, feed batch, or continuous stirred-tank reactor (CSTR) design. Preliminary product recovery may require steps such as filtration, distillation, or extraction. Final product recovery and purification steps may possibly be product-unique. In addition, biochemical and chemical-processing steps should be efficiently connected. Unresolved questions for the fermentation facility include the following: (1) whether or not the entire fermentation facility can/should be able to change from one product to another; (2) can multiple products be run in parallel, with shared use of common unit operations; (3) how should scheduling of unit operations be managed; and (4) how can in-plant inventories be minimized, while accommodating any changeovers required between different products for the same piece of equipment [61].

1.3.3   Green Biomass Fractionation and Energy Aspects

Today, green crops are used primarily as forage and as a source of leafy vegetables. In a process called wet-fractionation of green biomass, green crop fractionation can be used for simultaneous manufacture of both food and nonfood items [45].

The power and heat energy requirements of a forage fractionation of a protein concentrate production system are within practical limits for large farms and dehydrating plants [62]. Mechanical squeezing of the fresh crop results in energy savings of $1.577\,MJ\,ton^{-1}$ crop input, equal to 52% of the total energy input (compared to energetic drying of green biomass) [63]. Three simplified systems of wet green crop fractionation, which are characterized by the direct use of nutrient-rich green juice or deproteinized juice as feeding supplements for pigs or liquid fertilizer, have been described [64]. Wet green crop fractionation involves an energy saving of $538\,MJ\,ton^{-1}$ fresh crop, equal to 17.7% of the total energy input of crop drying [63]. Compared with conventional fractionation technology, membrane filtration results in an energy saving of $370\,MJ\,ton^{-1}$ crop input, which corresponds to 14.8% of the total energy input [64].

Via fractionation of green plants, green biorefineries are able to process amounts in the range of a few tons of green crops per hour (farm scale process) to more than $100\,t\,h^{-1}$ (industrial-scale commercial process). Careful wet-fractionation technology is used as a first step (primary refinery) to isolate the ingredients in their natural form. Thus, the green crops (or wet organic wastes) are separated into a fiber-rich press cake and a nutrient-rich GJ. Beside cellulose and starch, the PC contains valuable dyes and pigments, crude drugs, and other organics. The GJ contains proteins, free amino acids, organic acids, dyes, enzymes, hormones, further organic substances, and minerals. The application of biotechnological methods is particularly appropriate for conversion processes since the plant water can be used simultaneously for further treatments. In addition, the pulping of lignin–cellulose composites is easier compared to LCF materials. Starting from GJ, the main focus is directed to products such as lactic acid and corresponding derivatives, amino acids, ethanol, and proteins.

The PC can be used for production of green feed pellets; as raw material for production of chemicals, such as levulinic acid; and for conversion to syngas and hydrocarbons (synthetic biofuels). The residues of substantial conversion are applicable to the production of biogas combined with the generation of heat and electricity. Special attention is given to the mass and energy flows of the biorefining of green biomass.

1.3.4 Mass and Energy Flows for Green Biorefining

Green biorefining is described as an example of a type of agricultural factory in greenland-rich areas. Key figures are determined for mass and energy flow, feedstock, and product quantities (Fig. 1.13). Product quantities vary depending on the market and the demand for quality products. Mass flows (Scenario 1, Scenario 2) can be constructed from our own experimental results combined with market demand in the feed, cosmetic, and biotechnology industries. The technical and energy considerations of the fractionation processes of a green biorefinery, and production of the platform chemicals lactic acid and lysine are shown in Figure 1.13.

Using a mechanical press, about 20,000 t press juice [dry matter (DM): 5%] can be manufactured from 40,000 t biomass. First, the juice is the raw material for further
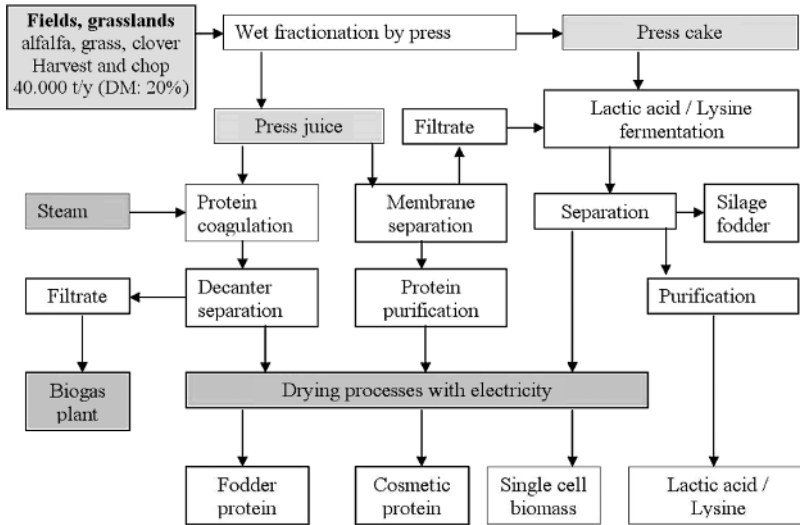
FIGURE 1.13 Selected and simplified processes of a green biorefinery [65].

products; and second, the green cut biomass contains much less moisture. Through fractionation of GJ proteins by different separation and drying processes, high-quality fodder proteins and proteins for the cosmetic industry can be produced [62, 66, 67]. The fodder proteins would be a complete substitute for soy proteins. They even have a nutritional physiological advantage due to their particular amino acid patterns [68]. Utilization of the easily fermentable sugar in the biomass and the available water offers an excellent biotechnological–chemical potential and makes possible the use of basic technologies such as the production of lactic acid or lysine.

In the next step (fermentation), the carbohydrates of the juice and one part of the PC can be used (after hydrolysis) for the production of lactic acid (Scenario 1 [69].) or lysine (Scenario 2 [70]). Thus, single-cell biomass, which can be applied after appropriate drying as a fodder protein, is produced.

The fermentation base in lactic acid fermentation is sodium hydroxide. By means of ultrafiltration, reverse osmosis, [71]. bipolar electrodialysis, and distillation, lactic acid (90%) is recovered from sodium lactate fermentation broth [72–74]. Lysine hydrochloride is the product of lysine fermentation [67]. After separation of the single-cell biomass by ultrafiltration and a membrane separation of water followed by a drying process, lysine hydrochloride (50%) is recovered [70, 71]. The broth that is left after separation from lactic acid or lysine, respectively, and single-cell biomass can be supplied to a biogas plant. Input and output data including required energy were estimated for the production of lysine hydrochloride, lactic acid, proteins for fodder and cosmetics and the utilization of the residue (PC) as silage fodder from 40,000 t green cut biomass (Table 1.1).

By drying, the PC could be manufactured into fodder-pellets. However, this drying is energetically very expensive. From an energy point of view it is far better to

TABLE 1.1   Combined Production of Lactic Acid, Lysine, Cosmetic-Protein, Single-Cell Biomass, Fodder, and Biogas with Energetic Input

Green Biorefinery	Scenario 1	Lactic Acid	
Input		Quantity	Unit
Green biomass (Lucerne, Clover, Grass)	DM: 20%	40,000	t
Steam		2,268	GJ
Electricity		1,300,000	kWh
Output			
Silage fodder	DM: 40%	13,000	t
Fodder-protein 80%	DM: 90%	400	t
Cosmetic-protein 90%	DM: 90%	29.6	t
Lactic acid 90%	DM: 90%	660	t
Residue to biogas plant TS: 2%		17,690	t
Single-cell biomass (as fodder-protein 60%)	DM: 90%	33	t
Green Biorefinery	Scenario 2	Lysine	
Input		Quantity	Unit
Cut Green Biomass (Lucerne, Clover, Grass)	DM: 20%	40,000	t
Steam		2,268	GJ
Electricity		492,000	kWh
Output			
Silage fodder	DM: 40%	13,000	t
Fodder-protein 80%	DM: 90%	400	t
Cosmetic-protein 90%	DM: 90%	29.6	t
Lysine–HCl, 50%	DM: 90%	620	t
Residue to biogas plant DM: 2%		17,770	t
Single-cell-Biomass (as fodder-protein 60%)	DM: 90%	31	t

Source: Ref. [65].
Note: DM, dry matter.

suggest that the PC be used as silage-feed. From an ecological and economical viewpoint, at this stage it has to be concluded that coupling of green biorefineries with green crop drying industry is necessary.

1.3.5 Assessment of Green Crop Fractionation Processes

Green biorefineries use different kinds of energy (steam and electricity) for the treatment of PC and press juice (intermediate products) to produce valuable end products. It is also possible to use the PC together with the press juice as a source of carbohydrate for the fermentation. For the separate processes mass balances were set up and thus the consumption of energy can be calculated by means of power consumption of the facilities (plants and machinery).

A linear programming model used to optimize the profitability and determine an optimized planning process for biorefineries is described in Annetts and Audsley

(2003) [75]. The raw materials are wheat (straw and grain) and rape, and therefore this would be a model for a whole-crop biorefinery and hardly applicable to a green biorefinery. At a capacity of 40,000 tons per year [t annum^{-1} (a)] fresh biomass (lucerne, wild-mixed-grass), and a operation time of 200 working days per year, an average of 200 t are converted per day. Under these conditions, the screw extrusion press used has an energy consumption of 135,000 kWh per year (kWh a^{-1}). It generates 100 t day^{-1} PC with DM ~35% and 100 t day^{-1} press juice with DM ~5%. Around 10 t of the 100 t press juice are fed to membrane-separation for a cosmetic-protein extraction. For separation of feed protein, 90 t press juice are put into a steam-coagulation. The required heat quantity as steam is 2268 GJ a^{-1}. The freshly pressed juice is preheated up to 45°C in a heat exchanger within a counter-current process. Via steaming, a temperature rise of the freshly pressed juice of up to 30°C is reached. Steam coagulation occurs at a temperature of 75°C. The following calculations are carried out according to Bruhn et al. (1978) [62]. For the separation of feeding proteins the following energy input is required: 1,500 kWh a^{-1} for skimming; 15,000 kWh a^{-1} for dehydration to ~50% DM; and 32,000 kWh a^{-1} for drying up to DM = 90%. Separation of cosmetic-proteins via ultrafiltration needs an energy input of 9700 kWh a^{-1}. For subsequent solvent extraction, a further energy input of about 507 kWh a^{-1} is generated via stirring [76].

For the separation via centrifugation 101 kWh a^{-1} are required and 2360 kWh a^{-1} for the subsequent spray-drying to DM = 90% [66, 77]. If the press-juice contains 2% proteins, 400 t feed proteins as protein concentrate and 29.6 t cosmetic proteins can be produced per year. Correspondingly increased quantities can be produced if the press juice contains a higher proportion of proteins. After protein-separation, 100 t fermentation-broth (~96.6 m^3 at a density of about 1035 kg L^{-1}) are available per working day. The energy input required for stirring during fermentation amounts to 150,000 kWh a^{-1} [70].

For lactic-acid fermentation, NaOH is added as a base, resulting in sodium lactate. The purification of lactic acid occurs with the following steps and corresponding energy yields: ultrafiltration 97,000 kWh a^{-1}, reverse osmosis 171,000 kWh a^{-1}, and bipolar electrodialysis 660,000 kWh a^{-1} [71, 72]. Bipolar electrodialysis is particu-larly energy-intensive. Subsequently, the lactic acid solution (45%) is concentrated up to a 90% lactic acid via vacuum distillation. The energy consumption for this single-stage distillation will amount 26,400 kWh a^{-1} [74]. The energy consumption for 660 t of 90% lactic-acid amounts 1104 MWh a^{-1} using this procedure.

If lysine fermentation is chosen instead of lactic acid, ultrafiltration and reverse osmosis are required for purification with the following corresponding energy yields: ultrafiltration (97,000 kWh a^{-1}) and reverse osmosis (171,000 kWh a^{-1}) [71]. After-wards the lysine hydrochloride is dried to DM of 90% with an energy requirement of 49,000 kWh a^{-1}) [75]. The energy consumption of 620 t lysine hydrochloride using this method results in 296,000 kWh a^{-1}.

In a biorefining plant processing 40,000 t green biomass for the combined production of 660 t lactic acid, 29.6 t cosmetic-protein, 33 t single-cell biomass, 400 t fodder-protein, 13,000 t silage fodder, and 17,690 t liquid residues for biogas production, the following energy input is required: 2,268 GJ heat, and 1.3 million

kWh electricity. The combined production of 620 t lysine, 29.6 t cosmetic protein, 31 t single-cell biomass, 400 t fodder protein, 13,000 t silage fodder, and 17,700 t liquid residues to produce biogas requires the following energy input: 2,268 GJ heat, and 0.492 million MWh electricity.

These results clearly demonstrate the quantity of products a green biorefinery can provide with the help of biotechnology, and the corresponding required energy input. The economic benefits of biorefining green biomass are the high yields of biomass per hectare and year, and synergetic effects via combination with established production processes in the agriculture and feed industries. Therefore, in the mid-term, it is reasonable to combine the economic potential of green agriculture and green-crop-drying-plants.

These data concerning quantity, quality, and required process energy form the basis of further economic considerations in connection with calculation of breakeven points when planning and establishing a green biorefinery. In future, energy inputs will be reduced further due to optimization of the corresponding biorefinery technology. The combination of biotechnological and chemical conversion processes will be a very important aspect in decreasing process energy input. Thus, the biotechnological production of aminium lactates, such as piperazinium dilactates as starting material for high-purity lactic acid and polylactic acid could be a new approach [69].

1.4 GREEN BIOREFINERY: ECONOMIC AND ECOLOGIC ASPECTS

Plant biomass is the only foreseeable sustainable source of organic fuels, chemicals, and materials. A variety of forms of biomass, notably many LCFs, are potentially available on a large scale and are cost-competitive with low-cost petroleum, whether considered on a mass or energy basis, in terms of price defined on a purchase or net basis for both current and projected mature technologies, or on a transfer basis for mature technology [78]. Green plant biomass in combination with LCF represents the dominant source of feedstocks for biotechnological processes for the production of chemicals and materials [24, 70, 79–81]. The development of integrated technologies for the conversion of biomass is essential for the economic and ecological production of products. The biomass industry, or bioindustry, at present produces basic chemicals such as ethanol (15 million t a^{-1}); amino acids (1.5 million t a^{-1}), of which L-lysine amounts to 500,000 million t a^{-1}; and lactic acid (200,000 million t a^{-1}) [82]. The target of a biorefinery is to establish a combination of a biomass–feedstock mix with a process and product mix [24, 80]. A life cycle assessment (LCA) is available for the production of polylactic acid (capacity 140,000 t a^{-1}) [83]. For total assessment of the utilization of biomass, one has to consider that cultivation of the plant has to fulfill certain economic and ecological criteria. Agriculture both creates pressure on the environment and plays an important role in maintaining many cultural landscapes and seminatural habitats [84]. Green crops, in particular, provide especially high yields.

Additionally, grassland can be cultivated in a sustainable way [85, 86]. European grassland experiments have shown that species-rich grassland cultivation

provides not only ecological but also economic advantages. With greater plant diversity, grassland is more productive and the soil is protected against nitrate leaching. Of the 71 species examined so far, 29 had a significant influence on productivity. *Trifolium pratense* has an especially important function regarding productivity. On sites where this species occurs, more than 50% of the total biomass has been produced by this species. Legumes such as clover and herbs also play an important role, as do fast-growing grasses [87]. An initial assessment of the concept of a green biorefinery has been carried out by Schidler and colleagues for the Austrian system approach [88, 89]. Furthermore, an Austrian-wide concept for the use of biomass and cultivable land for renewable resources has yet to be developed in Austria, which also holds true for Europe [90]. The size of such plants depends on the rural structures of the different regions. Concepts with more decentralized units would have a size of about $35,000\,t\,a^{-1}$ and central plants could have sizes of about $300,000–600,000\,t\,a^{-1}$ [90, 91].

1.5 OUTLOOK: PRODUCTION OF L-LYSINE-L-LACTATE FROM GREEN JUICES

The aminium lactate L-lysine-L-lactate was produced in fractionated juices from a green biorefinery. To investigate the effect of protein separation onto the lactic-acid fermentation, nontreated and deproteinized alfalfa press juice was compared to the MRS medium [92]. At a glucose concentration of $50\,g\,L^{-1}$, the production rates indicated that the separation of proteins from the press juice had no significant influence on the lactic-acid formation. Production rates were at the same level as the fermentation with the MRS medium. Experiments with alfalfa press juice reached higher final lactic-acid concentrations due to further carbohydrates in the press juice that could additionally be metabolized by strand DSMZ 2649 [93]. In further research, the complete carbohydrate composition of the alfalfa press juice and its single conversion to lactic acid is investigated. After increasing the glucose concentration up to $100\,g\,L^{-1}$, a significant nutrient limitation was observed during the fermentation with deproteinized press juice. The lactic-acid production rate dropped about 33% and the molar yield was 6% lower than in the fermentation with the semisynthetic medium, MRS. L-lysine-L-lactate could not be produced in the theoretical composition, because of the growing buffer capacity of the biomass with increasing substrate concentration. The pH that provides an equimolar composition of the aminium lactate has to be determined in further experiments. The results presented here show that the fermentative production of L-lysine-L-lactate can be integrated into the green biorefinery system, where deproteinized press juice accrues as a product. The usage of deproteinized press juice as a fermentation medium is technically and economically reasonable because of the stabilizing effect on the press juice and the surplus values from the gained proteins [94]. The N-supplementation that is necessary at high substrate concentrations could be realized by using biomass hydrolysates from previous fermentations. In future experiments, D-(+)-glucose will be substituted by hydrolysates from alfalfa press cakes to obtain a complete fermentation medium from a green biorefinery without any additional carbon source [93].

1.6 GENERAL CONCLUSION

There are various requirements for entering the industrial biorefinery technologies and the production of platform chemicals and materials. On the one hand, the production of substances on the basis of biogenic raw material in the already-existing production facilities of cellulose, starch, sugar, oil, and proteins has to be enlarged, on the other hand, the introduction and establishment of biorefinery demonstration plants is required. Conversion processes have to be developed in the biorefinery regime, that is, in defined product lines and product trees (platform chemicals → intermediate products → secondary products). The organic-technical chemistry has the task to position itself inside of the concept of "biobased products and biorefinery systems," among others things focusing itself on the linking of biological and chemical syntheses and technologies, especially integrating the sectors of reaction engineering, process intensification, and heterogenic catalysis.

Besides promoting the necessary research, development, and industrial implementation, a broader establishment of the specializing field "Chemistry of renewable raw materials/Biorefinery systems" in the education and in academic teaching needs to be achieved.

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