

International biorefinery systems*

Birgit Kamm^{1,‡} and Michael Kamm^{2,†}

¹*Research Institute Bioactive Polymer Systems e.V. and Brandenburg University of Technology Cottbus, Kantstrasse 55, D-14513 Teltow, Germany;* ²*Biorefinery.de GmbH, Stiftstrasse 2, D-14471 Potsdam, Germany*

Abstract: The development of biorefineries represents the key for access to an integrated production of food, feed, chemicals, materials, goods, and fuels of the future [1]. Biorefineries combine the necessary technologies of the biogenic raw materials with those of intermediates and final products. The main focus is directed on the precursor carbohydrates, lignins, oils, and proteins, and the combination between biotechnological and chemical conversion of substances. Currently, the lignocellulosic feedstock (LCF) biorefinery, green biorefinery, whole-crop biorefinery, and the so-called two-platform concept are favored in research, development, and industrial implementation.

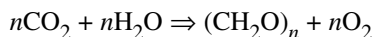
Keywords: biorefineries; biogenic raw materials; biobased industrial products; whole-crop biorefinery; green biorefinery; lignocellulosic feedstock biorefinery; two-platform concept.

INTRODUCTION

Sustainable economical growth requires the safe resources of raw materials for industrial production. Currently, the most frequently used industrial raw material, petroleum, is neither sustainable, because of its limited supply, nor environmentally friendly. While the economy of energy can be based on various alternative raw materials, such as wind, sun, water, biomass, as well as nuclear fission and fusion, the economy of substances fundamentally depends on biomass, in particular, biomass from plants. Special requirements are placed on both the substantial converting industry as well as research and development regarding the efficiency of raw materials and product lines as well as sustainability. “The development of biorefineries represents the key for the access to an integrated production of food, feed, chemicals, materials, goods, and fuels of the future” [1].

Nature is a permanently renewing production chain for chemicals, materials, fuels, cosmetics, and pharmaceuticals. Many of the currently used biobased industry products are results of a direct physical or chemical treatment and processing of biomass, such as cellulose, starch, oil, protein, lignin, and terpene. On one hand, one has to mention that due to the help of biotechnological processes and methods, feedstock chemicals such as ethanol, butanol, acetone, lactic acid, and itaconic acid as well as amino acids (e.g., glutamic acid, lysine, and tryptophan) are produced. On the other hand, currently only 6 billion tons of the yearly produced biomass, $1.7\text{--}2.0 \times 10^{11}$ tons, are used, and only 3.0 to 3.5 % of this amount is used in the non-food area, such as chemistry [2].

The basis reaction of the biomass is photosynthesis according to



Pure Appl. Chem.* **79, 1831–2100. An issue of reviews and research papers based on lectures presented at the 1st International IUPAC Conference on Green–Sustainable Chemistry, held in Dresden, Germany, 10–15 September 2006.

‡Corresponding author: E-mail: kamm@biopos.de

†E-mail: kamm@biorefinery.de

Industrial utilization of raw materials for the energy and materials industries coming from agriculture, forestry, and landscape care is still in the beginning phase. The majority of biological raw materials are produced in agriculture, forestry, and by microbial systems. Forest plants are excellent raw materials for the paper and cardboard, construction, and chemical industries. Field fruits represent an organically chemical pool, from which fuels, chemicals, and chemical products as well as biomaterials are produced (Fig. 1) [3]. Waste biomass and biomass of nature and landscape cultivation are valuable organic reservoirs of raw material and must be used in accordance with their organic composition. During the development of biorefinery systems, the term “waste biomass” will become obsolete in the medium term [4]. Because of low cost, plentiful supply, and amenability to biotechnology, carbohydrates appear likely to be the dominant source of feedstocks for biocommodity processing. Starch-rich and cellulosic materials each have important advantages in this context. Corn is by far the dominant feedstock for biological production of commodity products today. The advantages of cellulosic materials include a much larger ultimate supply, lower purchase and anticipated transfer cost, less erosion, and lower inputs of chemicals and energy required for production [5]. Recently, the goal of the U.S. Departments of Agriculture and Energy is the additional supply of 1 billion tons of biomass for a price of USD 35 per ton per year for industrial, chemical, and biotechnological utilization, without the restriction of today’s applications of biomass from agriculture and forestry [6].

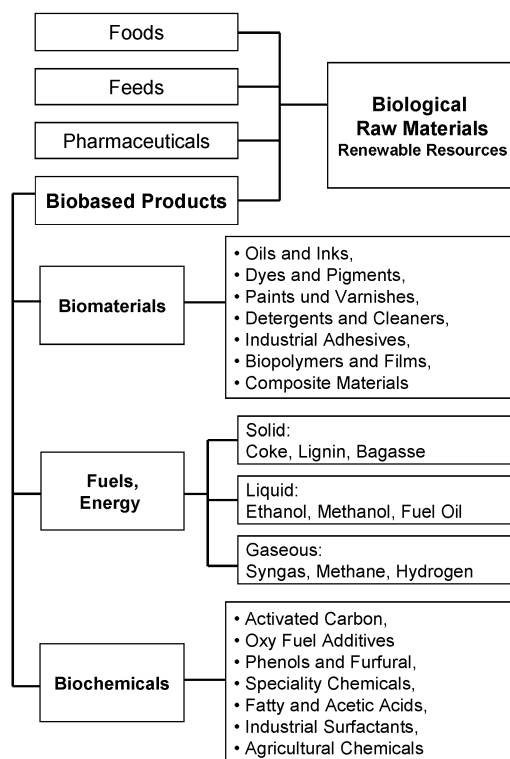


Fig. 1 Products and product classes based on biological raw materials [7].

PRINCIPLES OF BIOREFINERIES

Fundamentals

Biomass is similar to petroleum as a complex composition. Its primary separation into main groups of substances is appropriate. Subsequent treatment and processing of those substances lead to a whole palette of products. Petrochemistry is based on the principle of generating from hydrocarbons simple-to-handle and well-defined chemically pure elements in refineries. In efficient product lines, a system based on family trees has been built, in which basic chemicals, intermediate products, and sophisticated products are produced. This principle of petroleum refineries must be transferred to biorefineries. Biomass contains the synthesis performance of nature and has another C:H:O:N ratio than petroleum. The biotechnological conversion will become, besides the chemical, a big player in the future (Fig. 2).

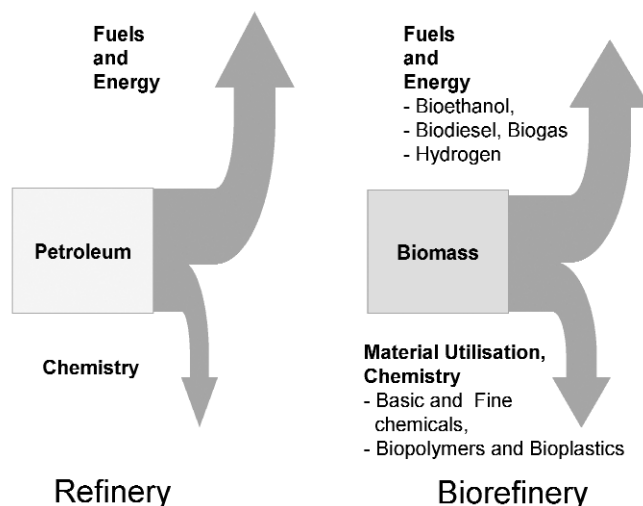


Fig. 2 Comparison of the basic principles of petroleum refineries and biorefineries [8].

Thus, biomass can already be modified within the process of genesis in such a way that it is adapted to the purpose of subsequent processing, and particular target products already have been formed. For those products, the term “precursors” is used.

Plant biomass always consists of the basic products carbohydrates, lignins, proteins, and fats, besides various substances such as vitamins, dyes, flavors, and aromatic essences of most different chemical structures. Biorefineries combine the essential technologies between biological raw materials and the industrial intermediates and final products (Fig. 3).

A technically feasible separation operation, which would allow a separate use or subsequent processing of all these basic compounds, exists up to now only in the form of an initial attempt. Assuming that out of the estimated annual production of biomass by biosynthesis of 170 billion tons, 75 % are carbohydrates (mainly in the form of cellulose, starch, and saccharose), 20 % are lignins, and only 5 % are other natural compounds such as fats (oils), proteins, and various substances [10], the main attention firstly should be focused on an efficient access to carbohydrates, their subsequent conversion to chemical bulk products, and corresponding final products. Glucose, accessible by microbial or chemical methods from starch, sugar, or cellulose, is among other things predestined for a key position as a basic chemical, because a broad palette of biotechnological or chemical products is accessible from glucose. In the case of starch, the advantage of enzymatic compared to chemical hydrolysis is already realized today [11,12].

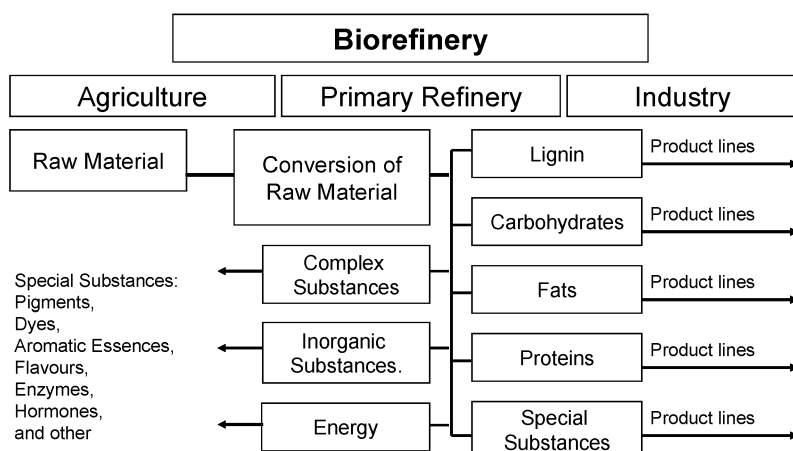


Fig. 3 Providing code-defined basic substances via fractionation for the development of relevant industrial product family trees [7,9].

In the case of cellulose, this advantage is not yet realized. Cellulose-hydrolyzing enzymes can only act effectively after pretreatment to break up the very stable lignin/cellulose/hemicellulose composites [13]. These treatments are still mostly thermal, thermomechanical, or thermochemical and require a considerable input of energy. The arsenal for microbial conversion of substances out of glucose is large, and the reactions are energetically profitable. It is necessary to combine the degradation processes via glucose to bulk chemicals with the building processes to their subsequent products and materials (Fig. 4).

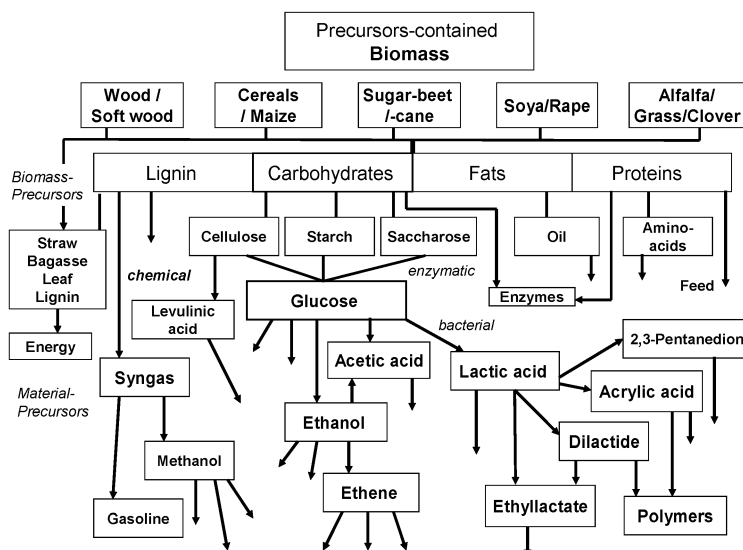


Fig. 4 Possible biorefinery rough scheme for precursors, containing biomass with preference of carbohydrate line, according to [7,9].

Among the variety of possibilities from glucose-accessible microbial and chemical products, in particular, lactic acid, ethanol, acetic acid, and levulinic acid, are favorable intermediates for the gener-

ation of industrially relevant product family trees. Here, two potential strategies are considered: first, the development of new, possibly biologically degradable products (follow-up products of lactic and levulinic acid) or secondly, the entry as intermediates into conventional product lines (acrylic acid, 2,3-pentandion) of petrochemical refineries [7].

Building blocks, chemicals, and potential screening

A team from PNNL and NREL submitted a list of 12 potential biobased chemicals [14]. A key area of the investigation includes biomass precursors, platforms, building blocks, secondary chemicals, intermediates, products, and uses (Fig. 5).

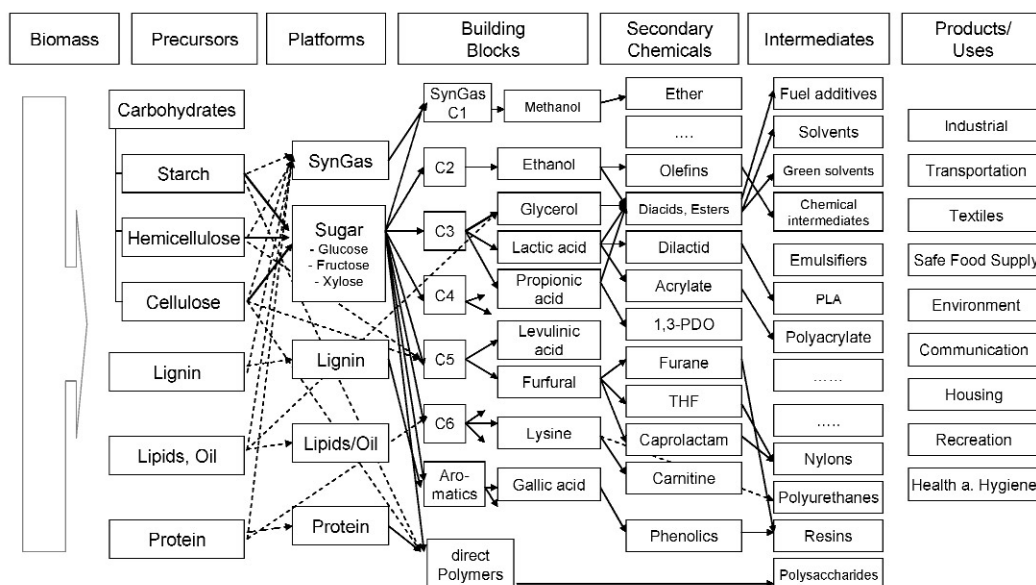


Fig. 5 Model of a biobased product flow-chart for biomass feedstock, cut out [14].

The final selection of 12 building blocks began with a list of more than 300 candidates. The 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 Pacific Northwest National Laboratory (PNNL) and National Renewable Energy Laboratory (NREL). This list of 30 candidates 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 reported block chemicals can be produced out of sugar via biological and chemical conversions. The building blocks can be subsequently 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 are 1,4-diacids (succinic, fumaric, and malic), 2,5-furan dicarboxylic acid, 3-hydroxypropionic acid, aspartic acid, glucaric acid, glutamic acid, itaconic acid, levulinic acid, 3-hydroxybutyrolactone, glycerol, sorbitol, and xylitol/arabinitol [14].

A second-tier group of building blocks was also identified as viable candidates. These include gluconic acid, lactic acid, malonic acid, propionic acid, the triacids, citric and aconitic; xylonic acid, acetoin, furfural, levoglucosan, lysine, serine, and threonine. Recommendations for moving forward in-

clude examining top-value products from biomass components such as aromatics, polysaccharides, and oils; evaluating technical challenges in more detail related to chemical and biological conversions; and increasing the suites of potential pathways to these candidates. From syngas, no further-down select products were undertaken. For the purposes of this study, hydrogen and methanol comprise the best near-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 [14].

BIOREFINERY SYSTEMS

Background

Biobased products are prepared for economical use by a meaningful combination of different methods and processes (physical, chemical, biological, and thermal). It is, therefore, necessary that biorefinery basis technologies have to be developed. Thus, profound interdisciplinary cooperation between the various compartment disciplines in research and development is inevitable. It appears, therefore, to be reasonable to refer to the term “biorefinery design”, which means: Bringing together well-sounded scientific and technological basics, with practice-near technologies, products, and product lines inside biorefineries. The basis 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 (M_1 - M_n) and the by-products (B_1 - B_n) will subsequently be subjected to microbiological or chemical methods. The follow-up products (F_1 - F_n) of the main and by-products can, furthermore, be converted or enter the conventional refinery (Fig. 4).

Currently, four complex biorefinery systems are the focus in research and development:

1. the lignocellulosic feedstock (LCF) biorefinery, which uses “nature-dry” raw materials such as cellulose-containing biomass and wastes;
2. the whole-crop biorefinery, which uses raw materials such as cereals or maize;
3. the green biorefinery, which uses “nature-wet” biomasses such as green grass, alfalfa, clover, or immature cereal [7,9]; and
4. the two-platform concept, which includes the sugar and syngas platforms [14].

Lignocellulosic feedstock biorefineries

Among the potential large-scale industrial biorefineries, the LCF biorefinery will most probably be pushed through with the highest success. On the one side, the raw materials situation is optimal (straw, reed, grass, wood, paper-waste, etc.), on the other side, conversion products have a good position in the traditional petrochemical as well as the future biobased product markets. An important point for utilization of biomass as chemical raw materials is the cost of the raw materials. Currently, the costs for corn stover or straw are: USD 30/ton; for corn USD 110/ton (USD 3/bushel) [15].

Lignocellulose materials consist of three primary chemical fractions or precursors: (a) hemicellulose/polyoses, a sugar-polymer of predominantly pentoses; (b) cellulose, a glucose-polymer; and (c) lignin, a polymer of phenols (Fig. 6).

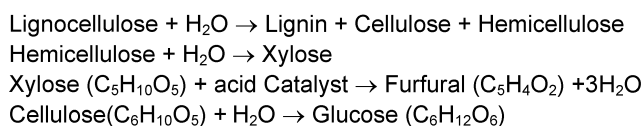


Fig. 6 Possible general equation of conversion at an LCF biorefinery.

The LCF biorefinery regime has a distinct ability for genealogical trees. The main advantage of this method is the fact that the natural structures and structure elements are preserved, the raw materials also have a low price, and large product varieties are possible (Fig. 7). Nevertheless, there is still development and optimization demand for these technologies, e.g., in the field of separation of cellulose, hemicellulose, and lignin as well as the lignin utilization in the chemical industry.

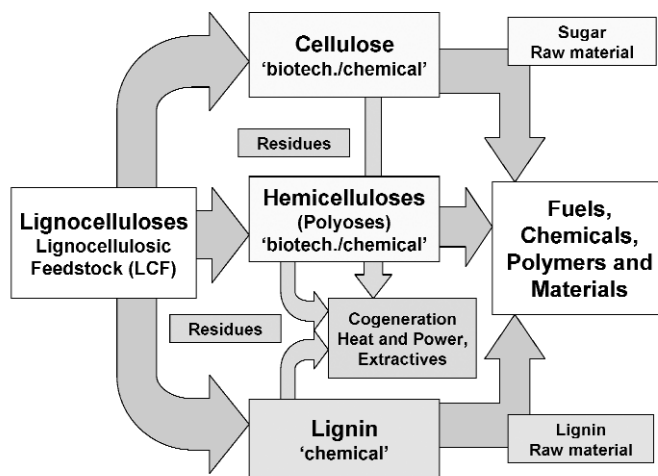


Fig. 7 LCF biorefinery [16].

In particular, furfural and hydroxymethylfurfural are interesting products. Furfural is the starting material for the production of nylon 6,6 and nylon 6. The original process for the production of nylon 6.6 was based on furfural. The last of these production plants was closed in 1961 in the United States due to economical reasons (the artificially low price of petroleum). Nevertheless, the market for nylon 6 is huge.

However, there are still some unsatisfactory parts within the LCF refinery, such as the utilization of lignin as fuel, adhesive, or binder. These parts are unsatisfactory because the lignin scaffold contains considerable amounts of mono-aromatic hydrocarbons, which, if isolated in an economically efficient way, could add a significant value increase to the primary processes. It should be noted that there are obviously no natural enzymes to split the naturally formed lignin into basic monomers as easily as possible as for the also naturally formed polymeric carbohydrates or proteins [17].

An attractive accompanying process to the biomass nylon process is the already mentioned hydrolysis of cellulose to glucose and the production of ethanol. Certain yeasts give a disproportionation of the glucose molecule during their generation of ethanol to glucose, which practically shifts its entire reduction ability into the ethanol and makes the last one obtainable in 90 % yield (w/w, regarding the formula turnover).

Based on recent technologies, a plant was conceived for the production of the main products furfural and ethanol from LC feedstock for the area of west central Missouri (USA). Optimal profitability can be reached with a daily consumption of about 4360 tons of feedstock. Annually, the plant produces 47.5 million gallons of ethanol and 323 000 tons of furfural [17].

Ethanol may be used as a fuel additive. Ethanol is also a connecting product for a petrochemical refinery. Ethanol can be converted into ethene by chemical methods. As is well known from petrochemically produced ethene, a whole series of large-scale technical chemical syntheses for the production of important commodities such as polyethylen or polyvinylacetate starts today. Further petrochemically produced substances can similarly be manufactured by microbial substantial conversion of glucose, such as hydrogen, methane, propanol, acetone, butanol, butandiol, itaconic acid, and succinic

acid [18–20]. DuPont has entered a 6-year alliance with Diversa in a biorefinery to produce sugar from husks, straw, and stovers and develop a process to coproduce bioethanol and value-added chemicals such as 1,3-propanediol [19]. Through metabolic engineering, an *Escheria coli* K12 microorganism produces 1,3-propanediol (PDO), in a simple glucose fermentation process developed by DuPont and Genencor. In a pilot plant operated by Tate & Lyle, the PDO yield reaches 135 gal⁻¹ at the rate of 4 gal⁻¹ h⁻¹. PDO is used for the production of PTT (polytrimethylen-terephthalate), a new polymer which is used for the production of high-quality fibers branded Sorona [20]. Production is predicted to reach 500 kt (kilotons) per year by 2010.

Whole-crop biorefineries

Raw materials for the whole-crop biorefinery are cereals such as rye, wheat, triticale, and maize (Fig. 8). The first step is the mechanical separation into corn and straw, whereas the portion of corn is approximately 10 % (w/w) and the portion of straw is 90 % (w/w) [21]. Straw means a mixture of chaff, nodes, ears, and leaves. The straw represents an LC feedstock and may further be processed in an LCF biorefinery regime.

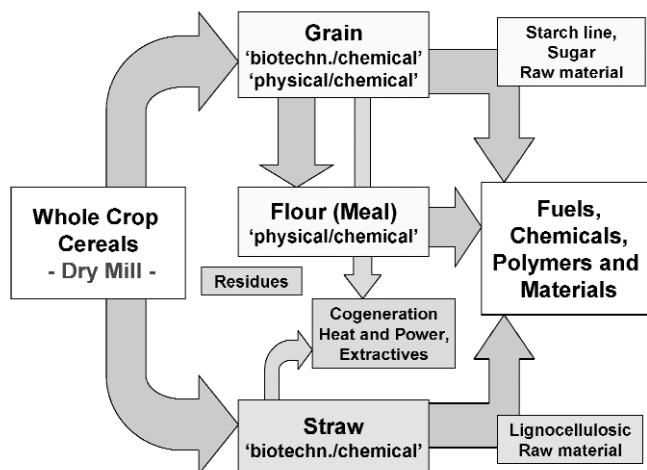


Fig. 8 Whole-crop biorefinery based on dry milling [16].

On the one side, there is the possibility of separation into cellulose, hemicellulose, lignin, and their further conversion within separate product lines, which are shown in the LCF biorefinery. Furthermore, the straw is a starting material for the production of syngas via pyrolysis technologies. Syngas is the basic material for the synthesis of fuels and methanol (Fig. 9).

The corn may either be converted into starch or directly used after grinding to meal. Further processing may be carried out in the four directions (a) breaking up, (b) plasticization, (c) chemical modification, or (d) biotechnological conversion via glucose. The meal can be treated and finished by extrusion into binders, adhesives, and fillers. 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 ethylen diamine a. o. and hydrogenative splitting into sorbitol, ethylenglycol, propylenglycol, and glycerin) [3,22,23].

Furthermore, starch can be converted by biotechnological methods into poly-3-hydroxybutyric acid in combination with the production of sugar and ethanol [24,25].

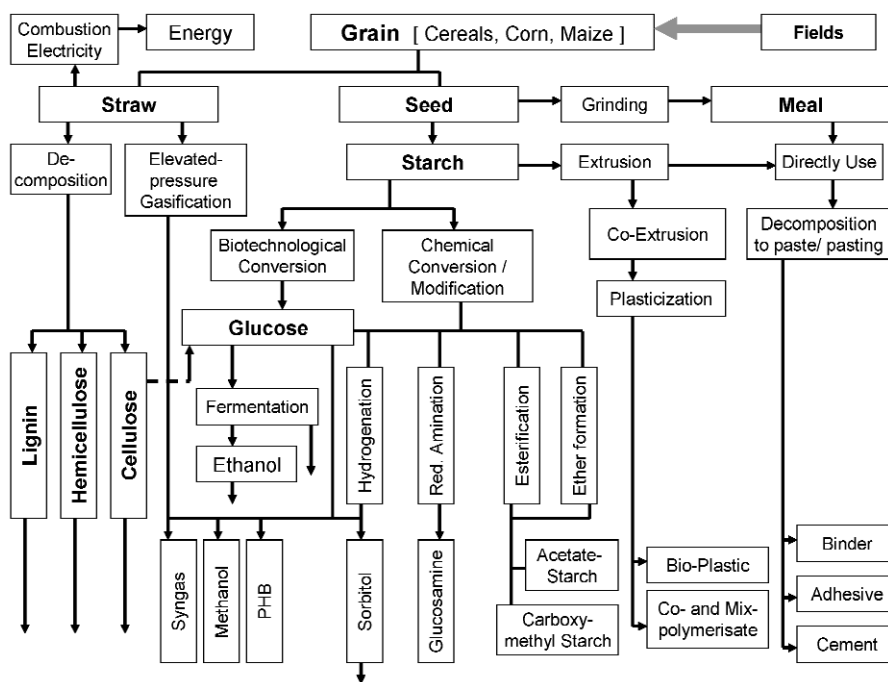


Fig. 9 Products from a whole-crop biorefinery [7,9].

Biopol, the copolymer poly-3-hydroxybutyrate/3-hydroxyvalerate, developed from Imperial Chemical Industries (ICI) is produced from wheat carbohydrates by fermentation using *Alcaligenes eutropius* [26].

An alternative to traditional dry fractionation of mature cereals into sole grains and straw has been developed by Kockums Construction, Ltd. (Sweden), later called Scandinavian Farming, Ltd. In this whole-crop harvest system, whole immature cereal plants are harvested. The whole 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 (leaves, ears, chaff, and nodes) (see also green biorefinery).

Fractions are suitable as raw materials for the starch polymer, feed, and cellulose industries and particle board producers, as gluten for the chemical industry, and as a solid fuel. Such a dry fractionation of the whole crop to optimize the utilization of all botanical components of the biomass has been described [27,28]. A biorefinery and its profitability is described in [29].

An expansion of the product lines to grain processing represents the whole-crop, wet mill-based biorefinery. The grain is swelled, and the grain germs are pressed, whereas high valuable oils are generated.

The advantages of the whole-crop biorefinery based on wet milling are that the receipt of the natural structures and structure elements such as starch, cellulose, oil, and amino acids (proteins) are kept to a large extent, and it is well known that basis technologies and processing lines can still be used. The disadvantages are high raw material costs and the necessity of industrial utilization of costly swell technologies. Otherwise, many products generate high prices, e.g., in pharmaceuticals and cosmetics (Figs. 10 and 11).

However, using the basic biorefinery technology, the corn wet mills used 11 % of the U.S. corn harvest in 1992, made products worth \$7 billion, and employed almost 10 000 people [1].

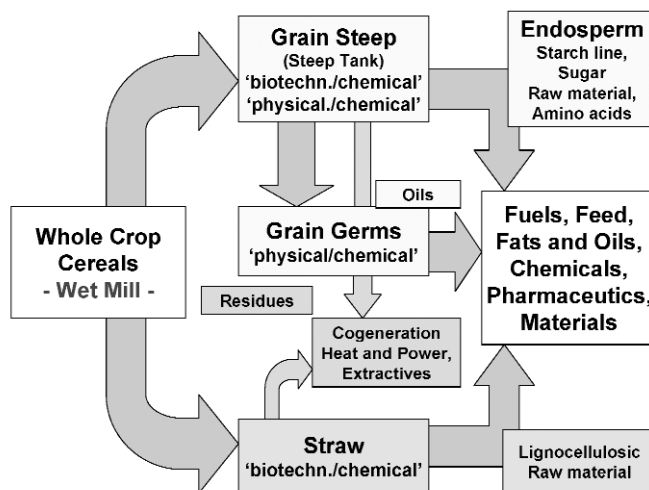


Fig. 10 Whole-crop biorefinery, wet-milling [16].

Wet-milling of corn yields corn oil, corn fiber, and corn starch. The starch products of the U.S. corn wet-milling industry are fuel alcohol (31 %), high-fructose corn syrup (36 %), starch (16 %), and dextrose (17 %). Corn wet-milling generates other products (e.g., gluten meal, gluten feed, oil) [30]. Figure 11 shows an overview of the product range.

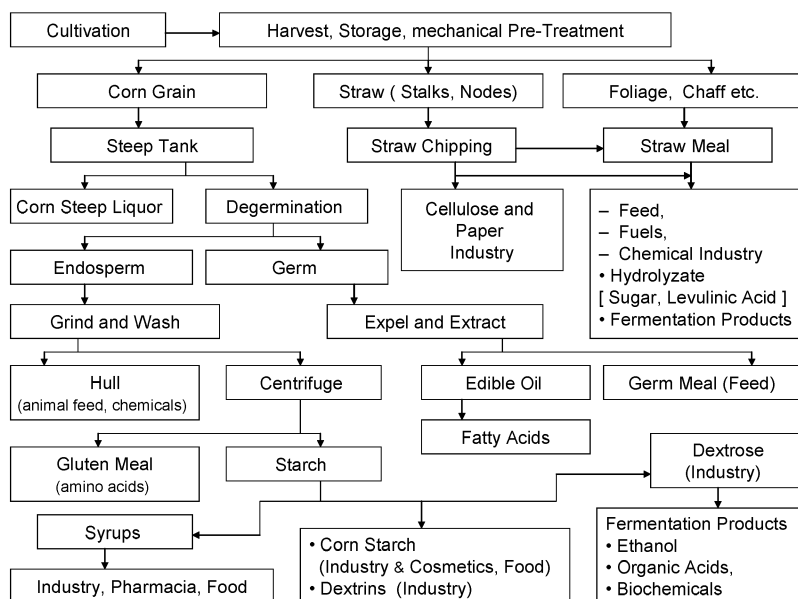


Fig. 11 Products from whole-crop, wet mill-based biorefinery.

Green biorefineries

Often, the economy of bioprocesses is still a problem because in the case of bulk products, the price is affected mainly by raw material costs [31]. The advantages of the green biorefinery are a high biomass profit per hectare and a good coupling with agricultural production, whereas the price segment of the

raw materials is still low. On one hand, simple basis technologies can be used and present a good biotechnical and chemical potential for further conversions (Fig. 12). On the other hand, a fast primary processing or the use of preservation methods such as silage or drying is necessary, both for the raw materials and the primary products. However, each preservation method changes the content materials.

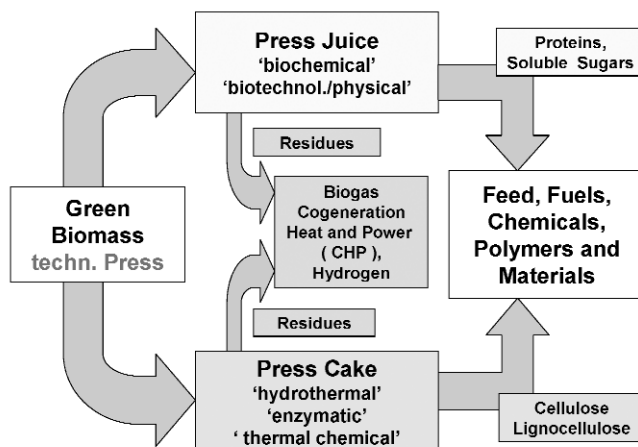


Fig. 12 Green biorefinery system [16].

Green biorefineries are also multiproduct systems and act according to their refinery cuts, fractions, and products in accordance with the physiology of the corresponding plant material, that is, maintenance and utilization of diversity of syntheses achieved by nature.

Green biomass is overriding green crops, for example, grass from cultivation of permanent grass land, closure fields, nature preserves, or green crops such as lucerne, clover, and immature cereals from extensive land cultivation. Thus, green crops represent a natural chemical factory and food plant.

Green crops are primarily used today as forage and a source of leafy vegetables. A process called wet fractionation of green biomass, green crop fractionation, can be used for simultaneous manufacturing of both food and non-food items [32].

Scientists in several countries developed green crop fractionation in Europe and elsewhere [33–35]. Green crop fractionation is now studied in about 80 countries [41]. Several hundreds of temperate and tropical plant species have been investigated for green crop fractionation [35–37]. However, more than 300 000 higher plants species are left for investigations. See reviews in refs. [33,34,38–41,44].

Green biorefineries can, by fractionation of green plants, process from a few tonnes of green crops per hour (farm-scale process) to more than 100 tonnes per hour (industrial-scale commercial process).

The careful wet fractionation technology is used as a first step (primary refinery) to isolate the content 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, the 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 the methods of biotechnology is predestined for conversions, because the plant water can simultaneously be used for further treatments. In addition, the lignin-cellulose composites are not so strong as 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, as well as for conversion to syngas and hydrocarbons (synthetic bio-

fuels). The residues of substantial conversion are suitable for the production of biogas combined with generation of heat and electricity (Fig. 13). For reviews of green biorefinery concepts, contents, and goals, see refs. [16,45,46].

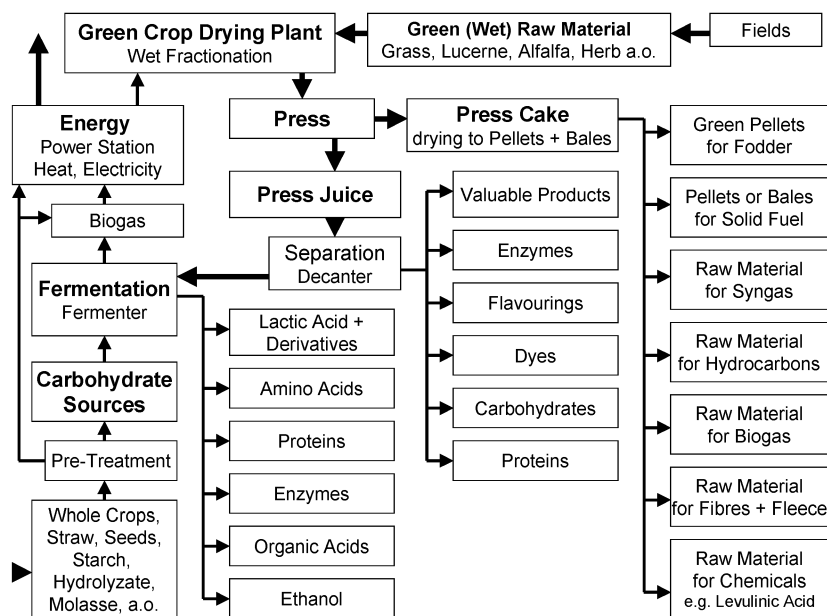


Fig. 13 Products from green biorefinery. A green biorefinery system combined with a green crop-drying plant [7,9].

Two-platform concept

The “two-platform concept” means (1) that the biomass on the average consists of 75 % of carbohydrates which can be standardized over an “intermediate sugar platform” as a basis for further conversions and (2) the biomass is converted thermochemically in syngas and the following 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 [14,33,42]. In addition to the gasification, other thermal and thermochemical biomass conversion methods have been described: hydrothermolysis, pyrolysis, thermolysis, and burning. The application is according to the water content of biomass [44].

The gasification and all thermochemical concepts concentrate on the utilization of the precursor carbohydrates as well as their imminent carbon and hydrogen content. The proteins, lignin, oils and lipids, amino acids, and general ingredients as well as *N*- and *S*-compounds occurring in every biomass are not taken into account in this case (Fig. 14).

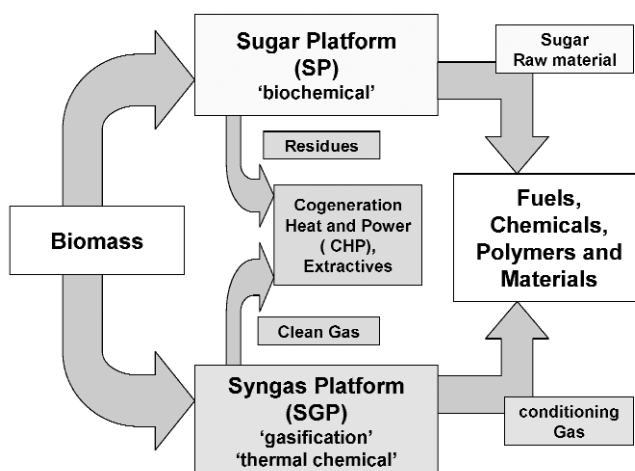


Fig. 14 Sugar platform and syngas platform [43].

REFERENCES

1. National Research Council. *Biobased Industrial Products: Priorities for Research and Commercialization*, National Academies Press, Washington, DC (2000).
2. H. Zoebelin (Ed). *Dictionary of Renewable Resources*, Wiley-VCH, Weinheim (2001).
3. D. J. Morris, I. Ahmed. *The Carbohydrate Economy, Making Chemicals and Industrial Materials from Plant Matter*, Institute of Local Self Reliance, Washington, DC (1992).
4. B. Kamm, M. Kamm, K. Richter, B. Linke, I. Starke, M. Narodoslawsky, K. D. Schwenke, S. Kromus, G. Filler, M. Kuhnt, B. Lange, U. Lubahn, A. Segert, S. Zierke. *Grüne BioRaffinerie Brandenburg - Beiträge zur Produkt- und Technologieentwicklung sowie Bewertung*, pp. 260–269, Brandenburgische Umwelt Berichte (2000).
5. L. R. Lynd, C. E. Wyman, T. U. Gerngross. *Biocommodity Eng., Biotechnol. Progr.* **15**, 777 (1999).
6. U.S. Department of Agriculture (USDA) and U.S. Department of Energy (DOE) (Eds). *Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply*, U.S. Department of Energy, Office of Scientific and Technical Information, Oak Ridge, TN (2005).
7. B. Kamm, M. Kamm. *Appl. Microbiol. Biotechnol.* **64**, 137 (2004).
8. B. Kamm, M. Kamm, P. Gruber (Eds). *Biorefineries: Industrial Processes and Products*, Wiley-VCH, Weinheim (2006).
9. B. Kamm, M. Kamm. *Chem. Biochem. Eng. Q.* **18**, 1 (2004).
10. H. Röper. *Perspektiven der industriellen Nutzung nachwachsender Rohstoffe, insbesondere von Stärke und Zucker*. Mitteilung der Fachgruppe Umweltchemie und Ökotoxikologie der Gesellschaft Deutscher Chemiker **7**, 6 (2001).
11. Y. Y. Linko, P. Javanainen. *Enzyme Microb. Technol.* **19**, 118 (1996).
12. K. J. Zielinska, K. M. Stecka, A. H. Miecznikowski, A. M. Suterska. *Pr. Inst. Lab. Badaw. Przem. Spozyw.* **55**, 22 (2000).
13. B. Kamm, M. Kamm, M. Schmidt, I. Starke, E. Kleinpeter. *Chemosphere* **62**, 97 (2006).
14. T. Werpy, G. Petersen (Eds.). *Top Value Added Chemicals from Biomass*, U.S. Department of Energy, Office of Scientific and Technical Information, Oak Ridge, TN (2004).
15. B. Dale. *Encyclopedia of Physical Science and Technology*, Vol. 2, 3rd ed., pp. 141–157, Academic Press, Amsterdam (2002).

16. S. Kromus, B. Kamm, M. Kamm, P. Fowler, M. Narodoslawsky. In *Biorefineries: Industrial Processes and Products*, Vol. 1, B. Kamm, M. Kamm, P. Gruber (Eds.), pp. 253–294, Wiley-VCH, Weinheim (2006).
17. M. Ringfeil. *Biobased Industrial Products and Biorefinery Systems – Industrielle Zukunft des 21. Jahrhunderts?* (2001).
18. K. D. Vorlop, Th. Willke, U. Prübe. “Biocatalytic and catalytic routes for the production of bulk and fine chemicals from renewable resources”, in *Biorefineries: Industrial Processes and Products*, Vol. 2, B. Kamm, M. Kamm, P. Gruber (Eds.), pp. 385–406, Wiley-VCH, Weinheim (2006).
19. *Chem World*, 20 May, 20 (2003).
20. DuPont. U.S. patent 5 686 276 (2004).
21. O. Wurz. *Zellstoff- und Papierherstellung aus Einjahrespflanzen*, Eduard Roether Verlag, Darmstadt (1960).
22. J. J. Bozell. “Alternative feedstocks for bioprocessing”, in *Encyclopedia of Plant and Crop Science*, R. M. Goodman (Ed.), Marcel Dekker, New York (2004).
23. C. Webb, A. A. Koutinas, R. Wang. *Adv. Biochem. Eng./Biotechnol.* **87**, 195 (2004).
24. R. V. Nonato, P. E. Mantellato, C. E. V. Rossel. *Appl. Microbiol. Biotechnol.* **57**, 1 (2001).
25. C. E. V. Rossel, P. E. Mantellato, A. M. Agnelli, J. Nascimento. “Sugar-based biorefinery: Technology for an integrated production of poly(3-hydroxybutyrate), sugar and ethanol”, in *Biorefineries: Industrial Processes and Products*, Vol. 1, B. Kamm, M. Kamm, P. Gruber (Eds.), pp. 209–226, Wiley-VCH, Weinheim (2006).
26. A. Fiechter. *Plastics from Bacteria and for Bacteria: Poly(β -hydroxyalkanoates) as Natural, Biocompatible, and Biodegradable Polyesters*, pp. 77–93, Springer Verlag, New York (1990).
27. F. Rexen. “New industrial application possibilities for straw”, Documentation of Svebio Phytochemistry Group (Danish), Fytokemi i Norden, Stockholm, Sweden, 1986-03-06 12 (1986).
28. J. Coombs, K. Hall. “The potential of cereals as industrial raw materials: Legal technical, commercial considerations”, in *Cereals: Novel Uses and Processes*, G. M. Campbell, C. Webb, S. L. McKee (Eds.), pp. 1–12, Plenum, New York (1997).
29. E. Audsley, J. E. Sells. “Determining the profitability of a whole crop biorefinery”, in *Biorefineries: Industrial Processes and Products*, Vol. 1, B. Kamm, M. Kamm, P. Gruber (Eds.), pp. 191–294, Wiley-VCH, Weinheim (2006).
30. A. J. Hacking. “The American wet milling industry”, in *Economic Aspects of Biotechnology*, pp. 214–221, Cambridge University Press, New York (1986).
31. Th. Willke, K. D. Vorlop. *Appl. Microbiol. Biotechnol.* **66**, 131 (2004).
32. R. Carlsson. “Sustainable primary production: Green crop fractionation: Effects of species, growth conditions, and physiological development”, in *Handbook of Plant and Crop Physiology*, M. Pessaraki (Ed.), pp. 941–963, Marcel Dekker, New York (1994).
33. N. W. Pirie. *Leaf Protein: Its Agronomy, Preparation, Quality, and Use*, Blackwell Scientific, Oxford (1971).
34. N. W. Pirie. *Leaf Protein and Its By-Products in Human and Animal Nutrition*, Cambridge University Press, Cambridge (1987).
35. R. Carlsson. “Status quo of the utilization of green biomass”, in *The Green Biorefinery, Proceedings of the 1st International Green Biorefinery Conference*, Neuruppin, Germany, 1997, S. Soyez, B. Kamm, M. Kamm (Eds.), Verlag GÖT, Berlin (1998).
36. R. Carlsson. “Leaf protein concentrate from plant sources in temperate climates”, in *Leaf Protein Concentrates*, L. Telek, H. D. Graham (Eds.), pp. 52–80, AVI Publishing, Westport, CT (1983).
37. L. Telek, H. D. Graham (Eds.). *Leaf Protein Concentrates*, AVI Publishing, Westport, CT (1983).
38. R. J. Wilkins (Ed.). *Green Crop Fractionation*, The British Grassland Society, c/o Grassland Research Institute, Hurley (1977).

39. I. Tasaki (Ed.). "Recent advances in leaf protein research", *Proceedings of the 2nd International Leaf Protein Research Conference*, Nagoya, Japan (1985).
40. P. Fantozzi (Ed.). *Proceedings of the 3rd International Leaf Protein Research Conference*, Pisa-Perugia-Viterbo, Italy (1989).
41. N. Singh (Ed.). *Green Vegetation Fractionation Technology*, Science Publishing, Lebanon, NH (1996).
42. D. H. White, D. Wolf. *Research in Thermochemical Biomass Conversion*, A. V. Bridgewater, J. L. Kuester (Eds.), Elsevier Applied Science, New York (1988).
43. National Renewable Energy Laboratory (NREL) (2005). <<http://www.nrel.gov/biomass/biorefinery.htm>>.
44. C. Okkerse, H. van Bekkum. *Green Chem.* **4**, 107 (1999).
45. B. Kamm, M. Kamm, K. Soyez (Eds.). "Die Grüne Bioraffinerie/The Green Biorefinery. Technologiekonzept", *Proceedings of the 1st International Symposium Green Biorefinery/Grüne Bioraffinerie*, Oct. 1997, Neuruppin, Germany (1998).
46. M. Narodoslawsky (Ed.). *Green Biorefinery, 2nd International Symposium Green Biorefinery*, October 13–14, 1999, Feldbach, Austria. Proceedings, SUSTAIN, Verein zur Koordination von Forschung über Nachhaltigkeit, Graz TU, Austria (1999).