

## **Part I**

### **Background and Outline – Principles and Fundamentals**



## 1

## Biorefinery Systems – An Overview

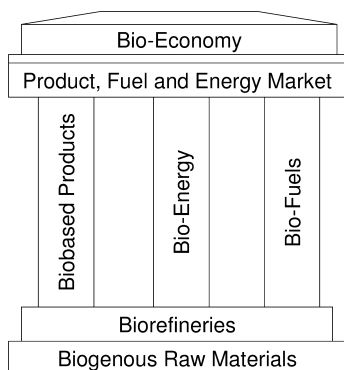
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## 1.1

### Introduction

The preservation and management of our diverse resources are fundamental political tasks to foster sustainable development in the 21st century. Sustainable economic growth requires safe and sustainable resources for industrial production, a long-term and confident investment and finance system, ecological safety, and sustainable life and work perspectives for the public. Fossil resources are not regarded as sustainable, however, and their availability is more than questionable in the long-term. Because of the increasing price of fossil resources, moreover, the feasibility of their utilization is declining.

It is, therefore, essential to establish solutions which reduce the rapid consumption of fossil resources, which are not renewable (petroleum, natural gas, coal, minerals). A forward looking approach is the stepwise conversion of large parts of the global economy into a sustainable biobased economy with bio-energy, biofuels, and biobased products as its main pillars (Fig. 1.1).



**Fig. 1.1** 3-Pillar model of a future biobased economy.

Whereas for energy production a variety of alternative raw materials (wind, sun, water, biomass, nuclear fission and fusion) can be established, industry based on conversion of sustainable material, for example the chemical industry, industrial biotechnology, and also the fuel generation, depends on biomass, in particular mainly on plant biomass.

Some change from the today's production of goods and services from fossil to biological raw materials will be essential. The rearrangement of whole economies to implement biological raw materials as a source with increased value requires completely new approaches in research and development. On the one hand, biological and chemical sciences will play a leading role in the generation of future industries in the 21st century. On the other hand, new synergies of biological, physical, chemical, and technical sciences must be elaborated and established. This will be combined with new traffic technology, media- and information technology, and economic and social sciences. Special requirements will be placed on both the substantial converting industry and research and development with regard to raw material and product line efficiency and sustainability.

The development of substance-converting basic product systems and poly-product systems, for example biorefineries, will be the "key for the access to an integrated production of food, feed, chemicals, materials, goods, and fuels of the future" [1].

## 1.2

### Historical Outline

#### 1.2.1

##### Historical Technological Outline and Industrial Resources

Today's biorefinery technologies are based (1) on the utilization of the whole plant or complex biomass and (2) on integration of traditional and modern processes for utilization of biological raw materials. In the 19th and the beginning of the 20th century large-scale utilization of renewable resources was focused on pulp and paper production from wood, saccharification of wood, nitration of cellulose for guncotton and viscose silk, production of soluble cellulose for fibers, fat curing, and the production of furfural for Nylon. Furthermore, the technology of sugar refining, starch production, and oil milling, the separation of proteins as feed, and the extraction of chlorophyll for industrial use with alfalfa as raw material were of great historical importance. But also processes like wet grinding of crops and biotechnological processes like the production of ethanol, acetic acid, lactic acid, and citric acid used to be fundamental in the 19th and 20th century.

## 1.2.2

**The Beginning – A Digest****1.2.2.1 Sugar Production**

The history of industrial conversion of renewable resources is longer than 200 years. Utilization of sugar cane has been known in Asia since 6000 BC and imports of cane sugar from oversea plantations have been established since the 15th century. The German scientist A.S. Marggraf was a key initiator of the modern sugar industry. In 1748 he published his research on the isolation of crystalline sugar from different roots and beet [2, 3]. Marggraf's student, F.C. Achard, was the first to establish a sugar refinery based on sugar beet, in Cütern/Schlesien, Poland, in 1801.

**1.2.2.2 Starch Hydrolysis**

In 1811, the German pharmacist G.S.C. Kirchhoff found that when potato starch was cooked in dilute acid the starch was converted into "grape sugar" (i.e. *D*-glucose or dextrose) [4]. This was not only a very important scientific result but also the starting point of the starch industry. In 1806 the French emperor Napoleon Bonaparte introduced an economic continental blockade which considerably limited overseas trade in cane sugar. Thus, starch hydrolysis became of interest for the economy. The first starch sugar plant was established in Weimar, Germany, in 1812, because of a recommendation of J.W. Döbereiner to grand duke Carl August von Sachsen-Weimar. Successful development of the sugar beet industry, however, initially obstructed further development of the starch industry [5]. In 1835, the Swedish Professor J.J. Berzelius developed enzymatic hydrolyses of starch into sugar and introduced the term "catalysis".

**1.2.2.3 Wood Saccharification**

In 1819 the French plant chemist H. Braconnot discovered that sugar (glucose) is formed by treatment of wood with concentrated sulfuric acid. 1855, G.F. Melsens reported that this conversion can be carried out with dilute acid also. Acid hydrolysis can be divided into two general approaches, based on (1) concentrated acid hydrolysis at low temperature and (2) dilute acid hydrolysis at high temperature. Historically, the first commercial processes, named wood saccharification, were developed in 1901 by A. Classen (Ger. Patent 130980), employing sulfuric acid, and in 1909 by M. Ewen and G. Tomlinson (US Patent 938208), working with dilute sulfuric acid. Several plants were in operation until the end of World War I. Yields of these processes were usually low, in the range 75–130 liter per ton wood dry matter only [6, 7]. Technologically viable processes were, however, developed in the years between World War I and World War II. The German chemist Friedrich Bergius was one of the developers. The sugar fractions generated by wood hydrolyses have a broad spectrum of application. An important fermentation product of wood sugar of increasing interest is ethanol.

Ethanol can be used as fuel either blended with traditional hydrocarbon fuel or as pure ethanol. Ethanol is also an important platform chemical for further processing [8].

#### 1.2.2.4 Furfural

Döbereiner was the first to report the formation and separation of furfural by distillation of bran with diluted sulfuric acid in 1831. In 1845 the English Chemist G. Fownes proposed the name “furfurol” (furfur – bran; oleum – oil). Later the suffix “ol” was changed to “al” because of the aldehyde function [9, 10].

Treatment of hemicellulose-rich raw materials with dry steam in the presence of hydrogen chloride gave especially good results [11]. Industrial technology for production of furfural from pentose is based on a development of an Anglo-American company named Quaker Oats. The process was been developed in the nineteen-twenties [E. P. 203 691 (1923), F. P. 570 531 (1923)]. Since 1922 Quaker Oats Cereal Mill in Cedar Rapids/Iowa, USA, has produced up to 2.5 tons of furfural per day from oat husks. Since 1934 the process had been established as an industrial furfural plant. Furfural was the cheapest aldehyde, at 16–17 cents per lb (lb=pound; 1 metric ton=1000 kg=2204.62442 lb; 1 kg=0.453592 lb) [12]. Until approximately 1960 DuPont used furfural as a precursor of Nylon-6.6. Furfural has since been substituted by fossil based precursors.

#### 1.2.2.5 Cellulose and Pulp

In 1839 the Frenchman A. Payen discovered that after treatment of wood with nitric acid and subsequent treatment with a sodium hydroxide solution a residue remained which he called “les cellules”, cellulose [13]. In 1854 caustic soda and steam were used by the Frenchman M.A. C. Mellier to disintegrate cellulose pulp from straw. In 1863 the American B.C. Tilgham registered the first patent for production of cellulose by use of calcium bisulfite. Together with his brother, Tilgham started the first industrial experiments to produce pulp from wood by treatment with hydrogen sulfite. This was 1866 at the paper mill Harding and Sons, Manayunk, close to Philadelphia. In 1872 the Swedish Engineer C.D. Ekman was the first to produce sulfite cellulose by using magnesium sulfite as cooking agent [14]. By 1900 approximately 5200 pulp and paper mills existed worldwide, most in the USA, approximately 1300 in Germany, and 512 in France.

#### 1.2.2.6 Levulinic Acid

In 1840 the Dutch Professor G.J. Mulder (who also introduced the name “protein”) synthesized levulinic acid (4-oxopentanoic acid,  $\gamma$ -ketovaleric acid) by heating fructose with hydrochloride for the first time. The former term “levulose” for fructose gave the levulinic acid its name [15]. Although levulinic acid has been well known since the 1870s when many of its reactions (e.g. esters) were

established, it has never reached commercial use in any significant volume. In the 1940s commercial levulinic acid production was begun in an autoclave in the United States by A. E. Staley, Dectur, Illinois [16]. At the same time utilization of hexoses from low-cost cellulose products was examined for the production of levulinic acid [17]. As early as 1956 levulinic acid was regarded as a platform chemical with high potential [18].

#### 1.2.2.7 Lipids

From 1850 onward European import of tropical plant fats, for example palm-oil and coconut oil, started. Together with the soda process, invented by the French N. Leblanc in 1791, the industrialization of the soap production began and soap changed from luxury goods into consumer goods. The developing textile industry also demanded fat based products. In 1902 the German chemist W. Normann discovered that liquid plant oils are converting into tempered fat by augmentation of hydrogen. Using nickel as catalyst Norman produced tempered stearic acid by catalytic hydration of liquid fatty acids [19]. The so called “fat hardening” led to the use of European plant oils in the food industry (margarine) and other industries.

#### 1.2.2.8 Vanillin from Lignin

In 1874 the German chemists W. Haarmann and F. Tiemann were the first to synthesize vanillin from the cambial juice of coniferous wood. In 1875 the company Haarmann and Reimer was founded. The first precursor for the production of vanillin was coniferin, the glucoside of coniferyl alcohol. This precursor of lignin made from cambial juice of coniferous trees was isolated, oxidized to glucovanillin, and then cleaved into glucose and vanillin [20]. This patented process [21] opened the way to industrial vanillin production. It was also the first industrial utilization of lignin. Besides the perfume industry, the invention was of great interest to the upcoming chocolate industry. Later, however, eugenol (1-allyl-4-hydroxy-3-methoxybenzene), isolated from clove oil, was used to produce vanillin. Today, vanillin production is based on lignosulfonic acid which is a side product of wood pulping. The lignosulfonic acid is oxidized with air under alkaline conditions [22, 23].

#### 1.2.2.9 Lactic Acid

In 1895 industrial lactic acid fermentation has been developed by the pharmaceutical entrepreneur A. Boehringer. The Swedish pharmacist C. W. Scheele had already discovered lactic acid in 1780 and the conversion of carbohydrates into lactic acid had been known for ages in food preservation (e.g. Sauerkraut) or agriculture (silage fermentation). Because of the activity of Boehringer the German company Boehringer-Ingelheim can be regarded as the pioneer of industrial biotechnology. Both the process and the demand for lactic acid by dyeing

factories, and the leather, textile, and food industries made the company the leading supplier. In 1932 W.H. Carothers, who was also the inventor of polyamide-6.6, developed, together with van Natta, a polyester made from lactic acid, poly(lactic acid) [24]. In the late 1990s this poly(lactic acid) was commercialized by the company NatureWorks (Cargill, the former Cargill Dow) [25].

### 1.2.3

#### **The Origins of Integrated Biobased Production**

In the year 1940 the German chemist P. von Walden (noted for his “Inversion of configuration at substitution reactions”, the so-called “Walden-Reversion”) calculated that in 1940 Germany produced 13 million tons of cellulose leaving 5 to 6 million tons of lignin suitable only as wastage. He then formulated the question: How long can national economy tolerate this [26]? Approaches to integrated production during industrial processing of renewable primary products have a long tradition, starting from the time when industrial cellulose production expanded continuously, as also did the related waste-products. Typical examples of this will be mentioned.

As early as 1878 A. Mitscherlich, a German chemist, started to improve the sulfite pulp process by fermentation of sugar to ethyl alcohol – it should be mentioned that sugar is a substance in the waste liquor during sulfite pulp production. He also put into practice a procedure to obtain paper glue from the waste liquor. Both processes were implemented in his plant located in Hof, Germany, in the year 1898 [27].

In 1927 the American Marathon Corporation assigned a group of chemists and engineers to the task of developing commercial products from the organic solids in the spent sulfite liquor from the Marathon's Rothschild pulp and paper operations close to Wausau, Wisconsin, USA. The first products to show promise were leather tanning agents. Later, the characteristics of lignin as dispersing agents became evident. By the mid 1930s, with a considerable amount of basic research accomplished, Marathon transferred operations from a research pilot plant to full-scale production [28].

One of the most well known examples is the production of furfural by the Quaker Oats Company since 1922, thus coupling food, i.e. oat flakes, production and chemical products obtained from the waste [10] (Section 1.2.2). On the basis of furfural a whole section of chemical production developed – furan chemistry.

Agribusiness, especially, strived to achieve combined production from the very beginning. Modern corn refining started in the middle of the 18th century when T. Kingsford commenced operation of his corn refining plant in Oswego, New York [29]. Corn refining is distinguished from corn milling because the refining process separates corn grain into its components, for example starch, fiber, protein and oil, and starch is further processed into a substantial number of products [30].

The extensive usage of green crops has been aim of industry for decades, because there are several advantages. Particularly worthy of mention is the work



of Osborn (1920) and Slade and Birkinshaw (1939) on the extraction of proteins from green crops, for example grass or alfalfa [31].

In 1937 N. W. Pirie developed the technical separation and extraction methods needed for this use of green crops [32, 33]. By means of sophisticated methods all the botanical material should have been used, both for production of animal feed, isolated proteins for human nutrition, and as raw material for further industrial processes, for example glue production. The residual material, juices rich in nutrients, had initially been used as fertilizer; later they were used for generation of fermentation heat based on biogas production [34, 35].

These developments resulted in market-leading technology, for example the Proxan and Alfaprox procedures, used for generation of protein-xanthophyll concentrates, including utilization of the by-products, however, predominantly in agriculture [36].

In the United States commercial production of chlorophyll and carotene by extraction from alfalfa leaf meal had started in 1930 [37, 38]. For example Strong, Cobb and Company produced 0.5 ton chlorophyll per day from alfalfa as early as 1952. The water-soluble chlorophyll, or chlorophyllin, found use as deodorizing agent in toothpastes, soaps, shampoos, candy, deodorants, and pharmaceuticals [39].

A historically important step for today's biorefinery developments was the industry-politics-approach of "Chemurgy", founded in 1925 in the US by the Chemist W. J. Hale, son-in-law of H. Dow, the founder of Dow Chemical, and C. H. Herty, a former President of the American Chemical Society. They soon found prominent support from H. Ford and T. A. Edisons. Chemurgy, an abbreviation of "chemistry" and "ergon", the Greek word for work [40], means by analogy "chemistry from the acre" that is the connection of agriculture with the chemical industry.

Chemurgy was soon shown to have a serious industrial political philosophy – the objective of utilizing agricultural resources, nowadays called renewable resources, in industry. There have been common conferences between agriculture, industry, and science since 1935 with a national council called the "National Farm Chemurgic Council" [41]. The end of Chemurgy started with the flooding of the world market with cheap crude oil after World War II; numerous inventions and production processes remained, however, and are again highly newsworthy. One was a car, introduced by Henry Ford 1941, whose car interior lining and car body consisted 100% of bio-synthetics; to be specific it had been made from a cellulose meal, soy meal, formaldehyde resin composite material in the proportions 70%:20%:10%, respectively. The alternative fuel for this car was pyrolysis methanol produced from cannabis. Throughout the thirties more than 30 industrial products based on soy bean were created by researchers from the Ford company; this made it necessary to apply complex conversion methods [42]. Hale was a Pioneer of ethyl alcohol and hydrocarbon fuel mixture (Power Alcohol, Gasohol) [43]. This fuel mixture, nowadays called E10-Fuel, consisting of 10 percent bioethanol and 90 percent hydrocarbon-based fuel, has been the national standard since the beginning of this millennium in the United States.

Associated with the work of Bergius, 1933 [44], and Scholler, 1923 and 1935 [45, 46], wood saccharification was reanimated at the end of WW II. Beside optimization of the process, use of lignocelluloses was of great interest. The continuously growing agribusiness left behind millions of tons of unused straw. Two Americans, Othmer and Katzen, were the main pioneers in the field of wood saccharification [47]. Between the years 1935 and 1960 several hydrolysis plants were built in Germany and the United States; in these deal, wood flour, surplus lumber, and also straw were hydrolyzed [48]. One of the most well known plants are those of Scholler/Tornesch located in Tornesch, Germany, with a production rate of 13,000 tons per year, in Dessau, Germany, production rate 42,000 tons per year, based on wood, in Holzminden, Germany, production rate of 24,000 tons per year, also based on wood, in Ems, Switzerland, with a production rate of 35,000 tons per year, also wood based, and the plants in Madison and Springfield, United States, and the Bergius plants in Rheinau, Germany (Rheinau I, built 1930, with a production rate of 8000 tons per year, based on surplus lumber; Rheinau II, built 1960 with a production rate of 1200 tons per year, based on wood) and the plant in Regensburg, Germany, with a production rate of 36,000 tons per year [49].

During WW II the plant in Springfield, Oregon, US (using the Scholler-Tornesch process as modified by Katzen) produced 15,000 gallons of ethyl alcohol per day from 300 tons wood flour and sawdust, i.e. 50 gallons per ton of wood [50]. The plant in Tornesch, Germany, has been producing approximately 200 liters of ethyl alcohol, purity 100%, per ton wood and approximately 40 kg yeast per ton of wood. In 1965 there were 14 plants in what was then the Soviet Union, with a total capacity of 700,000 tons per year and an overall annual wood consumption of 4 million tons [6].

During the nineteen-sixties wood chemistry had its climax. Projects had been developed, which made it possible to produce nearly all chemical products on the basis of wood. Examples are the complex chemical technological approaches of wood processing from Timell 1961 [51], Stamm 1964 [52], James 1969 [53], Brink and Pohlmann 1972 [54], and the wood-based chemical product trees by Oshima 1965 [55]. Although these developments did not make their way into industrial production, they are an outstanding platform for today's lignocellulose conversions, product family trees, and LCF biorefineries (Section 1.5.2).

Most of the above mentioned technologies and products, some of which were excellent, could not compete with the fossil-based industry and economy; nowadays, however, they are prevailing again. The basis for this revival started in the seventies, when the oil crisis and continuously increasing environmental pollution resulted in a broad awareness that plants could be more than food and animal feed. At the same time the disadvantages of intensive agricultural usage, for example over-fertilization, soil erosion, and the enormous amounts of waste, were revealed. From this situation developed complex concepts, which have been published, in which the aim was, and still is, technological and economical cooperation of agriculture, forestry, the food-production industry, and conventional industry, or at least consideration of integrated utilization of renewable resources.

Typical examples of this thinking were:

- integrated industrial utilization of wood and straw [56];
- industrial utilization of fast growing wood-grass [57, 58];
- complex utilization of green biomass, for example grass and alfalfa, by agriculture and industry [59–61];
- corn wet-grinding procedures with associated biotechnological and chemical product lines [62];
- modern aspects of thermochemical biomass conversion [63];
- discussion of the concept “organic chemicals from biomass” with main focus on biotechnological methods and products (white biotechnology) [64–66] and industrial utilization of biomass [67].

These rich experiences of the industrial utilization of renewable resources, new agricultural technology, biotechnology, and chemistry, and the changes in ecology, economics, and society led inevitably to the topic of complex and integrated substantial and energy utilization of biomass and, finally, to the biorefinery.

### 1.3

#### Situation

##### 1.3.1

#### Some Current Aspects of Biorefinery Research and Development

Since the beginning of the 1990s the utilization of renewable resources for production of non-food products has fostered research and development which has received increasing attention from industry and politicians [68–70]. Integrated processes, biomass refinery technology, and biorefinery technology have become object of research and development. Accordingly, the term “biorefinery” was established in the 1990s [1, 71–80]. The respective biorefinery projects are focused on the fabrication of fuels, solvents, chemicals, plastics, and food for human beings. In some countries these biorefinery products are made from waste biomass. At first the main processes in the biorefinery involved ethanol fermentation for fuels (ethanol-oriented biorefineries) [81–85], lactic acid (LA) fermentation [25, 86], propanediol (PDO) fermentation [87], and the lysine fermentation [88] especially for polymer production. The biobased polymers poly(lactic acid) [25], propandiol-derived polymers [89], and polylysine [88] have been completed by polyhydroxyalkanoates [90] and polymerized oils [91].

Many hybrid technologies were developed from different fields, for example bioengineering, polymer chemistry, food science and agriculture. Biorefinery systems based on cereals [92, 93], lignocelluloses [94, 95], and grass and alfalfa [35, 96], and biorefinery optimization tools are currently being developed [97, 98]. The integration of molecular plant genetics to support the raw material supply is currently being discussed intensely [99, 100].

Broin and Associates has begun the development of a second generation of dry mill refineries and E.I. du Pont de Nemours has developed an integrated corn-based biorefinery. In 2001 NatureWorks LCC (to Cargill, former Cargill Dow LLC) started the industrial production of PLA (PLA-oriented Biorefinery) on the basis of maize.

Biorefineries are of interest ecologically [101], economically, and to business, government, and politicians [102–107]. National programs [108, 109], biobased visions [110], and plans [111] have been developed and the international exchange of information is increasing, for example as a result, among others, of series of international congresses and symposia:

1. BIO World Congress on Industrial Biotechnology and Bioprocessing [112];
2. biomass conferences [113, 114];
3. The Green and Sustainable Chemistry Congress [115]; and
4. the Biorefinica symposia series [116, 117].

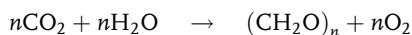
Currently, biorefinery systems are in the stage of development world-wide. An overview of the main aspects, activity, and discussions is the content of this book. An attempt to systematize the topic “Biorefinery” will be presented below.

### 1.3.2

#### Raw Material Biomass

Nature is a permanently renewing production chain for chemicals, materials, fuels, cosmetics, and pharmaceuticals. Many of the biobased industry products currently used are results of direct physical or chemical treatment and processing of biomass, for example cellulose, starch, oil, protein, lignin, and terpenes. On one hand one must mention that because of the help of biotechnological processes and methods, feedstock chemicals are produced such as ethanol, butanol, acetone, lactic acid, and itaconic acid, as also are amino acids, e.g. glutaminic acid, lysine, tryptophan. On the other hand, only 6 billion tons of the yearly produced biomass,  $1.7\text{--}2.0 \times 10^{11}$  tons, are currently used, and only 3 to 3.5% of this amount is used in non-food applications, for example chemistry [118].

The basic reaction of biomass is photosynthesis according to:



Industrial utilization of raw materials from agriculture, forestry, and agriculture is only just beginning. There are several definitions of the term “biomass” [118]:

- the complete living, organic matter in our ecological system (volume/non-specific)
- the plant material constantly produced by photosynthesis with an annual growth of 170 billion tons (marine plants excluded)
- the cell-mass of plants, animals, and microorganism used as raw materials in microbiological processes

Biomass is defined in a recent US program [108, 109]: “The term “biomass” means any organic matter that is available on a renewable or recurring basis (excluding old-growth timber), including dedicated energy crops and trees, agricultural food and feed crop residues, aquatic plants, wood and wood residues, animal wastes, and other waste materials.”

For this reason it is essential to define biomass in the context of the industrial utilization. A suggestion for a definition of “industrial biomass” [108, 109] is: “The term “industrial biomass” means any organic matter that is available on a renewable or recurring basis (excluding old-growth timber), including dedicated energy crops and trees, agricultural food and feed crop residues, aquatic plants, wood and wood residues, animal wastes, and other waste materials usable for industrial purposes (energy, fuels, chemicals, materials) and include wastes and co-wastes of food and feed processing.”

Most biological raw material is produced in agriculture and forestry and by microbial systems. Forestry plants are excellent raw materials for the paper and

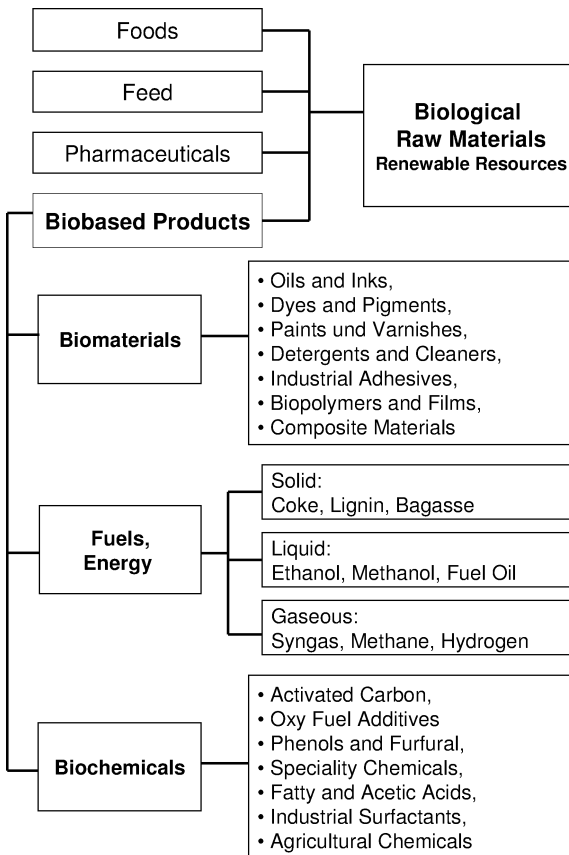


Fig. 1.2 Products and product classes based on biological raw materials [78].

cardboard, construction, and chemical industries. Field fruits are an pool of organic chemicals from which fuels, chemicals, chemical products, and biomaterials are produced (Fig. 1.2), [69]. Waste biomass and biomass of nature and agricultural 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 [119].

### 1.3.3

#### National Vision and Goals and Plan for Biomass Technology in the United States

Industrial development was pushed by the US President [108] and by the US congress [109], initially in 2000. In the USA it is intended that by 2020 at least 25% of organic-carbon-based industrial feedstock chemicals and 10% of liquid fuels (compared with levels in 1994) will be produced by biobased industry. This would mean that more than 90% of the consumption of organic chemicals in the US and up to 50% of liquid fuel needs would be biobased products [1].

The Biomass Technical Advisory Committee (BTAC) of the USA in which leading representatives of industrial companies, for example Dow Chemical, E.I. du Pont de Nemours, Cargill Dow LLC, and Genencor International, and Corn growers associations and the Natural Resources Defense Council are involved and which acts as advisor to the US government, has made a detailed plan with steps toward targets of 2030 with regard to bioenergy, biofuels, and bioproducts (Table 1.1) [110].

Simultaneously, the plan *Biomass Technology in the United States* has been published [111] in which research, development, and construction of biorefinery

**Table 1.1** The US national vision goals for biomass technologies by the Biomass Technical Advisory Committee [110].

Year	Current	2010	2020	2030
<b>BioPower</b> (BioEnergy)	2.8%	4%	5%	5%
Biomass share of electricity and heat demand in utilities and industry	(2.7 quad) <sup>a)</sup>	(3.2 quad)	(4.0 quad)	(5.0 quad)
<b>BioFuels</b>	0.5%	4%	10%	20%
Biomass share of demand for transportation fuels	(0.15 quad)	(1.3 quad)	(4.0 quad)	(9.5 quad)
<b>BioProducts</b>	5%	12%	18%	25%
Share of target chemicals that are biobased				

- a) 1 quad = 1 quadrillion BTU = 1 German billiarde BTU;  
 BTU = British thermal unit; 1 BTU = 0.252 kcal,  
 1 kW = 3413 BTU, 1 kcal = 4.186 kJ

demonstration plants are determined. Research and development are necessary to:

1. increase 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 efficiency and performance in conversion and distribution processes and technologies for development of a host of biobased products and
4. create the regulatory and market environment necessary for increased development and use of biobased products.

The Biomass Advisory Committee has established specific research and development objectives for feedstock production research. Target crops should include oil and cellulose-producing crops that can provide optimum energy content and usable plant components. Currently, however, there is a lack of understanding of plant biochemistry and inadequate genomic and metabolic information about many potential crops. Specific research to produce enhanced enzymes and chemical catalysts could advance biotechnology capabilities.

#### 1.3.4

##### **Vision and Goals and Plan for Biomass Technology in the European Union and Germany**

In Europe there are already regulations about substitution of nonrenewable resources by biomass in the field of biofuels for transportation [120] and the “Renewable energy law” of 2000 [121]. According to the EC Directive “On the promotion of the use of biofuels” the following products are regarded as “biofuels”:

- (a) “bioethanol”, (b) “biodiesel”, (c) “biogas”, (d) “biomethanol”, (e) “biodimethyl ether”,
- (f) “bio-ETBE (ethyl tertiary-butyl ether)” on the basis of bioethanol,
- (g) “bio-MTBE (methyl tertiary butyl ether)” on the basis of biomethanol, and
- (h) “synthetic biofuels”, (i) “biohydrogen”, (j) pure vegetable oil

Member States of the EU have been requested to define national guidelines for a minimum amounts of biofuels and other renewable fuels (with a reference value of 2% by 2005 and 5.75% by 2010 calculated on the basis of energy content of all petrol and diesel fuels for transport purposes). Table 1.2 summarizes this goal of the EU and also those of Germany with regard to establishment of renewable energy and biofuel [122, 123].

Today there are no guidelines concerning “biobased products” in the European Union and in Germany. After passing directives relating to bioenergy and biofuels, however, such a decision is on the political agenda. The “biofuels” directive already includes ethanol, methanol, dimethyl ether, hydrogen, and biomass pyrolysis which are fundamental product lines of the future biobased chemical industry.

**Table 1.2** Targets of the EU and Germany with regard to the introduction of technologies based on renewable resources.

Year	2001	2005	2010	2020–2050
<b>Bioenergy</b>	7.5%	–	12.5%	26% (2030)
Share of wind power, photovoltaics, biomass and geothermal electricity and heat demand in utilities and industry				58% (2050)
<b>Biofuels</b>	1.4%	2.8%	5.75%	20% (2020)
Biomass share of demand in transportation fuels (petrol and diesel fuels)				
<b>Biobased Products</b>	8%	–	–	–
Share of target chemicals that are biobased				

In the year 2003, an initiative group called “Biobased Industrial Products” consisting of members from industry, small and middle-class businesses, and research, and development facilities met and formulated a strategy paper, called “BioVision 2030” [124]. This strategy paper has been included in the resolution of the German Government (Deutscher Bundestag) on the topic “Accomplish basic conditions for the industrial utilization of renewable resources in Germany” [125]. An advisory committee consisting of members of the chemical industry, related organizations, research facilities, and universities has been established to generate a plan concerning the formulation of the objectives for the third column, bio-products in Europe (Table 1.2) [126].

## 1.4

### Principles of Biorefineries

#### 1.4.1

##### Fundamentals

Biomass, similar to petroleum, has a complex composition. Its primary separation into main groups of substances is appropriate. Subsequent treatment and processing of those substances lead to a whole range of products. Petrochemistry is based on the principle of generating simple to handle and well defined chemically pure products from hydrocarbons 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 the nature and has different C:H:O:N ratio from



petroleum. Biotechnological conversion will become, with chemical conversion, a big player in the future (Fig. 1.3).

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 have already been formed. For those products the term “precursors” is used. Plant biomass always consists of the basic products carbohydrates, lignin, proteins, and fats, and a variety of substances such as vitamins, dyes, flavors, aromatic essences of very different chemical structure. Biorefineries combine the essential technologies which convert biological raw materials into the industrial intermediates and final products (Fig. 1.4).

A technically feasible separation operation, which would enable separate use or subsequent processing of all these basic compounds, is currently in its initial stages only. Assuming that of the estimated annual production of biomass by biosynthesis of 170 billion tons 75% is carbohydrates, mainly in the form of cellulose, starch, and saccharose, 20% lignin, and only 5% other natural compounds such as fats (oils), proteins, and other substances [127], the main attention should first be focused on efficient access to carbohydrates, and 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 range of biotechnological or chemical products is accessible from glucose. For starch the advantage of enzymatic compared with chemical hydrolysis is already known [128].

For cellulose this is not yet realized. Cellulose-hydrolyzing enzymes can only act effectively after pretreatment to break up the very stable lignin/cellulose/

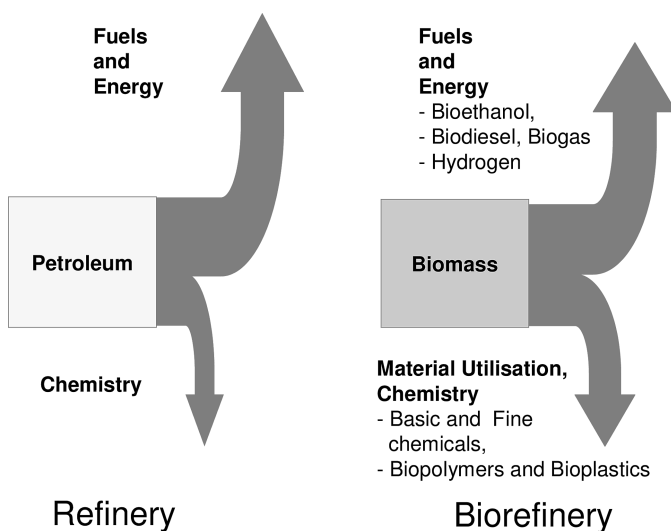
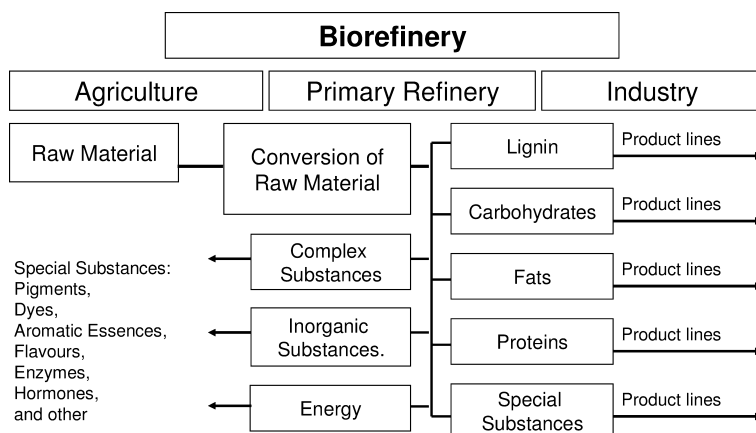
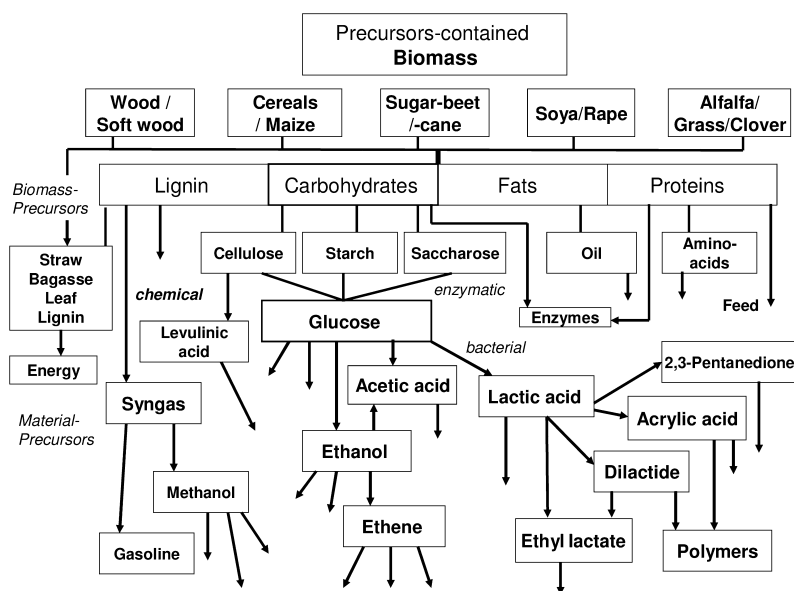


Fig. 1.3 Comparison of the basic-principles of the petroleum refinery and the biorefinery.



**Fig. 1.4** Providing code-defined basic substances (via fractionation) for development of relevant industrial product family trees [78, 79].



**Fig. 1.5** Possible schematic diagram of biorefinery for precursor-containing biomass with preference for carbohydrates [78, 79].

hemicellulose composites [129]. These treatments are still mostly thermal, thermomechanical, or thermochemical, and require considerable input of energy. The arsenal for microbial conversion of substances from glucose is large, and the reactions are energetically profitable. It is necessary to combine degradation

processes via glucose to bulk chemicals with the building processes to their subsequent products and materials (Fig. 1.5).

Among the variety of microbial and chemical products possibly accessible from glucose, lactic acid, ethanol, acetic acid, and levulinic acid, in particular, are favorable intermediates for generation of industrially relevant product family trees. Here, two potential strategies are considered: first, development of new, possibly biologically degradable products (follow-up products from lactic and levulinic acids) or, second, entry as intermediates into conventional product lines (acrylic acid, 2,3-pentanedione) of petrochemical refineries [78].

#### 1.4.2

##### Definition of the Term “Biorefinery”

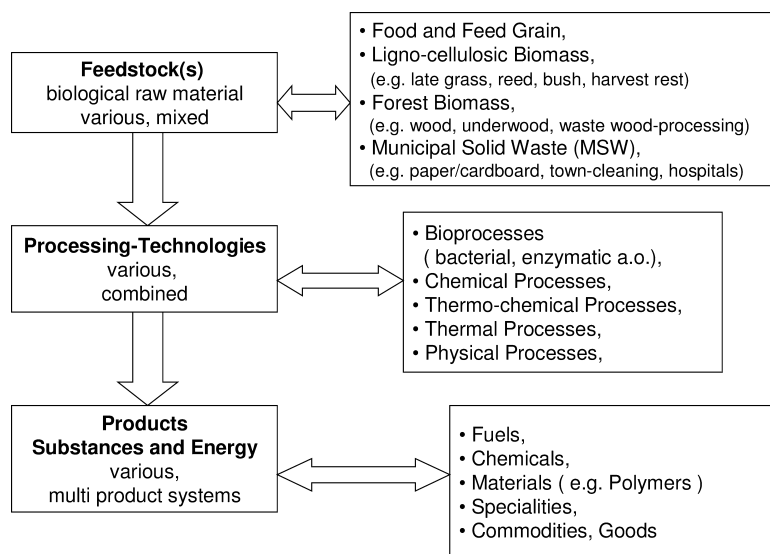
The young working field “Biorefinery Systems” in combination with “Biobased Industrial Products” is, in various respects, still an open field of knowledge. This is also reflected in the search for an appropriate description. A selection is given below.

The term “Green Biorefinery” was been defined in the year 1997 as: “Green biorefineries represent complex (to fully integrated) systems of sustainable, environmentally and resource-friendly technologies for the comprehensive (holistic) material and energetic utilization as well as exploitation of biological raw materials in form of green and residue biomass from a targeted sustainable regional land utilization” [73]. The original term used in Germany “complex construction and systems” was substituted by “fully integrated systems”. The US Department of Energy (DOE) uses the following definition [130]: “A biorefinery is an overall concept of a processing plant where biomass feedstocks are converted and extracted into a spectrum of valuable products. Based on the petrochemical refinery.” The American National Renewable Energy Laboratory (NREL) published the definition [131]: “A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass. The biorefinery concept is analogous to today’s petroleum refineries, which produce multiple fuels and products from petroleum. Industrial biorefineries have been identified as the most promising route to the creation of a new domestic biobased industry.”

There is an agreement about the *objective*, which is briefly defined as: “Developed biorefineries, so called “phase III-biorefineries” or “generation III-biorefineries”, start with a biomass–feedstock-mix to produce a multiplicity of most various products by a technologies-mix” [74] (Fig. 1.6).

An example of the type “generation-I biorefinery” is a dry milling ethanol plant. It uses grain as a feedstock, has a fixed processing capability, and produces a fixed amount of ethanol, feed co-products, and carbon dioxide. It has almost no flexibility in processing. Therefore, this type can be used for comparable purposes only.

An example of a type “generation-II biorefinery” is the current wet milling technology. This technology uses grain feedstock, yet has the capability to pro-



**Fig. 1.6** Basic principles of a biorefinery (generation III biorefinery) [78].

duce a variety of end products depending on product demand. Such products include starch, high-fructose corn syrup, ethanol, corn oil, plus corn gluten feed, and meal. This type opens numerous possibilities to connect industrial product lines with existing agricultural production units. “Generation-II biorefineries” are, furthermore, plants like NatureWorks PLA facility [25] (Sections 1.2 and 1.3.1) or ethanol biorefineries, for example Iogen’s wheat straw to ethanol plant [132].

Third generation (generation-III) and more advanced biorefineries have not yet been built but will use agricultural or forest biomass to produce multiple products streams, for example ethanol for fuels, chemicals, and plastics.

#### 1.4.3

#### The Role of Biotechnology

The application of biotechnological methods will be highly important with the development of biorefineries for production of basic chemicals, intermediate chemicals, and polymers [133–135]. The integration of biotechnological methods must be managed intelligently in respect of physical and chemical conversion of the biomass. Therefore the biotechnology cannot remain limited to glucose from sugar plants and starch from starch-producing plants. One main objective is the economic use of biomass containing lignocellulose and 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 basic chemicals is shown in subsequent sections.

### 1.4.3.1 Guidelines of Fermentation Section within Glucose-product Family Tree

Among the variety of chemical products, and derivatives of these, accessible microbially from glucose a product family tree can be developed, for example (C-1)-chemicals methane, carbon dioxide, methanol; (C-2)-chemicals ethanol, acetic acid, acetaldehyde, ethylene, (C-3)-chemicals lactic acid, propanediol, propylene, propylene oxide, acetone, acrylic acid, (C-4)-chemicals diethyl ether, acetic acid anhydride, malic acid, vinyl acetate, *n*-butanol, crotonaldehyde, butadiene, 2,3-butanediol, (C-5)-chemicals itaconic acid, 2,3-pentane dione, ethyl lactate, (C-6)-chemicals sorbic acid, parasorbic acid, citric acid, aconitic acid, isoascorbic acid, kojic acid, maltol, dilactide, (C-8)-chemicals 2-ethyl hexanol (Fig. 1.7).

Guidelines are currently being developed for the fermentation section of a biorefinery. The question of efficient arrangement of the technological design for production of bulk chemicals needs an answer. Considering the manufacture of lactic acid and ethanol, the basic technological operations are very similar. Selection of biotechnologically based products from biorefineries should be done in a way such that they can be produced from the substrates glucose or pentoses. Furthermore the fermentation products should be extracellular. Fermenters should have batch, feed batch, or CSTR design. Preliminary product recovery should require steps like filtration, distillation, or extraction. Final product recovery and purification steps should possibly be product-unique. In addition,

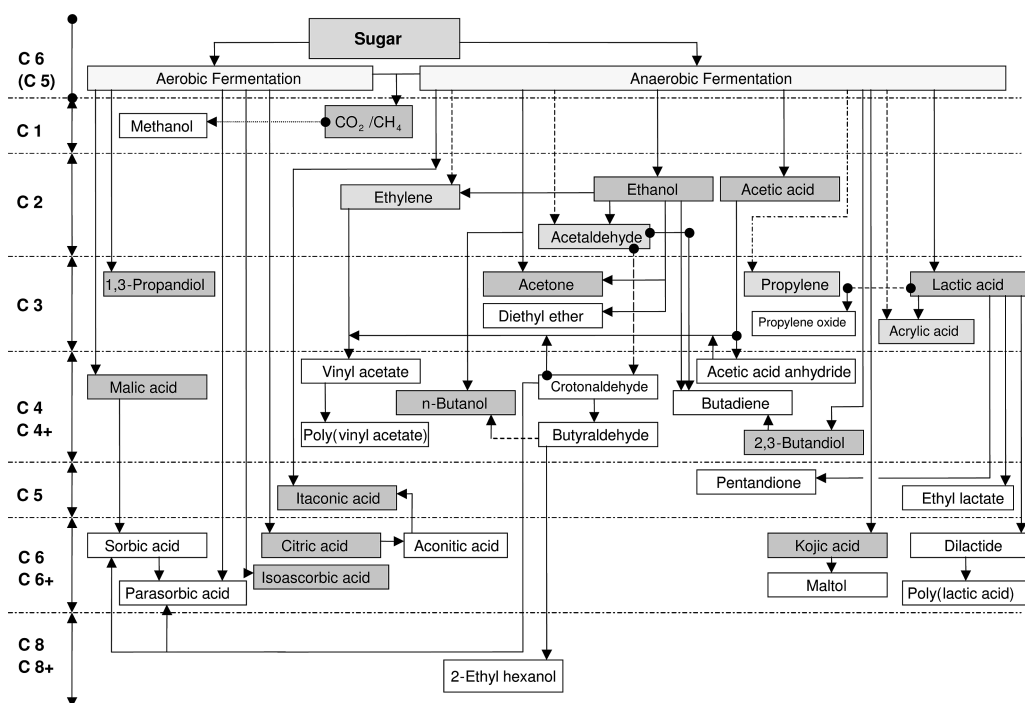


Fig. 1.7 Biotechnological sugar-based product family tree.

tion, biochemical and chemical processing steps should be advantageously connected.

Unresolved questions for the fermentation facility include:

1. whether or not the entire fermentation facility can/should be able to change from one product to another;
2. whether multiple products can be run in parallel, with shared use of common unit operations;
3. how to manage scheduling of unit operations; and
4. how to minimize in-plant inventories, while accommodating necessary change-overs between different products in the same piece of equipment [95].

#### 1.4.4

#### **Building Blocks, Chemicals and Potential Screening**

A team from Pacific Northwest National Laboratory (PNNL) and NREL submitted a list of twelve potential biobased chemicals [98]. A key area of the investigation as biomass precursors, platforms, building blocks, secondary chemicals, intermediates, products and uses (Fig. 1.8).

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 by 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 previous 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 synthetic pathways.

The reported block chemicals can be produced from sugar by biological and chemical conversions. The building blocks can be subsequently converted to several high-value biobased chemicals or materials. Building-block chemicals, as considered for this analysis, are molecules with multiple functional groups with the potential to be transformed into new families of useful molecules. The twelve sugar-based building blocks are 1,4-diacids (succinic, fumaric, and malic), 2,5-furandicarboxylic acid, 3-hydroxypropionic acid, aspartic acid, glucaric acid, glutamic acid, itaconic acid, levulinic acid, 3-hydroxybutyrolactone, glycerol, sorbitol, and xylitol/arabinitol [98].

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 include:

- examining top value products from biomass components, for example aromatic compounds, polysaccharides, and oils;
- evaluating technical challenges in more detail in relation to chemical and biological conversion; and
- increasing the suites of potential pathways to these candidates.

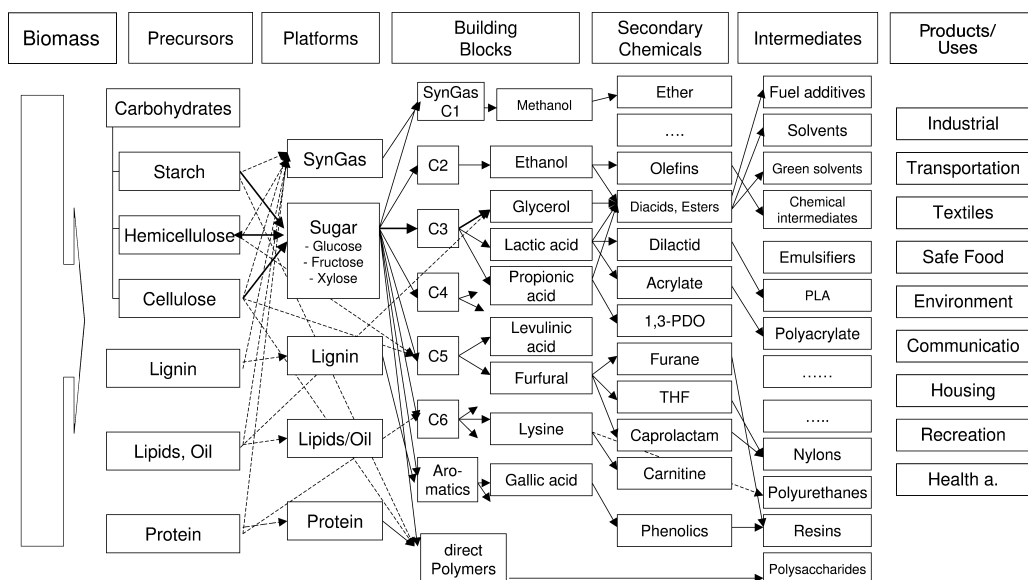


Fig. 1.8 Model of a biobased product flow-chart for biomass feedstock [98].

No products simpler than syngas were selected. For the purposes of this study hydrogen and methanol comprise 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 [98].

## 1.5 Biorefinery Systems and Design

### 1.5.1 Introduction

Biobased products are prepared for a usable economic use by meaningful combination of different methods and processes (physical, chemical, biological, and thermal). It is therefore necessary that basic biorefinery technologies are developed. For this reason profound interdisciplinary cooperation of various disciplines in research and development is inevitable. It seems reasonable, therefore, to refer to the term “biorefinery design”, which means: “bringing together well founded scientific and technological basics, with similar technologies, products, and product lines, inside biorefineries”. 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 ( $M_1$ – $M_n$ ) and the by-products ( $B_1$ – $B_n$ ) will subsequently be subjected to microbiological or chemi-

cal methods. The follow-up products ( $F_1$ – $F_n$ ) of the main and by-products can also be converted or enter the conventional refinery (Fig. 1.6).

Currently four complex biorefinery systems are used in research and development:

1. the “lignocellulosic feedstock biorefinery” which use “nature-dry” raw material, for example cellulose-containing biomass and waste;
2. the “whole crop biorefinery” which uses raw material such as cereals or maize;
3. the “green biorefineries” which use “nature-wet” biomasses such as green grass, alfalfa, clover, or immature cereal [78, 79]; and
4. the “biorefinery two platforms concept” includes the sugar platform and the syngas platform [98].

### 1.5.2

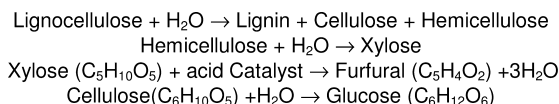
#### Lignocellulosic Feedstock Biorefinery

Among the potential large-scale industrial biorefineries the lignocellulose feedstock (LCF) biorefinery will most probably be pushed through with the greatest success. On the one side the raw material situation is optimum (straw, reed, grass, wood, paper-waste, etc.), on the other side conversion products have a good position on both the traditional petrochemical and future biobased product market. An important point for utilization of biomass as chemical raw material is the cost of raw material. Currently the cost of corn stover or straw is 30 US\$/ton and that of corn is 110 US\$/ton (3 US\$/ bushel; US bushel corn = 25.4012 kg = 56 lb) [136].

Lignocellulose materials consist of three primary chemical fractions or precursors:

- hemicellulose/polyoses, sugar polymers of, predominantly, pentoses;
- cellulose, a glucose polymer; and
- lignin, a polymer of phenols (Fig. 1.9).

The lignocellulosic biorefinery-regime is distinctly suitable for genealogical compound trees. The main advantages of this method is that the natural structures and structural elements are preserved, the raw materials are inexpensive, and large product varieties are possible (Fig. 1.10). Nevertheless there is still a demand for development and optimization of these technologies, e.g. in the field of separation of cellulose, hemicellulose and lignin, and utilization of the lignin in the chemical industry.



**Fig. 1.9** A possible general equation for conversion at the LCF biorefinery.



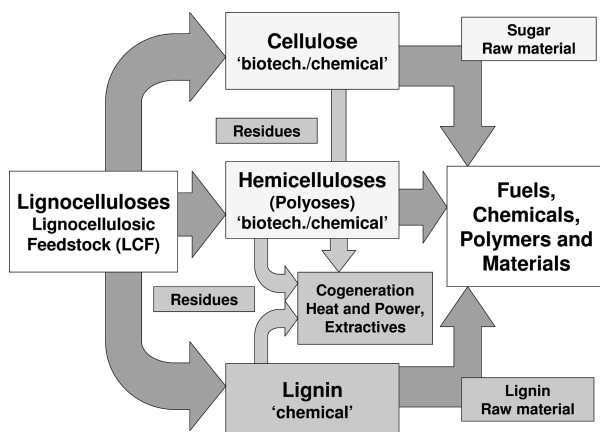


Fig. 1.10 Lignocellulosic feedstock biorefinery.

An overview of potential products of an LCF biorefinery is shown in Fig. 1.11. In particular furfural and hydroxymethylfurfural are interesting products. Furfural is a starting material for production of Nylon 6,6 and Nylon 6. The original process for production of Nylon-6,6 was based on furfural (see also Section 1.2.2). The last of these production plants was closed in 1961 in the USA, for economic reasons (the artificially low price of petroleum). Nevertheless the market for Nylon 6 is huge.

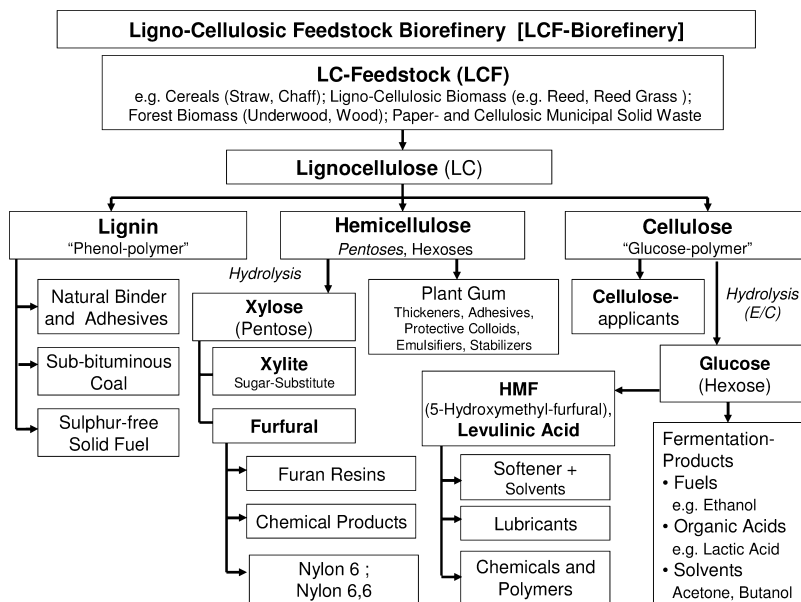


Fig. 1.11 Products of a lignocellulosic feedstock biorefinery (LCF-biorefinery, Phase III) [78, 79, 95].

There are, however, still some unsatisfactory aspects of the LCF, for example the utilization of lignin as fuel, adhesive, or binder. Unsatisfactory because the lignin scaffold contains substantial amounts of mono-aromatic hydrocarbons, which, if isolated in an economically efficient way, could add a significant increase in value to the primary processes. It should be noticed there are no natural enzymes capable of splitting the naturally formed lignin into basic monomers as easily as is possible for natural polymeric carbohydrates or proteins [137].

An attractive process accompanying the biomass-nylon-process is the already mentioned hydrolysis of the cellulose to glucose and the production of ethanol. Some yeasts cause disproportionation of the glucose molecule during their generation of ethanol from glucose, which shifts almost all its metabolism into ethanol production, making the compound obtainable in 90% yield (*w/w*; with regard to the chemical equation for the process).

On the basis of recent technology a plant has been conceived for production of the main products furfural and ethanol from LC feedstock from West Central Missouri (USA). Optimal profitability can be achieved with a daily consumption of approximately 4360 tons of feedstock. The plant produces 47.5 million gallon of ethanol and 323,000 tons of furfural annually [74].

Ethanol can be used as a fuel additive. It is also a connecting product to the petrochemical refinery, because it can be converted into ethene by chemical methods and it is well-known that ethene is at the start of a series of large-scale technical chemical syntheses for production of important commodities such as polyethylene or poly(vinyl acetate). Other petrochemically produced substances, for example hydrogen, methane, propanol, acetone, butanol, butandiol, itaconic acid, and succinic acid, can also be manufactured by microbial conversion of glucose [138, 139].

### 1.5.3

#### **Whole-crop Biorefinery**

Raw materials for the “whole crop biorefinery” are cereals such as rye, wheat, triticale, and maize. The first step is mechanical separation into corn and straw, approximately 10 and 90% (*w/w*), respectively [140]. Straw is a mixture of chaff, nodes, ears, and leaves. The straw is an LC feedstock and may further be processed in a LCF biorefinery.

There is the possibility of separation into cellulose, hemicellulose, and lignin and their further conversion in separate product lines which are shown in the LCF biorefinery. The straw is also a starting material for production of syngas by pyrolysis technology. Syngas is the basic material for synthesis of fuels and methanol (Fig. 1.13).

The corn may either be converted into starch or used directly after grinding to meal. Further processing may be conducted by four processes – breaking up, plasticization, chemical modification, or biotechnological conversion via glucose. The meal can be treated and finished by extrusion into binder, adhesives, and filler.

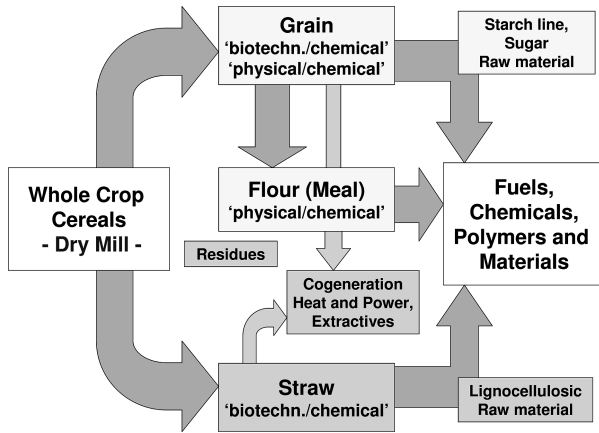


Fig. 1.12 Whole-crop biorefinery based on dry milling.

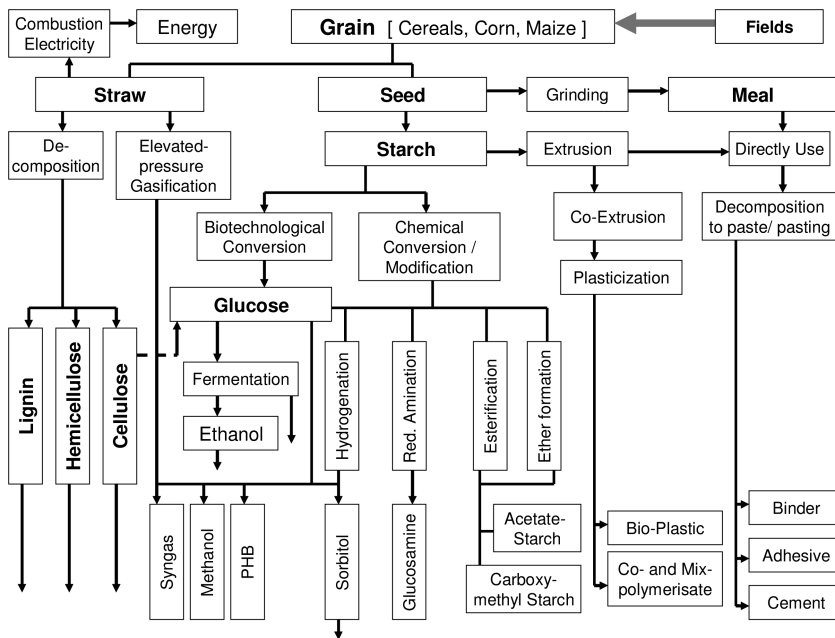


Fig. 1.13 Products from a whole-crop biorefinery [78, 79].

Starch can be finished by 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 ethylenediamine, etc., hydrogenative splitting into sorbitol, ethylene glycol, propylene glycol, and glycerin), and biotechnological conversion into poly-3-hydroxybutyric acid [69, 76, 92, 93, 141].

An alternative to traditional dry fractionation of mature cereals into grains and straw only was developed by Kockums Construction (Sweden), which later became Scandinavian Farming. In this 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 industry, the feed industry, the cellulose industry, and particle board producers, gluten can be used by the chemical industry and as a solid fuel. Such dry fractionation of the whole crop to optimize the utilization of all botanical components of the biomass has been described [142, 143]. A biorefinery and its profitability has been described elsewhere [144].

One expansion of the product lines in grain processing is the “whole crop wet mill-based biorefinery”. The grain is swelled and the grain germ is pressed, releasing high-value oils. The advantages of whole-crop biorefinery based on wet milling are that production of natural structures and structure elements such as starch, cellulose, oil, and amino acids (proteins) are kept high yet well known basic technology and processing lines can still be used. High raw material costs and, for industrial utilization, the necessary costly source technology are the disadvantages. Some of the products formed command high prices in, e.g., the pharmaceutical and cosmetics industries (Figs. 1.14 and 1.15). The basic biorefinery technology of corn wet mills used 11% of the US corn harvest in 1992, made products worth \$7.0 billion, and employed almost 10,000 people [1a].

Wet milling of corn yields corn oil, corn fiber, and corn starch. The starch products of the US corn wet milling industry are fuel alcohol (31%), high-fructose corn syrup (36%), starch (16%), and dextrose (17%). Corn wet milling also

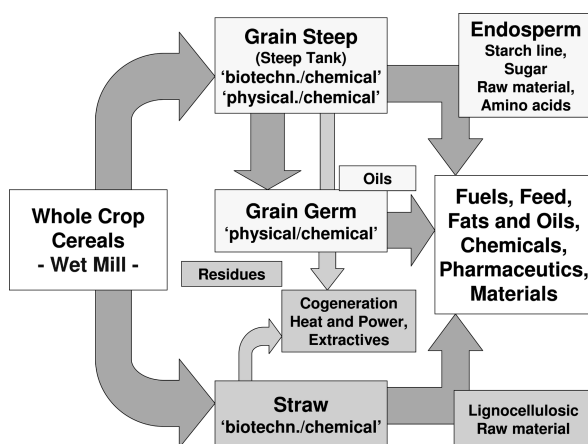


Fig. 1.14 Whole-crop biorefinery, wet-milling.

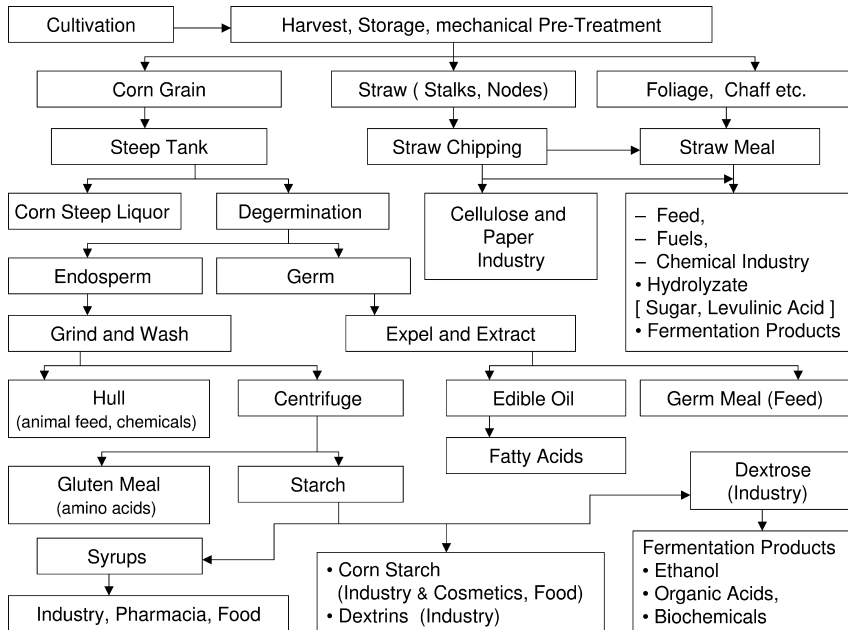


Fig. 1.15 Products from a whole-crop wet mill-based biorefinery.

generates other products (e.g. gluten meal, gluten feed, oil) [62]. An overview about the product range is shown in Fig. 1.15.

#### 1.5.4

#### Green Biorefinery

Green biorefineries are also multi-product systems and furnish cuts, fractions, and products in accordance with the physiology of the corresponding plant material, which maintains and utilizes the diversity of syntheses achieved by nature. Most green biomass is green crops, for example grass from cultivation of permanent grass land, closure fields, nature reserves, or green crops, such as lucerne, clover, and immature cereals from extensive land cultivation. Green crops are a natural chemical factory and food plant and are primarily used as forage and as a source of leafy vegetables. A process called wet-fractionation of green biomass, green crop fractionation, can be used for simultaneous manufacture of both food and non food items [145].

Scientists in several countries, in Europe and elsewhere, have developed green crop fractionation [146–148]. Green crop fractionation is now studied in approximately 80 countries [149]. Several hundred temperate and tropical plant species have been investigated for green crop fractionation [148, 150, 151] and more than 300,000 higher plants species have still to be investigated. The subject has been covered by several reviews [73, 146–148, 151–155]. 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).

Careful wet fractionation technology is used as a first step (primary refinery) to isolate the contents of the green crop (or humid organic waste goods) in their natural form. Thus, they are separated into a fiber-rich press cake (PC) and a nutrient-rich green juice (GJ).

The advantages of the green biorefinery are high biomass profit per hectare, good coupling with agricultural production, and low price of the raw materials. Simple technology can be used and there is good biotechnical and chemical potential for further conversion (Fig. 1.16). Rapid primary processing or use of preservation methods, for example silage production or drying, are necessary, both for the raw materials and the primary products, although each method of preservation changes the content of the materials.

In addition to cellulose and starch, the press cake contains valuable dyes and pigments, crude drugs and other organic compounds. The green juice contains proteins, free amino acids, organic acids, dyes, enzymes, hormones, other organic substances, and minerals. Application of the methods of biotechnology results in conversion, because the plant water can simultaneously be used for further treatment. In addition, the lignin–cellulose composite is not as intractable as lignocellulose-feedstock materials. Starting from green juice the main focus is directed toward products such as lactic acid and its derivatives, amino acids, ethanol, and proteins. The press cake can be used for production of green feed pellets, as raw material for production of chemicals, for example levulinic acid, and for conversion to syngas and hydrocarbons (synthetic biofuels). The residues of substantial conversion are suitable for production of biogas combined with generation of heat and electricity (Fig. 1.17). Reviews have been published on the concepts, contents, and goals of the green biorefinery [73, 75, 119].

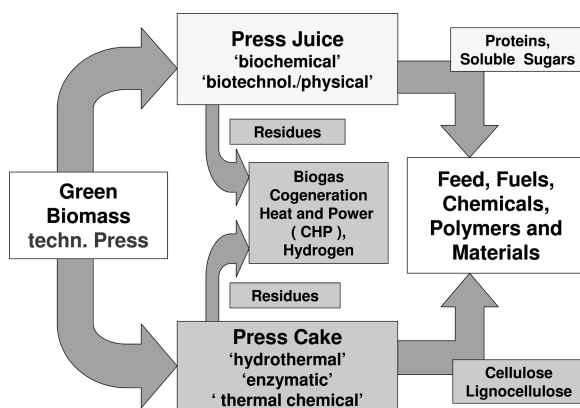
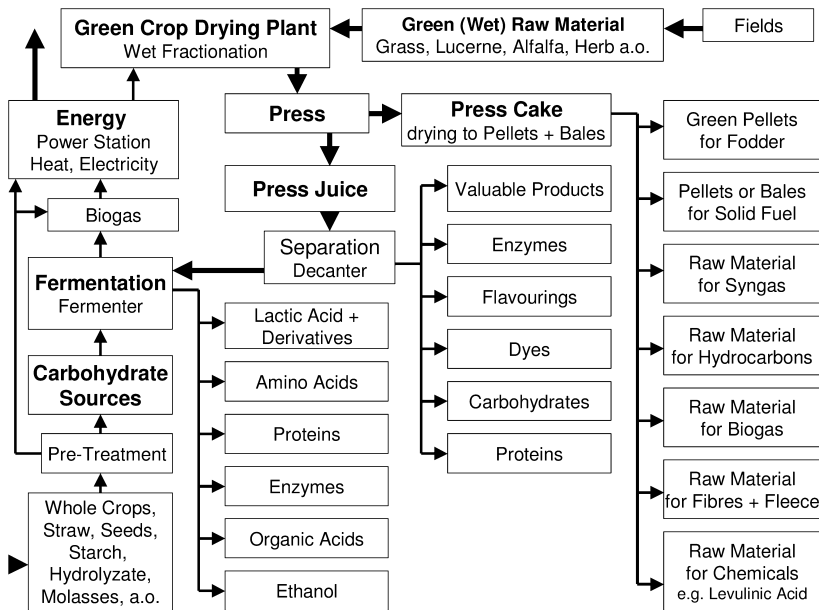


Fig. 1.16 A “green biorefinery” system.



**Fig. 1.17** Products from the green biorefinery. In this illustration a green biorefinery has been combined with a green crop-drying plant [78, 79].

### 1.5.5

#### Two-platform Concept and Syngas

The “two-platform concept” is one which uses biomass consisting, on average, of 75% carbohydrates which can be standardized as a “intermediate sugar platform”, as a basis for further conversion, but which can also be converted thermochemically into synthesis gas and the products made from this. The “sugar platform” is based on biochemical conversion processes and focuses on 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 [63, 98, 131]. In addition to the gasification other thermal and thermochemical biomass conversion methods have also been described – hydrothermolysis, pyrolysis, thermolysis, and burning. The application chosen depends on the water content of biomass [156].

The gasification and other thermochemical conversions concentrate on utilization of the precursor carbohydrates and their intrinsic carbon and hydrogen content. The proteins, lignin, oils and lipids, amino acids, and other nitrogen and sulfur-containing compounds occurring in all biomass are not taken into account (Fig. 1.18).

The advantage of this concept is that the production of energy, fuels, and bio-based products is possible using only slightly complex and low-tech technology,

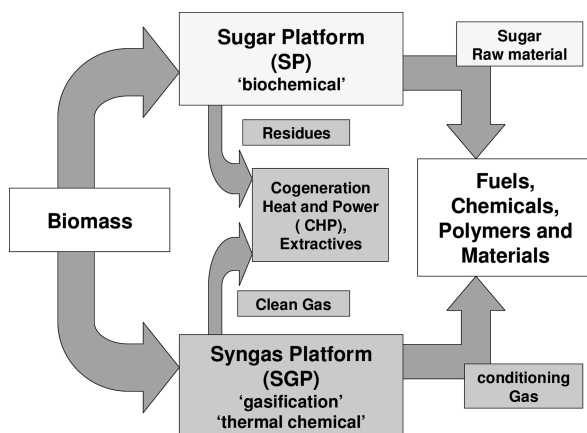


Fig. 1.18 The sugar platform and the syngas platform [131].

for example saccharification and syngas technology. The sugar platform also enables access to a huge range of family tree-capable chemicals (Figs. 1.7 and 1.8).

In-situ conversion of biomass feedstock into liquid or gas could be one way of using existing infrastructure (developed pipe network), but with the disadvantages of the need to remove hetero-atoms (O, N, S) and minerals present in the biomass and the highly endothermic nature of the syngas process [157]. Currently, production of simple alcohols, aldehydes, mixed alcohols, and Fischer-Tropsch liquids from biomass is not economically viable and additional developments are required [98] (Fig. 1.19).

## 1.6

### Outlook and Perspectives

Biorefineries are the production plants in which biomass is economically and ecologically converted to chemicals, materials, fuels, and energy. For successful development of “industrial biorefinery technologies” and “biobased products” several problems must be solved. It will be necessary to increase the production of substances (cellulose, starch, sugar, oil) from basic biogenic raw materials and to promote the introduction and establishment of biorefinery demonstration plants. Ecological transport of biomass must also be developed, for example utilization of already developed pipe networks.

Another important aspect is committing chemists, biotechnologists, and engineers to the concept of biobased products and biorefinery systems and promoting the combined biotechnological and chemical conversion of substances. Last, but not least, the development of systematic approaches to new synthesis and technologies is required to meet the sustainable principles of “ideal synthesis” and “principles of green chemistry and process engineering” [159–161].



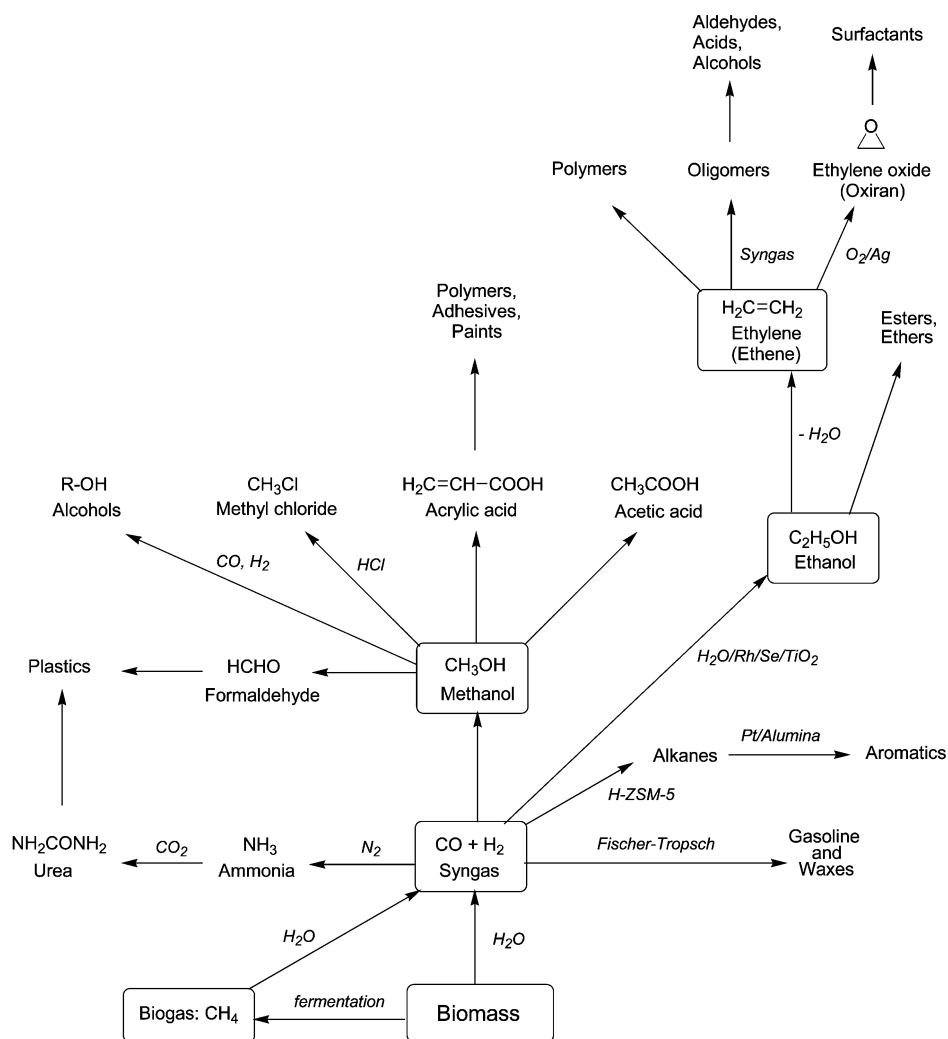


Fig. 1.19 Syngas-based product family tree [157, 158].

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