Biorefinery – Systems

Biorefineries combine necessary technologies between biogenic raw material and the industrial intermediates and final products. The paper represents the providing code-defined basic substances (via fractionation for the development of industrially relevant product family trees). The main focus is directed on precursor-containing biomass with preference of the carbohydrate line, in particulary on bulk chemical lactic acid and their sequence products, e.g. polylactic acid. Futhermore potential industrial biorefineries are described, such as lignocellulosic feedstock biorefinery, green biorefinery and whole corn biorefinery.

Keywords:
Biorefineries, biogenic raw material, biobased industrial products, poly(lactic acid)

Introduction

Sustainable economical growth requires safe resources of raw materials for the industrial production. Today's most frequently used industrial raw material, petroleum, is neither sustainable, because limited, 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 is fundamentally depending on biomass, in particularly on biomass of plants. Special requirements are placed to both, the substantial converting industry as well as research and development regarding the efficiency of the product line 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]

Whereas great successes regarding research and development in the young field of 'biorefinery system research' are most notable in Europe and Germany,[2–4] significant industrial developments are pushed by president[5] and congress[6] in the United States firstly in 2000. In the United States of America it is expected for 2020 to provide at least 25 % (compared to 1995) of organic carbon-based industrial feedstock chemicals and 10 % of liquid fuels from a biobased product industry. This would mean that more than 90 % of the consumption of organic chemical in the U.S. and up to 50 % of liquid fuel needs would be covered by biobased products.[1]

In Europe there are current regulations regarding substitution of non-renewable resources by biomass in the area of biofuels for transportation[7] beside the 'Renewable energy law' of the year 2000.[8] According to the EC-Directive "On the promotion of the use of biofuels" the following products are considered as 'biofuels': a) 'bioethanol', b) 'biodiesel', c) 'biogas', d) 'biomethanol', e) 'biodimethylether', f) 'bio-ETBE (ethyl-tertiär-butylether' on the basis of bioethanol, g) 'bio-MTBE (methyl-tertiär-butylether)' on the basis of biomethanol, h) 'synthetic biofuels', i) 'biohydrogen', j) pure vegetable oil.

Member States of the EU are requested to define national guidelines for a minimal amount 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).

Today there are no guidelines concerning 'Biobased Products' in the European Union and in Germany. However, after passing directives for bioenergie and biofuels such decission is on the political agenda. The directive of 'biofuels' already includes ethanol, methanol, dimethylether, hydrogen and biomass pyrolysis which are fundamental product lines of the future biobased chemical industry.

Some aspects of biorefinery-technologies

Currently three biorefinery systems are pursued in research and development. First, the 'Whole Crop Biorefinery' using raw material such as cereals or maize. Secondly, the 'Green Biorefinery', using 'nature-wet' biomasses such as green grass, lucerne, clover, or immature cereal. Third, the 'Lignocellulose

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Feedstock Biorefinery' using 'nature-dry' raw material, such as cellulose-containing biomass and wastes.

The Lignocellulose Feedstock (LCF) Biorefinery

Among the potential large-scale industrial biorefineries the Lignocellulose Feedstock (LCF)-Biorefinery will most probably be pushed through with highest success. On the one side the raw material situation is optimal (straw, reed, grass, wood, paper-waste etc.), on the other side conversion products have a good position, both, on the traditional petrochemical as well as on the future biobased product market. Lignocellulose materials consist of three primary chemical fractions or precursors: a) hemicellulose/polyoses, a sugar-polymer of pentoses predominantly; b) cellulose, a glucose-polymer; and c) lignin, a polymer of phenols (Fig. 1).

$$\text{Lignocellulose} + H_2O \rightarrow \text{Lignin} + \text{Cellulose} + \text{Hemicellulose}$$
$$\text{Hemicellulose} + H_2O \rightarrow \text{Xylose}$$
$$\text{Xylose } (C_5H_{10}O_5) + \text{acid Catalyst} \rightarrow \text{Furfural } (C_5H_4O_2) + 3H_20$$
$$\text{Cellulose}(C_6H_{10}O_5) + H_2O \rightarrow \text{Glucose } (C_6H_{12}O_6)$$

Fig. 1 – *The general equation of conversion of the LCF-Biorefinery*

An overview about potential products of a LCF-biorefinery is shown in Figure 6. 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 U.S.A. due to economic reasons (the artificial low prize of petroleum). Nevertheless, the market for Nylon 6 is huge (Fig. 2).

However, there are still some unsatisfactory parts within the LCF, such as utilization of lignin as fuel, adhesive or binder. Unsatisfactory because the

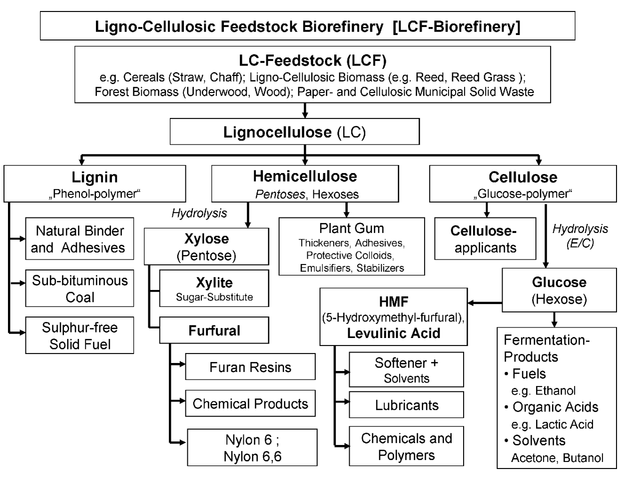


Fig. 2 – *Ligno-cellulosic feedstock biorefinery (LCF-Biorefinery)*

lignin structure 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 noticed that there are obviously no natural enzymes to split the naturally formed lignin into basic monomers as easy as this is possible for the also naturally formed polymeric carbohydrates or proteins.[9]

An attractive accompanying process to the biomass-nylon-process is the already mentioned hydrolysis of the 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 it obtainable in 90 % yield (w/w; regarding to the formula turnover).

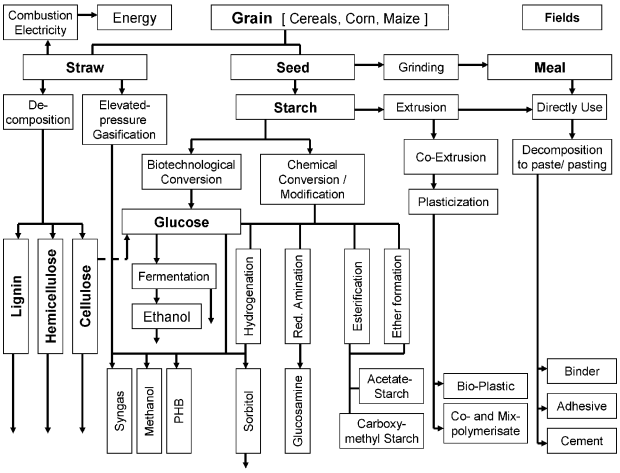
Based on recent technologies a plant was conceived for the production of the main products furfural and ethanol from LC-feedstock for the area West Central Missouri (U.S.A.). Optimal profitability can be reached with a daily consumption of about 4360 tons of feedstock. Annually the plant produces 213.75 million l (47.5 million gallon) of ethanol and 323 000 tons of furfural.[24]

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

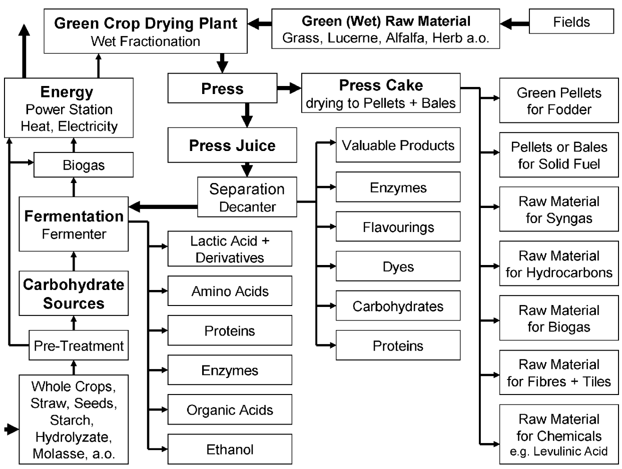
The Whole Crop Biorefinery

Raw materials for the 'Whole Crop Biorefinery' are cereals, such as rye, wheat, triticale as well as maize. The first step is the mechanical separation into corn and straw, which are obtained in almost the same amount. The straw represents a LC-Feedstock and may further be processed in a LCF-Biorefinery regime. 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 production of syngas via pyrolysis technologies. Syngas is the basic material for the synthesis of fuels and methanol (Fig.3).

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)



F i g . 3 – *The whole crop biorefinery. Raw material: cereals, maize etc.*



F i g . 4 – *A System Green Biorefinery combined with a green crop drying plant. Concept of Havelland-Biorefinery, Selbelang, State of Brandenburg, Germany*

breaking up, b) plasticization, c) chemical modification or d) biotechnological conversion via glucose. The meal can be treated and finished by extrusion into binder, adhesives and filler. Starch can be finished via plasticization (co- and mix-polymerization, compounding with other polymers), chemical modification (etherification into carboxy-methyl starch; esterification and re-esterification into fatty acid esters via acetic starch; splitting reductive amination into ethylen diamine a. o., hydrogenative splitting into sorbitol, ethylenglycol, propylenglycol, glycerin) and biotechnological conversion to poly-3-hydroxybutyricacid.[25]

The Green Biorefinery

Green Biorefineries are also multi-product-systems and act regarding 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.

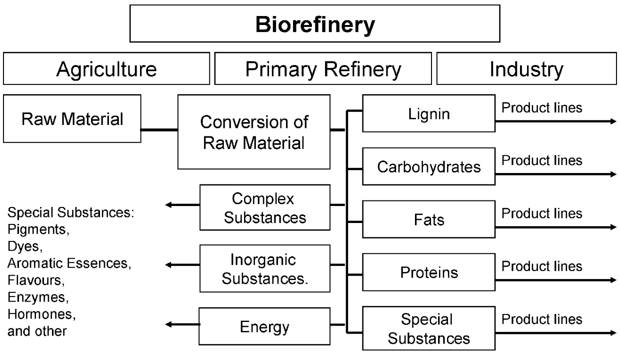
Green biomass are for example grass from cultivation of permanent grass land, closure fields, nature preserves or green crops, such as lucerne, clover, immature cereals from extensive land cultivation. Thus, green plants represent a natural chemical factory and food plant. The careful wet fractionation technology is used as 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) (Fig 4).

Beside cellulose and starch, the press cake contains valuable dyes and pigments, crude drugs and other organics. The green juice 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 predestinated for conversions, because the plant water can simultaneously be used for further treatments. Additionally, by the lignin-cellulose composite are not strong as in lignocellulose-feedstock materials. Starting from green juice the main focus is directed to products such as lactic acid and corresponding 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, such as levulinic acid, as well as for conversion to syngas and hydrocarbons (synthetic biofuels). The residues of substantial conversion are suitable for the production of biogas combined with generation of heat and electricity. Reviews to Green Biorefinery concepts, contents and goals, are published.[2–4] In Europe Green Biorefinery activities are concentrated in Germany, Denmark, Austria and Switzerland.

Biorefinery rough scheme and guidelines for designing the fermentation section of a biorefinery

Biogenic raw material (biomass) has, similar to petroleum, a complex composition. Its primary separation into main groups of substances is appropriate. Subsequent treatment and processing of those substances leads to a whole palette of products. An important difference is, that petroleum is obtained by extraction, whereas biomass already exists as product – mostly that of an agricultural conversion process. 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.[9]

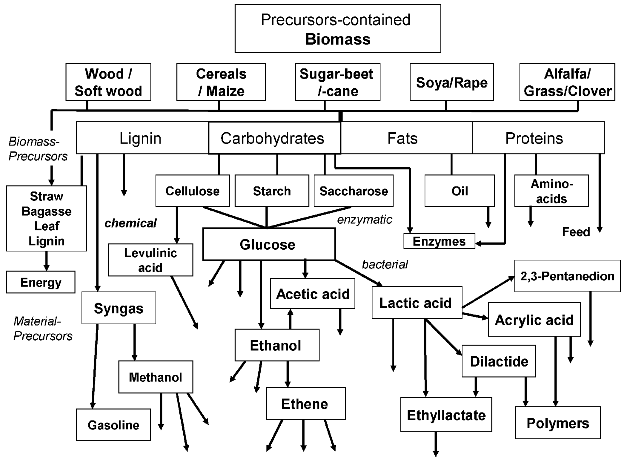
Plant biomass always consists of the basic products carbohydrates, lignin, proteins and fats, beside various substances such as vitamins, dyes, flavours, aromatic essences of most different chemical structure. Biorefineries combine the essential technologies between biological raw materials and the industrial intermediates and final products (Fig. 5).



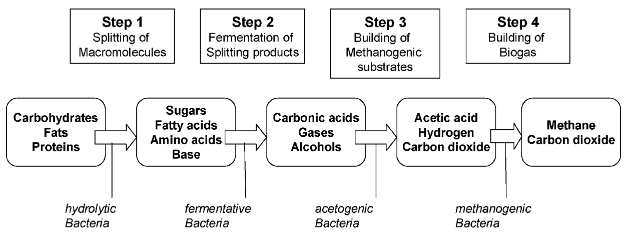
F i g . 5 – *Providing code-defined basic substances (via fractionation) for the development of relevant industrial product family trees*

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 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 form of cellulose, starch and saccharose, 20 % lignin and only 5 % compounds of other nature such as fats (oils), proteins and various substances,[10] the main attention should be focused firstly on an efficient access to carbohydrates, their subsequent conversion to chemical bulk products and on corresponding final products. It is necessary to combine the degradation processes via glucose to bulk chemicals with the building processes to their subsequent products and materials. Among the variety of possibly accessible microbial and chemical products from glucose, in particular lactic acid, ethanol, acetic acid and levulinic acid are favorable intermediates for the generation 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), and secondy, the entry as intermediates into conventional product lines (acrylic acid; 2,3-pentandion) of petrochemical refineries (Fig. 6).

Glucose, accessible by microbial or chemical methods from starch, sugar or cellulose, is among other things predestined for a key position as basic chemical, because a broad palette of biotechnological or chemical products are accessible from Glucose. In the case of starch the advantage of enzymatic compared to chemical hydrolysis is today already realized.[11] In the case of cellulose this is not yet realized. Cellulose-hydrolyzing enzymes can only act effectively after pre-treatment to break up the very stable lignin/cellulose/hemicellulose composites. These treatments are still mostly thermal, thermo-mechanical or thermo-chemical and require a considerable input of energy. Once in this condition, the acidic hydrolysis can be finished, although only low yields of glucose can then be achieved compared to treatments using enzyme-combinations. There is the question, whether recent developments, such as using of expansins,[12] will bring a breakthrough regarding low energy break up processes. The arsenal for microbial conversion of substances out of glucose is large, the reactions are energetically profitable. By biotechnological processes and methods feedstock chemicals are produced such as ethanol, butanol, aceton, lactic acid and itaconic acid as well as amino acids, e.g. glutaminic acid, lysine, tryptophan (Fig. 7).



F i g . 6 – *Biorefinery rough-scheme for precursors-containing biomass with preference of carbohydrate line*



F i g . 7 – *Simplified presentation of a microbial biomass-breakdown regime*

Currently guidelines are developed for the fermentation section of a biorefinery. The question for an efficient arrangement of the technological design for the production of bulk chemicals needs an answer.

Considering the manufacture of lactic acid and ethanol, the technological basic operations are very similar. The selection of biotechnologically based products from biorefineries should be done in such a way that they can be produced from the substrates glucose or pentose. Futhermore, the fermentation products should be extracellular. Fermentors should have either 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, biochemical and chemical processing steps should be advantageously connected.

Unresolved questions for the fermentation facility include: a) whether or not the entire fermentation facility can /should be able to change from one product to another; b) if multiple products can be run in parallel, with shared use of common unit operations, c) how to manage scheduling of unit operations, and d) how to minimize in-plant inventories, while accommodating necessary change-overs between different products in the same piece of equipment.[13]

Lactic acid – Sequence product poly(lactic acid)

Lactic acid has the potential to become a commodity chemical. High growth rates are expected: an annual volume of 1.36 to 1.8 million tons for lactic acid sequence products alone for the U.S.- market.[14] Chemical products of sequence are propylene glycol, propylene oxide, and epoxides. Propylene oxide is a starting material for the production of polyester, polycarbonates, polyurethanes. Further products are acrylic acid as monomer for polyacrylic acid and resins as well as alkyllactates for application as 'green solvents'. Furthermore, enantiomeric forms of lactic acid are applied in drugs, pharmaceuticals and agrochemicals. Classical areas of application are such as so-called *culinary delight* lactic acid, e.g. in food industry and technical processes such as tanneries, textile industry, chemical industry.[15,16]

Enormously growing amounts are expected for polymeric materials of lactic acid, poly(lactic) acid. Polylactide is a versatile thermoplastic, which can be processed in manifold ways: e.g. spinning fibres, melting spinning fibres, extrusion foils, injection moulding, thermoforming sheets, extrusion coating for paper and board, and many other applications. It is fully biodegradable and compostable and does not disturb the normal process of biodegradation in compost.

Especially for the market segments of food packaging and food service, e.g. one-way-consumption article) and performance-products for agriculture as well as fibres for textiles PLA is a very interesting material.

In 1993, a market volume of 140 000 – 900 000 tons per year for biodegradable polymers on basis of lactic acid was estimated for the U.S.A.[26] Since then efforts were increased to build major industrial capacities. The company Cargill Dow LLC has built a commercial production facility for polylactide (PLA) in Blair Nebraska, U.S.A.. The Blair facility started its operations in late 2002 and has a maximum capacity of 140 000 metric tons (140 000 t) of PLA per year.[17] The establishment of further capacities of the company shall follow within the next 10 years up to a capacity of 140 000 metric tons (140 000 t) in Asia and Europe. So it is expected that the price will decrease within the next years to the level of petrochemical based thermoplastics.[18]

The *Polylactid technology* starts with the classical variant of lactic acid fermentation (primary production of anorganic salts of lactic acid) via further steps of production of lactic acid and oligomeric lactic acid, subsequently synthesis of cyclic diesters of lactic acid, from which the polylactide is accessible by ring opening reaction.[14] In this technology principle the two processing steps (biotechnological production of lactic acid and the subsequent chemical steps) are clearly separated.[15]

A new technology principle is patented by our institutions and briefly drafted in Figure 4.[19–21] Aminium-lactates act as alternative coupling reagents to connect biotechnological and chemical conversion (synthesis of dilactide). Requirements on amium-lactates are low melting points, good crystallinity and good thermal or hydrolytic dissociation ability. Requirements on amines are good water solubility, a pH-value within basic area, sufficient thermal, acid and catalyst stability for the recycling according to the cyclization process, ecological harmlessness and economical availibility. Piperazine dilactate is for example a well investigated model substance,[21–23] (Fig. 8).

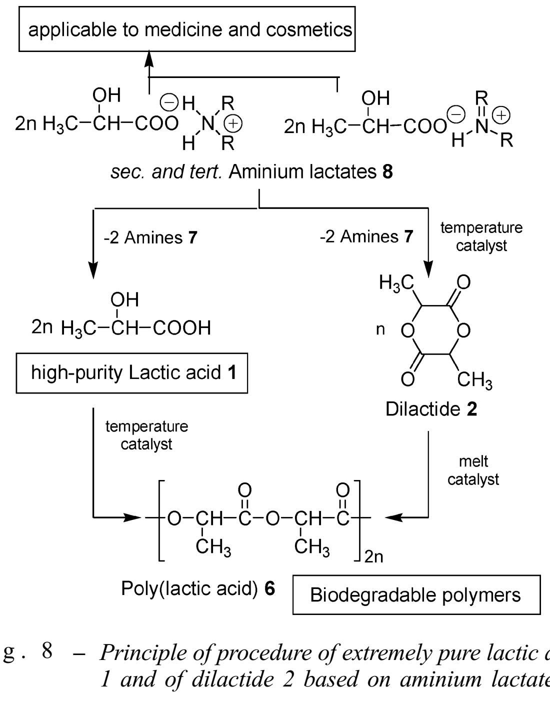


Fig. 8 – *Principle of procedure of extremely pure lactic acid 1 and of dilactide 2 based on aminium lactates 8*

Conclusion

There are several requirements to enter the development of 'Industrial Biorefinery Technologies' and 'Biobased Products'. On the one side it is necessary to increase the production of substances (cellulose, starch, sugar, and oil) on the base of biogenic raw materials, on the other side to push the introduction and establishment of biorefinery demonstration plants. Research and development are necessary for (1) increasing the scientific understanding of biomass resources and better tailoring of those resources, (2) improving sustainable systems for developing, harvesting, and processing biomass resources, (3) improving efficiency and performance in conversion and distribution processes and technologies for a host of products development of biobased products and (4) creating the regulatory and market environment necessary for increased development and use of biobased products. Important points are to get the commitment of the chemistry, particularly organic chemistry, for the concept of biobased products and biorefinery systems as well as to force the combination of biotechnological and chemical conversion of substances.

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