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THE LCF-BIOREFINERY PRODUCTION OF PLATFORM CHEMICALS AND INTERMEDIATES

Lignocellulosic materials based biorefineries development could be a key for future economy. State-of-art, perspectives and problems are here presented, focusing on chemical production from biomasses.

One-hundred-and-fifty years after the beginning of coal-based chemistry and 50 years after the beginning of the petroleum-based chemistry industrial chemistry, is now entering a new era. In the twenty-first century utilization of renewable raw materials will gain importance in the chemical conversion of substances in industry. Partial or even complete re-adjustment of whole economics to renewable raw materials will require completely new approaches in research, development and production.
One approach is the development of biorefinery technologies and systems. Biorefining is the transfer of the efficiency and logic of the fossil-based chemistry and substantial converting industry as well as the energy production onto the biomass industry [1].

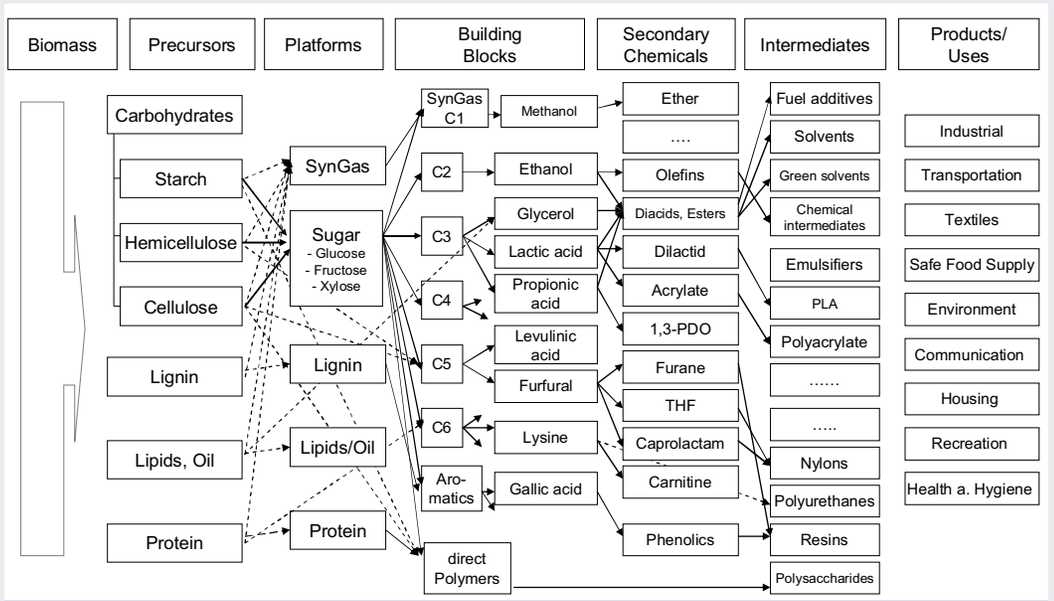


Fig. 1 - Model of a Biobased Product Flow-chart for Biomass Feedstock (according [1], cut from [2])

Plant biomass always consists of the basic precursors 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.

In this paper, the focus is directed to the Lignocellulosic feedstock biorefinery system, technologies and products, in particular of the platform chemicals (building blocks) [2] (Fig. 1).

Lignocellulosic Feedstock 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 on the traditional petrochemical as well as on the future biobased product market. An important point for utilization of biomass as chemical raw material is the cost of raw material.

Lignocellulose materials consist of three primary chemical fractions or precursors:

a) hemicellulose/polyoses, a sugar-polymer of predominantly pentoses;

b) cellulose, a glucose-polymer;

c) lignin, a polymer of phenols (Fig. 2).

The lignocellulosic biorefinery system has a distinct ability for creating genealogical trees. The main advantages of this method are that the natural structures and structure elements are preserved, the raw materials also have low price, and many product varieties are possible (Fig. 3). Nevertheless, there is still a requirement for development and optimization of these technologies, e.g. in the field of separating cellulose, hemicellulose and lignin as well as the use of Lignin in the chemical industry.

Model building blocks by chemical methods

Furfural, in particular is produced by acidic hydrolysis from hemicellulose in the scale of approximately 142,000 t/a [4]. 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 USA for economic reasons (the artificially low price of petroleum). Nevertheless, the market for Nylon 6 is huge.

However, there are still some unsatisfactory areas within the LCF system, such as the utilization of lignin as a fuel, adhesive or binder. 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 observed that there are no obvious natural enzymes to split the naturally formed lignin into basic monomers as easily as is possible for the also naturally formed polymeric carbohydrates or proteins.

A major role as platform chemical obtained from biomass is levulinic acid, which can be obtained from cellulose and lignocellulose. During

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

Fig. 2 - A possible general equation of conversion at the LCF Biorefinery

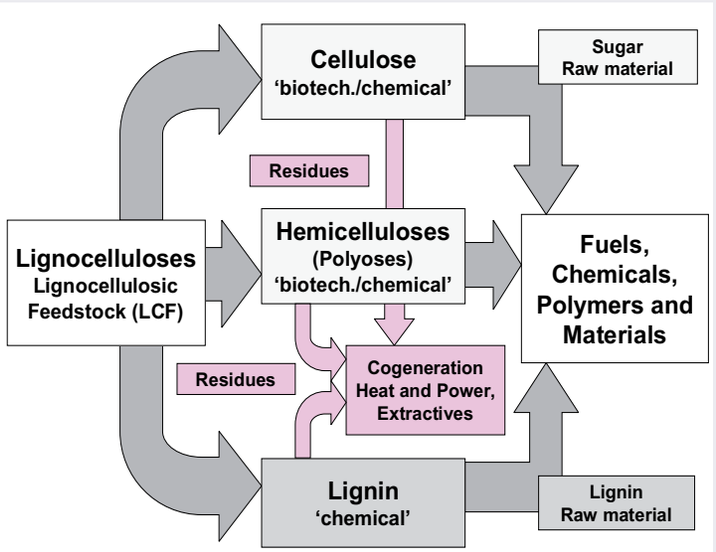


Fig. 3 - Lignocellulosic feedstock biorefinery [3]

the conversion, 5-hydroxymetylfurfural (HMF) is formed via acid catalyzed dehydration, which can be split via dehydration into levulinic acid and metanoic acid (formic acid). Even with raw materials that strongly vary in their quality from batch to batch, the yields that can be obtained are very high. The formic acid can be removed via distillation for further use. Today, hydrolysis processes of lignocellulosic material are carried out as a thermochemical (acid catalyzed/steam assisted) of fungal (enzymatic) catalyzed reactions. Acid catalysis encounters the disadvantages of corrosive nature of reaction media, which must be recovered before further steps while enzymatic reaction leads to longer residence time.

Levulinic acid is a vertile chemical intermediate [5-7] (Fig. 4).

To decrease the waste problems, the State of New York (USA) has built two levulinic acid pilot plants (1 t per day). In these pilot plants, different possibilities shell be tested for the exploitation of the whole variety of carbohydrate-rich and humid waste materials (waste paper, sewage sludge) for levulinic acid production. Thermo-chemical processes tolerate fluctuations in feedstock compositions. In the future, decentralized facilities are planned with volumes of 50 to 1,000 t/day and more. The high prices of levulinic acid has inhibited large-scale use. It currently has a world wide market of about one million pounds per year at a price of $4 to $6 per pound. The New York *biofine*-process is projected to be capable of producing levulinic acid at $0.04 to $0.32 per pound, depending on the scale of operation [8, 9].

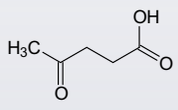
A further commercial plant for levulinic acid production is built in Caserta, Italy and convert 3,000 t/day of raw material (waste sludge from tobacco and paper industry). The process employs a two-stage reaction scheme: continual pre-hydrolysis at higher temperatures (210-230 °C) with short residence time (13-25 s) in diluted acids and hydrolysis of first stage product in second batch reactor at temperatures of 195-215 °C and longer residence time (15-30 min.). The yield is between 60-70% of the theoretical yield based on hexose content of the biomass.

Recently, research has been carried out to study new methods of pre-treatment of biomass. Sub- and supercritical water have been gaining increasing attentions as attractive solvent and reaction media for a variety of application. It is cheap, non-toxic and non-flammable and offers some other advantages in field of "green chemistry". At high temperatures water develops acidic characteristics and accelerates cleavage of chemical bonds and lignocellulose decomposition. One of the major motivations in hydrolysis of polymeric sugars in hemicellulose and cellulose is to implement sub- and supercritical water as environmentally friendly solvent in pre-treatment stage.

Model building blocks by biotechnological methods

An attractive accompanying process to the biomass-nylon process is the previously mentioned hydrolysis of cellulose to glucose and the production of ethanol. Certain yeasts produce a disproportionate amount of the glucose molecule during their generation of ethanol to glucose, which effectively shifts the entire reduction ability into the ethanol and makes the latter obtainable at 90% yield (w/w; with regard to the formula turnover).

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 the use of petrochemically produced ethene, nowadays it is the raw material for a whole series of large-scale technical chemical syntheses for the production of important commodities, such as polyethylene, or polyvinylacetate.



Levulinic acid

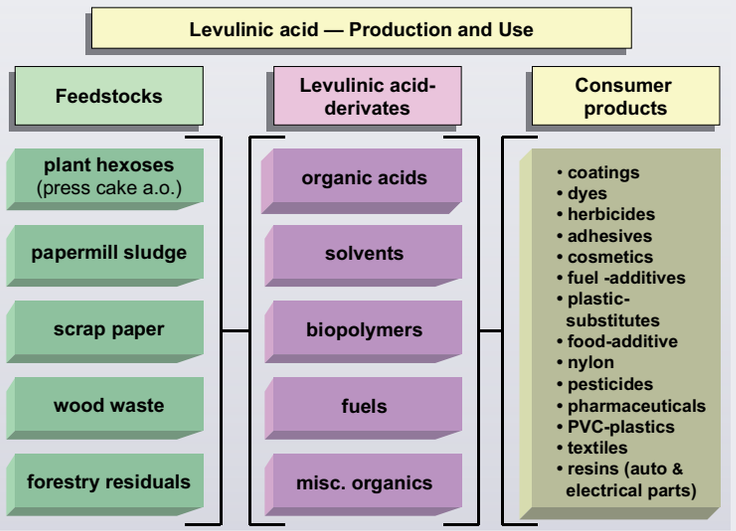


Fig. 4 - Levulinic acid-production and use

The company Dow Chemical one of world leading producers of polyethylene, and the company Crystalsev, one of the most important Brazilian ethanol producers, have announced the establishment of a new polyethylene facility based on sugar cane [10]. Ethanol is produced from sugar by fermentation, converted to ethylene by dehydration and finely polymerised. The start-up is planned for 2011 at an annual capacity of 350,000 tons comparable with modern petrochemical based polyethylene plants. Polyethylene is marketed as versatile mass-produced plastic in the key sectors infrastructure, e.g. pipe systems, cables and conduits, automotive and up-market packaging.

DuPont has entered into a 6-year alliance with Diversa in a biorefinery to produce sugar from husks, straw and corn stover, and to develop processes to co-produce bioethanol and value-added chemicals, such as 1,3-propandiol [11]. Through metabolic engineering, an Escheria coli K12 microorganism produces 1,3-propandiol (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 gL^{-1} at the rate of 4 gL^{-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 fibres with the brand name Sorona [12]. Production is predicted to reach 500 kt per year by 2010.

Outlook

Further petrochemically produced substances can similarly be manufactured by substantial microbial conversion of glucose, such as hydrogen, methane, propanol, aceton, butanol, butandiol, itaconic acid and succinic acid [13, 14, 1].

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RIASSUNTO

Conversione catalitica di biomassa in combustibile ed energia

Lo sviluppo delle bioraffinerie basate su materiali lignocellulosici può rappresentare la chiave dell'economia futura. Lo stato dell'arte, le prospettive e le relative problematiche sono qui esaminate in particolare per produrre prodotti chimici a partire da biomasse. La presente review è stata oggetto di una conferenza dell'autore a Sorrento durante il recente congresso nazionale della SCI.