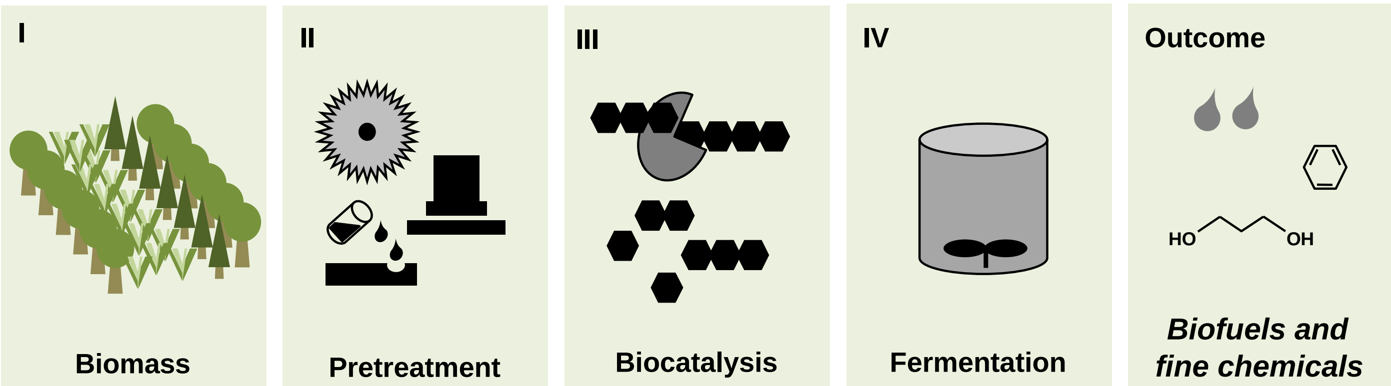
BIOMASS TO FUEL THE WORLD – A CURSE OR A BLESSING?

There is a constantly increasing demand for energy in rapidly industrializing nations. Globally, most energy requirements are met by fossil fuels, but versatile alternative energy sources have been monitored in recent years to displace industrial petrochemical routes and petrol fuels in particular in the long term. In this context, plant-derived biomass has been evaluated to be a sustainable resource used for both, liquid fuel production and fine chemicals to compete with the petroleum industry. However, further technological developments are mandatory to establish an environmentally-friendly biorefinery that does not compete with food industry.



Schematic diagram depicting conversion steps to produce second-generation biofuels and platform chemicals from plant-derived lignocellulosic biomass.

Technical background on bio-based energy

PETROLEUM is still the most important source of energy that is available today with its largest fraction being used as transportation fuel. In addition, there is a constantly increasing demand for energy in rapidly industrializing nations. Around 90% of fossils fuels are used to produce energy, while 10% serves to produce chemicals and materials. Therefore, versatile alternative energy resources have been monitored in recent years to displace industrial petrochemical routes and petrol fuels particularly in the long term. For this purpose, plant-derived biomass has been evaluated to be the only sustainable resource used for liquid fuel production and manufacture of bulk and fine chemicals (e.g. polymers, bioplastics etc.). Since the 1970s and at a high level since the mid-1990s, biofuels (in particular biodiesel and bioethanol) have been produced and implemented for transportation issues in different countries [1].

It has been proposed that mainly bioethanol has both the potential to act as an additive or to completely replace petroleum derived transportation fuels in the future. However, the energy amount of bioethanol is lower compared to petrol ethanol due to the partial oxidation of the carbon content. It is approximately 66% of the volumetric energy fraction of gasoline indicating a reduction of one-third in the total driving kilometres [2]. Bioethanol displays corrosive effects to metal pipes and containers in the existing infrastructure, which demands the development of specific corrosion inhibitors. There are current efforts to replace crude oil by oils from different biological feedstocks that can be directly fed into existing refineries [3].

An integrated bioethanol producing process on the basis of renewable, sustainable biomass would thereby reduce the dependence of most countries on foreign oil and would help to combat climate change in an environmentally favorable green future. However, bioenergy must first become commercially competitive, profitable and environmentally responsible not to loose out in the marketplace. In this context, progress in versatile scientific fields including agriculture and white biotechnology (industrial biotechnology) is mandatory to produce optimally adjusted plant-derived biomass to be used in cost-effective and sustainable processes for the production of energy and fine chemicals as an alternative to the traditional processing of petrochemicals [4]. Although, bioenergy is the major renewable energy source nowadays accounting for 10% of all human energy use, large amounts of available biomass are still unused [5]. It was estimated that over 1 billion tons of biomass per year are used to generate alternative energies, which could replace around 300 million litres (<2 million barrels) of fossil fuels.

I - Biomass resources

BIOMASS is produced by plant-mediated carbon fixation during photosynthesis and bioethanol is the most promising and suitable fuel resource when produced from lignocellulose. Lignocellulose in plant-derived biomass is composed of cellulose (30-50%), which is the most abundant polysaccharide on earth, hemicellulose (15-35%) and lignin (10-30%). Nowadays, bioethanol is mainly produced in starch-based processes from corn in the United States and from sugar cane in Brazil, while biodiesel is generated from vegetable oils and animal fats at lower levels. Starch is the major energy storage component in cereal crops such as corn or wheat. It can be broken down to monomeric sugar molecules either by chemical methods (such as acid hydrolysis) or by more environmentally friendly techniques including enzymatic hydrolysis to be later microbially fermented to give bioethanol [6]. These so called first-generation biofuels are being exclusively produced from edible plants and compete with food production. A sustainable shift from first- to second-generation biofuels might be favorable to overcome the “FOOD-VS-FUEL” debate.

Sources for second-generation biofuels are the non-edible lignocellulosic parts of plants. Bioenergy crops used as potential feedstocks to produce second-generation biofuels are composed of agricultural and forest residues and waste materials like sugarcane bagasse, wood or straw providing the required attributes to reduce greenhouse gas emissions. It has been estimated that a major part of municipal solid waste is also composed of lignocellulose. Moreover, lignocellulosic biomass is abundant and renewable. In principle, agricultural crops, waste vegetable oils or woody biomass are all potential sources to produce bioethanol and building block chemicals, but offer different advantages and disadvantages, i.e. sugarcane is highly efficient with regard to its biomass production per growing area in contrast to corn. However, the search for alternative energy sources is urgent. New and innovative cellulosic feedstocks that can be brought to the market must be identified and applied soon. Therefore, it is important to note that the lignocellulosic composition of unlike plant materials including hardwoods, softwoods and grasses display diverse chemical and physical properties and are differently affected by pretreatment methods and enzymatic hydrolysis. Further plants that have been discussed to be promising lignocellulose sources are switchgrass, poplar, maize stover, energy cane, elephant grass, *Miscanthus*, giant king grass, napier grass or various *Agave* species [7]. The development and choice of an optimal agroecosystem will be mainly evaluated with regard to the feedstock’s water-efficiency. Although, commercial-scale lignocellulosic biofuels production was a recent historic achievement in few small commercial facilities in the United States and in Europe including Italy and Germany, the perfect feasible method for the breakdown of (hemi-) cellulosic sugars is still a dream of the future. So far, these “proof-of-principle” demonstrations were predominately based on the degradation of wheat straw and corn stover. In such a zero-waste biorefinery process, raw material, lignocellulose pretreatment and tailor-made biocatalysts comprise the most significant cost fractions.

II - Pretreatment

AMONG the most important technological drawbacks of bioethanol production from lignocellulosic feedstocks is the separation of lignin from the sugar components cellulose and hemicellulose and the further decomposition of the polysaccharides to give small and fermentable sugars. Enzymes cannot attack the tightly bound structure of lignocellulose in the cell wall, which is a natural protection against pathogens in plants. The polymeric compounds display a complex organization and interact with each other. Therefore, a harsh pretreatment is indispensable in a biorefinery to modify the physical and chemical properties of the plant cell wall. This pretreatment step is considered to impact all following operation steps in the process including downstream processing, handling of waste residues, and selection of the fermenting microorganism as well as ethanol recovery. Moreover, the pretreated biomass itself and the polysaccharide degrading biocatalysts are highly dependent on the methodology. Biomass is treated by versatile chemical, physical or physicochemical pretreatment methods including hot water, steam explosion, milling or acid treatment to separate (hemi-) cellulose and lignin. Pretreatment procedures can be assigned to four different categories including biological (enzymatic), chemical (acidic, alkaline oxidative pretreatment methods) and physical (vibratory or milling) methodologies [8]. Moreover, different solvent fractionation methods are routinely used to disrupt the hydrogen bonds between microfibrils. The most often used methods are ionic liquids or phosphoric acid fraction and the organosolv process. The latter procedure can be used to extract lignin at high temperatures (90-220°C depending on the biomass source) from the remaining biomass combined with a mild acid hydrolysis of the polysaccharides into fermentable sugars. Fragmentation makes use of ionic liquid's capability to form hydrogen bonds with cellulose at high temperatures. In contrast to the organosolv process and ionic liquid fragmentation, phosphoric acid can be used at 50°C to fractionate the biomass into cellulose, hemicellulose and lignin [9]. Afterwards, lignin is usually combusted in industrial processes to supply the required process energy, but it also represents an important material to manufacture valuable fine chemicals. Finally, an advantage of biological pretreatment technologies over the other techniques is the fact that they are not energy-intensive, but they usually require prolonged residence times and consume available carbohydrates. White rot basidiomycetous fungi were applied to remove lignin from the biomass by the action of extracellular laccases and lignin peroxidases. However, thermochemical pretreatment technologies are considered to be the most promising procedures nowadays [9]. A thermochemical pretreatment dissolves the tight structure of lignocellulose and enables a 3-10 fold increase of enzymatic hydrolysis. However, such pretreatment methods represent a large expense and consume high rates of energy. Moreover, cooling of a reactor vessel for subsequent enzymatic hydrolysis and fermentation is also highly cost intensive.

III - Biocatalysis

DURING the process of biocatalysis, polysaccharidic sugars are further converted into monosaccharides and small oligosaccharides by the concerted action of cellulases and hemicellulases. This second step in lignocellulose conversion applies different biocatalysts to convert polysaccharides into fermentable sugars. Cellulose is a linear polysaccharide composed of β-1,4-linked monomers of glucose, while hemicellulose is heterogenous mainly consisting of β-1,4-linked xylose connected to other sugar components such as arabinose, galactose, glucose or mannose. The most important enzymes are endo-acting cellulases (endoglucanases) and xylanases (endoxylanases) that randomly cleave these polysaccharides to produce oligo- and disaccharides. Afterwards, oligo- and disaccharides are further processed to finally give monosaccharidic pentoses and hexoses [10]. The action of biocatalysts at labile process conditions is highly susceptible to non-specific binding to lignin and other components, inactivation by product intermediates, enzyme interactions with degradation products or high process temperatures. To circumvent the problem of active reactor cooling, extremozymes (enzymes from extremophilic microorganisms) that withstand harsh conditions including high temperatures might be an attractive future process improvement [11].

IV - Fermentation

IN a final step, released sugars will be fermented to give bioethanol by tailor-made microorganisms such as engineered bakers yeast *Saccharomyces cerevisiae* or the production of bulk chemicals from sugars or lignin components is conducted. Mono- and oligosaccharidic sugar molecules are usually fermented by fuel producing microbial strains of bacterial or fungal origin. Bakers yeast is the traditional and still preferred microorganism for bioethanol production due to its versatile applicability, genetic engineering and extensive characterization. Nevertheless, the efficiency of the overall process must be increased by the combined fermentation of hexose and pentose sugars to become economically attractive. Therefore, yeast strains with high product yields were recently engineered to be capable of using xylose for biofuel production as well. Moreover, another desirable strategy is to consolidate enzymatic saccharification and microbial fermentation by generating (hemi-)cellulolytic microorganisms that are capable of producing bioethanol or other biochemicals and biomaterials [12]. In this context, engineering thermophilic fermenting microorganisms might also be very promising to establish future consolidated bioprocessing technologies to compete with petrochemical production routes indicating that research on optimized bioethanol production combines different fields including biotechnology, genetic engineering, data mining, systems biology, process engineering, measurements and analysis.

Further alternatives

Another promising feedstock for future applications is algae. Algal biomass can easily be produced at high-speed exclusively needing light, water and carbon dioxide, which is extremely attractive for industrial applications. The most important advantage over second-generation feedstocks is the fact that algae do not contain lignin in their plant cell walls, simplifying the access to their valuable sugar sources. However, alginate (the algal saccharide) is only weakly attacked by routinely used biotechnologically relevant microorganisms. Therefore, scientists screen for potential alginate lyase candidates from different sources. A complete degradation pathway including ethanol fermentation from brown macroalgae has recently been presented for a synthetic yeast platform [13]. Suchlike macroalgae are also commercially grown and harvested as animal feed or human food source.

Executive summary

Many efforts were undertaken in the production of bioethanol during the past years. Nowadays, first generation biofuels are produced at a high level, but they compete with the food industry, while the production of second generation biofuels from biological waste materials is very promising, but not yet feasible. Finally, it is well accepted to replace fossil fuels by bioethanol in some countries, while it is controversially debated in others.

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