1 General Introduction

1.1 Forced replacement of fossil-based compounds by bio-based products from renewable resources

1.1.1 Fossil-based products and their drawbacks

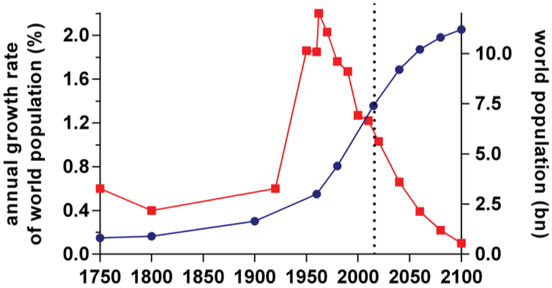

Figure 1: World population growth and its annual growth rate from 1750 to 2010 and projections up to 2100 (modified from [1]).

The world population has increased from 1 billion to over 7 billion humans within the last 200 years [2]. Within only 100 years, from 1900 to 2000 marking the beginning of modernity, a drastic increase in population size from 1.5 to 6.1 billion was registered. Due to lower fertility rates, world population growth decelerates ending up with an estimated annual growth rate of 0.1 % by 2100. Nevertheless, world population will grow by another 3 billion people in the next 80 years [1]. This means a gigantic global demand for food, energy, fuels, and chemicals to maintain and improve human living standards. Agricultural production for instance has to be increased by 70 to reach 100 % until 2050 in order to meet global food demands [3–5]. Depending on the scenario, energy supply is supposed to reach levels in 2040 that are up to 45 % higher than in 2012 [6]. The accomplishment of these needs is mainly based on fossil resources leading to an already huge and still increasing dependency on coal, petroleum, and natural gas [7]. Due to their formation process taking millions of years, these resources are finite and will decrease in availability until completely depleted [8]. This trend will extremely increase prizes and dependency on countries still possessing fossil sources. Additionally, fossil fuel burning negatively affects air quality by increasing pollutant concentrations locally, while contributing to global warming on a larger scale. Increased concentrations of greenhouse gases, such as carbon dioxide, methane, and nitrous oxide, in the troposphere trap solar radiation in form of heat leading to a warming of the earth atmosphere and surface [9,10]. Another issue regarding the consumption of sulfur-containing fossil fuels is the formation of acid rain due to sulfur dioxide and nitrogen oxide emissions [11]. To fight these drawbacks and make alternatives competitive, a replacement of fossil-based by bio-based renewable resources as carbon feedstock is indispensable.

1.1.2 Production of fuels and chemicals from biomass feedstocks

While at the beginning of the 20th century, trees and agricultural crops were used for the production of a variety of industrial materials, a shift towards petroleum occurred in the late 1960s. Despite the energy crisis in the 1970s that accelerated the interest in bio resources-based production, until today most of the worldwide energy market heavily relies on fossil fuels for the generation of thermal energy, fuels in gaseous, liquid, and solid form, and chemicals [12–14]. Depletion of fossil reserves, climate change and dependency on countries exporting fossil materials drives the search for alternative resources [15]. In terms of a short formation period, biomass represents the only renewable CO_2-based source available in abundance. CO_2 has the potential to replace fossil resources applied in the production of chemicals, energy, and fuels, but its use on a commercial scale is still very limited [8,12,16]. Burning biomass indeed causes some pollutants like dust and subsequently acid rain, when no filters are used. But due to comparatively low sulfur contents, wood consumption for example emits 90 % less sulfur than coal. Regarding the greenhouse gas effect, the amount of released carbon dioxide balances with the carbon dioxide absorbed by the plants. Biomass is therefore indicated as carbon dioxide neutral [7].

Biomass is defined as “all non-fossil-based living or dead organisms and organic material that have an intrinsic chemical energy content” [8]. This includes plant material such as algae, animal products, and manure, or agricultural and forestry by-products [8,17]. Biomass classification in terms of its major component differs i.a. between sugars, starch, cellulose, hemicellulose, lignin, oils, and proteins [18]. It is assumed that 146 billion metric tons of biomass are produced worldwide per year, mostly in the form of wild plant growth of which only a fraction of less than 1 % is used. The largest feedstock is cellulose with 49 %, followed by other sugar polymers including starch with 23 %, and proteins with 12 % [18–20]. Regarding biofuel production, biomass is also divided into the categories “first”, “second”, and “third generation feedstock”. “First generation biofuels” directly originate from biomass that is edible including sugar cane, corn, whey, barley, and sugar beets. Ethanol and biodiesel, e.g., are considered as first-generation biofuels, depending on the carbon source and synthesis route. Bioethanol is commonly produced in fermentation processes using C6 sugars (mostly glucose) and yeast strains such as *Saccharomyces cerevisiae*. In order to do so, sugarcane is crushed in warm water to remove sucrose which is then purified for the production of ethanol. Before corn can be used as feedstock for ethanol production, starch has to be hydrolyzed to make the containing sugars accessible. The production process of biodiesel (monoalkyl esters) is quite different. Oils are extracted from the biomass of oily plants and seeds to convert them into biodiesel by a process called transesterification. During this process, glycerol is separated from the bound long chain fatty acids and is replaced by methanol [21,22]. With the use of arable land for biofuel feedstocks, however, the food versus fuel dilemma appeared. Farmland and crops are diverted that are needed to ensure the world’s food supply. The large increase in biofuel production in recent years have resulted in an increase in food prices due to limited feedstocks, needed for both production processes, and restricted farmland [23].

The “food vs. fuel” debate drove the development of second generation or advanced biofuels like cellulosic ethanol and Fischer-Tropsch liquids. These biofuels are derived from cellulose, hemicellulose, lignin, or pectin (e.g., agricultural and forestry wastes) and therefore from sources not digestible by humans. Before sugar monomers can be fermented to ethanol, the fibrous matrix structure of lignocellulose has to be broken up into hemicellulose, cellulose chains, and lignin and hexose and pentose sugars have to be hydrolyzed from the separation products [24].

Feedstocks formed by aquatic autotrophic organisms (e.g., algae) are termed as “third generation feedstocks” [25]. Due to their high lipid productivity meaning the product of lipid content and biomass productivity, microalgae are an attractive alternative for vegetable oil and therefore biodiesel production [26]. Several algae species produce 50 to 60 % of their dry weight in lipid form making them up to 20 times more efficient per unit area than the best oil-seed crop [27,28]. Species featuring high lipid productivity are, e.g., *Amphora*, *Ankistrodesmus falctaus*, *Chlorella sorokiniana*, and *Tetraselmis suecica*. Other advantages are their rapid growth and their ability to grow in marginal regions, in the ocean, or in brackish water. The latter reduces the conversion of areas that are needed for food supply. But despite these great advantages, biodiesel production from algae is not yet economically profitable [26,29].

Biobased raw material has different application fields. On the one hand, it is used as biofuels, such as biogas, ethanol, methanol, and biodiesel, as an alternative to petroleum fuels. On the other hand, it is applied in bioenergy production instead of petroleum or coal, or as feedstocks for chemical industry by biorefining [30]. A biobased product is characterized by a biomass content of at least 90 % (besides water and other inorganic components) as measured by its volume or weight. Examples for biobased products are paper and paper-like products, wooden composites, paints, lubricants, textiles, wooden furniture, insecticides, and fertilizers, pharmaceuticals, and cosmetics, but also food, drinks, and food supplements [31].

In the biobased process of fuel and chemical production, biomass can be converted in different ways, either by chemical or enzymatic catalysis, or by biological conversion using microorganisms. Each pathway goes along with advantages and disadvantages. High volume throughput, but less molecular structure specificity can be achieved by chemical synthesis. In contrast, biological conversion can result in high specificity, but the production parameters have to be chosen with respect to the microorganisms used [32]. Nevertheless, biological conversion – also called fermentation – has several advantages over the petro chemistry: Each raw material containing carbohydrates can basically be used as substrate. Therefore, besides biomass organic waste or side products from agricultural manufacture such as straw or wood waste can be applied, and more importantly even mixtures of carbon sources. Fermentation processes go along with low pressures and temperatures often resulting in lower initial costs. Most of the by-products are nontoxic. While petroleum and chemical feedstocks mostly have to be imported, raw material for fermentation processes usually has a homemade origin. This improves foreign trade balance and decreases political and economic dependency on countries holding fossil resources. Currently, a main disadvantage of biomass converting factories is the plant capacity which is limited by costs for biomass, transport, and storage [31].

In recent years, the production of valuable chemicals from biomass feedstocks using microorganisms attracted more and more attention and each increase in commodity