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Introduction to Renewable Resources in the Chemical Industry

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Processes in the chemical industry are historically based on fossil resources. During industrial revolution, energy sources like peat and such renewable biomasses as wood were substituted by coal and later on by natural gas and petroleum oil. The latter has been, until now, the main resource for raw materials and the energy supply for the private sector. Due to its very beneficial properties in terms of chemical synthesis processes, only a minor proportion of approximately 10% of this plentiful resource is used for such purposes, whereas 90% is utilized for energy and transport. With regard to the increasing population and energy demand and oil consumption of developing countries, the limited availability of crude oil, and financially motivated trading operations, the price of oil rises steadily and reached a peak of nearly 150 USD per barrel in 2008. It is assumed that most of the known so-called supergiant oil-fields cross the oil-peak, which comes along with a decrease in the discovery of novel oil springs. Therefore, alternatives have to be introduced to reduce the dependency on these transient fossil fuels. But one has to keep in mind that alternative fuels and resources for chemical building blocks have to compete against classical fossil compounds.

Currently, the prices of most bulk and specialty chemicals are too low for biotechnological routes to compete. It is estimated that competition begins at feedstock prices above $2 per kilogram. Nevertheless, the share of biotechnologically produced chemicals is expected to increase from approximately 5% to 20% in the year 2010. The greatest impact is expected in the segment of fine and specialty chemicals with up to 60% of the products based on biotechnological processes. Interfacing with green biotechnology for enhanced crop properties and increased plant breeding can be expected. More attention is paid to the lignocellulose feedstock, which is extensively discussed and examined to be used as a sustainable raw material for ethanol production. In addition, a few current trends focus on C1 carbonic compounds such as methanol and methane, fatty acids and glycerol from plant oil, and whey-based substrates that can be used as input compounds for a chemical refinery.

If one has a closer look to current activities of oil companies, it is obvious that the time is changing. Several efforts to utilize sustainable biomass feedstocks for recovering fuel substitutes were carried out by these companies. But the

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exploitation and utilization of the biomass feedstock have to be implemented very carefully to avoid such an already occurred competition of energy crops with food production, if first-generation biomass fuels were considered. However, the complete substitution of fossil resources by biobased fuels and raw materials within the near future is quite improbable, considering the current process operation's dependency on large amount of biomass feedstock. Therefore, socioeconomic trends must focus on a holistic approach, where fossil as well as biological resources have to be used in a complementary way. At least at the laboratory scale, for 6 of the 10 best sellers of the chemical industry alternative biotechnological production processes are under development (ethylene, ethylene oxide, dichloroethane, propylene, formaldehyde, and propylene oxide). In Western Europe alone, the annual demand for ethylene and propylene is 40.5 million tonnes. World production of the basic building blocks of the chemical industry, including polymers, exceeds 500 million tonnes. This fact clearly shows that large quantities of renewable raw materials must be made available for the production of bulk chemicals. Despite the 5.6 million hectares of arable land currently lying fallow in the EU, this cannot be limited to the provision of sugar or starch. On the contrary, what is required is the holistic utilization of diverse renewable resources. Nature provides around 170 billion tonnes of plant biomass, of which hitherto only approximately 3–4% have been commercially exploited. The crux of the matter is how much can, and indeed may, be used of the remaining 96% in a sustainable way? And how much energy will this entail?

If one considers the biomass feedstock, the number of different categories is enormous and includes grains, sugar crops, oilseed crops, agricultural wastes, food-processing wastes (liquid and solid), wood, wood chips, bark, mill residues, forest residues, pulping liquors, manures, and algae. With regard to an increasing utilization of crops in the material and energy sector, the prices for comestible goods also increase and a couple of social problems arise. Therefore, the exploitation of forest residues or special planted wood-based biomass is – based on our current knowledge – accompanied only by insignificant social problems. Especially for European countries, prosperous predictions for utilization of such materials do exist. Owing to a declining population, the need for agricultural crop lands for food supply will decrease and could be used for industrial plantations. As a positive consequence, new collaborations between producers (farmers) and chemical manufacturers will be established in analogy to the already existing collaborations between the starch-processing companies and manufacturers.

One potential starting point is the development of the lignocellulose biorefinery. However, the sustainable development of the biorefinery depends on the extensive process integration. A concept devised solely for the production of basic and fine chemicals may well fail to achieve its target. More importantly, the materials applied should be used both for energy (in the form of heat and power) and for the production of chemicals and materials. All planning must allow for the fact that the renewable resources in question should not only be allocated to biotechnology but also in fact in the area of energy supply where there is a tendency to draw increasingly on biomass. Hütermann and Metzger, for example, state that

"... global energy provision on the basis of biomass is feasible without detriment to food production. ..." According to their calculations, a biobased economy would require 22.3 billion tonnes of bio-oil from pyrolysis. This corresponds to approximately 35 billion tonnes of biomass solely for conversion into energy. In the construction materials sector, too, there is a growing trend to utilize renewable resources. To quote the "Informationsknoten nachwachsende Rohstoffe" (Renewable Resources Information Centre), "... nature provides a huge range of plant and animal raw materials that are suitable for a variety of applications. The challenge for the future is to exploit this inexhaustible raw materials potential without detriment either to man or to the environment and without impairing the standard of living of the population. ...". Only the concerted efforts of all interest groups in the field of renewable resources can pave the way for a meaningful development. In the following chapters, the options for the biotechnological and chemical industries will be examined in more detail. In view of the raw materials figures initially mentioned, one of the priorities will be (ligno)cellulose as, with around 95%, it accounts for the bulk of renewable raw materials. A further priority will be the more intensive utilization of methane and methanol from both fossil and renewable sources.

Assuming an estimated annual biomass production of 170 billion tonnes by biosynthesis, of which 75% are carbohydrates mainly in the form of cellulose, chitin, starch, and sucrose, 20% lignin, and only 5% other natural products such as fats (oils), proteins, and diverse ingredients, the prime concern should be efficient access to carbohydrates and processing them into chemical mass products and finished products. This will not take place overnight since the relevant technologies first have to be developed; moreover a shift from fossil to sustainable processes can only be implemented if it is seen to be economically viable. The substitution of fossil resources by renewable resources can, therefore, only proceed in stages. To combine the markets for fossil and renewable resources would only make a prognosis of the most favorable time for the change more difficult.

Raw materials on the basis of biomass cannot simply be converted into conventional plants like naphtha crackers; hence it is postulated that new processes for the conversion of biomass first need to be developed. If used intelligently, chemical reaction technology, including catalysis and process engineering together with biotechnology, may provide economic solutions to this technological problem. The following strategies are, in principle, possible:

- utilization of the chemical structures produced by nature without any chemical modification;
- one-step modification of these structures;
- multistep chemical modification;
- total degradation to C-1 fragments (e.g., synthesis gas or methane) and controlled synthesis to obtain the desired molecules.

The chemical industry owes its success to the principle of unit construction: from simple basic substances, like ethylene, carbon monoxide, or hydrogen, more complex precursors can be produced under controlled conditions by chemical reactions; due to the variety of combination options, the latter can in turn be converted into inconceivable quantities of derivatives and end products. Chemistry learned how to produce chemically pure basic substances from oil that are simple to handle and exactly defined; this is performed highly efficiently in refineries. This was the key to its success. Without exact knowledge of this functional principle, the triumphant success of plastics would have been just as impossible as the production of thousands of other chemical products that today make our lives safe and comfortable.

Within the following chapters, this book tries to answer some of the important questions to establish biorefineries within the existing chemical industry. What should be the impact from plant breeding for new biorefineries? Is it possible to design new and better plants which fulfill most of the requirements (high contents of fermentable raw materials, less by-products, easy to hydrolyze)? Initially the chemical industry considered fermentation of plant carbohydrates as the only viable solution. But now, with the increasing success of globally grown genetically modified plants, plant enzymes, cell cultures, and whole plants have been taken seriously for chemical production processes. Pharmaceutical proteins, SMDs, and fine chemicals have been the first choice for production. But with ever-rising prices of fossil resources, chemical commodities such as platform chemicals (e.g., succinate, itaconic acid), intermediates, or polymers are now considered as economically viable (see Chapter 2). However, is the world agro capacity big enough to deliver all raw materials needed? The primary purpose of agriculture is food production and has been so throughout human history. During the last decade, environmental and economic concerns have led to growing interest in fuel and energy crop production. Therefore, the production of renewable chemicals from agricultural raw materials will be in direct competition with both food and fuel production for space, resources, labor, and funds. Although the high value of chemical products may make them economically viable, they may have an undesirable competitive effect on food production. However, food, fuel, and chemical production are not necessarily mutually exclusive. The biorefinery concept aims to make best use of whole crop plants by producing numerous products from a single resource (discussed in Chapter 3). In comparison to their fossil counterparts, process chains based on renewable raw materials differ in many aspects. Operations for cultivation, harvesting, and provision of renewable raw materials take place in a natural environment. The raw materials accrue spatially distributed on large areas. Amount and characteristics of the resources underlie seasonal variances and restrictions. As a rule, the abilities and capabilities for storage are limited. Long-distance transports are disadvantageous because of comparable high water content and low calorific values. Thus, Chapter 4 explains the essential adjustments for the logistics of renewable raw materials. Looking at the existing value chain of industrial biotechnology, all fermentation processes which have been commercialized in the last decades for the production of one of the building blocks such as ethanol or amino acids presently rely on carbohydrates as feedstock. Moreover, the majority of fermentation processes, which recently are in the feasibility stage, also start from these feedstocks at the moment. Chapter 5 gives an overview about the existing value chains and the products already produced in the so-called type-one biorefineries, whereas future biorefineries are described in Chapter 6. The establishment of new industrial firms, such as a biorefinery, in a rural area can be seen as an opportunity to revitalize the local economy, and to revert the negative demographic trend, which very often characterizes those areas. However, apart from the scarce density of capital and human resources locally existing, the development of a biorefinery in those places strictly depends on the acceptance level of the local communities which, in assessing the socioeconomic and environmental implications, take into account a series of concerns particularly related to understand how their quality of life may change as a result of the industrial project implementation. These economic and social implications of the industrial use of renewable raw materials are discussed in Chapter 7. Potential markets for bioproducts are wide ranging, including polymers, lubricants, solvents, adhesives, herbicides, and pharmaceuticals. While bioproducts have already penetrated most of these markets to some extent, new products and technologies are emerging with the potential to further enhance performance, cost competitiveness, and market share. The market needs and opportunities for products produced by the existing and proposed new types of biorefineries are explained in Chapter 8. One major reason for the interest in biobased products is their potential contribution to the mitigation of climate change since biobased products are made from renewable resources which, during their growth, take up the same amount of CO_2 as is released by biological degradation or energetic conversion in the end of the product's life. This is a generic advantage compared to the use of fossil resources, which release the inventory of carbon accumulated and stored in the ground millions years before. However, is this true for all biobased products? Chapter 9 tries to answer this by discussing the life cycle analysis of biobased products.

The aim of this book is to highlight all areas which have to be regarded in order to realize the vision of a "biobased economy" as a sustainable industrial future based on renewable resources is often termed. The choice of the chapters is inspired by the scientific framework and the business conditions with an influence on the development of a biobased economy. How do the different authors as specialists in their fields appraise the application of renewable raw materials? Where do they see chances, where do they see need of action? "May you live in interesting times" stated Wim Soetaert in regard to the progress of biorefineries (see Soetaert, W. [2009] May you live in interesting times! *Biofuels, Bioprod. Biorefin.*, **3**, 491–492, DOI: 10.1002/bbb.173). We hope that you will have interesting time while reading this book!