Bioenergy – Chances and Limits

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Statement

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The “Executive Summary and Recommendations”, in German and English, is printed in a separate booklet. The short- and long version are also found under www.leopoldina.org
Back in 2009, the German National Academy of Sciences Leopoldina, the German National Academy of Science and Engineering and the Berlin-Brandenburg Academy of Sciences and Humanities outlined the necessary scope of future energy research in their “Concept for an integrated energy research programme for Germany”. The Leopoldina updated the concept last year when it issued its statement entitled "Energy and research policy recommendations following the events in Fukushima".

The present study now provides a comprehensive analysis of the use of bioenergy.

In recent years Germany has seen a steady rise in the number of energy crops being cultivated for the production of biofuels and biogas. Because bioenergy is so versatile and easy to store, the German Federal Government wants to ensure that it continues to play a major role in the future.

Over the past one-and-a-half years, a group of experts from various disciplines have been helping the Leopoldina investigate how Germany can best harness biomass in ways that make sense from the point of view of energy and the climate. The statement on the opportunities and limits of bioenergy analyses the availability and feasibility of using biomass in Germany, provides an overview of energy conversion technologies and introduces promising approaches to producing hydrogen from renewable resources.

The recommendations contained in this statement are intended to provide parliaments, ministries, associations and companies with well-founded and unbiased support in making the important decisions that will lay the foundations for a climate-friendly, secure and sustainable use of bioenergy.

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Professor Jörg Hacker
President of the German National Academy of Sciences Leopoldina
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Bioenergy is energy derived from non-fossilized plant and algal biomass. The energy stored in biomass can be released either directly, by simply burning the harvested material, or indirectly after its conversion into a liquid biofuel such as bioethanol and biodiesel or into a gaseous biofuel such as biogas, hydrogen or synthesis gas. The aim of this Leopoldina report is to evaluate the chances and limits of bioenergy as an energy source for Germany with a European and a global perspective. First “The availability and sustainability of plant biomass as energy source” are discussed. This is followed by a chapter on “Conversion of biomass into marketed energy carriers and precursors for chemical synthesis” including the thermochemical path from biomass to fuels. Finally the topic “Biological and bio-inspired solar dihydrogen production” is addressed – a presently much discussed area – although this research has not yet provided operationally usable devices. Economic and socioeconomic aspects of bioenergy are only touched upon in a few cases as an aid to understanding.

The general conclusions and recommendations are published as a German and English version:

The use of fossil fuels as an energy source is of concern, because the amounts of easily accessible coal, gas and especially oil, are limited, and because the combustion of fossil fuels is associated with the formation of carbon dioxide (CO₂), whose concentration in the atmosphere has increased considerably since the beginning of the industrial revolution. The increase in atmospheric CO₂ correlates with the presently observed climate change and is responsible for the acidification of the oceans. CO₂ is a greenhouse gas (GHG) absorbing infrared light and when dissolved in water it creates a weak acid, which negatively affects the formation of calcium carbonate required in the formation and maintenance of coral reefs and carbonate based shells and structures. There is thus a search for renewable energy sources that are climate and environment friendly. The one discussed here is Bioenergy.

The aim of this report is to evaluate the chances and limits of bioenergy as an energy source for Germany. Although the focus is on Germany the discussion includes Europe (EU-25) and has a global perspective. The report discusses mainly the present situation with some extrapolations into the future.

Bioenergy generally refers to energy from the sun stored in plant biomass by photosynthesis. The energy can be released from the biomass by direct combustion (solid biofuels like wood and straw) or after conversion to liquid biofuels such as bioethanol and biodiesel, or gaseous biofuels such as biogas, syngas or hydrogen. Bioenergy also includes the energy stored in hydrogen generated from water involving photosynthesis.

Bioenergy is often considered to be renewable and CO₂ neutral because the generation of biomass through photosynthesis absorbs the same amount of CO₂ as is released when that biomass is burnt as an energy source; but this disregards the following three important facts: (a) The carbon cycle is intimately linked with the nutrient cycles of nitrogen (N), phosphorus, sulfur, and metals, of which biomass is also composed, and with the water consumed to produce it (Figure 1). Whenever biomass is produced, soil nutrients are consumed. Whenever biomass is repeatedly removed from an ecosystem or its production is accelerated, nutrients need to be added via fertilizers. Yet, N-containing fertilizer application induces release of nitrous oxide (N₂O) with a much higher global warming potential than that of CO₂; (b) in addition to N₂O, intensive agriculture is almost always accompanied by emissions of the GHGs CO₂ and methane (CH₄) as a result of land management, of application of fertilizers and pesticides, and of livestock husbandry. Also, carbon costs in the production and transformation processes and the inherent costs of human resources have to be considered; and (c) There is a third reason why CO₂ fixation by plant growth does not in itself justify neglecting the CO₂ emissions upon combustion of the harvested biomass. If the area used for the growth of energy crops were not used for that purpose it would be grassland or forests. For example, if not used for bioenergy, abandoned cropland often reverts to forests. As forest it would remove carbon from the atmosphere and would increase the carbon stock in biota and soils for decades or centuries until a new equilibrium is reached. This lost carbon sequestration through land-use change can be
The carbon cycle cannot be separated from the nutrient cycle

\[ \text{CO}_2 \]

\[ \text{Carbon cycle} \]

\[ \text{Nutrient cycle} \]

Figure 1: Coupling of the carbon cycle and the mineral nutrients cycle. Any assessment of the sustainability of biomass utilization must account for the fact that biomass is not just composed of carbon, but also of nitrogen, phosphorus, sulfur, metals, etc., as well as water. Therefore, biomass production taps the nutrient capital of the ecosystem. Any acceleration of the carbon cycle (higher productivity) must accelerate the nutrient cycle, including the production of the N-based greenhouse gas \( \text{N}_2\text{O} \) and of methane: gases with a much higher global warming potential than that of \( \text{CO}_2 \). If soil organic nitrogen mineralized following land-use change and \( \text{NO}_x \) deposits from the atmosphere are included, then the \( \text{N}_2\text{O} \) emission factor (% N as fertilizer or biologically fixed N emitted as \( \text{N}_2\text{O} \)) is about 4 % (100 % = N-content of the biomass). c

Quite significant. All three cost factors and the environmental and ecological consequences and impacts on biodiversity of large scale biomass cultivation have to be considered in a full life-cycle assessment (Chapter 1.7). In some cases these costs can lessen or even neutralize the net greenhouse gas mitigation impacts of using biomass as energy source. In these cases bioenergy is neither renewable nor carbon neutral, instead it is energy- and \( \text{CO}_2 \) negative.

Despite these limitations, the European Union (EU) has the objective that by 2020 at least 10 % of the fuel used for transport and mobility should come from liquid biofuels. It is acknowledged that the EU directive requires that the biofuels meet certain criteria including GHG saving minimums (35 % now and more than 50 % from 2017 on). c The biofuels should not be produced using raw materials from land with high biodiversity value or with high carbon stock. These criteria will be difficult to meet if additionally it is considered that biomass for fuel production should not compete with biomass for human food, animal feed or industrial purposes.

The reduction of GHG emissions, especially of \( \text{CO}_2 \), is only one of the driving forces for enhancing biomass-based energy. In the case of biofuels, an additional motivation is to become less dependent on oil imports both for transportation and for the synthesis of petrochemicals. Development of sustainable biofuel production techniques is also of commercial interest, because of its potential role in maintaining Germany’s industrial exports.

To address these issues, a working group of the German National Academy of Sciences Leopoldina organized an international workshop on “Biofuels and Bioconversion” at the Alfried Krupp Wissenschaftskolleg Greifswald, in October 2010. Scientists from various disciplines (biology, biophysics, biotechnology, chemistry and ecology) discussed the following topics:
- Availability and sustainability of biomass generated by photosynthesis as an energy source considering also the direct and indirect production and transformation costs (Chapter 1);
- Conversion of biomass into biofuels (biogas, bioethanol, biodiesel) and petrochemicals (Chapter 2);
- Biological and bio-inspired solar-driven hydrogen generation from water (Chapter 3).

The report does not deal with economic and socioeconomic aspects such as the present inability of bioenergy to compete with other energy sources without financial subsidies. d The effect on food prices of competition between the food market and the energy market is also not included. These issues are only touched upon in a few cases as an aid to understanding; they have already been intensively discussed elsewhere. e


After almost completion of the Leopoldina report, the Intergovernmental Panel on Climate Change (IPCC) Special Report 2012 on Renewable Energy (SRREN)\textsuperscript{10} was published; in Chapter 2 of that report more than 100 pages are dedicated to bioenergy with a global focus. The report provides best case and worst-case deployment scenarios. However, in the Executive Summary it is mainly the best case that is highlighted. Partly because of this emphasis, the special report paints a too optimistic picture of the greenhouse-gas mitigation potential of bioenergy and the technical potential of biomass to produce bioenergy. Likewise, the BioÖkonomieRat of the German Federal Republic recently published a report\textsuperscript{11} in which a scenario is discussed that by 2050, 23\% of the energy consumed in Germany could be derived from bioenergy, mainly from imports (Chapter 1.9).

The Leopoldina report is much less optimistic about the future of bioenergy. This is largely because it is judged that almost all of the biomass that can be grown sustainably worldwide may in the future be required to provide the growing world population with food and goods derived from biomass if countries like Brazil, China and India reach European living standards and will adopt the diet currently appreciated in the industrialized world. Sustainable growth in this context means that the environmental, ecological and climate consequences and the impact on biodiversity of large scale biomass cultivation will be minor, also taking into account that the availability of irrigation water (Chapter 1.13) and of phosphate fertilizers (Chapter 1.14) is limited.

The statement “Bioenergy – chances and limits” by the German National Academy of Sciences Leopoldina takes into consideration previous publications by other Academies\textsuperscript{3,12-14} and complements its previous assessments on “Concept for an integrated energy research programme for Germany” (2009)\textsuperscript{15} and on “Energy policy and research policy recommendations after the events in Fukushima” (2011).\textsuperscript{16}

Parallel to the Leopoldina Report, which mainly deals with science aspects of bioenergy, the Deutsche Akademie der Technikwissenschaften (acatech) published a supplementary report on “Biotechnologische Energieumwandlungen in Deutschland”, which mainly deals with the technical aspects.
REFERENCES


Plant biomass, mainly wood, has been used as an energy source by humans since they first discovered the use of fire. Since then the number of people on Earth has increased to now more than 7 billion \((10^9)\) and the amount of energy used per person has increased on average way more than 10 fold in the last few hundreds of years. Concomitantly, global crop production has increased substantially, e.g. between 1965 and 1985 by 56%; however, between 1985 and 2005 production increased only by 20%, indicating that the rate of increase is slowing. Irrigated land accounts for 34% of agricultural production, and in the past 50 years the world’s irrigated cropland area has roughly doubled (Chapter 1.13). Yet, despite crop production having increased, global net primary production is decreasing due, amongst other causes, to more land being used for infrastructure and to soil degradation (Chapter 1.12).

The question discussed here is what percentage of the plant biomass generated annually is possibly available as an energy source for transportation, households, industry, services etc., but considering that plant biomass is also required for human food and animal feed and that the plant biomass has to be shared by all other living beings on Earth. The sustainability of the biosphere from which bioenergy can be drawn has to be taken into account. We also consider how intensive agriculture can have negative ecological impacts, such as a decrease in biodiversity and that increased biomass production through land-use change, land management and fertilization is often associated with the net formation of greenhouse gases (GHGs) thus contributing to the predicted anthropogenic climate change. The fossil energy inputs required for farming and processing often cancel out most of the energy delivered. This is of concern because biomass production for bioenergy then makes no contribution to the reduction of GHGs. As already mentioned, the focus of the discussion is on Germany and the EU-25, but with a global perspective. The global perspective is of importance since Germany and most other European countries are substantial net importers of biomass and of biomass products.

The chapter draws on relevant publications and on two treatises on net primary production and bioenergy (“Nettoprimärproduktion und Bioenergie”) by Schulze and Körner, and on human appropriation of net primary production in Europe (“Menschliche Aneignung von Nettoprimärproduktion in Europa”) by Haberl et al. The two treatises, which contain data especially acquired for this statement, can be found in the supplement.

Much of the data were taken from information provided by the Federal Agency of Statistics of Germany (Statistisches Bundesamt Deutschland). The data are mostly based on averages and extrapolations and therefore involve relatively large uncertainties with margins of error of at least + 10 %, However, despite these uncertainties, it was possible to derive a reliable estimate of the availability and sustainability of biomass as an energy source.

For any country, the availability of biomass as an energy source depends on the demands for land to satisfy other requirements such as human food, animal feed and industrial pur-
poses and on the primary-energy consumption. The relatively low availability of biomass in most countries will be the primary focus of this study because it is the driver of intensive land use with all its climate and ecological risks. Including GHG emissions caused by creating new farmland from forests, farming is one of the largest single sources of man-made GHGs.19

After explaining how much solar energy is continuously stored in biomass and discussing the difference between primary-energy and final-energy consumption (Chapter 1.1), we describe the net amount of terrestrial biomass which can be harvested sustainably (Chapter 1.2), analyze the percentage of net primary production that is already being appropriated by humans (Chapter 1.3) and compare the net primary production with primary-energy consumption (Chapter 1.2). The fossil fuel costs and GHG emissions associated with biomass production are outlined in Chapters 1.4 to 1.8, showing that the GHG mitigation potential of using biomass as an energy source is small. In Chapter 1.9 it is pointed out that Germany meets about 30% of its biomass demands from imports of plant growth from outside Germany. Chapters 1.10 and 1.11 critically address “wastes” in the human food production chain and the availability of agricultural and municipal wastes and of straw as energy sources. Concern over changes in soil quality, water availability and phosphate limitations are discussed in Chapters 1.12 to 1.14. What we can expect from plant breeding of energy crops and of sustainable intensification is discussed in Chapters 1.15 and 1.16, from growing algae in Chapter 1.7 and from exploiting the oceans for bioenergy in Chapter 1.18.

From the information given in the 18 subchapters it becomes evident that the expectations set for bioenergy have been too high. It emerges that in Germany the availability of biomass as an energy source is very low relative to Germany’s primary-energy consumption and that few bioenergy sources are without environmental, ecological and climate risks. Without biomass imports only a few percent of Germany’s primary-energy consumption can sustainably come from biomass (mostly renewable wastes; Chapter 1.4).

1.1. Carbon and energy content of biomass, primary energy and final energy

The carbon (C) content of biomass is approximately 50%. This carbon is derived from atmospheric CO₂ during photosynthesis. One gram of C in biomass is derived from 3.67 g CO₂. The average energy content (gross calorific value) of biomass is 37 x 10³ J per g C. In the case of wood, biomass is often reported in solid cubic meters (m³); 1 m³ of wood contains on average about 250 kg C (it varies considerably depending on the water content and wood density).

To estimate the availability of biomass as an energy source, the annual amount of energy fixed into biomass is compared with the primary and final energy consumptions of a country. Primary energy is the energy contained in natural resources, before undergoing any conversions or transformations. In the case of biomass, coal and oil it is the energy of combustion. In the case of non-combustible energy sources, including nuclear energy and all non-combustible regenerative energies, primary energy is the secondary energy that they produce (e.g. electricity). This accounting method (there are others) may lead to an overestimation of the contribution of bioenergy compared to non-combustible regenerative energies by a factor of 1.2 to 3, because of the relatively large conversion losses from biomass (primary energy) to biofuels (final energy) such as bioethanol or biodiesel.16 The final energy is the energy sold to the end-consumers after conversion of the primary energy to useful energy such as electricity, heat and fuels.

The world’s primary-energy consumption is estimated to be 500 x 10¹⁸ J yr⁻¹ and its final-energy consumption to be 350 x 10¹⁸ J yr⁻¹.1 The numbers for Germany in 2010 are about 14 x 10¹⁸ J yr⁻¹ (primary-energy consumption) and 9 x 10¹⁸ J yr⁻¹ (final energy consumption). On average 28% of primary energy is lost during energy conversion and about 7% are used as primary energy for non-energy purposes such as the formation of plastics, paints and synthetic rubber.20
1.2. Net primary production (NPP) in terrestrial systems and primary energy consumption

The net primary production (NPP) is the amount of plant biomass that grows within a year in a given area, neglecting emissions of volatile organic compounds and root exudates as well as above- and belowground litter recycled within a year. It is generally given in grams carbon per square meter and year (g C m\(^{-2}\) yr\(^{-1}\)), or for countries in metric tonnes (t) carbon per year (t C yr\(^{-1}\)). The gross primary production (GPP), which is a measure of the annual photosynthesis of the plants in a given area, is almost twice as high because approximately 50 % of the photosynthesis products are respired by the plants for maintenance and growth.\(^{21}\) NPP is dependent on the solar photon flux, the length of the growing season, the temperature, and the water and mineral supply; the latter can limit growth rates either directly or via photosynthesis and can affect plant respiration. NPP in the absence of human interventions such as deforestation, land use for infrastructure, fertilization, irrigation or soil sealing (Chapter 1.12), is referred to as NPP\(_o\).\(^{22}\)

Aboveground and belowground NPP: In agricultural systems, 20 – 40 % of grassland NPP\(^{23}\) and 70 – 90 % of cropland NPP\(^{24,25}\) generally goes to aboveground biomass.\(^{26}\) In the case of trees 50 – 80 % of the NPP is aboveground.\(^{27-29}\) Averaged by area globally, about 60 % (57 % in Ref. 6) of the NPP are estimated to be aboveground. In countries like Germany with large areas of cropland the average aboveground NPP can be as high as 70%. Of the aboveground NPP on average less than 50 % can be sustainably harvested. In the case of trees only 25 % of the aboveground NPP can be harvested, which can be as low as 12.5 % of the total NPP because in these long-lived organisms most of the NPP is used for leaf and root turn-over, which cannot be harvested.

Limitation of NPP by solar irradiation: When the growth of plants is not limited by lack of nutrients, by water availability (Chapter 1.13) and by temperature (seasonality), NPP is determined by light intensity. The global solar radiation that reaches the earth’s surface and that is absorbed there is about 170 W m\(^{-2}\) (power average during 365 days and 24 hours per day, also accounting for clouds etc.). At the Equator, the average intensity of solar radiation can be more than twice the global average and in Germany it is 115 W m\(^{-2}\) (Chapter 1.4). But the light intensity is not only determined by the geographic zone: for example, in northern Germany the average light intensity is lower (100 W m\(^{-2}\)) than in southern Germany (130 W m\(^{-2}\)), not only because the light intensity increases with decreasing latitude but also because in southern Germany there are more days without clouds, which are also warmer. This is reflected in differences in NPP\(_o\) (Figures 1.1 and 1.2). Consistent with light intensity being the dominant factor is the finding that in the area of the EU-25 the GPP (see above) is almost identical for croplands, grasslands and forests (about 1,200 g C m\(^{-2}\) yr\(^{-1}\)).\(^{8}\) The higher growth rates of crop plants are apparently almost compensated by the longer growth periods of the more slowly growing trees. The average NPP of forests and of cropland in the EU-25 are almost the same (518 g C m\(^{-2}\) yr\(^{-1}\) and 550 g C m\(^{-2}\) yr\(^{-1}\), respectively), whereas the average NPP of the grasslands is about 30 % higher (750 g C m\(^{-2}\) yr\(^{-1}\)).\(^{8}\)

1.2.1. Global net primary production (NPP) and primary energy consumption

On average, the global terrestrial NPP without human intervention (NPP\(_o\)) is approximately 430 g C m\(^{-2}\) yr\(^{-1}\), equivalent to an energy flux of about 16 million J m\(^{-2}\) yr\(^{-1}\) (Figure 1.1). Based on a global terrestrial land area of about 150 x 10\(^{12}\) m\(^{2}\), this results in a terrestrial NPP\(_o\) of about 65 billion t C yr\(^{-1}\) (Table 1.1), which is equivalent to an energy flux of 2,400 x 10\(^{16}\) J yr\(^{-1}\). The actual NPP is estimated to be 10 % lower (60 billion t C yr\(^{-1}\)) than NPP\(_o\) due to human intervention\(^6\) (see below). The global aboveground NPP is estimated to be 34 billion t C yr\(^{-1}\), of which probably less than 50 % with a calorific value of less than 650 x 10\(^{18}\) J yr\(^{-1}\) can be sustainably harvested (Table 1.1).
The global terrestrial NPP is derived from the global terrestrial gross primary production (GPP ≈ 2 x NPP) which has been estimated by various methods to be about 120 billion t C yr⁻¹, a value generally considered as the carbon gold standard. However, recent calculations based on H₂¹⁸O/CO₂ isotope exchange data, although still tentative, suggest that the GPP could be 25 – 45 % greater.

Figure 1.1: Global terrestrial net primary production (NPP) in the year 2000 (modified after Ref. 8). Net primary production (NPP) is the amount of plant biomass that grows within a year in a given area. NPP in the absence of human interventions such as fertilization, irrigation or soil sealing is referred to as NPP_o. Global NPP is estimated to be 65 billion t C yr⁻¹ and global NPP to be 60 billion t C yr⁻¹. The average NPP_o per m² is approximately 430 g C yr⁻¹ using the total land area and 650 g C yr⁻¹ based on only the vegetated area. The global surface area is 510 x 10^{12} m². The global terrestrial land area is about 150 x 10^{12} m², of which only 100 x 10^{12} m² is vegetated land area. Of this global terrestrial land area of 150 x 10^{12} m² about 50 x 10^{12} m² (33 %) are used for agriculture: about 15 x 10^{12} m² (10 %) are croplands and about 34 x 10^{12} m² (23 %) are pastures and grazing lands. About 28 % of the terrestrial area is covered with forests (41.6 x 10^{12} m²). Deserts, mountains, tundra, cities and other land unsuitable for agriculture cover much of the rest of the land. In 2011 the world's average population density was 47 people per km².

**NPP of croplands, grasslands and forests:** Of the global land area of about 150 x 10^{12} m² about 49 x 10^{12} m² (33 %) are used for agriculture: 15.3 x 10^{12} m² (10 %) are croplands and about 34 x 10^{12} m² (23 %) are pastures and grazing lands. About 28 % of the terrestrial area are covered with forests (41.6 x 10^{12} m²). And much of the rest of the land is covered by deserts, mountains, tundra, cities and other land unsuitable for agriculture. The average NPP_o on the vegetated area is about 650 g C m⁻² yr⁻¹ (Figure 1.1). The average NPP on croplands is somewhat higher (about 10 %) than that of forests and somewhat lower (about 20 %) than that on grassland. The NPP_o of vegetated lands can be as high as 1,500 g C m⁻² yr⁻¹, whereas the NPP_o of marginal lands can be less than half the average (Figures 1.1 and 1.2). The NPP on arable land seldomly exceeds 1,500 g C m⁻² yr⁻¹, even under optimal conditions of fertilizer application, water supply (Chapter 1.13) and sunlight exposure (Chapter 1.15 and 1.16).

An expansion of the agricultural area is problematic since worldwide agriculture has already cleared or appropriated 70 % of the grassland, 50 % of the savanna, 45 % of the temperate deciduous forest and 27 % of the tropical forest biomes. This conversion of land for agriculture has made tremendous impacts on habitats, biodiversity, carbon storage, soil conditions and freshwater availability.

Between 1985 and 2005 the world’s croplands and pastures expanded by 1.54 x 10^{12} m² (about 3 % increase) with significant expansion in some areas (the tropics) and little change or even a decrease in others (the temperate zone). The result is a net redistribution of agricultural land towards the tropics with all its environmental threats.
Current and future energy- and biomass demands: Currently, primary-energy demand from industry, transport, and the households of the about 7 billion people on Earth amounts to approximately $500 \times 10^{18} \text{ J yr}^{-1}$. The primary energy is provided from fossil fuel, from nuclear power, and from renewable sources including biomass. Bioenergy contributes with $50 \times 10^{18} \text{ J yr}^{-1}$ to about 10%. The amounts of biomass used directly by humans for food, indirectly for animal feed and for industrial- and energy purposes add up to about $225 \times 10^{18} \text{ J yr}^{-1}$ (Table 1.1).

The global annual primary-energy consumption per person is presently about $70 \times 10^{9} \text{ J per person per year}$. This global annual average is much lower than the average in Europe ($150 \times 10^{9} \text{ J per person per year}$) or in the USA ($320 \times 10^{9} \text{ J per person per year}$). As the wealth of other continents increases, the global annual average is expected at least to double within the next 40 years resulting in a global primary-energy consumption of $1,000 \times 10^{18} \text{ J yr}^{-1}$. Similarly, the amount of biomass used directly and indirectly as food and for industrial purposes may be expected to double over its present value of $225 \times 10^{18} \text{ J yr}^{-1}$ (Table 1.1) if countries like Brazil, China and India reach European living standards and will adopt the diet currently enjoyed in industrialized countries. At the same time the increase in arable land area between 2005 and 2050 is estimated to be about 40%, of which on average less than 50% can be sustainably harvested. For example, the harvest index for forests with an NPP of $22 \times 10^{18} \text{ t C yr}^{-1}$ is only 12 to 13%.

Energy maximally available from wood: The global NPP of forests is near $22 \times 10^{18} \text{ t C yr}^{-1}$ (calculated from the forested area and a global average NPP in forests of about $520 \text{ g C m}^{-2} \text{ yr}^{-1}$). Based on a harvest index for forests of 12.5%, the amount of wood that can be felled sustainably is $2.8 \times 10^{9} \text{ t C yr}^{-1}$ with a calorific value of $37 \times 10^{18} \text{ J yr}^{-1}$. Thus, if all the wood that can be sustainably felled were used for energy purposes, which is unrealistic because some is required for other purposes, then wood could contribute to only 20% of the present world’s primary-energy consumption of $500 \times 10^{18} \text{ J yr}^{-1}$. Carbon accounting suggests that extensive bioenergy production from forest biomass does not reduce anthropogenic climate forcing on decadal time scales. There is a substantial risk of sacrificing forest integrity and sustainability for maintaining or even increasing energy production without mitigating climate change. FAO estimates are that presently firewood with a calorific value of about $24 \times 10^{18} \text{ J yr}^{-1}$ are globally consumed.

### Table 1.1: Global net primary production (NPP) and primary energy consumption in the year 2010

<table>
<thead>
<tr>
<th>Description</th>
<th>NPP $\text{ Billion t C yr}^{-1}$</th>
<th>Calorific value $10^{18} \text{ J yr}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPP $\text{(above- and belowground)}^{a}$</td>
<td>65</td>
<td>2400</td>
</tr>
<tr>
<td>NPP $\text{(above- and belowground)}^{b}$</td>
<td>60</td>
<td>2200</td>
</tr>
<tr>
<td>NPP $\text{(aboveground)}^{b}$</td>
<td>34</td>
<td>1300</td>
</tr>
<tr>
<td>NPP used by humans $^{c}$</td>
<td>6</td>
<td>225</td>
</tr>
<tr>
<td>Primary-energy consumption (2010)</td>
<td></td>
<td>500</td>
</tr>
</tbody>
</table>

---

a) NPP without human intervention.
b) Averaged by area globally, about 60% of the NPP is estimated to be aboveground (57% in Ref. 6), of which on average less than 50% can be sustainably harvested. For example, the harvest index of forests with an NPP of $22 \times 10^{18} \text{ t C yr}^{-1}$ is only 12 to 13%.
c) The amounts of biomass used directly by humans for food, indirectly for animal feed and for industrial purposes.

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[317x482] (www.globalcarbonproject.org)
Potential for future NPP increases: The world’s population of presently 7 billion people is still growing by 70 million per year and this growth (1 % per year) together with the expected growth of primary-energy consumption (5 % in 2010) is not paralleled by an increase in NPP. Rather, the global net primary production has decreased by about 10 % since humans appeared on the scene (Table 1.1). One major reason for this is that many agro-ecosystems have a lower NPP than the vegetation they replace. In addition, NPP is lost due to soil sealing and degradation (the latter resulting from past and present land use) (Chapter 1.12). The overall decrease in net primary production has not been matched by the increase of net primary production from agriculture, although current NPP surmounts the NPP of potential vegetation in some intensively used regions, e.g. northwest Europe and irrigated dry lands such as the Nile valley (Chapter 1.13). As mentioned above, only about 10 % of the terrestrial area is cropland. The continuous increase in crop yields achieved over the last 50 years has in the last years leveled off; past increases were not only due to plant breeding but also to fertilizer application and irrigation (Chapters 1.15 and 1.16) with all the associated climate and environmental risks (Chapters 1.4 – 1.8). Therefore, whether it will be possible to raise NPP over its natural potential over large regions and longer periods of time seems questionable.

Bioenergy potential: Of the $500 \times 10^{18}$ J yr$^{-1}$ global primary energy consumption about 10 % ($50 \times 10^{18}$ J yr$^{-1}$) are presently provided by bioenergy ($1.5 \times 10^9$ t C yr$^{-1}$), which is the main energy source in most underdeveloped countries. This percentage will in the future probably decrease, rather than increase, because the primary energy consumption will increase (see above), whereas the amount of biomass available for bioenergy will probably not increase. At present more than a billion people are suffering malnutrition and lack of food security, because of regional food scarcity. As indicated above, the world’s population of 7 billion is growing by 1 % annually and the amount of biomass used directly and indirectly as food and for industrial and energy purposes is expected to increase from $6 \times 10^9$ t C yr$^{-1}$ (Table 1.1) to $12 \times 10^9$ t C yr$^{-1}$ (without bioenergy) within the next 40 years. Therefore, in the near future it is most likely that almost all the biomass that can be sustainably harvested on Earth will be required for human food (protein, starch, fats and oils), as animal feed (cellulose), as construction materials (wood) or as platform chemicals. These demands leave only very little room for the use of biomass, except for wastes (Chapter 1.11), as an energy source.

The point is frequently made that if the lignocellulosic part of crop plants and grasses could be converted to bioethanol (second generation biofuels) then a larger percentage of the net primary production would become available as an energy source. Since humans cannot digest cellulose there would also be no competition between fuel and fork. However, this argument must be balanced against the use of cellulose by ruminants (cattle, sheep, goats etc) who can digest it and who provide a source of nutrition for humans. Furthermore, the lignocellulosic part of crop plants is also required to replenish the soil carbon, as will be outlined in Chapter 1.12. Cellulose and wood are also major products with a range of other uses.

Comparison of bioenergy with other energies: It is difficult to compare climate and ecological risks caused by generating biofuels from crops with those related to other renewable fuels and to fossil fuels because the use of crop biomass as an energy source competes with its use for human food and for animal feed, which is not relevant to the other energy sources. Suffice to mention that other renewable energies such as photovoltaic electricity and wind turbine electricity rather than bioenergy have to be backed up by conventional power plants for times where there is not enough sun light or not enough wind (Chapter 1.4) and that the mining for fossil fuels can be environmentally very unfriendly and even hazardous. But this cannot be the reason to use crops as energy source where they are needed as food and feed. Even more so, it is important that the immense losses in the human food production chain are reduced (Chapter 1.10).
1.2.2. NPP and primary-energy consumption in Germany

NPP of croplands, grasslands and forests: In Germany approximately 11% of the land is used for infrastructure, 34% for agriculture (NPP = 550 ± 50 g C m⁻² yr⁻¹) and 24% as grassland (NPP = 750 ± 150 g C m⁻² yr⁻¹); the remaining 30% of the land is forested (NPP = 518 ± 67 g C m⁻² yr⁻¹); the NPP in brackets are European averages. The land area of Germany is 357 x 10⁹ m², on which about 82 million people live (230 people per km²). Germany’s annual average NPP (on 89% of the area) is close to 650 g C m⁻². The annual average NPP, on 100% of the area, is about 580 g C m⁻² (Figure 1.2). The NPP of special croplands optimally fertilized, provided with water and exposed to sunlight can be more than twice the average, whereas the NPP of marginal lands can be less than half the average (Chapter 1.15).

Aboveground NPP harvested and grazed: Detailed analyses have revealed two different estimates for Germany’s actual NPP: one by Schulze et al. yielding 175 – 195 million t C yr⁻¹ and the other by Haberl et al. yielding 210 ± 20 million t C yr⁻¹. Their estimates for actual aboveground NPP are 130 million t C yr⁻¹ and 160 million t C yr⁻¹ (Table 1.2). About 70 million t C yr⁻¹ of this actual aboveground NPP are directly removed from ecosystems and used by society as food, animal feed and raw materials. In addition to this, ruminants graze about 20 million t C yr⁻¹.

Of the about 90 million t C yr⁻¹ harvested and grazed, about 10 million t C yr⁻¹ are used as vegetal food for humans, 53 million t C yr⁻¹ as animal feed (including grazed biomass), about 14 million t C yr⁻¹ as industrial wood and firewood (eight year average) and 10 million t C yr⁻¹ for other purposes (mainly seed and industrial uses of agricultural biomass including losses within the processing chain). The about 90 million t C yr⁻¹ do not in-
include approximately 20 million t C yr\(^{-1}\) of straw associated with the harvest of the aboveground NPP (Table 1.2).

**Calorific value of the harvested and grazed biomass:** The aboveground harvested and grazed biomass in Germany (about 90 million t C yr\(^{-1}\)) has an energy equivalent of about 3.4 \(\times 10^{18}\) J yr\(^{-1}\) (Table 1.2), which for comparison is equal to 24 % of Germany’s primary-energy consumption of 14 \(\times 10^{18}\) J yr\(^{-1}\) (Figure 1.3). But this does not mean that 24 % of the primary-energy consumption in Germany could be covered by biomass because most of this biomass is required for food, animal feed and industrial products. The significant energy cost for production of fertilizers, pesticides and machines, as well as the energy needed for manpower, transport and for farm operations (from plowing to harvest) also have to be considered (Chapter 1.4).

**Biomass used for bioenergy:** According to a preliminary assessment for 2010,\(^{44}\) approximately 6 % of the primary-energy consumption in Germany are presently derived from biomass or biomass products plus 0.7 % from renewable wastes: 0.5 \(\times 10^{18}\) J yr\(^{-1}\) from solid fuels, mainly wood; 0.22 \(\times 10^{18}\) J yr\(^{-1}\) from biogas; and 0.19 \(\times 10^{18}\) J yr\(^{-1}\) from liquid fuels (mainly biodiesel and bioethanol; Table 1.2). Most of the biomass is used for heating and electricity production (most of the biogas) rather than for transport, which is of concern since transport fuels are in the long run probably most difficult to replace (Chapter 1.4).

<table>
<thead>
<tr>
<th>NPP (above- and belowground)</th>
<th>185 / 210</th>
<th>6.8 / 7.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPP (aboveground) (^{a})</td>
<td>130 / 160</td>
<td>4.8 / 5.9</td>
</tr>
<tr>
<td>NPP harvested and grazed</td>
<td>89 / 93</td>
<td>3.3 / 3.5</td>
</tr>
<tr>
<td>- Vegetal food for humans</td>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td>- Animal feed including 20 million t C yr(^{-1}) grazed</td>
<td>53</td>
<td>2</td>
</tr>
<tr>
<td>- Industrial wood and firewood (^{b})</td>
<td>14</td>
<td>0.5</td>
</tr>
<tr>
<td>- Other uses (^{c})</td>
<td>10</td>
<td>0.4</td>
</tr>
<tr>
<td>Cereal and rape straw (^{d})</td>
<td>20</td>
<td>0.7</td>
</tr>
<tr>
<td>Embodied NPP from abroad via imports (Chapter 1.9)</td>
<td>70</td>
<td>2.6</td>
</tr>
<tr>
<td>Primary-energy consumption (total)</td>
<td></td>
<td>14</td>
</tr>
<tr>
<td>Primary energy from biomass products (2010) (^{e})</td>
<td>30</td>
<td>1</td>
</tr>
<tr>
<td>- Solid fuels (mainly wood)</td>
<td></td>
<td>14</td>
</tr>
<tr>
<td>- Biogas (^{f})</td>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>- Liquid biofuels (biodiesel and bioethanol)</td>
<td></td>
<td>0.2</td>
</tr>
<tr>
<td>- Renewable wastes including land fill gas</td>
<td></td>
<td>0.2</td>
</tr>
</tbody>
</table>

\(^{a}\) Averaged by area (croplands, grasslands, forests), about 75 % of the NPP is aboveground.

\(^{b}\) Calculated from an average of 56 million m\(^3\) timber per year (2002 – 2009 average) (for calculation and uncertainties see Ref. 28).

\(^{c}\) The value includes seed and industrial uses of agricultural biomass including losses within the processing chain.

\(^{d}\) The value includes about 4 million t C yr\(^{-1}\) of straw used as bedding material for animal husbandry and about 13 million t C of straw left on the fields for humus formation.

\(^{e}\) The energy values do not contain the primary-energy costs for producing this product (see Chapter 1.4).

\(^{f}\) Produced in about 7,000 biogas production plants (beginning 2011) generating together electrical power of about 2,500 MW with an efficiency of 35 %.
In 2008, of the biomass used directly as an energy source, about 20 % were imported; the remaining 80 % were grown in Germany. However, the 80 % domestic biomass for bioenergy were only available because additional biomass for animal feed was imported (Chapter 1.9). The use of wood in Germany as an energy source is quantitatively limited by the amount of wood that can be sustainably cut annually; over the years this has been at an average of about 56 million m³ wood per year, or about 14 million t C yr⁻¹ (2002 – 2009 average) with a calorific value of 0.5 x 10¹⁸ J yr⁻¹ to 0.6 x 10¹⁸ J yr⁻¹ (Table 1.2). Of the felled wood only about 40 % are directly used as an energy source, about 60 % are used for wood products, some of which may be burned later. If all the wood presently felled in Germany were used as an energy source this would contribute about 4 % to the primary-energy requirement of Germany. And even this low contribution would – in the long run – not be sustainable because the amount of wood that is presently felled exceeds the harvest index of 12.5 % for forest by almost a factor of two. The amount of wood presently used as energy source is dependent on imports (see chapter 1.9).

### 1.2.3. NPP in other countries

On average the NPP₀ in the EU-25 is about 550 g C m⁻² yr⁻¹ (Figure 1.2). NPP₀ in Germany is 580 g C m⁻² yr⁻¹, in France 680 g C m⁻² yr⁻¹, in Italy 590 g C m⁻² yr⁻¹, in Great Britain plus Ireland 550 g C m⁻² yr⁻¹, in Poland 560 g C m⁻² yr⁻¹ in Portugal plus Spain 500 g C m⁻² yr⁻¹, in Sweden 430 g C m⁻² yr⁻¹ and in Finland 400 g C m⁻² yr⁻¹ (all figures are approximate, from Table 3 in Ref. 43). Due to human intervention the aboveground NPP in France, Germany and Great Britain plus Ireland is 10 to 20 % higher than the NPP₀, whereas in Poland, Spain and Portugal it is about 10 % lower (see Table 2 in Ref. 43). Only the latter countries have the potential to significantly increase their NPP by land management and fertilization. In North America the average NPP, is near 450 g C m⁻² yr⁻¹, in Latin America and the Caribbean near 800 g C m⁻² yr⁻¹ and in South-eastern Asia near 1,000 g C m⁻² yr⁻¹ (Figure 1.1). In all these countries the actual NPP is some 10 % to 20 % lower than NPP₀ due to human interventions that have led to a net decrease of NPP. The availability of biomass as an energy source varies from country to country (Figures 1.1 and 1.2) and depends mainly on the primary-energy consumption per person, the population density, the natural endowment of the respective country and its yield gap, i.e. the difference between actual and potential future yields. One would expect that the lower the primary-energy consumption per person and the population density, the higher would be the percentage of harvestable biomass that can be used as an energy source. For example, in Germany both the primary-energy consumption per person (170 x 10⁹ J per person per year) and the population density (230 persons per km²) are considerably higher than in Brazil (52 x 10⁹ J per person per year and 22 persons per km²). The difference between Germany and Brazil is even larger considering that in Brazil the NPP is on average about 2 times higher than in Germany (see Figure 1.1). But even in Brazil, bioenergy (mainly bioethanol from sugar cane) presently covers only approximately 30 % of the primary-energy consumption of this country (see Chapter 2.12) and its production is considered to generate environmental and social problems. As other examples: in 2010 the primary-energy...
consumption and population density in France are $180 \times 10^6$ kJ per person per year and 110 persons per km$^2$, in the USA $320 \times 10^6$ kJ per person per year and 30 persons per km$^2$, and in China $62 \times 10^9$ J per person per year and 138 persons per km$^2$.

### 1.3 Human appropriation of net primary production and bioenergy potential

What fraction of the NPP in a given country can be used for energy production, what is the bioenergy potential? In addressing that question, we must consider the NPP that is currently already appropriated by humans for food, animal feed, and for industrial purposes and/or by the negative human impacts on the productivity of ecosystems (e.g. soil sealing; Chapter 1.12).

**Human appropriation of NPP (HANPP):** HANPP is equal to the NPP of the potential vegetation in an ecosystem in the absence of humans (NPP$_o$) minus the fraction of the NPP of the actual vegetation in the ecosystem left after human use. For example, HANPP is 0 % in a wilderness area and 100 % on sealed soils. In land use such as forestry, where stocks (i.e. accumulated biomass over the course of years, decades or centuries) are harvested, HANPP can even be much larger than 100 % of the annual NPP, flow. This occurs if harvest exceeds annual growth. HANPP does not include the energy cost of producing the NPP (fossil fuel energy needed for production of fertilizers, pesticides, cultivation, and harvest).

In Germany the NPP is larger than NPP$_o$; the difference, $\Delta$NPP, is up to -100 g C m$^-2$ yr$^-1$ (Figure 1.4 A). The HANPP is estimated to be $340$ g C m$^-2$ yr$^-1$ (120 million t C yr$^-1$; see Tables 2 and 6 in Ref. 43) which is close to 60 % of the NPP$_o$ of $580$ g C m$^-2$ yr$^-1$ (210 million t C yr$^-1$). Within the EU-25 HANPP is highest in the country group of Belgium, the Netherlands, Luxembourg and Denmark (69 %) followed by Great Britain and Ireland (67 %), Poland (60 %), Germany (59 %), Austria (57 %), Italy (52 %), and Spain and Portugal (44 %) and lowest in Sweden (25 %; Figure 1.4 B). On average, HANPP in the EU-25 is 50 %.

**Bioenergy potential:** Because of the relatively high HANPP in Europe, the potential for increasing the use of biomass as an energy source in the EU-25 is low. Exploitation of the entire bioenergy potential implies risks such as higher contamination of water bodies with fertilizers and pesticides, release of N$_2$O and other GHGs into the atmosphere, and a detrimental impact on biodiversity. The land presently not used by crops is the final remaining habitat for many organisms, and EU-FFH (Fauna–Flora–Habitat–Directive) regulation does not permit action that would result in deterioration of these habitats. Increasing biomass imports, the only option to overcome this constraint, exports the ecological and social risks to other countries (see below).

Based on the relatively high HANPP in Europe (50 % on average), the potential for using biomass as an energy source in the EU-25 has been estimated to be only about 4 % of the current primary-energy consumption in the EU-25. For Germany with an HANPP of 60 % the estimated potential is less than 3 %. However, even this rather small potential disregards the ecological risks of intensive agriculture. Nor does this analysis consider that during the next decades, biomass will be increasingly needed to feed the growing world population and to substitute fossil fuels as raw material for the petrochemical industry.

**1.4 Fossil fuel costs of net primary production, energy returns on investment, area efficiencies and capacity credits**

**Fossil fuel costs:** As already mentioned the figures for the energy equivalent of the harvested and grazed biomass do not consider the fossil energy that is needed to produce and operate the means of biomass production. The fossil energy cost for the production of fertilizers, pesticides and machines as well as the energy needed to drive them and for farm operations (from plowing to harvest) can take a considerable share of the energy produced. The literature, e.g. contains different estimates of the size of this share.

A detailed estimate of the fossil energy costs of biomass production in the EU-25 is given by
The energy costs (as a percentage of the energy equivalent of the harvested biomass) were calculated from CO2 emissions due to fossil fuels burnt in biomass production. These costs were found to be 11% for cropland, 7% for grassland and 3% for forests (see Table 1.4). The analysis assumed that cropland is plowed, harrowed, planted and harvested at least once per year. In addition it is fertilized twice per year and sprayed with pesticides four times per year. All grassland is cultivated and harvested at least once per year and fertilized twice per year. The energy cost of fertilizer production is distributed over crop and grassland in proportion to their surface area. In forestry, 10% of the forest are thinned each year; another 10% are harvested and planted. The harvested timber is transported using a 40 t truck over a distance of at least 30 km (20 km for countries smaller than 100,000 km²). The analysis did not include the energy consumed by the work force or the energy costs of water. Estimates of energy costs of crop biomass production in Switzerland and in the USA have yielded much higher values.

Production of bioenergy also has to include the energy costs of conversion of the harvested biomass to biofuels: such as the costs of lignocellulose pretreatment, ethanol distillation, lipid extraction, and biofuel storage and transport. These costs can range from as low as 10% for wood-chip production from wood, to as high as 100% in the case of first generation liquid-fuel production from maize (Chapter 1.6).

**Energy return on investments (EROI):**

The overall production costs of bioenergy can be quantified by the EROI, which denotes the amount of energy that is returned (energy output) per unit of energy invested (energy input) during biomass production and conversion to, for example, liquid biofuels or electricity. EROI in bioenergy production generally only considers the energy input from fossil fuels (Table 1.3). Thus in bioethanol production from maize or sugar cane the energy costs for distillation are not taken into account if provided through burning of maize stover, sugar-cane straw, wood or renewable electricity.

EROI is high for solid biomass used directly as energy source, e.g. about 10 for wood chips/pellets. EROI is generally much lower for liquid and gaseous fuels formed from biomass, in some cases it may be even less than 1. EROI for biodiesel from rapeseed has been reported to be less than 2,51 for bioethanol from maize in the USA to be between 1 and 1.6,59,60 from sugar beet in Germany to be 3.5,3 and for bioethanol from sugar cane in Brazil to be 8. EROI for bioethanol from switch grass has been estimated to be 5.4,58 EROI for bio-butanol from maize is below 1,54 and for biogas from maize silage in Germany it is 4.8 (combustion energy) and 1.4 (electricity). EROI for biogas derived electricity can be as high as 4.5 if the biogas is converted to electricity with using the low-temperature waste heat output. The EROI of bioethanol production can be considerably increased when wood, or another...
renewable energy sources, provides the energy for ethanol distillation, however this comes at the price of a lower area efficiency. With respect to the EROI, bioenergy production is still a young industry and there is some room for improvements in efficiency.

The EROI of bioenergy, especially first generation biofuels in Europe and the USA, is rather low when compared to other energy technologies. For example, for photovoltaics the EROI is around 7,66,67 for the most modern wind turbines around 18 and for hydro-

power69 it can even be above 100. EROI estimates of nuclear power lie between 10 and 20, but estimates as low as 1 and as high as 50 can also be found in the literature.70 The EROI estimates for nuclear power are problematic because of the still poorly developed database for the costs of deconstruction and making good the damage caused by catastrophes. It should be noted that a technology with a high EROI might still in practice be uneconomic due to the high capital outlay required; this is presently one of the problems of photovoltaics.

**Table 1.3: Energy return on investment (EROI) and area efficiencies of fuel production.** EROI = Energy output/fossil energy input. Fossil energy input includes fossil fuels required for land management, for the synthesis of fertilizers and pesticides, for sawing and harvest as well as for the conversion of the biomass to biofuels. The values given are the highest values found and reasonably documented. The area efficiencies on farming plots are generally lower than on experimental plots. For literature see the text.

<table>
<thead>
<tr>
<th>EROI</th>
<th>Area efficiency (W m⁻²) (year’s average)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Firewood (Germany)</td>
<td>10 a)</td>
</tr>
<tr>
<td>Biodiesel from rapeseed (Germany)</td>
<td>&lt; 2 a)</td>
</tr>
<tr>
<td>Bioethanol from maize (USA)</td>
<td>1.5 a)</td>
</tr>
<tr>
<td>Bioethanol from sugar beet (Germany)</td>
<td>3.5 a)</td>
</tr>
<tr>
<td>Bioethanol from sugar cane (Brazil)</td>
<td>8 x (b)</td>
</tr>
<tr>
<td>Bioethanol from Triticale/maize (Germany) (combined production) (Chapter 2.11)</td>
<td>8 a)</td>
</tr>
<tr>
<td>Bioethanol methane and electricity from lignocellulose (Chapter 2.11)</td>
<td>3</td>
</tr>
<tr>
<td>Bioethanol from switch grass (USA)</td>
<td>5.4 a)</td>
</tr>
<tr>
<td>Bio-butanol</td>
<td>&lt; 1 a)</td>
</tr>
<tr>
<td>Biodiesel from algae (Chapter 1.17)</td>
<td>&lt; 1 a)</td>
</tr>
<tr>
<td>Biogas from maize silage (Germany)</td>
<td>4.8 a)</td>
</tr>
<tr>
<td>Biogas from maize silage (Germany) (electricity)</td>
<td>1.4</td>
</tr>
<tr>
<td>Photovoltaic (Germany) (electricity)</td>
<td>7</td>
</tr>
<tr>
<td>Photovoltaic (Brazil) (electricity)</td>
<td>7</td>
</tr>
<tr>
<td>Wind turbine (Germany) (electricity)</td>
<td>18</td>
</tr>
<tr>
<td>Nuclear power (electricity)</td>
<td>10 – 20 d)</td>
</tr>
<tr>
<td>Hydropower (electricity)</td>
<td>100</td>
</tr>
</tbody>
</table>

a) Combustion energy
b) This high EROI is reached only when bagasse (the residue from sugar cane after it has been crushed to extract the juice) is used as the main energy source for distillation, which is not sustainable because of the resulting loss in soil carbon (Chapter 1.12)
c) Land based standard wind farms; the land between the turbines may be used for agricultural or other purposes.
d) EROI estimates for nuclear power as low as 1 and as high as 50 can be found in the literature.70 The estimates are problematic because of the still poorly developed database for the costs of deconstruction and making good the damage caused by catastrophes.
e) Average power during 365 days and 24 hours a day
Area efficiencies: The total solar energy that annually reaches the Earth’s terrestrial vegetated surface (100 x 10^12 m^2; Figure 1.1) and is absorbed there is about 0.5 x 10^24 J (about 170 W m^-2; average power during 365 days and 24 hours a day, also accounting for clouds etc.). Of this energy, at global scale, only approximately 2.2 x 10^21 J (about 0.5 %) are harvested by plants via the net formation of biomass (60 x 10^9 t C yr^-1; Table 1.1). There are several reasons for this low efficiency: (a) The photosynthetic pigments absorb and use only 47 % (energy wise) of the sun light. Green light, UV- and IR light are not used; (b) only about 10 % of the light energy are stored in the form of NADPH (Chapter 3, Figure 3.2); (c) about one third of the energy stored in NADPH is consumed by photorespiration due to the reaction of ribulose bisphosphate with O_2 catalyzed by ribulose bisphosphate carboxylase; (d) The efficiency is further reduced by continuous damages of photosystem II (D1-protein), which has – at high light intensities – to be repaired three times per hour (Chapter 3); and (e) the photosystems have evolved to optimally use the sun light from sunrise to sunset during which the light intensity increases from 0 W m^-2 to 680 W m^-2 (global average) at noon to then decrease to 0 W m^-2 again. The optimization price is that at light intensities above 150 – 200 W m^-2 (Chapter 1.15) photosynthesis becomes limiting. Under light limitation the maximal efficiency of photosynthesis is 4.5 %, but in nature even an efficiency of 1 % is seldomly reached.8

In Germany the solar radiation that reaches the earth’s surface and is absorbed there is about 115 W m^-2 (100 – 140 W m^-2; year’s average power). An average annual NPP of ca. 650 g C m^-2 in Germany is equivalent to an average rate of about 0.8 W m^-2. The area efficiency of NPP in Germany expressed as a percentage of incident solar energy is thus less than 1 % (0.7 %).9 Even with rich soils and fertilization on experimental plots the efficiency of NPP seldom exceeds 1 % of the average solar energy flux. Furthermore, the percentages are much lower if only the annually produced biofuel is considered. Thus, in the case of biodiesel from rapeseed in Germany the area efficiency is only 60 x 10^9 J ha^-1 yr^-1 (about 1,600 l; 0.18 W m^-2; Table 1.3).9 Finally, the efficiencies on farming plots are always lower than on experimental plots.

The area efficiency of bioethanol from maize in the USA is about 81 x 10^9 J ha^-1 yr^-1 (3,800 l; 0.26 W m^-2), from sugar beet in Europe about 117 x 10^9 J ha^-1 yr^-1 (5,500 l; 0.37 W m^-2), and from sugar cane in Brazil about 150 x 10^9 J ha^-1 yr^-1 (7,000 l; 0.47 W m^-2; density of ethanol at 20 °C is 0.79 g l^-1).3 The small scale combined production of ethanol and biogas from Triticale (two third) and maize (one third) in Germany yields ethanol with an area efficiency of 80 x 10^9 J ha^-1 yr^-1 (3700 l; 0.25 W m^-2; Chapter 2.11). Triticale is a hybrid of wheat (Triticum) and rye (Secale).

The area efficiency of bioethanol from sugar cane in Brazil of 0.47 W m^-2 has to be compared with the solar radiation of 250 W m^-2 (year’s average power) that reaches the earth’s surface in Brazil and is absorbed there. The efficiency of conversion of light energy into bioethanol expressed as a percentage of incident solar energy is thus less than 0.2 % and lower than in Germany where in the case of bioethanol from sugar beet it is 0.23 % (0.26 W m^-2 / 115 W m^-2).

Bioethanol formation from lignocelluloses biomass is most efficient when starchy raw material is added to the lignocelluloses biomass. This scenario leads to an estimated delivery of 65 x 10^9 J ha^-1 yr^-1 ethanol (0.2 W m^-2), electric power of about 5 x 10^9 J ha^-1 yr^-1, and about 90 x 10^9 J ha^-1 yr^-1 methane. This results in an energy gain estimated at 140 x 10^9 J ha^-1 yr^-1 (0.44 W m^-2) and an energy balance calculated as an energy output to fossil energy input ratio of above 3 : 1 (Chapter 2.11). Bioethanol formation from Switchgrass has been estimated to yield 60 x 10^9 J ha^-1 yr^-1 (0.19 W m^-2) with an EROI of 5.4.58

The area efficiency of biogas formation in Germany from Triticale can be as high as 140 x 10^9 J ha^-1 yr^-1 (4,000 Nm³ methane; 0.44 W m^-2) and from maize silage about

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8 see the editorial by H. Michel: Vom Unsinn der Biokraftstoffe; Angewandte Chemie 124, 2566–2568, 2012.
For maize silage area efficiencies can reach under experimental conditions about 350 x 10^9 J ha^{-1} yr^{-1} (10,000 Nm^3; 1.1 W; Table 1.3).

**Comparisons with other renewable energies:** Relative to other energy technologies, bioenergy has only low area efficiencies as exemplified by a comparison with photovoltaics and wind turbine electricity. In Germany the power density of photovoltaic panels is generally above 5 W m^{-2} and of standard land-based wind farms between 2 – 3 W m^{-2} (average power during 365 days and 24 hours a day; Table 1.3). This higher efficiency is not adversely by a higher fossil energy input associated with the construction and installation of solar panels and wind turbines, since their EROIs – as mentioned above – are high: around 7 for photovoltaics, and as high as 18 for wind turbines (Table 1.3). Once installed, photovoltaic cells and land based wind turbines have hardly any maintenance cost.

Non-surprisingly, of the sun-derived energies, bioenergy contributes least to the reduction of GHGs and has the highest financial price per ton of CO2 saved.

**Capacity credits:** Although NPP has a much lower area efficiency of sunlight harvest than photovoltaics and wind turbine electricity, it does have the advantage that its product (biomass and biofuels generated from it) can be stored for later use in large amounts and at high energy density. This is a requirement for applications such as fuels for aircraft, for heavy goods vehicles and for large ships which also in future will most probably not be able to run by electricity. Currently there is limited capacity for storing large amounts of electricity, which is why photovoltaic electricity (during night times and cloudy weather) and wind turbine electricity (when there is no wind) has to be backed up by electricity generated from conventional power plants for times when there is not sufficient sunlight or wind. Thus bioenergy has an advantage as an energy source that can be used to reliably meet fluctuating demands, it has a capacity credit. Bioenergy can support grid stability by providing balancing and reserve power to an energy system with increasing proportions supplied by fluctuating renewable sources. However, this advantage is partly cancelled out by the much lower EROI and the higher net GHG emission.

### 1.5. Greenhouse gas fluxes associated with net primary production

Biomass formation via photosynthesis involves sequestration of the GHG CO2 from the atmosphere. When the biomass is re-mineralized by organisms or burnt the same amount of CO2 is released back into the atmosphere as had previously been removed. But the GHG balance has to additionally consider (a) that biomass growth can lead to oxidation of soil carbon, (b) that intensive cultivation also has a CO2 cost for land management, for the production of fertilizers and pesticides, and for sawing, harvest and transport and (c) that intensive agriculture almost always lead to an increased emission of the GHGs nitrous oxide (N2O) and methane (CH4) as a result of land management, livestock husbandry and the use of fertilizers. In the GHGs balance the CO2 fixed during plant growth has to be disregarded if the biomass used as an energy source is biomass “that merely displaces biomass now used to meet other human needs, or biomass used to maintain or build carbon stocks in plants and soil”.

**CO2 emissions from microbial oxidation of soil carbon:** Intensive cultivation to increase NPP can lead to microbial oxidation of soil carbon to CO2 as a result of plant and microbial activities. Thus net CO2 emission from soil carbon of about 4 % (100 % = CO2 fixed into harvested biomass) occurs in crop-lands in the EU-25 where too much crop residue (e.g. straw) is removed from the fields (see Chapter 1.12). On the other hand, soil carbon is presently increasing in grassland soils and in forest soils: in the case of grassland an equivalent of about 26 %, and in the case of forest about 32 %, of the CO2 net assimilation into harvested biomass ends up as soil carbon (Table 1.4). It is at present difficult to judge whether and when there will be a saturation point of soil-carbon accumulation. The
amount of carbon that can be accumulated in soils depends on the availability of metal ions, such as iron or aluminum.

**CO₂ emissions due to fossil fuel consumption:** Intensive cultivation also has a CO₂ cost for land management, for the production of fertilizers and pesticides, and for sawing, harvest and transport. Fossil fuels are consumed in all these operations generating CO₂. These CO₂ costs are largest for cropland (an equivalent of about +11 % of the net CO₂ assimilated into harvested biomass), less for grassland (+7 %) and lowest for forests (+3 %)⁴⁶ (Table 1.4; see also Chapter 1.4).

Fertilizer production in the Haber-Bosch process has increased by over 800 % in the past 50 years.⁵ GHG emissions from the fossil fuel required for H₂ formation and N₂ reduction increased somewhat less because of higher process efficiency. Presently, more than 1 % of the global primary energy is consumed in this process. ¹⁸

**N₂O and CH₄ emissions associated with the use of fertilizers:** In addition to the CO₂ cost mentioned above, intensive agriculture almost always leads to an increased emission of the GHGs nitrous oxide (N₂O) and of CH₄ (mainly from paddy fields and livestock husbandry) as a result of the use of fertilizers and of land management. The fertilization-associated GHG emissions, which include those from manure, are largest for grasslands (an equivalent of +38 % of the net CO₂ assimilation into harvested biomass) followed by croplands (+26 %) and forests (+22 %; Table 1.4).

**Nitrogen fertilizers are generally applied at a rate of 10 – 20 g N m⁻² per year with approximately 2 to 3 % of the N ending up as N₂O that escapes into the atmosphere.⁶⁶ The N₂O emission factor (percentage of N as fertilizer or biologically fixed N emitted as N₂O), including soil organic nitrogen mineralized following land-use change and NOₓ deposits from the atmosphere, was recently reconfirmed to be about 4 %.⁶⁶ The emission occurs irrespective of whether the applied form of nitrogen is organic or inorganic N (see Figure 1, Introduction, p. 6).

**Greenhouse gas (GHG) potentials:** N₂O and CH₄ have a much higher potential greenhouse effect than CO₂, about 25 fold in the case of CH₄ and about 300 fold in the case of N₂O on a 100 year horizon.⁶⁷,7⁹ Although the tropospheric CH₄ concentration curve has transiently leveled off within the last 20 years⁸⁰,⁸¹ that of tropospheric N₂O has increased linearly with time since the “green revolution”,⁸²,⁸³ as has the CO₂ concentration since the “industrial revolution”. The present tropospheric concentrations of CO₂, CH₄ and N₂O are 390 ppm, 1.8 ppm and 0.32 ppm, respectively.

Nitrogen fertilizers have recently been shown to also be a source of atmospheric nitrous acid (HONO) and OH radicals which strongly influence the oxidation capacity of the atmosphere⁸⁴ and may therefore affect, e.g., the average residence time of tropospheric CH₄.

**Contributions to the anthropogenic greenhouse effect:** Intensive agriculture

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**Table 1.4:** Greenhouse gas fluxes associated with biomass growth in percent of the CO₂ fixed into harvested biomass. The data given are for the EU-25. The margins of error are at least ±10 %. For details see Ref. 46. In forestry about 20 % of the felled material remains in the forest.⁶,¹⁸ Negative numbers refer to uptake of CO₂ / GHGs from the atmosphere and positive numbers losses of CO₂ / GHGs to the atmosphere.

<table>
<thead>
<tr>
<th></th>
<th>CO₂ from soil carbon</th>
<th>CO₂ from fossil fuels</th>
<th>GHGs from manure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Croplands</td>
<td>4 %</td>
<td>11 %</td>
<td>14 %</td>
</tr>
<tr>
<td>Grasslands</td>
<td>-26 %</td>
<td>7 %</td>
<td>18 %</td>
</tr>
<tr>
<td>Forests</td>
<td>-32 %</td>
<td>3 %</td>
<td>21 %</td>
</tr>
</tbody>
</table>

a) Harvest rests
b) Emissions due to the application of fertilizers
contributes considerably to the anthropogenic greenhouse effect and that occurs whether the crops are grown for food (81%, 9.2 million ha), industrial purposes (3%; 0.32 million ha) or biofuels (16%; 1.96 million ha; numbers refer to Germany 2011). Estimates are that agriculture is responsible for 30 – 35% of global greenhouse gas emissions, largely from deforestation, methane emissions from livestock and rice cultivation, and nitrous oxide emissions from fertilizers.

If managed sustainably, the growth of trees in forests is more or less GHG neutral because then they are in a steady state with as many trees being felled as are re-grown and because forests are normally not fertilized. However, it should be noted that forests in Europe are indirectly fertilized through atmospheric N deposition which in turn results in GHG emissions. This deposition is a side effect of burning fossil fuels and intensive agriculture. The GHG balance of forests becomes negative (less CO₂ emitted than assimilated) mainly when the forest area or standing biomass increases. Globally, in the last few years, the world’s forests have been estimate to be a sink of $2.4 \pm 0.4 \times 10^9$ t C yr⁻¹. However, at present harvesting rates in Germany the total biomass decreases, i.e. forests become a CO₂ source.

1.6. Greenhouse gas mitigation potential of using biomass as an energy source and effects of land use change

The emission of CO₂ and N₂O and CH₄ (the latter mainly in paddy fields) as microbial byproducts of plant growth in the presence of fertilizers strongly reduces the mitigation potential of using biomass as an energy source in Europe: by about 42% in the case of croplands, by about 19% in the case of grasslands and by -7% in the case of forests (Table 1.4).

Land use Change: The differences in GHG emissions have to be additionally accounted for when land use is directly changed for energy-plant production. Thus, when forest land is converted to croplands in Europe, the emissions increase by 49%. On the other hand, when croplands are converted to forests there is 49% decrease in GHG emissions which often is larger than the mitigation potential of using the crop biomass as an energy source.

There is also indirect land use change which has to be considered. It occurs if crop-land previously used for food crops is used for bioenergy crops and food production moves elsewhere. This may result in deforestation in other regions. The extent of indirect land use change depends (a) on changes in the food system (i.e. whether the lost food crop production is replaced or not – if not, however, this may result in more hunger), (b) on changes in the yields of food crops (e.g., if food crop production can be maintained through yields increases, indirect land use changes may be reduced or even absent, although in this case the additional emissions from land-use intensification must be taken into account) and (c) on the area required for bioenergy (and therefore the volume to be produced). The scientific uncertainties associated with GHGs emissions due to indirect land use change are still high.

CO₂ costs of biomass conversion into biofuels: Besides the GHG emissions associated with the growth of the biomass, the conversion of biomass into biofuels (wood, bioethanol, biodiesel, biogas) generally has an additional CO₂ cost. With liquid biofuels and biogas from crops and grasses this cost is large and therefore a considerable part of the energy output must always be offset against the fossil fuels used in their production. For example, in biodiesel production with an EROI of 2 (Table 1.3) the fossil fuel CO₂ costs are 50%, in bioethanol production with an EROI of 1.6 the CO₂ costs are about 60%, in bioethanol production from sugar cane with an EROI of 8 the CO₂ costs are about 12% and in firewood production with an EROI of 10 the CO₂ costs are 10% of the CO₂ released upon combustion of the biofuel.

GHG mitigation potential of liquid and gaseous biofuel production: Life-cycle analyses (see below) including land-use change indicate that in most countries, including Brazil, the net-GHG balance of bioethanol or biodiesel production (including CO₂ production from biofuel combustion) is
positive (i.e. net production of GHG). In some cases more than twice as much GHGs are emitted than are fixed indicating that using liquid biofuels instead of fossil fuels does not reduce GHG emissions.\textsuperscript{6,44} Only if fertilization in crop or grass growth is maintained at a low level, if the percentage of biomass converted into biofuels is high, and if the fossil fuel requirement of biomass conversion into biofuels is low, is the emission of GHGs significantly reduced compared to that obtained from burning fossil fuels.\textsuperscript{92}

Application of fertilizers can be kept at a low level in crop and grass growth if only the cellulose part of the plants is fermented to biogas or bioethanol and the fermentation residue (mainly non-fermented lignin and lignocellulose) is subsequently applied to the fields as fertilizer and to increase soil humus formation, thereby closing part of the nutrient cycle.\textsuperscript{65} However, this does not avoid N\textsubscript{2}O emissions resulting from agro-fertilizer application.

**GHG mitigation potential of using wood as energy source:** Life-cycle assessments (see below) indicate that using wood as an energy source can be GHG neutral since growth of trees, if not fertilized, is not associated with a net production of greenhouse gases (Table 1.4) and since the CO\textsubscript{2} costs of firewood production are only about 10 % of the CO\textsubscript{2} released upon wood combustion (Table 1.3). However, because in the long run only 12 to 13 % of the NPP can be sustainably harvested, the amount of wood available as an energy source is relatively limited (Tables 1.1 and 1.2). Yet, wood fuel is only good for the environment if the forests, from which the wood is taken, are sustainably managed and if proper techniques are employed to reduce chimney emissions, especially of particulate matter (black carbon aerosols).\textsuperscript{93} Heating homes with wood gathered illegally in forests and using older home wood-burning stoves is frequently anything but environmentally friendly.

**In summary,** it is judged unlikely that — with the possible exception of wood — biofuels will reduce emissions by even close to 80 – 90 % of the fossil energy baseline as thought possible in the best case scenario in the SRREN.\textsuperscript{84}

### 1.7. Life-cycle assessments and carbon capture

**Life-cycle assessments** of biofuels must include all GHG emitted in managing the land and converting the biomass into usable biofuels, as well as the fossil fuels required to produce the fertilizers and pesticides. The fate of co-products must also be included, such as: straw from cereal crops used for combustion, protein meal from oilseed crops and distillers’ grains used for animal feed. They should include GHG emissions associated with direct and indirect land-use change.\textsuperscript{95} The treatment of the co-products and the way impacts are allocated to them both in the agricultural and the processing phase can significantly change the overall results of an analysis.\textsuperscript{96}

Life-cycle assessments generally do not include ecosystem services such as soil quality and biodiversity changes, fertilization associated emissions of ammonia leading to soil acidification, contamination of groundwater, lakes and rivers with nitrates and phosphates leading to eutrophication, or — in the case of irrigation — effects on the water table and salinization. Life-cycle assessments will be incomplete until these environmental issues are taken into account.\textsuperscript{16,74}

Full life-cycle assessments are difficult to achieve and are subject to ongoing research.\textsuperscript{97} Particular difficulty is caused by: (a) the need to take into account indirect effects such as relocation or intensification of food crop production resulting from bioenergy deployment; (b) these indirect effects depend not only on the production chain, but also on the volume of bioenergy to be produced as well as on the location of production; and (c) the full carbon balance of bioenergy production can only be understood in the context of the entire global land system (i.e. all other land uses).

Life-cycle assessments indicate that liquid biofuel (bioethanol and biodiesel) production and consumption is not sustainable when all important factors are fully taken into account. Bioethanol production from sugar cane in Brazil is no exception.\textsuperscript{91,98} Although the special conditions for biogas result in somewhat more optimistic assessments,\textsuperscript{99–103} the Advisory Board “Agrarpolitik” beim Bundesministerium für
Ernährung, Landwirtschaft und Verbraucherschutz concludes that for the EU the promotion of biogas production should not be continued in its current form. This conclusion was reached mainly because the current promotion of biogas is not convincing in terms of climate policy due to very high carbon avoidance costs and because the resulting cost reductions are very limited.\textsuperscript{104} Biogas can only make a relatively small net contribution to energy supply. Finally, it tends to increase agricultural prices, thus putting a strain on consumers.\textsuperscript{104}

**Carbon Capture:** It has been suggested the production of bioethanol be combined with carbon capture and carbon storage in the form of CO\textsubscript{2} as a means to remove CO\textsubscript{2} from the atmosphere.\textsuperscript{105} This would, however, significantly increase the operational cost. Another possibility to improve the greenhouse gas balance is to convert biomass into charcoal either via pyrolysis (biochar) or via hydrothermal carbonization (HTC). The objective would be to obtain carbon that can be mixed with soil where it is assumed to have a residence time of many hundreds of years. However this assumption has now been shown to be invalid – the residence time is only 2 to 29 years.\textsuperscript{106,107} There is also at present no indication that these techniques can be economically employed at a large scale.\textsuperscript{108} The energy costs of only 3.5\% as claimed in the SRREN (Chapter 2.6.3.3, page 289)\textsuperscript{94} appear unrealistic.

**1.8. Accounting of greenhouse gas emissions from agriculture in international agreements**

In the EU-25 the net GHG balance of agricultural goods production and re-mineralization is positive (i.e., net GHG formation) with Germany probably being, in absolute numbers, the largest agricultural GHG emitter.\textsuperscript{18} Therefore, if in Germany the goal is to reduce GHG emissions, then probably the most promising way would be to move to less intensive agricultural land management for food-crop production (especially less fertilizers and pesticides) rather than to develop intensive energy-crop production. The effect of moving to less intensive agriculture on reducing GHG emissions would be larger than the use of 18\% of the arable land for biofuel production and industrial purposes as is presently the case in Germany.\textsuperscript{97} Such a change could be initiated if all countries of the EU-25 were to include an account of their GHG emissions from agriculture in future international agreements. Germany, Great Britain, France, Italy and others have elected against accounting for agricultural GHG emissions under Article 3, paragraph 4 of the Kyoto protocol.\textsuperscript{109}

In a comprehensive climate policy framework, all greenhouse gas emissions (CO\textsubscript{2}, N\textsubscript{2}O, CH\textsubscript{4}) from agriculture, bioenergy production, and direct and indirect land-use change have to be included, preferably by including these sectors in an emission-trading scheme. This is necessary to provide the right incentives for switching towards low-emission production technologies in agriculture (e.g., mixed systems, precision farming) and restricting additional land conversion for bioenergy production. To prepare for this step, further research is required (a) on measurement of land-use related emissions, and (b) on consequential comprehensive life-cycle assessments of different production systems for agriculture, food, and bioenergy including the use of fossil fuel and manpower for operation as well as GHG emissions. Consequential life-cycle assessments have to be based on multi-sector economic models, which are able to calculate the total marginal change in global GHG emissions due to bioenergy deployment. These comprehensive approaches are complementary to attributional life-cycle assessments, which are based on specific process accounting.\textsuperscript{94}

As indicated in the “Introduction” the European Union (EU) has the objective that by 2020 about 10\% of the fuel used for transport and mobility should come from liquid biofuels. Based on the arguments outlined in the previous chapters and the chapters to come, Germany should insist that the EU 2020 target is given up.

**1.9. Import of biomass**

The net biomass import of countries like Germany results in considerable human appropriation of net primary production (HANPP) elsewhere. This can be quantified using the
indicator of ‘embodied HANPP’ that accounts for all HANPP caused by the production of biomass consumed in the country under consideration (e.g. Germany), including net imports/exports of biomass.\textsuperscript{110} Conceptually, embodied HANPP is similar to ‘virtual water’, i.e. the water required for the production of traded goods.\textsuperscript{111} For Germany’s territory the above and belowground HANPP (about 120 million t C yr\textsuperscript{-1}; 340 g C m\textsuperscript{-2} yr\textsuperscript{-1}) is considerably lower than the ‘embodied HANPP’ (about 190 million t C yr\textsuperscript{-1}; 530 g C m\textsuperscript{-2} yr\textsuperscript{-1}; see Table 6 in Ref. 43) resulting from biomass-based products produced abroad but consumed in Germany. The embodied HANPP (above and below ground) via imports amounts to about 70 million t C yr\textsuperscript{-1} (Table 1.2). This implies that Germany is strongly (about 37 %) dependent on appropriating NPP outside its own borders in order to cover its current biomass consumption. That is, Germany, exports the potential ecological risks and GHG emissions associated with intensive arable land management and forestry\textsuperscript{43} unless it is ascertained that imports (a) are derived from biomass that is grown and harvested sustainably in the exporting countries, (b) do not negatively affect the provision of food and fodder in the exporting countries and (c) do not contribute to environmental conflicts in the exporting countries (e.g. deforestation).

The largest net imports of biomass into Germany are presently approximately 5.4 million t yr\textsuperscript{-1} of soybeans and soybean products that are used mainly as animal feedstuff. This is followed by the net import of about 2.3 million t yr\textsuperscript{-1} of rapeseed, 1.2 million t yr\textsuperscript{-1} of maize and the many products such as coffee that cannot be grown in Germany.\textsuperscript{112,113}

In Germany, on average (2002 to 2009) approximately 56 million m\textsuperscript{3} timber per year (about 14 million t C yr\textsuperscript{-1}, energy equivalent to about 0.50 x 10\textsuperscript{18} J yr\textsuperscript{-1}) are harvested.\textsuperscript{50} This amount is smaller than the amount of timber, wood products and paper that is imported into Germany (111 million m\textsuperscript{3} in the year 2009). However, Germany also exports timber, wood products and paper in considerable quantities (123 million m\textsuperscript{3} in the year 2009). This creates a net-export (12 million m\textsuperscript{3} in the year 2009) of timber and wood-products from Germany.\textsuperscript{50} A flow diagram for the year 2009 is shown in Figure 1.5. Nonetheless, it’s important to note that the wood industry is crucially dependent on this large external trade of wood and wood products. Without wood imports, it would not be possible to export timber, wood products and paper while at the same time gaining, as presently, 0.5 x 10\textsuperscript{18} J yr\textsuperscript{-1} from wood combustion equivalent to about 4 % of Germany’s primary-energy consumption (Table 1.2).\textsuperscript{48}

Although Germany is a net exporter not only of timber and wood-products but also of other agricultural commodities such as wheat (4.5 million t yr\textsuperscript{-1} in 2008), the overall physical trade balance results in an embodied HANPP for Germany that is considerably higher than the HANPP within its own territory, as discussed above.
Also, other European countries strongly depend on appropriating NPP outside their own borders in order to cover their current biomass consumption. Within the EU-25, only France (-15 %), Finland (-27 %), Estonia, Latvia and Lithuania (-18 %) and Sweden (-12 %) are net ‘exporters’ of embodied HANPP. The EU-25 average is about 33% (see Table 6 in Ref. 43).

1.10. Losses in the human food production chain

**Biomass required for food and feed:** On average (all ages, both sexes) the metabolic rate of humans is approximately 11,000 kJ per person per day (127 W). The food energy required to sustain this metabolic rate adds up to \(0.33 \times 10^{18}\) J yr\(^{-1}\) for the 82 million people making up the German population. In Germany and most of Europe, about two-thirds of the food energy is provided by plant products and about one-third by animal products (meat, milk and eggs etc.; e.g., in Germany 62 % plant products and 38 % animal products and in Italy 67 % and 33 %, respectively).\textsuperscript{14,11,19} Globally it is about 80 % from plant products and 20 % from animal products.\textsuperscript{17} To produce the vegetal food in Germany each year approximately 10 million t C plant biomass are harvested (Table 1.2). To feed the animals, about 53 million t C of plant biomass are harvested or grazed annually (Table 1.2) and about 9 million t C are net imported (presently about 5.4 million t yr\(^{-1}\) soybeans and soybean products, about 2.3 million t yr\(^{-1}\) of rapeseed and about 1.2 million t yr\(^{-1}\) of maize; see Chapter 1.9). The calorific value of the more than 70 million t C of plant biomass is > 2.6 \(\times 10^{18}\) J yr\(^{-1}\).

**Losses in the production chain:** To sustain the metabolic rate of the German population calorie wise only 9 million t C of biomass (0.33 \(\times 10^{18}\) J) would be required. In reality 73 million t C are consumed. The calorific losses in the human food production chain are thus enormous. One reason is that the cellulosic part of the biomass, which can be more than 50 %, cannot be digested by humans and that the lignin part can be digested neither by animals nor humans. The main reason is, however, the high consumption of animal products. The immense losses in the animal products production chain are mainly due to the metabolic rate of the animals but also amongst others to the production of about 10 million t C of animal manure (see Chapter 1.11). Globally, the losses in the human food production chain have been estimated to be about 60 %.\textsuperscript{17} Above that, a large volume of food (estimates lie between 30 % and 50 %) is never consumed but instead discarded or consumed by pests along the food supply chain.\textsuperscript{5,18}

The production of animal-based products, such as meat and milk, requires different amounts of plant biomass depending on the particular animal and the feeding strategy. Different animal species have different conversion rates. For example, producing 1 kg of fresh beef meat may require about 13 kg of grain and 30 kg of hay, while 1 kg of chicken meat requires only about 2.3 kg of feed.\textsuperscript{119} As a global average, about 40 % of total global cereal production is fed to animals to produce meat, milk, cheese and other foods derived from animals; this trend is increasing.\textsuperscript{117} Presently astonishing 75 % of the world’s agricultural land is devoted to raising animals.\textsuperscript{5}

Since the losses are highest in the animal products production chain, considerably more plant biomass would be available as a bioenergy source if less animal products were consumed as human food. A reduction in the eating of animal products would also significantly reduce GHG emissions since in Germany most of the agricultural methane emissions are derived from farm animals. It would also provide the land area required for a further move from an intensive to an extensive (less fertilizers, less pesticides, less land management, less animals) agriculture as recommended above (Chapter 1.8).

**Fuel for food discussion:** Globally, maize, wheat, rice and soybeans constitute roughly 75 % of the calories that humans directly or indirectly consume.\textsuperscript{120} The production of fuels from these crops have been assumed to have caused the 2008 spike in food prices which has triggered a food-versus-biofuel debate.\textsuperscript{41} But in a world where a large part of the population is overweight and food is wasted, and another part where much of the population is undernourished, other aspects of food security are just as important to consider:
these include consumer behavior and the access to food through governance, trade agreements and distribution.\textsuperscript{121}

\subsection{1.11. Availability of agricultural and municipal wastes and of straw}

For the application of organic residues and wastes for biofuel production it must be taken into consideration that in Germany nearly all waste materials are currently used in well-established utilization processes and only few residues and wastes are not completely utilized.\textsuperscript{122}

The waste quantity of many production processes is recorded periodically by the Federal Statistical Office ("Statistisches Bundesamt") and presented in the yearly statistic handbook ("Statistisches Jahrbuch").\textsuperscript{123} Residues from agriculture and agro-industry are typically used for animal feeding, compost and biogas production, whereas wastes from municipal collection and wastewater treatment are mostly used in incineration and composting plants.\textsuperscript{124} As a consequence, the utilization of wastes for biofuel production is in the majority of cases in strong competition to existing utilization routes.

We still lack a clear definition of "waste". For example, straw is a major source of carbon for agricultural soils. If too much straw is removed from the fields, the soil carbon content decreases.\textsuperscript{125} Thus, straw should only be regarded as "waste", if the soil carbon content is not being depleted. In the following we do not consider straw to be an agricultural waste (Figure 1.6).

\textbf{Agricultural and municipal wastes:} Wastes from agriculture and agro-industry in Germany add up to about 13.5 million t C yr\textsuperscript{-1}, the largest contributors being beet and potato leaves (3.1 million t C yr\textsuperscript{-1}), liquid manure (5.5 million t C yr\textsuperscript{-1}), farmyard manure (4.4 million t C yr\textsuperscript{-1}) and sugar beet slice residues (0.5 million t C yr\textsuperscript{-1}). The wastes from landscape preservation (1.7 million t C yr\textsuperscript{-1}), municipal waste disposal (2.4 million t C yr\textsuperscript{-1}) and rendering plants (0.4 million t C yr\textsuperscript{-1}) adding up to about 4.5 million t C yr\textsuperscript{-1}) are comparatively low. There are thus about 20 million t C waste per year of which more than half is manure. The numbers given are theoretical potentials.\textsuperscript{126}

Of the manure (10 million t C yr\textsuperscript{-1}) only approximately 15 \% of the theoretical potential is presently used for biogas production.\textsuperscript{127} Liquid manure contains only 6 – 10 \% dry matter making the transport to central conversion plants not energy-efficient when the biogas production units (presently about 7,000 in Germany) are too far away. After fermentation the residues are generally transferred to the fields as fertilizer containing – as liquid manure – high concentrations of ammonium that in the soil is converted to nitrate and nitrite. There are indications of increasing groundwater contamination with nitrate and nitrite near biogas production sites, clearly indicating the need for greater enforcement of existing regulations of the amount of fermentation residue used as fertilizer.

\begin{center}
\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig16.png}
\caption{Amounts of agricultural and municipal wastes and of straw in Germany. The wastes and straw are given in metric tonnes (t) carbon (C) per year (yr)}
\end{figure}
\end{center}
Other residues from agriculture and industrial processing are typically converted into animal feed or are composted, whereas wastes from municipal collection and wastewater treatment are mostly incinerated or composted. Scrap paper is almost completely recycled. Thus the quantity of unused agricultural and municipal wastes (without the unused manure) available for biofuel production is relatively low, probably only about 40% of the waste of 10 million t C yr⁻¹ (without manure), i.e. some 4 million t C yr⁻¹; in energy terms this is equivalent to about 1% of the annual primary-energy consumption in Germany. And even this small percentage in part exists only because imports replace the domestically grown biomass as animal feed.

Although in Germany almost all wastes are already used this does not mean that they cannot be used in more energy-efficient ways. For example, bio-wastes could first be used for biogas production with the non-fermented residues then being composted.¹²⁸

**Straw:** Of Germany’s annual harvest of about 15 million t C of cereal straw and 5 million t C rape straw, approximately 4 million t C are used as bedding material in animal husbandry, and about 13 million t C remain on the field for soil-humus formation leaving at most 3 million t C for various energy applications.¹²⁹⁻¹³¹ Humus formation from straw plowed into the soil is the main input of organic matter to maintain carbon in agricultural soils (e.g. Ref. 132). Without adding new organic matter to soils in excess of root biomass, soils would lose humus, thereby reducing their water and nutrient holding capacities.¹³⁵ At present, the soil carbon pool of cropland soils in most countries is decreasing annually by an estimated 2.6% (see also Table 1.4),⁷⁸ which indicates that harvest by grazing or by farmers exceeds the sustainability limit. In some areas of the world soil is being lost 100 times faster than it is formed (Figure 1.7). Significant losses are also the result of salinization due to irrigation (see below) and of soil sealing by changing the soil so that it behaves as an impermeable medium: for example, compacting by agricultural machinery or covering by impervious materials such as concrete or asphalt. There is general agreement that land-use management and soil fertility should now be a research priority.

Globally, soil carbon contains two to three times as much carbon as either the atmosphere (820 x 10⁹ t C) or the terrestrial vegetation (800 x 10⁹ t C). Soil carbon is mostly organic matter, some of which persists for millennia, whereas other soil organic matter decomposes readily. Molecular structure alone does not control soil organic matter stability; in fact environmental and biological controls predominate.⁵³

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1.12. **Soil quality and intensive agriculture**

Soil does far more than support farming and forestry.¹²⁰⁻¹³³ It stores carbon, filters water, transforms nutrients and sustains biodiversity. In the past the question of how global soils will cope with intensive agriculture has largely been avoided. But it must always be remembered that when the carbon content of soils is not maintained soils lose some of these properties. At present, the soil-carbon pool of cropland soils in most countries is decreasing annually by an estimated 2.6% (see also Table 1.4),⁷⁸ which indicates that harvest by grazing or by farmers exceeds the sustainability limit. In some areas of the world soil is being lost 100 times faster than it is formed (Figure 1.7). Significant losses are also the result of salinization due to irrigation (see below) and of soil sealing by changing the soil so that it behaves as an impermeable medium: for example, compacting by agricultural machinery or covering by impervious materials such as concrete or asphalt. There is general agreement that land-use management and soil fertility should now be a research priority.

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Figure 1.7: Soil quality worldwide (Figure from Ref. 134). Stable soils are those where the rate of soil formation equals, or is higher than that of soil losses by soil being washed from fields by rain, blown away by dust storms during drought, degraded by pollution, by salts concentrated from evaporating irrigation water, by compaction by heavy machinery, by soil carbon being oxidized to CO$_2$ or by soil being literally sealed up as cities pave and roof over it. Soils are formed as rocks break up and dissolve, with help from soil organisms, creating particles that bind with decaying biomass and living microbes to form larger aggregates. These aggregates provide a good balance of mineral and organic nutrients, which are processed by microbes into forms useful for plants. The pores within and between soil aggregates retain sufficient moisture for biological growth, facilitate drainage and allow oxygen to reach plant roots (text from Ref. 133).

1.13. Water requirement of NPP and effects of global warming on NPP

Water requirements of NPP: Plants generally require a lot of water for optimal growth. The water requirement depends on the crop-type, climate and soil conditions. The amount of water needed to grow 1 kg C is 700 l for maize, 900 l for sugar beet and 1,050 l for wheat. Yet, only 0.2 to 0.3 % of the necessary water is used for the formation of organic substances, the vast majority of water is used for transpiration. Maize has the highest water demand in the northern hemisphere in July and August with at least 1,000 m$^3$ water per hectare per month (equivalent to 100 mm rain). In Germany, because of the moderate temperature and relatively high rainfall, cultivation of crop plants does not normally require irrigation. However, in countries with less rain high yields can only be obtained with irrigation and irrigation-dependent NPP is associated with salinisation of soils. The contribution of irrigation to global agricultural productivity is very significant. Irrigation is currently responsible for water withdrawal of about 2,800 km$^3$ yr$^{-1}$ from groundwater, lakes and rivers (70 % of global fresh water withdrawals), is used on about 24 % of the croplands, and is responsible for delivering 34 % of the agricultural production. In the past 50 years the world’s irrigated cropland area roughly doubled. But concomitantly, significant areas have also been lost due to salinisation. The ecological costs of irrigation can thus be high.

Breeding or genetic engineering of plants requiring less water and tolerating higher salt concentrations is one of the pressing goals, but improvement is limited by the fact that CO$_2$ and water vapor are exchanged through the same openings in the leaves, the stomata. Saving water results inevitably in decreased CO$_2$ fixation and thus decreases plant production. Nevertheless, some irrigated crops require less than 0.1 l water per kJ of food while others require twice as much. Irrigation water used for agriculture has to be properly priced in order to avoid over-use and to select for the most sustainable production technologies.
Water requirement for biofuel production: Another problem concerning water is that conversion of biomass to biofuels such as ethanol requires a lot of water (> 10 l water per l bioethanol) which has to be cleaned up after the fermentation in an energy requiring process before it can be released into the environment or be reused again.

Energy costs of ocean water desalination: There are almost unlimited amounts of water in the world’s oceans, but the theoretical energy costs of desalination are already about one half of the energy conserved during plant growth. The calculation is included here because if, as sometimes assumed, the energy cost of desalination was small then in principle water could be available in the future for the irrigation of desert land on which biomass could then be grown as an energy source. The calculation is based on the following facts: The concentration of salt (NaCl) in seawater is 0.6 M (0.6 Mol/l = 3.5 %), this has to be reduced to a concentration of lower than 0.1 mM for the water to be used for continuous plant irrigation; the reduction of the NaCl concentration by a factor of \(10^4\) consumes 22.8 kJ mol\(^{-1}\) NaCl under equilibrium conditions (\(4 \times 5.7 \text{kJ mol}^{-1}\)); under non-equilibrium conditions the energy costs are at least twice as high; for the growth of 1 g C biomass 500 – 1000 ml H\(_2\)O are required; the calorific value of 1 g C biomass is 37 kJ. Using these values it is calculated that about 14 – 28 kJ of energy has to be invested in removing most of the NaCl from seawater in order to be able to use the water for the growth of 1 g C biomass. And this calculation does not consider the energy required to remove the about 30 mM Na\(_2\)SO\(_4\), for water transport to the fields and the water losses during transport. A counter argument could be that if the energy for desalination comes from the sun, then it is for free. However, this is not a valid argument because any process capable of desalination would also be technically capable of directly producing electricity.

Effects of global warming on NPP: Since 1980 the global temperature has increased by 0.13 °C per decade but the warming has not been the same in all cropping regions of the world. Europe, for example, experienced a significant warming, while the United States experienced a slight cooling over the period. At the same time, the precipitation has changed; but the change patterns for precipitation do not always match the temperature change patterns. The impact of these recent climate trends on major crop yields has been modeled for maize, wheat, rice, and soybeans which provide about 75 % of the calories that humans directly or indirectly consume. The data-based model predicts that in the last 30 years global maize and wheat production declined by 3.8 and 5.5 %, respectively. For soybeans and rice, winners and losers largely balanced out. In the United states, which accounts for ca. 40 % of global maize and soybean production, the estimated changes were negligible.

1.14. Phosphate limitation of net primary production in terrestrial systems

Any plans to develop a sustainable use of biomass for energy supply must also acknowledge that the phosphate reserves needed for fertilizers are finite and, although this has recently been questioned, they will possibly soon become limiting. Phosphate fertilization is generally required to produce a high crop yield. However, although sufficient phosphates are normally present in the soils they occur as insoluble phosphates which can be mobilized by the plants only slowly. Microbes interacting with plant roots (mycorrhiza) by excreting organic acids (e.g. citric acid which tightly complexes calcium ions) may enhance the mobilization process thus promoting plant growth. Breeding of energy crops with better mycorrhiza formation is therefore another prerequisite for the long-term use of biomass as a sustainable energy source.

Efficient recycling and recovery of phosphates for re-use in agriculture has to be another goal. German agriculture currently needs about 650,000 t phosphates (\(\text{P}_2\text{O}_5\)) per year of which approximately half is imported. Nearly 300,000 t of the demand can be covered by the application of manure. Additionally, substantial amounts of phosphate can be extracted from municipal and industrial wastewater treatment plants. But wastewater sludge
is incinerated producing insoluble phosphates with an additional energy demand for recovery and conversion to plant-usable phosphates. Also, industrial and city wastes are usually contaminated by heavy metals and their use as fertilizer in forests and fields is prohibited unless contaminating heavy metals are removed. However, this is now technically possible, but does have an extra energy cost.

When agricultural crops are used for biogas production, the phosphate content of the biomass can be recycled completely by using the digestate for fertilization. The anaerobic conversion process used in generating biogas increases the proportion of phosphate, which is then biologically available for crops. However, in the digestate the nitrogen to phosphate ratio can be higher than required by the plants with the result that too much nitrogen is applied to the fields with the fertilizer. Enriched harmful substances and micro-organisms may be another problem.

1.15. Plant breeding for energy crops

Generally, selection and breeding of plants for food production has led to plants with only a slightly higher NPP potential (not much more than 10 % of NPP) in which the NPP is, however, redistributed (e.g. more grains and less straw). A comparison of C_3 and C_4 species growing at ambient CO_2 concentrations revealed that, when sufficient water and nutrients are available, the growth rate (integrated over the year) of plants is limited by available light (below 150 – 200 W m^-2). Consistently, in the area of the EU-25 the gross primary production, which is a measure of the annual photosynthesis of the plants in a given area, is almost identical for croplands, grasslands and forests (about 1,200 g C m^-2 yr^-1). The higher growth rates of crop plants are apparently almost compensated by the longer growth periods of the more slowly growing trees. The average NPP of forests and of cropland in the EU-25 are almost the same (518 g C m^-2 yr^-1 and 550 g C m^-2 yr^-1, respectively), whereas the average NPP of the grasslands is higher by about 30 % (750 g C m^-2 yr^-1). Growth of plants is often co-limited by nutrient and water supply as indicated by increased NPP upon fertilization and irrigation. A growing body of evidence suggests that much of the observed genetic gain in yield during the past 30 years can be attributed to greater resistance rather than to an increase in yield potential.

**Increases in crop yields:** Since 1965 individual crop yields have increased by 70 – 80 %, but the rate of increase has decreased in the last few years. The continuous increase was only partly the result of plant breeding for better allocation of carbon into grain (increased harvest index). It mainly resulted from more intense land management, fertilizer and pesticide application (over 800 % for nitrogen alone) and irrigation, which are associated with the climate and environmental costs outlined above.

Plant breeding, genetic modification and synthetic biology approaches are hoped to lead to new variants of plants with substantially higher net primary production and/or a lower requirement for water and fertilizers. This development would enhance biomass availability at lower ecological costs. However, there is a physical upper limit of production set by available photons (light conversion efficiency into biomass), water, and plant structure; this limit cannot be exceeded, either by applying fertilizer and pesticides or by bioengineering. There is not yet general agreement, where exactly this limit is. A NPP of about 1,500 g C m^-2 yr^-1 is the highest observed under natural conditions (Figure 1.1).

In Europe, the C_4 perennial biomass crop Miscanthus x giganteus has been claimed to yield an average 1,100 g C m^-2 yr^-1 of harvestable aboveground biomass, if the growth of the grass is not limited by the supply of water and nutrients. This finding shows that plants may have evolved with a much higher aboveground NPP than trees or food crops. These species have only recently been introduced into agriculture and therefore are wild species that still need domestication (adoption to the human need exploiting their present properties). Although it is realized that breeding of e.g. Miscanthus may not be that easy, the expectations are high. One of the visions is to engineer grasses that can fix all of their required nitrogen in symbiosis with...
bacteria and thus become at least independent of nitrogen fertilizers.145

Differences between crop and energy plants: With respect to breeding goals, there is an important difference between crop and energy plants. For crop plants, yield is the harvest of seeds or tubers. Seeds and tubers are high-quality products with constituents like starch, lipids and proteins that can be digested. However, their production is energetically inefficient, because it involves re-allocation of resources to store, that no longer contribute to growth of the parent plant. For energy plants, yield is the harvest of the vast majority of the vegetative mass – leaves and stems – composed of a mixture of cellulose, other complex polysaccharides and lignin, which are difficult to digest and also difficult to convert by fermentation to a liquid biofuel.

Currently, there is intensive research aimed at finding ways to use vegetative plant biomass as a source for, e.g., bioethanol production. This will open up new goals for plant breeding. Even in existing crop plants, the goal will shift to maximizing biomass formation, independent of the constraint that this needs to be converted to starch, protein or lipid in seeds or tubers. There may also be considerable potential to breed for or engineer plants that accumulate large amounts of starch, lipids or other high-energy compounds in their leaves and stems. Sugar cane is an effective energy plant because it accumulates large amounts of sugar during vegetative growth in its leaves and stem.147

The high growth rate – high energy content dilemma: In addition to these general problems, the dilemma faced by plant breeders is that bioenergy crops with high growth rates and high energy content per volume are wanted. Plants with high growth rates such as maize, sugar cane and switch grass, generally have low energy contents per volume and a low carbon to nitrogen ratio. They therefore require nitrogen fertilizer for rapid growth; but application of this fertilizer results in emissions of N₂O. On the other hand, plants with high energy content per volume generally have a high carbon to nitrogen ratio and grow slowly. This class would include the full range of existing tree species such as pine, oak, ash and poplar. Trees with a higher growth rate have a lower energy content per unit volume: e.g., the higher growth rate of poplar as compared to oak and ash results in poplar having an energy content which is only half of that of ash and oak (3.6 x 10⁹ J m⁻³ versus 7 x 10⁹ J m⁻³). Therefore, it will be quite a challenge to create a crop with the energy content and carbon to nitrogen ratio of oak or ash and the growth rate of poplar. One way to ameliorate this problem is to use perennials like switch grass, in which nutrients can be recycled form the aboveground parts to the storage roots in the autumn, and then remobilized the next year to support growth again. Maximization of the efficiency of the recycling of nutrients would here be an important and achievable breeding goal.

Other goals of plant breeding: A current goal of plant breeding is to select and breed plants that will expand the land area on which the energy crops can be grown, e.g., plants that are frost or salt tolerant. Candidate energy crops include several grasses (e.g. china grass [Miscanthus], switch grass, reed canary grass, sorghum, woody crops such as willow, poplar, eucalyptus) and oil crops (e.g. in some countries physic nut [Jatropha]). They all potentially have the advantage of being able to grow on more marginal land and to therefore avoid direct competition with food crops. However, such marginal land would probably be also suitable for native tree growth, and most marginal lands are protected under nature conservation rules.

Existing energy crops have already been selected for high yield; hence the potential for further rapid gains in target traits such as yield is likely to be less for these crops than starting with new, less productive crops.150 Such new crops would need to be selected for regional growth conditions in order to optimize yield as compared to native plants.

An interesting goal of plant breeding is to modify plants such that they are better suited as substrates, e.g. for the production of cellulosic ethanol. Modifications to the cell wall composition, which will make the vegetative biomass of maize or of poplar better suited for conversion into fermentable sugars without affecting plant stability, is just one example.146
1.16. Sustainable intensification of crop yields

There are only a few reported cases where a significant increase in yield has been achieved without a corresponding environmental price (increase in greenhouse gas emissions etc.). In some very special cases, alternative agricultural practices, may have led to emissions being reduced while productivity increased. Agroforestry has been reported to be an example of such a sustainable intensification.\(^n\) Undoubtedly, this is an important area of future research.

Whereas in Germany and most EU-25 countries the farm crop yields are already very high, considerable yield gaps as well as abandoned farmland exist in other parts of the world, including Eastern Europe. For example, the average farm maize yield in the Ukraine is presently about 5 t per ha, which is less than 80 % of the yields in most EU-25 countries.\(^h\) Comparison of the farm yields with yields determined on experimental plots suggests that the yields obtained in future could be even higher. However, farm yields are always much lower than the yield potentials determined experimentally under optimal conditions of water and nutrient supply, pesticide control and sun light exposure.

But not only the crop yields per hectare can be increased in Eastern Europe. Additionally, in the Ukraine and Russia there are thousands of hectares of abandoned agricultural land that could probably be re-cultivated. Worldwide, the amount of abandoned and marginal land that could be turned to agricultural use is in the order of millions of hectares (5 % of the arable land). There is therefore still technical potential for increasing the global crop yield. Whether this can be achieved in a sustainable manner requires further investigation. However, the full GHG consequences of using forest land or abandoned agricultural land for bioenergy production will need to be taken into account before embarking on large-scale programs to realize these potentials. Abandoned land can be a substantial carbon sink for decades or even centuries. This carbon sink would be reduced or even nullified if that land were to be used to produce energy crops.\(^m\)

The potential to increase biomass production in a sustainable and carbon-neutral, or at least low-carbon fashion is, in our view, overestimated. For example, the total amount of biomass used by humans in the year 2000 (about 17 % of the aboveground NPP) had an energy value (gross calorific value) of \(225 \times 10^{18} \text{ J yr}^{-1}\); Table 1.1). This includes all biomass used directly and indirectly for human food, including grazing by livestock, use of biomass as a raw material (pulp, paper, construction wood, clothing, etc.), as well as bioenergy. To adequately feed a growing world population and to reduce malnutrition and hunger, the amount of biomass available per year for all these purposes will probably have to double by 2050.\(^n\) The ecological consequences of an additional production of biomass equivalent to \(100 – 500 \times 10^{18} \text{ J yr}^{-1}\) for bioenergy, as thought to be possible in SRREN in the best case scenario, are not comprehensively discussed in the SRREN.\(^s\)

1.17. Net primary production by algae

Microalgae can produce a highly productive and sustainable source of feedstock for biofuels (such as oil for biodiesel) and for other high value products. Microalgae possess several features that make them suitable for exploitation – these include fast growth rates, efficient photosynthesis and high oil yields (up to 75 % of dry weight for \(Chlorella\) and \(Nannochloropsis\) species, for example). As algae are aquatic, they can be cultured in conditions and locations unsuitable for terrestrial crops and do not compete for agricultural land (or freshwater in the case of marine species). Productivity and oil yields per unit area of algae are simply unparalleled within the plant kingdom. Whereas, the NPP of terrestrial plants is on average near 600 g C m\(^{-2}\) yr\(^{-1}\) (Figure 1.1) that of algae can be up to 5,000 g C m\(^{-2}\) yr\(^{-1}\).\(^t\) Microalgal growth systems such as photobioreactors have a small environmental impact and can be incorporated into existing indus-

\(^h\) http://www.indexmundi.com/agriculture/?country=ua&commodity=corn&graph=production.)
trial production chains where carbon and nutrient-rich streams (e.g. CO₂ from flue gases; nitrogenous wastes from municipal and farming operations) can be processed. After the algal cells have been concentrated and dehydrated, oils can be extracted from the biomass paste while the remainder of the biomass can be converted to biogas or refined into a variety of products. A bio-refinery concept, including the production of a range of high value compounds, and recycling of residues would add value to waste products, while offsetting the cost of producing fuels such as biodiesel.

In photobioreactors the high NPP of algae is only obtained with substantial energy input. This energy is needed to continuously mix the algal culture to guarantee a constant exposure of all the cells to light during the day and a constant supply of oxygen at night. Under optimal conditions the energy output only slightly exceeds the energy input from fossil fuels, although more optimistic estimates have been published. A significant scaling up in dimensions would be required for biofuel production with a higher energy return on investment (EROI) and that is not yet in sight. Algal biomass as a biodiesel feedstock demands not only high quality raw material but also large quantities of algal biomass and energy-efficient downstream processing. The industry requires advances in the algal cultivation technology and also an improvement in the cell recovery and extraction processes. Particular problems yet to be solved are large-scale harvesting, the spread of algal diseases, and the extraction of the algal biomass (only about 10 g dry mass per liter of water).

Currently, large volumes of microalgae are cultivated either using extensive and usually low-tech open raceway systems or in contained photobioreactors. At low latitudes, open raceway systems benefit from the high solar irradiation and warm temperature during daytime. Photobioreactors enable cultivation of a wider number of species under more constant conditions and with enhanced areal productivity. Nevertheless considerable optimization is required to increase the scale and efficiency of some commercial equipment – for example, installation of highly efficient artificial lighting may be a key engineering improvement. Since artificial lighting is very energy, and thus cost intensive, it can only be economically employed when the algae are grown for high value products.

With the current perspective, it is not very likely that within the near future algae will contribute significantly to biofuel production. However, algae are already now of interest to industry as a raw material for the production of small quantities of high value compounds. The large scale production of commodity chemicals from main algal biomass constituents in a bio-refinery is also envisaged. The application of algae to the production of bio-solar hydrogen is discussed in Chapter 3 (p. 63).

1.18. Net primary production in oceans

Although globally total gross primary production in the oceans is of similar magnitude to that on land (but only one quarter per unit area if one accounts for the far smaller vegetated land area), there is a striking difference between the standing stock of biomass in the two biomes. About 650 x 10⁹ t C are bound in terrestrial vegetation, whereas in the ocean the standing stock of total plankton biomass at any given moment is only 3 x 10⁹ t C. The difference is partially explained by a much faster turnover of the unicellular phytoplankton due to grazing by zooplankton, but there are other causes of mortality. Hence, more than half of the biomass in the ocean is in form of bacteria and animals living in the water column or on the sea floor, with phytoplankton contributing much less. This is the reason why the oceans can provide humans with so much animal biomass whereas phytoplankton biomass is generally not harvested, although as an exception some algae are harvested and eaten by humans as vegetables. From these observations it is concluded that the oceans are not suited as source of biomass for large scale biofuel production.
REFERENCES

16. NPP, can be higher or lower than the actual NPP. E.g. NPP of land decreases to 0 g C m-2 yr-1 when the land is used for infrastructure. In the case of forests NPPo and NPP are not very different. Conversion of forests into cropland is, in the case of intensive cultivation systems, associated with only a minor increase in NPP because the increased growth rate of crops due to fertilization and land management is compensated by a shorter growing period. When desert land is converted into croplands via irrigation and fertilization NPP is much larger than NPPd.
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39. Seintsch, B. Holzbilanzen 2009 und 2010 für die Bundesrepublik Deutschland. in Arbeitsbericht des Institutes für Ökonomie der Forst- und Holzwirtschaft (Johann Heinrich von Thünen-Institut) (2011).

40. Actually the amount of wood felled presently is – in the long run – not sustainable because it exceeds the harvest index of 12.5% for forest by almost a factor of two. (30% of the area of Germany is forested with a NPP of near 520 g m$^{-2}$ yr$^{-1}$ or 56 million t C per year. 12.5% of the NPP is 7 million t C per year rather than 14 million t C per year). That 14 million t C per year could be felled within the last years can be explained by the fact that the second world war much more wood was felled than sustainably grown so the forests had to be reafforested and that these stocks are now ready for harvest. Another reason is that trees are now felled earlier, after 70 to 80 years rather than after 90 to 100 years. Thus the amount of wood felled in German forests will decrease again to less than 7 million t C per year because the uneven age structure will remain.


43. For details see Haberl. Menschliche Aneignung von Nettoprimärproduktion in Europa: Schlussfolgerungen für Bioenergiepotentiale, in the supplement.


46. For details see Schulze. Nettoprimärproduktion und Bioenergie, in the supplement.

69. The Energy, harvest efficiency of green plant photosynthesis, at non-saturating light, is about 20% when considering only the photosynthetic reaction centers, about 10% after the inevitable losses in the chloroplast and is reduce it to 5% during the peak month of vegetation in the field down to 1% in the yearly average.
71. The Energy harvest efficiency of green plant photosynthesis, at non-saturating light, is about 20% when considering only the photosynthetic reaction centers, about 10% after the inevitable losses in the chloroplast and is reduced to 5% during the peak month of vegetation in the field down to 1% in the yearly average.


95. An example of direct land use change is the conversion of grassland to cropland for bioenergy production. Indirect land-use change (iLUC) occurs if cropland previously used for food crops is used for bioenergy crops and food production moves elsewhere. This may result in deforestation in other regions. The extent of iLUC depends on (i) changes in the food system (i.e. whether the lost food crop production is replaced or not – if not, however, this may result in more hunger), (ii) changes in the yields of food crops (e.g., if food crop production can be maintained through yields increases iLUC may be reduced or even absent, although in this case the additional emissions from land-use intensification must be taken into account) and (iii) the area required for bioenergy (and therefore the volume to be produced).


2. CONVERSION OF BIOMASS INTO MARKETED ENERGY CARRIERS AND PRECURSORS FOR CHEMICAL SYNTHESIS

NICOLAUS DAHLEN, ECKHARD DINJUS, PETER DÜRRE, GERD KOHLHEPP, KATHARINA KOHSE-HÖINGHAUS, BERNHARD SCHINK, THOMAS SENN, RUDOLF K. THAUER, PETER WEILAND AND KAREN WILSON

Fossil fuels are the main source of the world’s energy supply. By 2030, the worldwide energy consumption is projected to have grown by about 60 %, but while it is questionable exactly how long fossil fuel resources will last, they are certainly limited. As the easily accessible fossil fuel resources are increasingly exhausted crude oil prices reach new highs, surpassing US$ 145 per barrel in July 2008. Unconventional sources such as tar sands and oil shale then become economically feasible. Biofuels have been proposed and are already being used as alternative energy resources in the rapidly growing transportation sector (an annual average growth of 3 % is projected over the next twenty years, largely due to increasing mobility in China and India). Transport accounts for 20 % of the primary energy used worldwide and 70 % of all liquid fuels. However, only bioethanol, biodiesel, and renewable diesel are produced at an industrial scale today (approximately $10^9$ l bioethanol and $7 \times 10^9$ l biodiesel in 2007). While Brazil and the United States produced approximately 80 % of the world’s bioethanol, Europe produced about 70 % of all biodiesel in 2007.

Biofuels are made from abundant resources that are available on a global scale. In contrast to conventional fossil fuels, the development of renewable energy sources is not limited by resource availability. Butanol, methanol, and hydrogen. In addition, electricity can be generated from biomass using biofuel cells. In the subsequent text, the production and utilization of these energy carriers will be compared contrasting their energy efficiency and the feasibility of their utilization. The limitations of biomass supply as a general source for biofuel production have been discussed in detail in Chapter 1 (p. 9). The different energy carriers are compared with respect to their Energy Return on Investment (EROI) values and area efficiency in Chapter 1.4 (p. 18) and Table 1.3 (p. 20).
Lignocellulose (wood, straw) is mainly composed of cellulose, hemicellulose, and lignin, of which lignin and cellulose are very difficult to degrade. Although both lignin and cellulose are rather heterogeneous polymers and differ considerably depending on their origin they are termed here in the singular as “lignin” and “cellulose”. Hemicelluloses, which are composed of pentoses and hexoses are relatively easy to hydrolyze when present alone, but are protected from hydrolysis when in a complex linkage with lignin and cellulose. Lignin is a polymer of phenolic constituents that can be degraded only aerobically, mainly by aerobic fungi. The hydrolysis of cellulose to fermentable sugars is catalyzed by cellulases, which are produced by microorganisms but not by most animals. Cellulase-catalyzed cellulose hydrolysis is slow relative to amylase-catalyzed starch hydrolysis, but it is even slower if the cellulose is in a complex linkage with lignin. The formation of biofuels from lignocellulose is therefore dependent on a lignocellulose pre-treatment in order to make all the celluloses and hemicelluloses accessible to cellulases and hemicellulases in a reasonable time. If such a pre-treatment is not possible, biofuel formation from these compounds will be very slow. Pre-treatment of lignocellulose (Figure 2.1) involves mechanical steps followed by the extraction of the celluloses and hemicelluloses with acid or ammonia, and is an energy-intensive process. Alternatively, lignocelluloses can be sub-oxidized with air to syngas (synthesis gas; H\textsubscript{2}, CO and CO\textsubscript{2}) from which liquid fuels can then be formed microbiologically or chemically.

The conventional initial acid-hydrolysis/extraction step in degradation of lignocellulose is the most wasteful step in the process. Recent papers\textsuperscript{6} have reported the use of ball milling as an effective means to induce ‘mechano-catalysis’ between cellulose and clay-based catalysts with layered structures. Alternative approaches make use of ionic liquids that can dissolve cellulose and, if coupled with acidic reagents, also generate selected platform chemicals.\textsuperscript{7,8} Recently, this approach has been applied with solid catalysts\textsuperscript{9} offering both the ease of separation of a solid catalyst with the dissolving power of the ionic liquid – this combination generates exciting prospects for cleaner conversion of cellulose to chemicals. The dissolution of cellulose can be accelerated by a combined application of strong acids with milling.\textsuperscript{10}

2.2. Biogas
The microbial formation of methane and CO\textsubscript{2} (biogas) from biomass is a well-established process, which is equivalent to the degradation
of organic matter in anoxic biotopes such as lake sediments. The process is slow but highly efficient; in principle, the process can be formulated with the non-ligninaceous part of the biomass being converted to methane plus \( \text{CO}_2 \), i.e., one hexose unit forms 3 \( \text{CH}_4 \) and 3 \( \text{CO}_2 \). It is not only sugars and polysaccharides that can be converted to biogas; proteins, fats and other lipids, detergents, nucleic acids, and other products of biological or synthetic origin can also be converted. Lignified biomass (wood, but also parts of grass, hay, straw) is only very slowly converted because – as mentioned above – the wood polymer lignin is not utilized anaerobically and also protects a considerable part of the cellulose from degradation.

Biogas is produced intensively both in large-scale plants and in small local reactors that are distributed across rural areas and are used to dispose of agricultural waste and generate energy on-site. The reactor feed typically consists of animal manure mixed with green waste from field production, and varying amounts of whole-crop silage to maintain a balanced carbon-to-nitrogen ratio. The sludge produced as a by-product is typically applied to crop fields, thus recovering phosphorus and nitrogen fertilizer. Anaerobic biogas reactors are also used to stabilize the sludge produced in wastewater treatment using the “activated sludge process”. More recently, solid household wastes (organic waste; “Biomüll”) are also being treated through a “biogas” process rather than through aerobic composting. Certain branches of industry (food industry, breweries, sugar refineries, paper and fiber industry, etc.), which produce very rich wastewater, prefer to treat this waste by a methanogenic pre-purification in the so-called “Upflow Anaerobic Sludge Blanket” (UASB) reactors and use the biogas produced as an energy source, rather than paying high fees for wastewater treatment at municipal sewage treatment plants.

At present (2011) there are almost 7,000 biogas plants (not including the numerous reactors employed in wastewater treatment) operating in Germany, with a total installed electrical power output of about 2,500 million W.\(^\text{12}\)

In contrast to all other fermentation processes, methane formation has the advantage that it does not depend on pure cultures and therefore does not require microbiologically controlled processing. Moreover, methane escapes the fermentation broth easily and does not require energy-intensive distillation. The disadvantages of this process are the slow growth of the microorganisms catalyzing it and, with this, the low adaptability and sluggish reaction of the system to changing conditions, e.g., changes in the feed composition. Either a one-step or a two-step process can be used; in the latter, (faster) acid-producing fermentations are separated from the subsequent final methanogenic step. This mode is preferred especially with irregular or discontinuous feed supply, as may occur due to the seasonality in the sugar industry. To improve the process and develop shorter turnover times or higher methane yields, thermo-mechanical pre-treatment of the substrate feed or the addition of depolymerizing enzymes (cellulases, hemicellulases, pectinases, etc.) are being applied and further developed.

Of the different biofuels, biogas presently has the highest area efficiency (Table 1.3, p. 20).

### 2.3. Bioethanol

Ethanol is produced from sugarcane in Brazil, from maize in the USA, and from wheat and sugar beet in Europe. In principle, all reducing power (electrons) of the substrate can be converted into ethanol; the process is well-established and can be applied at an industrial scale (see also chapters below). Its major disadvantage compared to methane production is that the production of burnable ethanol requires distillation from the fermentation broth and this requires a major investment of thermal energy. Moreover, ethanol production has so far been limited to the sugar and starch fractions of plants (first-generation bioethanol) and cellulose containing fraction (second-generation bioethanol).

Practical disadvantages of ethanol are that ethanol is corrosive and hygroscopic. Aluminum parts are especially vulnerable to corrosion. As a result, ethanol cannot be distributed in pipelines and must be transported by tanker trucks, rail car, or river barges.\(^\text{16}\) Blending gasoline with ethanol is not feasible at the
production facility or refinery before distribution; blending must occur shortly before use.16

**First-generation bioethanol** fermentation is a mature technology and the product is widely used as a biofuel extender, i.e., as a gasoline additive. Most common are batch fermentations with the yeast *Sacccharomyces cerevisiae*. During the last few years, industrial production strains of yeast have been improved for higher ethanol yields, specific ethanol productivity, inhibitor insensitivity, and product tolerance (up to 20 % ethanol). However, optimal ethanol production rates are obtained at lower ethanol concentrations, in the range of 8 – 9 % ethanol. These low product concentrations require in turn a high energy investment in the distillation process; although, as in Brazil, this may be covered by incineration of the by-product bagasse (stems and leaves of the sugarcane plant). Worldwide, a total of 50 x 10^9 l of bioethanol were used as biofuel in 2007.15 The increasing demand for sugar cane and maize for ethanol production are in serious competition with the food supply. The use of large areas of land for growing monocultures is also criticized as environmentally hazardous. The technical and environmental implications of large-scale bioethanol production from sugar cane will be discussed with the example of Brazil in Chapter 2.12.

**Second generation:** The use of biomass such as wood, agricultural residues, and municipal solid waste is being developed as an alternative raw material for ethanol production, and all efforts should be concentrated on the fermentation of the lignocellulosic fraction, i.e., to producing second-generation bioethanol. The space-time yields that have been achieved for fermentative ethanol production from cellulose still lie below the economic limit. Possible improvements are envisaged in optimizing mechanical, chemical and/or enzymatic (cellulases, hemicellulases) pre-treatment of the lignocelluloses (see Chapter 2.1) and the application of recombinant plants with more easily degradable lignocelluloses. Industrial-scale second-generation bioethanol production is unlikely to be feasible without the use of genetically modified organisms (GMO), which will test the limits of public acceptance. As already mentioned above, second-generation biofuels (Figure 2.1) are currently at a pre-commercial phase, and if they are to meet targets for implementation by 2015 – 2020, significant technical hurdles to the transformation of the lignocellulosic biomass need to be overcome.

**Bioethanol from CO₂, CO, and H₂:** Another option being explored is the thermal sub-oxidation of lignocellulosic agricultural waste materials (but also of carbon-containing waste, such as automobile tires) to CO, H₂, and CO₂ (syngas; see Chapter 2.14), followed by fermentation of these gases to ethanol by specific acetogenic bacteria (e.g., *Clostridium ljungdahlii*). This option is explored with pilot plants by several start-up companies in the USA and in New Zealand. In China the first demonstration plant has gone into operation.

### 2.4. Biodiesel and renewable diesel

**Biodiesel** is the name of the methyl, ethyl, or butyl esters of lipid fatty acids, and the term “renewable biodiesel” is used for the catalytic reduction product of triglycerides with H₂ to hydrocarbons.

**Biodiesel** today is typically a transesterification product of vegetable or animal fats with methanol, yielding fatty acid alkyl esters and glycerol (Figure 2.2). Starting substrates are typically vegetable oils (rapeseed, sunflower, coconut, and palm oil). Worldwide, more than 6.7 billion liter were used in 2007, either as a pure fuel or fuel additive.1,4,5 Biodiesel is produced by transesterification of the parent oil with an alcohol, mostly petrochemically derived methanol because of its low price, but ethanol or butanol can be used as well. The resulting products are FAME (fatty acid methyl esters), FAEE (fatty acid ethyl esters), or FABE (fatty acid butyl esters), respectively, with C₁₄ to C₂₀ carbon chains. The reaction is catalyzed by acids, alkali, or lipase enzymes,7,18 and glycerol is produced as a co-product. Since the oil phase is easily separated from the aqueous starting solution, no distillation is required for this energy carrier. While biodiesel can be isolated by phase separation rather than distillation, there are a number of undesirable energy-intensive purification steps required to ensure that the fuel is free from impurities when using current technology.
Ultimately, climate and economics determine which vegetable oil is used for biodiesel production. While the US rely on soybean oil (400 – 446 l oil per ha) as the major feedstock, European countries prefer rapeseed (Canola) oil (1100 – 1190 l oil per ha) and tropical countries palm oil (2400 – 5950 l oil per ha). Sunflower oil (690 l oil per ha), groundnut oil, cottonseed oil, castor oil, and safflower oil are also being used commercially. In addition, there is growing interest in using oil from aquatic biomass, namely from algae such as *Chlorella spp.*, *Nannochloropsis spp.*, and *Botryococcus braunii*.21

The cost effectiveness of biodiesel synthesis is determined mainly by the manner in which the transesterification step is performed. Conventionally, homogeneous basic catalysts are used, including sodium or potassium hydroxides, carbonates, or alkoxides. Removal of the base and any trace amounts of alkali after the reaction is essential, but is a major problem since aqueous quenching results in the formation of stable emulsions and saponification, making separation of the methyl ester a very energy intensive step.22 Free fatty acids must be removed from the starting oils by an acid-catalyzed esterification step, necessitating additional quenching and neutralization steps, which further increase the energy demands of the process. The use of solid acid or base catalysts offers several process advantages including the elimination of a quenching step (and associated contaminated water waste) to isolate the products, and the opportunity to operate as a continuous process.23-25 In addition, the co-product glycerol will have a higher purity, thus adding value to the overall process.

Basically, biodiesel shares many characteristics with fossil fuel diesel. However, there are significant differences between the biodiesel fuels produced from various vegetable sources, which can lead to damage of diesel engines. Critical points are dilution of motor oil, coking of piston rings, corrosion of hydraulic components, and deposits in the injection system resulting from the production process and fuel aging. These problems have resulted in several automotive manufacturers refusing to sanction the use of biodiesel in some of their models. Newly developed, highly efficient motor technologies require fuel with low sulfur and saturated hydrocarbons, without aromatic compounds. A way out of this problem would be the use of renewable diesel and diesel from BtL (biomass to liquid) biofuels (see below).

The fact that “first-generation” biodiesel was produced from edible oils including palm, rapeseed, sunflower, or soybean oil caused serious issues with changes in land use. In the production of biodiesel, only the lipid fraction of the biomass is used, which amounts to 20 – 50 % of the plant dry mass. The energy yield per m² of agricultural land used for biodiesel is thus lower than that for bio-ethanol, and much lower than for biogas. Consequently, first-generation bio-based fuels and chemicals derived from edible plant materials caused much anguish over competition between land used for fuel crops versus traditional agricultural cultivation. Of equal concern is the deforestation, notably in Indonesia, where vast tracts of rainforest and peatland are being cleared to support oil palm plantations.
The term “renewable diesel” has become standard in the US, while “hydro-treated vegetable oil” (HVO) is still more common in Europe. However, the term HVO is not strictly accurate, because vegetable oil is not the only constituent, it also contains components of animal fat, such as lard and tallow. The triglycerides react with H₂ at a catalyst, thereby forming propane (from the glycerol moiety), CO₂, H₂O, and hydrocarbons (from the fatty acids by splitting the ester bond and removing the carboxyl group; Figure 2.3). Propane can be used as a fuel as well, or as feedstock for the chemical industry. Bio-gasoline (chain lengths from C₄ to C₁₂) is produced as a by-product. The major hydrocarbons of chain lengths between C₁₂ and C₂₀ (well in the diesel range of C₁₀ to C₂₅) are fully saturated, and free of O₂ and aromatic compounds. They are low in sulfur content and produce little nitrous oxide upon combustion, they are thus a superior bio-based diesel fuel, chemically equivalent to fossil fuel diesel. Renewable diesel is about to enter the market in large quantities. In 2006, ConocoPhillips started to produce renewable diesel commercially, and output from its Whitegate refinery in Cork, Ireland has now reached 150,000 l (39,600 US gallons) per day. Neste Oil Corporation announced in May 2008 that it intended to produce 170,000 t of renewable synthetic diesel (brand name: NExBTL) per year from its Porvoo refinery, Finland. Feedstocks include palm oil, rapeseed oil, and animal fats. The same company opened an 800,000 t per year plant for renewable diesel production in 2010 in Singapore.

Figure 2.3: Hydro-treatment routes to convert triglycerides (common neutral fats, center) to renewable diesel (left and right).

Figure 2.4: Production of biodiesel, “renewable diesel”, and “synthetic diesel”.

Conversion of biomass into marketed energy carriers and precursors for chemical synthesis
Renewable diesel can also be produced from biomass after gasification, especially with relatively dry types of biomass. The resulting synthesis gas (syngas) is used in the “Fischer-Tropsch process” and modifications thereof. Such fuel (“synthetic diesel”; Figure 2.4) is known under the brand names SunFuel® or SunDiesel® (a cooperation between Shell, Volkswagen, and Daimler). So-called “renewable jet fuels” with shorter alkane chain lengths and lower freezing points can also be synthesized through this process.

2.5. Butanol

The fermentative formation of butanol and acetone (always as a mixture, together with ethanol) from sugars and starch had started before World War I and was already being applied intensively in the 1930s and 1940s in the USA and South Africa. Subsequently, it became uneconomical because of the availability of inexpensive crude oil. Today, the possibilities of this technique are being reconsidered in the context of advanced process optimization and the use of recombinant microorganisms. In particular, there appears to be a chance to overcome the toxicity barrier of 2% butanol concentration in this fermentation process. Unfortunately, the literature on this subject is often contradictory and does not differentiate sufficiently between the toxicity of externally administered butanol and the tolerance towards internally produced butanol, which may be substantially higher. As with ethanol formation, the second generation of butanol formation through fermentation must largely rely on lignocellulose as the substrate (see Chapter 2.1).

While alcohol fuels have similar properties to gasoline, butanol provides a number of advantages over ethanol. Its energy density is significantly higher. The octane rating of butanol is lower than that of ethanol, but similar to that of gasoline. Butanol has a lower vapor pressure and is thus safer to handle. It is less corrosive and less hygroscopic than ethanol, giving it several advantages over ethanol (see Chapter 2.3).

Butanol can be blended with gasoline well ahead of distribution and can be transported by the existing infrastructure. While ethanol can be blended only up to 85% with gasoline before existing car engines must be modified; butanol can be blended at any concentration without engine modification. Despite its advantageous properties, butanol has not yet entered the biofuel market. However, there is a large market for butanol as a commodity chemical, in which biobutanol is gaining increasing importance (see Chapter 2.9).

2.6. Methanol and hydrogen

Methanol is released by microorganisms from the plant polymer pectin, which makes up only a small amount of plant tissue. Fermentation of biomass to methanol and CO2 is thermodynamically not possible, and neither is the anaerobic conversion of methane to methanol. An incomplete oxidation of methane to methanol with O2 using aerobic microorganisms as a catalyst has been attempted, but has never been achieved industrially. Chemical synthesis of methanol from CO + H2 (syngas) is at present the main source of methanol, substantial amounts of which are used in the transesterification of vegetable oils to “biodiesel” (see above).

Fermentative H2 production is limited by thermodynamics, and at most only one-third (usually substantially less) of the electrons available in biomass can be finally recovered as molecular hydrogen. The major part of the electrons (at least two-thirds) is bound in the acetate residues formed as the most important product of biomass fermentation, and cannot be released as H2 for energetic reasons. Even the optimal fermentation of hexoses (as important representatives of biomass) to 2 acetate, 2 CO2 and 4 H2 is reached only at enhanced temperatures (>60 °C), otherwise, butyrate or ethanol are formed as by-products, with substantially lower H2 yields. Thus, H2 production by biological processes will gain importance only if coupled to photosynthetic reactions (see Chapter 3, p. 63).

2.7. Advanced biofuels

In addition to conventional fermentation products such as methane, ethanol, and n-butanol, there is a range of liquid, readily combustible compounds such as isobutanol (2-methylpropanol) and isoprenes, which can be formed by recombinant microorganisms in anabolism
and are termed “advanced biofuels”. In spite of beneficial properties, these “anabolic fuels” are formed under aerobic conditions and have, with this, the disadvantage that the energy recovered in them is less than 50 % of the energy that was contained in the substrate from which they were synthesized. With “catabolic biofuels” (biofuels produced anaerobically through fermentation), this percentage is in the range of 80 to 90 %. Therefore, such advanced biofuels will be viable only if special properties are required; for example, low freezing points, as with fuels such as “biokerosenes” used to replace conventional jet fuels, together with “renewable jet fuels” (Chapter 2.4).

“Advanced biofuels” such as isobutanol, isopentenol and fatty acid esters produced from plant biomass offer advantages such as higher energy density, lower hygroscopicity, lower vapor pressure, and compatibility with existing transportation infrastructure, as compared to the traditional biofuel, ethanol. Examples of advanced “anabolic” biofuels are isobutanol, isopentenol, and fatty acid ethyl esters produced by recombinant strains of Escherichia coli (Figure 2.5).

2.8. Microbial fuel cells
In fuel cells, electrons from the oxidation of a substrate are transferred directly to an anode from where they flow to an oxygenated cathode, thus establishing an electrical circuit. In microbial fuel cells, bacteria act as the catalyst in the oxidation of organic matter and transfer the electrons to the anode, either via suitable dissolved electron carriers or directly to the anode surface after attachment to it. The mechanism by which electrons can be transferred directly from microbial cells to anode surfaces is not known exactly; among others, so-called nanowires have been proposed as being possible conductors. Ideally, electrons from the oxidation of organic matter arising at the redox potential of the NAD/NADH-couple (-320 mV) could flow through such a device to O$_2$ at a redox potential of +810 mV, thus establishing a voltage of 1.13 V. In reality, maximum voltages in the range of only 0.4 – 0.7 V are reached, because there are voltage losses in all electron transfer processes and also the bacteria consume part of the electrochemical potential for their own energy metabolism. Microbial fuel cells have been discussed as possible energy sources. The limiting factor in this technology is the provision of a sufficiently reactive electrode surface for the active bacteria to become attached to. With this, the process is surface-limited, which curtails its applicability at large scale. Moreover, the microbial communities settling on the electrode surfaces age and need to be replaced with time to avoid a decrease in electron transfer effi-

Figure 2.5: Advanced biofuels that can be produced in genetically engineered Escherichia coli strains. Isopropanol and n-butanol are produced via the traditional fermentation pathways (catabolic biofuels, shaded in gray) under anaerobic conditions, whereas all other alcohols are produced via biosynthetic pathways (anabolic biofuels, shown in red) under aerobic conditions (modified after Ref. 37).
ciency. So far, maximum current densities of $4 - 7 \text{ W m}^{-2}$ have been reached in laboratory-scale reactors for short periods of time and $0.56 \text{ W m}^{-2}$ in pilot wastewater treatment plants. The efficiency of electron transfer to the anode and the maintenance of the anode surface at high electron transfer capacity are the limiting factors in this technology. Thus, although biofuel cells might be applicable in certain niches such as power supply for deep-sea recording devices, there is little chance of them being applied on a large scale for extended periods of time.

2.9. Commodity chemicals

An important component of the strategy to save fossil resources must include substitution not only of fuels but also of the raw materials for the synthesis of chemical compounds of economic interest.

Recent reports have identified several building-block chemicals that can be produced through biological or chemical conversion of biomass. Examples include ethanol ($\text{C}_2$), glycerol ($\text{C}_3$), fumaric acid ($\text{C}_4$), xylitol ($\text{C}_5$), and sorbitol ($\text{C}_6$), but these are all highly oxygenated (typically $\text{C}_x(\text{H}_2\text{O})_y$), and thus very different from traditional hydrocarbons from petrochemical sources. Transformation of these feedstock compounds has to apply a chemistry that proceeds from highly functional to more reduced compounds, quite different from conventional oil-based chemistry which has always had to add functional groups to otherwise inert hydrocarbon structures.

The Department of Energy of the USA (US DoE) identified 12 platform chemicals that can be produced from sugars through chemical or biochemical transformation of lignocellulose biomass (Figure 2.6). When generated from fermentation processes, these molecules are often present at low concentrations (typically $< 10\%$) in aqueous solutions in the presence of other polar molecules. Purification of such fermentation broths is particularly difficult and energetically not feasible – a way of directly transforming the aqueous solution is needed. This chemistry requires catalysts capable of performing organic chemistry in water that are also resistant to impurities present in the fermentation broth and that can transform these platform molecules to a wide range of useful chemical feedstocks.

![Figure 2.6: Possible platform chemicals produced from cellulosic biomass.](image-url)
Such catalysts have to be hydrophilic, stable over a wide pH range, and resistant towards leaching under reaction conditions. The use of organic-inorganic hybrid catalysts may be an option as these allow the hydrophobicity of the catalyst to be tuned to affect the adsorption properties of polar molecules. Mesoporous carbons may also prove suitable for use with biomass conversion, as carbon supports tend to be highly resistant to acidic and chelating media. To transform the functional groups on platform chemicals, catalysts capable of performing dehydration, hydrogenolysis (already discussed in the context of glycerol utilization), and hydrogenation will be required. Many of these reactions employ conventional homogeneous reagents or commercial catalysts. Other popular platform molecules are 3-hydroxypropionic acid as a basis for acrylic acid and its derivatives, and 5-hydroxymethylfurfural (HMF). The latter is produced by dehydration of hexoses and may serve as a basis for the synthesis of a variety of useful acids, aldehydes, alcohols, and amines, as well as the promising fuel 2,5-dimethylfuran (DMF). Levulinic acid is another valuable precursor to a range of chemical intermediates which can likewise be generated by acid-catalyzed dehydration, esterification or metal-catalyzed reduction. While there are a number of studies investigating reduction, there has been surprisingly little work on the esterification of platform molecules using solid acid catalysts. Development of new catalysts and overall process optimization for biomass conversion to fuels or chemicals can be achieved only through interdisciplinary research that will require collaboration between organic chemists, physical chemists, biologists, chemical engineers, and experts in molecular simulation to take advantage of innovative reactor designs.

Using biobutanol as feedstock for the production of commodity chemicals is another valuable option because: i) their market price is higher than that of fuels and ii) production of sustainable materials from bio-based feedstocks is economically more reasonable than their being burnt as biofuels. Traditionally, biobutanol was obtained by fermentation using solventogenic clostridia (Clostridium acetobutylicum, C. beijerinckii, C. saccharobutylicum, C. saccharoperbutylacetonicum). Currently (2011), 11 fermentation plants for butanol production are in operation in China (plus an additional two under construction) and one in Brazil. They all are based on the conventional procedure, using either starch or sugars (from molasses) as a carbon source and separating butanol from other fermentation products by distillation. Compared to current technology, improvement in strains used (engineered for less by-products, higher solvent titer and tolerance), process technology (semicontinuous, continuous), and downstream processing (gas stripping, pervaporation, liquid-liquid-extraction) is possible and will render the fermentation economically competitive and even superior to ethanol fermentation. Also, lignocellulose hydrolysates can already be used, as the clostridia mentioned above use both, C₅ and C₆ sugars. Finally, syngas fermentation has also now entered the commercial stage. The genome sequence of C. ljungdahlii has been determined and a recombinant strain for butanol formation was constructed by using genes from C. acetobutylicum. This paves the way for engineering other constructs, forming essential bulk and specialty chemicals from waste gases, while in parallel reducing greenhouse gas emissions. The genomic blueprint of another carbon monoxide-utilizer has also recently been resolved.

2.10. Biofuel combustion-associated emissions

Biofuels can cause problems when applied in practice, as mentioned in some examples above, i.e., the high hygroscopicity of ethanol and associated corrosion problems, and the heterogeneity of biodiesel products. Further application problems arise with their combustion behaviour, as detailed in this chapter.

The combustion of fuels is a complex series of fast oxidation reactions. Conventional fuels are hydrocarbons consisting only of C and H atoms. Combustion of these compounds produces a series of partly oxidized by-products (aldehydes, unsaturated aldehydes, CO), most of which are harmful to human health.
like conventional fuels, biofuel molecules also contain O atoms (ethanol, biodiesel, etc.), and as a result their behaviour in combustion is far more complex than that of conventional fuels. Most of them produce increased aldehyde emission, a fact that has recently been discussed with respect to air quality in Brazil and related photo-smog formation. Biofuels may also contain nitrogen constituents, e.g., from fertilizers, which can give rise to $\text{N}_2\text{O}$ emission. Other by-products may include hydrogen cyanide, ammonia, iso cyanic acid as well as acrylamide, acetonitrile, propene nitrile, or aromatic nitrogenated compounds. Further problems can arise with fuel viscosity (plant oils), incomplete combustion inside the combustor, formation of solid deposits, and production of by-products in the exhaust gas. Whereas stationary large-scale power generators can be optimized towards combustion efficiency and minimization of by-product formation, e.g., by exhaust gas after-treatment, vehicle engines in particular may face substantial problems from the use of complex fuel mixtures and changes in fuel composition, especially regarding cold starting, temperature fluctuations, ignition behavior, etc. The strict regulations on exhaust gas quality, developed for conventional fuel combustion, will be hard to meet with complex fuel mixtures of biological origin. Pollutant emissions from such novel and diverse fuel sources will require new regulations.

Thus, the assessment of the suitability of a bio-derived fuel should include the downstream aspects of hazardous combustion emissions. Knowledge on some chemical families of pollutants is becoming available, while others may be undetected or underestimated. Exhaust gas after-treatment for biofuel combustion will probably necessitate changes in catalysts to reduce such emissions. As another caveat, the term biofuel suggests a homogeneous class of chemicals, while in reality their molecular structures and combustion reactions are widely different. Each biofuel must thus be assessed separately for its value, including its pollutant emission potential. With growing demands for biofuel application in many regions of the world, informed choices will be crucial.

2.11. **Best practice example: Combined production of ethanol and biogas**

Bioethanol is usually produced in large-scale plants (100,000 t per year from 50,000 ha), in North America and Europe mostly from cereals but with an increasing contribution from sugar beet in Europe. This process usually operates with an energy output: fossil energy input ratio of less than 5:1 (Table 1.3, p. 20) provided that the residue from the distillation process, the dried distillers grains and solubles (DDGS), is included as high value feedstock in the energy and eco balances. For life-cycle analyses of large-scale first-generation ethanol production the reader is referred to the reports of Rettenmaier et al.

**Bioethanol from Triticale:** Compared to large-scale ethanol production, bioethanol production in small-scale regional production plants is more sustainable. These plants are able to produce about 5,000 t ethanol per year from 2,500 ha of field area. This technology could be put into practice in Germany without any harmful land-use change effects by using existing farm distilleries that are leaving the state monopoly. The characteristic of these regional production plants (Figure 2.7) is the combination of a distillery (milling of grain, mashing, fermentation, and distillation) with a biogas plant. The scenario begins with crop production, which uses two-thirds of the cultivated area for Triticale production and one-third for the production of maize silage. With this methodology, ethanol is produced only from the Triticale grains. The maize is harvested as intact plants and stored as silage. One-third of the Triticale straw is harvested, while the residual straw is left on-site to maintain the soil carbon content. This scenario represents conditions in the Münsterland area in Germany.

The maize silage and the harvested straw together with the residue remaining after distillation are used for biogas production. The methane produced is then used in a combined heat-and-power production plant to supply the distillery with electricity and heat, the fermentation residues are used as fertilizer for the following crop. The final products are ethanol, a
surplus of methane that is not needed for energy supply, and a small surplus of electric power.

Sustainable ethanol production as described here results in greenhouse gas (GHG) emissions of only 19.7 g CO₂-equivalent per 10⁶ J for ethanol and 22.4 g CO₂-equivalent per 10⁶ J for methane production. This results in an overall GHG reduction of 76.5 % (detailed analysis in Table 2.1). This sustainable agrarian production of ethanol and biogas is one of the most efficient bioenergy pathways known.

From the energy point of view, this sustainable method of ethanol production results in an energy gain of about 80 x 10⁹ J ha⁻¹ yr⁻¹. Growing maize under the same conditions on 100 % of the land area and using it to produce only biogas would be the most efficient process of energy production from biomass. The energy gain would be about 104 x 10⁹ J ha⁻¹ yr⁻¹: comprising 51 x 10⁹ J ha⁻¹ yr⁻¹ of energy delivered as electric power and 53 x 10⁹ J ha⁻¹ yr⁻¹ as heat. This comparison shows that the energy gained from producing a liquid, dense, and easy to handle energy source in the form of bioethanol and biogas production. The distillery is an ideal heat sink for the biogas plant.

**Bioethanol from lignocelluloses:** With second-generation bioethanol, one has to take into consideration some basic limitations of ethanol fermentation from biomass. Some facts are shown in Table 2.2. The data clearly show that besides biomass pre-treatment and cellulose hydrolysis, additional process steps are necessary to convert lignocellulose biomass to ethanol. Distillation consumes 65 to 80 % of all the energy consumed in the process of generating ethanol from cereals; figures calculated without accounting for drying the distillation residue and assuming an ethanol content of about 11 to 14 % by volume. Distilling a mash containing only 5 % or less ethanol needs three times more energy. Thus, one has either to accept this energy demand or to develop new methods of concentrating mash via evaporation or membrane technology.

If regional plants in combination with biogas production are used for lignocelluloses biomass ethanol production there is a simple solution to the energy problem: namely, to add starchy raw material to the lignocelluloses biomass mash after cellulose hydrolysis, this would ensure ethanol concentration of about 11 % by volume or more.
Table 2.1: Greenhouse gas (GHG) emissions of process steps in regional bioethanol production. EtOH = Ethanol.

<table>
<thead>
<tr>
<th>Process</th>
<th>GHG emissions, g CO₂ equiv. / 10⁶ J EtOH without allocation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Crop production</strong></td>
<td></td>
</tr>
<tr>
<td>Seed supply</td>
<td>0.68</td>
</tr>
<tr>
<td>Supply of fertilizers</td>
<td>2.4</td>
</tr>
<tr>
<td>Emissions from N-fertilization (N₂O)</td>
<td>19.58</td>
</tr>
<tr>
<td>Supply of pesticide</td>
<td>1.05</td>
</tr>
<tr>
<td>Diesel oil consumption</td>
<td>4.98</td>
</tr>
<tr>
<td>Sum of crop production</td>
<td>28.69</td>
</tr>
<tr>
<td>Diesel oil consumption in transport to conversion: all crops 25 km</td>
<td>0.88</td>
</tr>
<tr>
<td><strong>Ethanol processing</strong></td>
<td></td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>0.085</td>
</tr>
<tr>
<td>Water supply</td>
<td>0.087</td>
</tr>
<tr>
<td><strong>Biogas production</strong></td>
<td></td>
</tr>
<tr>
<td>Methane losses 1 %</td>
<td>9.02</td>
</tr>
<tr>
<td>Transportation of fermentation residues 25 km</td>
<td>2.75</td>
</tr>
<tr>
<td><strong>Sum of conversion</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>11.95</td>
</tr>
<tr>
<td><strong>Transportation of ethanol to station 100 km</strong></td>
<td>0.51</td>
</tr>
</tbody>
</table>

Table 2.2: Restrictions of ethanol production from lignocellulose biomass with respect to the ethanol concentrations that can be reached after fermentation. LA = Liter alcohol; DS = dry substance; EtOH = Ethanol.

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Glucan content %</th>
<th>Pentosan content %</th>
<th>Theoretical ethanol yield LA/100 kg DS</th>
<th>Possible DS content in process %</th>
<th>EtOH in mash % vol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maize silage</td>
<td>30 – 50</td>
<td>15 – 20</td>
<td>30.5 – 47.0</td>
<td>22</td>
<td>6.7 – 10.3</td>
</tr>
<tr>
<td>Straw</td>
<td>32</td>
<td>21</td>
<td>31</td>
<td>15</td>
<td>4.7</td>
</tr>
<tr>
<td>Grass silage</td>
<td>25</td>
<td>21</td>
<td>28.5</td>
<td>10</td>
<td>2.85</td>
</tr>
</tbody>
</table>

As an example, maize silage is pre-treated mechanically and hydrothermally. Fine-milled grain is then added directly to this lignocelluloses biomass mash giving a natural pH value of 4.0 – 4.2. At present, the best method of degrading the starch is the use of the Stargen® enzyme complexes. After two hours of starch pre-hydrolysis in parallel to the continued enzymatic cellulose hydrolysis, fermentation is started as an SSF-process by addition of yeast and saccharifying enzymes.

This scenario leads to an estimated delivery of electric power of 4 x 10⁹ to 5 x 10⁹ J ha⁻¹ yr⁻¹, 65 x 10⁹ J ethanol per ha per year, and about 90 x 10⁹ J methane per ha per year. This results in an energy gain estimated at 140 x 10⁹ J ha⁻¹ yr⁻¹ and an energy in calculated as an energy output to fossil energy input ratio of above 3 : 1. The estimated amount of avoided GHG emissions will sum up to 12.3 t of CO₂-equivalent per ha per year, i.e., a reduction by about 82 % compared to the use of fossil fuels.⁶⁸

### 2.12. Large-scale bioethanol production in Brazil

In 2009, about 47 % of the total energy supply of Brazil was derived from renewable resources, mainly biomass (32 %; Chapter 1.2, p. 11) and hydropower (15 %). The biomass resource comprised 18 % biofuels, and 14 % firewood and charcoal. Eolic (wind power) and solar energy are still in their infancy, but may
have good prospects. The remaining 53 % was from fossil fuels, comprising: crude oil 38 %, natural gas 9 %, coal 5 %, with nuclear power only 1 %.\textsuperscript{69} The Brazilian population density is only about 10 % and the energy consumption per person only about 30 % of that in Germany, while the average net primary production (NPP) in Brazil is two to three times higher than that in Germany. Thus, the conditions for biofuels to contribute significantly to the primary-energy consumption are more than 50 times more favorable in Brazil than in Germany (Chapter 1.2, p. 11).

Ethanol production in Brazil is based on sugar cane. Crop area and production of sugar cane has increased enormously in the last two decades, from 270 million t cut sugar cane on 4.3 million ha in 1987, to about 600 million t on 8.7 million ha in 2009 (the latter amounts to 11.3 % of the total cultivated area of Brazil; 2.3 % of total farm area). Today, about 50 % of the sugar cane area (Figure 2.8) is used for ethanol production. Sugar cane production is concentrated in the state of São Paulo (62 %), but is expanding to the states of Paraná, Goiás, Mato Grosso do Sul, and Mato Grosso.

The productivity per ha of Brazilian ethanol from sugar cane (7,000 l; 0.5 W m\textsuperscript{-2}; Table 1.3) exceeds European sugar beet (5,500 l), and is much higher than that of ethanol from maize in the US (3,800 l) and wheat in the EU (2,500 l)\textsuperscript{70,71} (Chapter 1.4, p. 18). The US Environmental Protection Agency (EPA) considers sugar cane ethanol from Brazil to be the best renewable low-carbon fuel. After the United States, Brazil is the second largest and above all the cheapest producer (40 % of the US cost per liter) and the largest exporter of fuel-grade ethanol. Ethanol production becomes profitable at an oil price of more than US$ 40 per barrel.

The energy return of investment (EROI) of ethanol production in Brazil (energy output / fossil energy input) is about eight and cannot be matched by ethanol production from grains in the United States (EROI < 2; Table 1.3).\textsuperscript{74} The exceptional efficiency of Brazilian ethanol production depends mainly on sugar cane as source of substrate, productive soil conditions and favorable climate, but also on inexpensive labor, and a high level of technological expertise.

In 2009, more ethanol than gasoline was used in light vehicles in Brazil. At the end of 2010, 430 ethanol distillation plants existed in Brazil: 43 % in the state of São Paulo, 9 % in Minas Gerais, and 8 % each in Pernambuco, Alagoas and Paraná, with small-scale production developing in Mato Grosso do Sul, the Triângulo Mineiro, and Goiás. Widespread interest of oil companies in participating in ethanol production can be observed. Today, 22 % of the distillation units are controlled by foreign capital.

Currently, more than 92 % of all new light vehicles in Brazil (12 million cars or 43 % of the total fleet of cars) are using flex-fuel engines. First introduced in 2003, flex-fuel engines are a German invention that can be fueled with gasoline, ethanol, or any mixture of both. Thus, it is possible to choose the type of fuel according to the price. Nearly all international car manufacturers are producing vehicles in Brazil, which can use fuel with a much higher proportion of ethanol (E25 – E100) than proposed in Germany (E10), obviously without major technical problems.

According to European criteria, Brazilian ethanol has a CO\textsubscript{2} reduction standard of about 70 %;
the International Energy Agency calculated it to be above 80%. Since 1975, the use of ethanol (E25) instead of gasoline is claimed to have avoided more than 600 million t CO₂ emissions in Brazil. Nonetheless, the ethical, social, and ecological implications of large-scale sugar cane production are also being disputed with serious criticism.75

It has been argued76 that ethanol production is not to be blamed for tropical deforestation because sugar cane plantations and potential crop areas are far from the rainforest of Amazonia (which is not the case for soybean cultivation for biodiesel production). Sugarcane expansion into the savanna (campos cerrados) is also not considered to be the main cause for the creation of livestock pasture in Amazonia and thus not to cause deforestation; livestock farming in the campos cerrados is intensifying as rough pasture is improved. Also, the typical energy crop versus food crops rivalry is not a major topic in Brazil, because grains are not used for ethanol production, as they are in ethanol formation from maize. The shifting and in some cases the reduction of food cropland is claimed to be more than compensated by the increasing productivity of food production at the national scale, in the case of beans and rice between 1990 and 2010 productivity increased by 44% and 53%. In Brazil, rising basic food prices have probably not been due to diminishing production, rather they have mainly been caused by higher oil prices, increases in the price of fertilizer and pesticides, transport costs as well as capital market speculation. Finally, the ecological and social conditions of ethanol production have greatly improved in recent years, especially in the Brazilian main production area of the state of São Paulo, thus approaching European standards (in detail, see Ref. 70). The German-Brazilian Agreement on Energy in May 2008 underlines the principles of European legislation: imports of Brazilian ethanol are subject to criteria on the ecological and social sustainability of their production.

Full life cycle assessment (Chapters 1.6 and 1.7, pp. 24 and 25) indicate that bioethanol production in Brazil is much less environmentally and climate friendly than outlined in the paragraph above.

### 2.13. Hydrogen storage via microbial methane formation

There is also a biological perspective to the storage of H₂. Methanogenic archaebacteria transform 4 H₂ with CO₂ to methane, which still contains about 80% of the energy initially present in H₂, i.e., one liter of methane gas contains about 80% of the caloric value of four liters of H₂ gas. Due to its far lower boiling point, methane can be stored much more easily than H₂. The CO₂ required could be derived from coal-fired power plants, thus rendering this storage process greenhouse gas neutral. Nonetheless, the energy needed for fast and efficient transition of H₂ and CO₂ from the gaseous into the liquid phase must first be minimized before this process can be applied at an industrial scale.77,78

### 2.14. Thermochemical path from biomass to fuels

The biochemical processes described above proceed in aqueous solutions at ambient temperature or slightly above. Thermochemical reactions like pyrolysis, combustion and gasification proceed at high temperatures using dry biomass, mainly low moisture lignocellulosics like wood or straw. These technologies for converting biomass to H₂ or various organic chemicals and fuels have profited greatly from well-known coal conversion technologies. The different chemical behavior of coal and biomass is due to the different elemental composition. Dry and ash-free lignocellulosics – the most abundant type of biomass – can be considered to a close approximation as a 50:50 (percentage by weight) mixture of C and H₂O, but with about 20% higher heating value due to the presence of C–H and C–OH bonds.

#### Basic thermochemical process concept:

For the production of organic chemicals and fuels, biomass is usually first converted into syngas, a mixture of CO and H₂. Syngas is a versatile chemical intermediate (platform chemical) for the production of different chemical products. To convert syngas to a particular product requires highly selective catalysts at defined temperatures and pressures and a suitable...
H₂/CO–ratio. The synthesis processes downstream from syngas generation are well-known and mature technology. Table 2.3 summarizes the operating conditions and catalysts for major products. Because syngas can be produced from coal, natural gas, oil or biomass, at present the major development efforts for thermochemical biomass conversion processes are focussed on the front-end steps in syngas generation, i.e., the conversion of biomass to syngas.

**Energy efficiency**: In the thermochemical conversion process, about 50 % of the initial chemical energy is recovered in the final products, the other half being converted to (high temperature) heat, steam or electric power. This energy serves to supply the process itself, after which any surplus can be exported, for example as electricity, acting as an energy “credit” for the main product.

**Outline of a thermochemical biomass to liquid (BtL) process**: here we describe the bioliq process developed by the Karlsruhe Institute of Technology (KIT).79 This is a typical example of the worldwide development effort that is working towards an economic BtL conversion. Currently, the KIT bioliq facilities for biomass pyrolysis, gasification, syngas cleaning and synthesis are operating as pilot experiments. Commercial and economic operation would require a scaling-up by at least 20-fold for the pyrolysis in the front-end section and about 1,000-fold scaling-up for the gasification, gas cleaning and synthesis section. For large commercial plants with a biogas output of at least 1 Mt per year – about 10 % of a modern oil refinery – a biosyngas-based fuel manufacturing cost is estimated at about € 1 per liter. With the present crude oil price of some US$ 110 per barrel, petroleum is about 1.5 times cheaper. In central Europe, biosyngas-based fuels will become attractive at crude oil prices above US$ 150 per barrel.

**Description of the BtL process**: The KIT bioliq process developed in Karlsruhe, Germany, consists of five successive steps:

1. **Biomass pyrolysis**: Low-moisture lignocellulosic biomass is rapidly decomposed by fast pyrolysis at about 500 °C to solid charcoal, liquid tar, aqueous pyrolysis condensate and pyrolysis gases. Pyrolysis gas combustion supplies the heat required for the pyrolysis process.

2. **Bio-slurry preparation**: Pyrolysis condensates and pyrolysis charcoal powder are mixed to a very compact liquid bio-slurry or pasty bio-sludge. This condensed, compact bio-sludge can be transported economically in silo vessels over large distances to a large-scale central facility.

3. **Entrained flow gasification**: The bio-sludge is pumped into a large slagging pressurized entrained-flow gasifier and is atomized with O₂. A tar-free, low-methane syngas is generated at 1,200 °C or more at high pressure (up to about 100 bar above the downstream synthesis pressure) with an H₂/CO ratio of 0.5 – 1.0.

### Table 2.3: Important products from catalytic syngas conversion.

<table>
<thead>
<tr>
<th>Product</th>
<th>Annual World Production</th>
<th>Catalyst</th>
<th>H₂/CO-feed volume ratio</th>
<th>p bar</th>
<th>T °C</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>?</td>
<td>High T: Cr/Fe Low T: Cu/Zn</td>
<td>any</td>
<td>any</td>
<td>~400 &gt;200</td>
<td>H₂ production</td>
</tr>
<tr>
<td>Methane</td>
<td>?</td>
<td>Ni</td>
<td>3</td>
<td>1-100</td>
<td>~250</td>
<td>Fuel gas</td>
</tr>
<tr>
<td>Methanol</td>
<td>~40 Mt</td>
<td>Cu/Zn/Al₂O₃</td>
<td>2+</td>
<td>~50+</td>
<td>~250</td>
<td>Platform chemical, fuel</td>
</tr>
<tr>
<td>Dimethyl-ether</td>
<td>?</td>
<td>Cu/Zn/Al₂O₃ plus γ-Al₂O₃ or Zeolite</td>
<td>1</td>
<td>~50+</td>
<td>~250</td>
<td>Platform chemical, fuel</td>
</tr>
<tr>
<td>Fischer-Tropsch Hydro-carbons</td>
<td>~10 Mt</td>
<td>Co-based Fe-based</td>
<td>~2 1-2</td>
<td>10-40 250 350</td>
<td>Fuel (chemicals)</td>
<td></td>
</tr>
</tbody>
</table>
4. **Syngas purification**: The raw syngas is purified and the $\text{H}_2/\text{CO}$ ratio is adjusted via the catalyzed water gas shift reaction to the optimum for the chosen product synthesis.

5. **Fuel synthesis**: The pure and adjusted syngas is converted at defined temperatures and pressures to the desired product with a selective catalyst (see Table 2.3). Some workup of the raw product might be required to ensure marketability.

The KIT bioliq process allows decentralized pre-treatment of biomass in regionally distributed fast-pyrolysis plants. The high-energy intermediate bio-slurry or bio-syncrude – a pumpable mix of pyrolysis char and pyrolysis liquid – can be transported economically, even over large distances, and subjected to further processing in the required large-scale plants.
REFERENCES


3. BIOLOGICAL AND BIO-INSPIRED SOLAR DIHYDROGEN PRODUCTION

FRASER A. ARMSTRONG, VINCENT ARTERO, HOLGER DAU, BÄRBEL FRIEDRICH, THOMAS HAPPE, PHILIPP KURZ, WOLFGANG LUBITZ AND MATTHIAS RÖGNER
(Bärbel Friedrich, coordinator and corresponding author)

Dihydrogen (H₂) is a uniquely clean renewable energy carrier; its oxidation for production of heat or electricity yields water (H₂O) as the only product. Furthermore, H₂ is highly important for many industrial processes, e.g. the production of ammonia (for fertilizers) by the “Haber-Bosch” process. Free H₂ occurs only in trace amounts on our planet. Thus, more than 90 % of the H₂ is currently generated from natural gas by steam-reforming with an efficiency of approximately 80 %.

To develop a viable H₂-based economy, production of H₂ has to be significantly increased while employing renewable non-fossil resources. Carbon-neutral routes to H₂ are mainly based on the electrolysis of water. Large-scale production usually relies on costly high-pressure and high-temperature systems that improve the efficiency of electrolysis. Photovoltaic hydrogen generation is expected to have a promising future but is currently limited by costs that are about ten times higher than those for conventional H₂ production. Additional options for biomass-related H₂ production are discussed in Chapter 2 (p. 43).

The exploitation of solar energy for either chemical or biological generation of H₂ is an attractive and environmentally friendly technological endeavor; yet it is highly challenging and still at the level of basic research. It is still an open question whether these strategies will ever lead to processes that may be used in practice on a large scale. A rapidly expanding research field is focussed on direct H₂ production by artificial photosynthetic systems, which do not rely on intermediate energy carriers such as electricity, biomass or energy-rich metabolites. Since these processes integrate fewer energy transduction steps, they offer the potential to improve the overall efficiency and to lower the costs of capital investment.

One option for biological H₂ generation is the photosynthetic conversion of sunlight and water directly to H₂ and di-oxygen (O₂); both water and light are available to an almost unlimited extent and because only H₂ and O₂ are formed in this reaction, no greenhouse gases are generated. The total solar energy that reaches the Earth’s surface and is absorbed there is about 2.7 x 10²³ J yr⁻¹ (170 W m⁻²; year’s average). This is 5,400 times the primary energy consumed by the world’s population in a whole year (500 x 10¹⁸ J in 2010). Biological conversion of solar energy to H₂ requires efficient, stable, selective, O₂-tolerant and highly active catalytic systems. Extensive molecular, biochemical and biophysical investigations have contributed to a deeper understanding of the structure and function of the biological catalysts that are involved in photosynthesis and H₂ activation. This wealth of information has inspired chemists to develop synthetic catalysts for renewable fuel production.

Chapter 3 presents an overview on the current state of research regarding biological and bio-inspired solar H₂ production, addressing the following issues:

a) technical routes to hydrogen production using solar energy;
b) biological routes to hydrogen production based on water and sunlight;
c) bio-inspired catalysts for solar water-splitting and H₂ production.
3.1. Technical routes to hydrogen production using solar energy

Two technical routes of solar hydrogen production have been established: One method makes use of biomass gasification, i.e., processing of renewable biological resources instead of natural gas and coal (see Chapter 2; p. 43). The second route does not involve photosynthetic biomass production but instead produces $H_2$ through electrolysis of water, applying electricity generated from solar energy by photovoltaic cells or by thermal conversion (Figure 3.1). A third approach, which is the subject of ongoing research and development, is focused on direct production of $H_2$ from sunlight and water. Each of these methods is directed at producing hydrogen with zero overall emission of greenhouse gases.

None of the techniques exploiting renewable energy sources for $H_2$ production are currently competitive with fossil resources based on market prices. As a reference figure, the price for $H_2$ generation from natural gas reforming (the cheapest way to produce $H_2$) is about €1 per kg of $H_2$. From biomass, $H_2$ is currently obtained at a price of about €7 per kg of $H_2$ by gasification in a midsize plant. This price reflects higher feedstock, distribution, and fixed and capital costs, but does not take into account fertilizer costs and the environmental impact associated with the production, harvest, and transport of biomass.

Of all the greenhouse-gas free methods for $H_2$ production, alkaline electrolysis is currently the most economically viable, with a cost of about €3 per kg of $H_2$. The cost consists of 50% capital investment in the electrolysis and storage devices and 50% for electrical power. Alkaline water electrolysis is carried out from concentrated potassium hydroxide solutions (30 to 60% by weight) at low-cost electrodes fabricated from nickel (Ni) and iron (Fe). The overall yield depends on the current flowing through the device but is optimistically around 70% for bipolar devices.

Electrolyzers working under acidic conditions are the most promising and adaptable, due to the use of potentially low cost organic materials, operating at low ambient temperatures. Such devices are efficient over a wide...
range of power supply (0.1 W to 100 kW) with an overall yield of 50 to 80%. However, manufacture of proton exchange membrane devices is still expensive due to the high cost of materials like fluorinated acid polymer membranes of the Nafion® type and especially the precious metal catalysts required at both anode and cathode (at least 1 mg of platinum per Watt of nominal power; iridium oxide can also be used at the anode).

The photo-electrochemical approach (Figure 3.1), in which an electrolyzer is coupled directly to a solar photovoltaic device could enable H₂ to be produced at a similar cost to its production from biomass and at a reasonable efficiency (around 10% overall energy conversion from sunlight to H₂). This analysis was made in 2004 and is based on the capital investment in an alkaline electrolyzer (€ 125 per kW) with 70% yield and for solar cells with a module cost of € 1 per Wₚ – competitive with conventional technologies for electricity production alone. However bipolar alkaline electrolyzers able to display such high yields are sensitive to sudden variations in intensity and require a minimum power level to be maintained. As a result, they are not suitable for coupling with intermittent power sources such as solar panels. For such applications, monopolar alkaline electrolyzers should be used instead; however, they are especially cumbersome and often display a lower yield of 60% or less. By contrast, coupling a photovoltaic device with a photo-electrochemical electrolyzer operating at 80% efficiency is much more promising, and could provide an overall solar to hydrogen conversion yield of 10 to 15%. In both cases, the photovoltaic panel, based on crystalline silicon or composite materials, and the platinum/iridium (Pt/Ir) catalysts account for about 80% of the costs. Thus alternative, fully integrated photo-electrochemical devices, based on low-cost nanostructured semiconductors or metal oxides and using bio-inspired noble-metal-free catalytic and photocatalytic systems (Figure 3.1) are expected to be economically viable, provided they can be developed into a robust form.

For molecules able to absorb a major fraction of the visible solar spectrum, a lifetime target of 20 years corresponds to about 10⁹ photons absorbed per individual light-harvesting unit. In order to optimize the utilization of these harvested incident solar photons, directly linked catalysts for water oxidation and reduction should combine both high turnover frequencies, exceeding 10 s⁻¹ (hydrogen molecules produced per molecular unit of catalyst) and high surface densities, about ten catalytic sites per square nanometer (nm²). The surface density issue severely restricts the volume or "footprint" of each molecular catalytic unit because even 10 sites per nm² correspond to 20 monolayers of a rather small molecule such as ferrocene on a flat surface. Furthermore, if the energy of red and near infrared photons is to be used so that the maximum fraction of the sun’s energy can be converted into chemical energy, these catalysts should operate as close as possible to the thermodynamic potential of the redox reaction. We emphasize, that any existing photo-electrochemical device currently does not meet the above figures. The devices represent targets for future research and development. Sizable research activities are required for assessment of technical feasibility and economic viability.

Once electrical energy is available from solar power, it is important to optimize the rates and efficiencies of the electrode reactions at both cathode (producing H₂) and anode (evolving O₂). The efficiency of electrochemical processes is defined by the current density and by the electrode potential, relative to the thermodynamic potential, at which the current density starts to rise (the overpotential requirement, often called the overvoltage). A large overpotential requirement at either anode or cathode means that energy is wasted. An electrolyzer typically operates at a voltage above 2 V (compared to the reversible, thermodynamic cell potential of 1.2 V) reflecting the sizable overpotential requirements at both anode and cathode. It should be noted that the same principle applies to proton-exchange membrane fuel cells, as their output voltage is typically as low as 0.7 V. Production and oxidation of H₂ is very efficient at Pt metals because the electrode reaction is fully reversible, i.e. requires only a small overpotential in either direction to drive the reactions. On the other
Biological and bio-inspired solar dihydrogen production

Hand, even at Pt (or iridium oxide, IrO₂) water oxidation requires a sizable overpotential, usually above 0.3 V. Although Pt (cathode) and IrO₂ (anode) are the best catalysts, both Pt and Ir are limited, expensive resources. Alternatives must be found if green H₂ technology is to be sustainable and cheap. Replacing noble metals is the “holy grail” for future renewable energy and great efforts are being made to find ways of producing proficient catalysts from abundant metals.

3.2. Biological routes to hydrogen production based on water and sunlight

“Learning from biology” means copying the principles by which enzymes catalyze reactions at rates that are often many orders of magnitude higher than for synthetic catalysts. The metals at the active site of enzymes are indeed abundant, sustainable and cheap. The same principle applies to electro-catalysis because despite their large size, many enzymes are superb electro-catalysts on a per site basis, providing high rates (current density) at small overpotentials and often yielding fully reversible electrochemistry. Thus hydrogenases, enzymes that catalyze the reversible conversion of H₂ into protons and electrons, host active sites containing Fe and in some cases Ni in addition to Fe. They exhibit activities for H₂ production and H₂ oxidation that are comparable, on a per site basis, to Pt. Likewise copper (Cu) enzymes known as ‘blue’ Cu oxidases reduce O₂ to water at smaller overpotentials than Pt and even Pt-Ni. In photosynthesis, the water-oxidizing manganese (Mn) complex operates at reasonably low overpotential and a rate (turnover frequency) that exceeds typical synthetic catalysts by orders of magnitude. The key enzymes involved in biological H₂ production from water will now be described in more detail.

3.2.1. Photosynthetic hydrogen formation from water

In photosynthetic microorganisms such as green algae and cyanobacteria light-induced cleavage of H₂O yields O₂ and biochemically usable energy that under certain physiological conditions is released as H₂. This naturally occurring process involves two photosynthetic protein complexes, the H₂O-splitting photosystem II (PS II) and the electron-delivering photosystem I (PS I). Protons (H⁺) and electrons (e⁻) released during H₂O oxidation are converted by the enzyme hydrogenase to molecular hydrogen (H₂) as depicted in Figure 3.2. An alternative highly energy-consuming pathway for natural H₂ production by oxygenic photosynthetic microbes is the use of the enzyme nitrogenase, which can produce high levels of H₂ under certain external conditions.¹¹

The key catalysts of biosolar H₂ production, the two photosystems (PS I, PS II) and hydrogenase (Figure 3.2), contain intricate metal cofactors embedded in a network of amino acids that form the protein pocket and providing

![Figure 3.2: Photosynthetic H₂ production from water. Oxygenic photosynthesis is functionally divided into two parts: (i) the light-dependent reactions where light energy is converted to chemical energy and (ii) the light-independent reactions where carbon dioxide is converted into biomass. The light-dependent reactions occur at membranes catalyzed by complexes of proteins, chlorophylls and other cofactors. Photosystem II (PS II, on the left) captures light energy at 680 nm exciting electrons (e⁻) that enter the electron transport chain. Electrons are replaced with electrons stripped from water (the water-splitting reaction) creating O₂ as a by-product. The energized electrons are shuttled from PS II via components of the respiratory chain to photosystem I (PS I, on the right) capturing light energy at 700 nm. The e⁻ transfer releases energy to pump protons (H⁺) across the membrane (not shown) forming a reservoir for the synthesis of chemical energy, primarily ATP. In PS I light energy excites electrons, and this time electrons are captured by the electron carrier molecule NADP⁺, which is reduced to NADPH. The reduction process involves ferredoxin (Fd) as electron carrier molecule and the enzyme ferredoxin-NADP⁺ reductase (FNR). The product NADPH is used in addition to ATP (not shown) for fixation of carbon dioxide in the light-independent reactions of the Calvin Cycle.](image-url)
tunnels for the substrate H$_2$O and the products O$_2$ protons (H$^+$) and electrons (e$^-$). The electrons released from water in a light-dependent reaction by PS II are shuttled via membrane-associated components (Cyt b$_6$f) to PS I, which captures light energy for the reduction of the electron carrier ferredoxin. Reduced ferredoxin can either serve as direct electron donor for the reduction of protons by hydrogenase or for the reduction of NADP$^+$ by ferredoxin-NADP$^+$ reductase (FNR). Reduced NADPH is normally utilized by the cells for autotrophic carbon dioxide fixation via the light-independent reactions of the Calvin Cycle yielding biomass.$^{5,6}$

3.2.2. Photosystem II

A broad inventory of molecular, biochemical and biophysical methods provided the tools to derive detailed insights into the structure and function of the photosynthetic apparatus. In particular, recent progress has been achieved on the water-splitting PS II complex, which constitutes a membrane-spanning protein complex composed of more than 20 polypeptides (Figure 3.2). The molecular structure was recently analyzed at very high resolution (1.9 Å) with a protein preparation from the thermophilic cyanobacterium Thermosynechococcus vulcanus.$^{12}$ The central proteins D$_1$ and D$_2$ carry several cofactors, including a Mn$_4$O$_5$Ca cluster. The Mn cofactor is the site where photolysis of water and the evolution of O$_2$ take place (Figure 3.3).

Oxidation of H$_2$O is a four-electron transfer process (Figure 3.3) powered by light-induced charge separation across the photosynthetic membrane. The model predicts that H$_2$O binds to the Mn cluster in a stepwise cycle (S$_0$ to S$_4$). Oxidation occurs by successive subtraction of 4 H$^+$ accompanied by liberation of O$_2$ in the last step. Advanced spectroscopic analyses in concert with theoretical calculations$^{13-15}$ contributed to a functional model as depicted in Figure 3.3. The recently published protein structure with considerably improved resolution$^{12}$ is considered as a major breakthrough in understanding this elementary process of life. Needless to emphasize that in addition to the metal cofactor the protein matrix of PS II plays an important role in the photosynthetic reaction.

![Figure 3.3: The catalytic site of photosystem II.](image)

The function of other protein-associated components such as chlorophylls, quinones, carotenoids and lipids is only partially understood, they are active in light harvesting, charge separation, electron and proton transfer, and contribute to the stability and protection of the biocatalyst.

3.2.3. Hydrogenases

The second partner in biological hydrogen production is the enzyme hydrogenase. Hydrogenases, microbial metal proteins that catalyse rapid H$^+/H_2$ inter-conversion, are usually considered as very O$_2$-sensitive enzymes.$^{16}$ Based on the composition and structure of their active
sites, three classes of hydrogenases are distinguished: the mono-iron [Fe]-, di-iron [FeFe]-, and nickel-iron [NiFe]-hydrogenases.17,18 [FeFe]-hydrogenases are highly productive in H₂ evolution (turnover rates up to 10,000 s⁻¹) but are irreversibly inactivated by traces of O₂.19 [NiFe]-hydrogenases preferentially catalyse H₂ oxidation and are less sensitive to O₂ 6,20 (Figure 3.4). Typically [NiFe]-hydrogenases and [FeFe]-hydrogenases consist minimally of a large subunit that accommodates the bimetallic active site and at least one electron-transferring iron-sulfur (Fe-S) cluster usually located in a separate subunit as illustrated in Figure 3.4. In both cases the metals are bound to cysteine residues and varying numbers of carbonyl (CO) and cyanide (CN⁻) ligands. This fragile environment is a target for O₂ and most of the “standard” hydrogenases, which are instrumental under anaerobic conditions in nature, are inactivated by traces of O₂.18 However, some [NiFe]-hydrogenases display high catalytic activity for sustained periods under aerobic conditions and are therefore characterized as “O₂-tolerant”.20 An important clue to explain O₂ tolerance is a modified iron-sulfur cluster (4Fe-3S) coordinated by six instead of four cysteine residues (Figure 3.4) that is proximal to the [NiFe] active site.21-24 Any ability of hydrogenases to remain active in air is important for the design of H₂-producing cellular systems and inspired synthetic catalysts for future H₂ energy technologies.6,25

![Figure 3.4: The catalytic sites of most common hydrogenases.](image)

The [NiFe] active site (left) and the [FeFe] active site (right) are shown in a stick and sphere representation with their carbonyl ligands (red) and cyanide ligands (blue). The cysteine residues that coordinate the proximal Fe-S cluster are shown in yellow. The two supernumerary cysteine residues that are found only in O₂-tolerant [NiFe]-hydrogenases are highlighted in magenta.

### 3.3. Cellular and semi-artificial systems for H₂ production

Oxygenic photosynthesis evolved in cyanobacteria approximately 2.8 billion years ago. Recruiting PS II enabled the organism to generate organic carbon compounds and cell material from CO₂ and water using sunlight as a source of energy (Figure 3.2). This achievement represents one of the major milestones in the evolution of our planet, yielding all fossil resources and the total amount of currently available biomass. In the course of this process O₂ was liberated and accumulated gradually in the atmosphere providing conditions for the development of the O₂-respiring organisms.

Biological H₂ conversion in nature is a common metabolic trait. Microorganisms exist that preferentially use H₂ as an energy source and others that produce H₂ to dispose of excess reducing power during anaerobic fermentation of organic biomass as discussed in Chapter 2 (p. 43). Anaerobic H₂ production either occurs in the dark or is powered by a photosynthetic process. Here we focus on H₂ production by photolysis of water carried out by oxygenic phototrophic microbes such as unicellular green algae and cyanobacteria. This process requires
two membrane-bound photosystems, PS I and PS II, which act in series as demonstrated in Figure 3.5. The electron carrier ferredoxin (Fd) functions as a distributor of electrons. It can either reduce [FeFe]-hydrogenases present in green algae thereby producing H₂ as a biofuel or alternatively donate electrons to NADP⁺, which once reduced to NADPH is mainly used for CO₂ fixation, finally yielding biomass (Figure 3.5). It is anticipated that in cyanobacteria NADPH can also feed electrons into [NiFe]-hydrogenases to form H₂.

Figure 3.5: Cellular H₂ production from water. A cellular model for designing an H₂-evolving cell is the cyanobacterium Synechocystis (left). To increase the efficiency of the system the flow of electrons from the photosystems (PS I and PS II) and the electron carrier ferredoxin (Fd) should be tightly coupled to the enzyme hydrogenase (H₂-ase) instead of producing biomass via autotrophic CO₂ fixation.

Bio-photolysis of water is an attractive option for energy generation. To exploit this process as an efficient and economically viable process for H₂ production several requirements have to be met: tight coupling of PS I and hydrogenase, avoidance of the detrimental effect of the by-product O₂ on hydrogenases, and improvement of the natural repair system to stabilize PS II which is destroyed by light-induced reactive oxygen species. These are the most challenging tasks for biosolar H₂ research.

Up to now, protection of H₂ formation against detrimental effects of O₂ has mostly been achieved through indirect bio-photolysis in which H₂ production is spatially or temporally separated from water-splitting photosynthesis. Spatial separation is realized, for instance in cyanobacterial cells, that differentiate into heterocysts, which can fix molecular nitrogen to ammonia. These modified cells contain the nitrogen-fixing oxygen-sensitive enzyme nitrogenase that coproduces H₂ in a highly energy-consuming process. The system is protected against O₂ damage due to the lack of PS II and a special morphology of the host cells that guarantees a low O₂ content. Most recently a high potential H₂-producing cyanobacterium has been reported which is even active in air, producing up to ten times more H₂ than organisms under anaerobic conditions – although not on a continuous basis.

Temporal separation of H₂ production from oxygenic photosynthesis can experimentally be achieved by anaerobic fermentation of storage compounds such as starch or glycogen accumulated during light-driven CO₂ fixation. The most intensively studied form of indirect bio-photolysis is to grow Chlamydomonas reinhardtii photosynthetically, i.e. under air, and then expose the cells to a sulfur-limiting medium to decrease PS II activity. Under these conditions, the O₂-producing water-splitting reaction is suppressed while respiration proceeds at a high rate, thereby maintaining a low O₂ concentration and allowing for H₂ production discontinuously. Reported H₂ production yields from one liter of algal culture after six days in sulfur-free medium are about 170 ml H₂ using C. reinhardtii wild type cells while the light conversion efficiencies are very low (up to 1.6 %).

3.3.1. Using immobilized enzymes for H₂ production
Several approaches have been initiated to accelerate the photosynthetic electron transport
by coupling the photosystems tightly with hydrogenase and to channel the bulk of electrons to proton reduction rather than CO₂ fixation (Figure 3.5). These approaches were first tested by in vitro assays. One device used genetic engineering to construct a protein fusion between a small stromal subunit of PS I from the cyanobacterium *Synechocystis* and the electron-transferring subunit of an O₂-tolerant [NiFe]-hydrogenase from the aerobic bacterium *Ralstonia eutropha*. This procedure arranged PS I sufficiently close to the hydrogenase to outcompete charge recombination within PS I and direct the electron flow towards the hydrogenase. The recombinant PS I-hydrogenase hybrid complex, immobilized on a gold electrode, evolves H₂ at a fairly high rate of 3,000 µmol mg chlorophyll⁻¹ hr⁻¹. 31,32

Another attempt used a synthetic biological approach by tethering the redox cofactors of both PS I and a [FeFe]-hydrogenase through a chemically synthesized molecular wire to build a direct connection between the electron transfer chains of PS I and hydrogenase. After self-assembly of the modified proteins the complex showed light-induced H₂ evolution. 33 More recently this nano-construct could be improved yielding an H₂ production rate of 2,200 µmol mg chlorophyll⁻¹ hr⁻¹, which is equivalent to 105 e⁻ PS I⁻¹ s⁻¹. 34

An alternative design is focused on the immobilization of PS I and PS II using osmium-polymer structures on gold electrodes (Figure 3.6). The photosynthetic electron transport reactions are divided into two compartments, of which one is aerobic (due to water photolysis) and the other one anaerobic as required by O₂ sensitive hydrogenases, all components can then be changed individually aiming at the design of an efficient photosynthetic cellular system. As both half-cells have already been improved considerably the system is now available for attaching various hydrogenases. 35

### 3.3.2. On the way to H₂ producing design cells

To establish an economically viable biosolar H₂ technology the efficiency of the existing cellular systems needs to be increased by a factor of about 100. 36 This means that 75 % of the photosynthetic energy derived from water oxidation should be channeled towards H₂ instead of forming biomass. Such an optimized system is expected to produce 250 ml H₂ per liter culture within one hour. 37
Two cellular targets are amenable to optimization using genetic engineering techniques. Considerable improvement has been achieved by reduction of the antenna size for decreasing the light sensitivity. Systems employed in practice should take advantage of living cells which are capable of self-repair by replacing the D1 protein of PS II, which has a half-life of 20 minutes, by an intact possibly even more stable component. Current research is therefore directed at: (i) Systematic screening for novel phototrophic organisms (cyanobacteria and green algae, especially marine systems) with thus far unprecedented H2-producing capacity. However, the outcome of such an approach is difficult to estimate. (ii) Genetic engineering of existing microbes to design super H2-producing cells taking into account the progress of scientific knowledge in this field. This approach is expected to lead to an acceleration of H2 production rates. However, it remains elusive whether the resulting capacity can compete with other technologies. (iii) Both natural and design cells need to be cultivated more efficiently under low-operational costs. This implies the application of new materials for the construction of photobioreactors especially in view of the transmission of light and maintenance of homogeneous cell suspensions. Investigations on continuous cell cultivation using specifically designed flat-bed reactors are currently in progress.

3.4 Bio-inspired systems for solar water splitting and hydrogen production

“Learning from biology” means replacing enzymes by small molecular counterparts, not necessarily by analogues that mimic the structures of the active sites, but rather by “functional” analogues that conform to the same mechanistic principles, i.e. abilities to carry out multiple proton-electron transfers at potentials not too different from the thermodynamic potentials of the reactions being driven. In the long term, the new catalysts that are functional analogues of the enzyme active sites must be robust and inexpensive to produce, but at the current stage of research and development the priorities are to ascertain what is possible and identify any special principles of mechanism or synthesis that have not so far been obvious. Two examples of functional analogues are a nickel (Ni)-based system for production and oxidation of H2 and a cobalt (Co)-based system for photolysis of water. Bio-inspired systems for H2 production are still at a relatively early stage of mostly basic research, whereas research on biological H2 production using self-reproducing photosynthetic microorganisms has been investigated for longer. The maximum solar-energy conversion efficiency is limited and a photo-bioreactor is unlikely to become a stand-alone system with low operational costs. The concept of artificial photosynthesis has been developed to go beyond natural photosynthesis by utilization of photosynthetic microorganisms (cyanobacteria, algae) for H2 production. Researchers in this field also aim at systems for transformation of solar energy into chemical energy. However, instead of using organisms, they copy key processes of natural photosynthesis and H2 cycling systems. In artificial photosynthesis, systems are built up from synthetic modules, without involvement of photosynthetic organisms or biomass. These modules never represent a direct copy of the photosystems and hydrogenases found in microorganisms. It is merely the function and frequently also the elemental composition and structure of the active site in proteins that is copied – never the natural protein itself. Depending on the level of similarity to the biological paragon, a synthetic module or technological system is considered to be biomimetic or bio-inspired. Crucial points that characterize a bio-inspired system (Figure 3.7) of artificial photosynthesis are:

- Energetically the overall process is driven by solar energy. The final synthesized product is not electricity but a fuel, that is, an energy-rich chemical.
- The system can cope with a fluctuating solar energy supply.
- Water is the only feedstock if molecular hydrogen (H2) is to be produced as a fuel. For the synthesis of carbon-based fuels, both water and atmospheric carbon dioxide are used as starting material.
- Reactions proceed at “physiological” temperatures (<100 °C). Moreover extreme pressures and pH-regimes as well as aggressive solvents are largely avoided.
For the catalytic entities, abundant first-row transition metals (V, Mn, Fe, Co, Ni) are the primary choice as in biological redox catalysis where these metals also constitute the active sites of metalloproteins. The use of rare and/or expensive elements like platinum group metals is avoided.

The light-driven transformation of H₂O into H₂ and O₂ is currently the predominant target of research in artificial photosynthesis. A basic view on the system is illustrated in Figure 3.7. Key processes to be addressed are those discussed in the previous chapter:

- The oxidation of H₂O to O₂, which in nature is catalyzed by the Mn-Ca complex of PS II in photosynthesizing organisms (see also Chapter 3.3).
- The reduction of protons to H₂, which in intact organisms is not facilitated by proteins of the photosynthetic apparatus but by hydrogenases, these are enzymes that can use reducing equivalents provided by PS I.
- The coupling of these two catalytic processes to the primary light reactions, where in natural photosynthesis the chlorophyll molecules of PS II and PS I are the key players.

**Figure 3.7:** A bio-inspired system for H₂-formation from H₂O. A, electron acceptor; D, electron donor. The gray box labeled, as ‘PS II mimic’ comprises the reactions for light-driven water oxidation; the box labeled, as ‘PS I / H₂ase mimic’ comprises the light-driven reductive reactions resulting in the formation of H₂. The two boxes are coupled via an electron relay R. Alternatively, electrodes may substitute for the molecular electron relay.42

### 3.4.1. Light reactions

Coupling the catalytic processes with the primary light reactions can be addressed by employing conventional and new concepts developed in various fields of physical and chemical science. Following the natural example closely, organic or metal-organic pigments (dyes) can be used both as light-absorbing photosensitizers and primary electron acceptors (A) and donors (D) in Figure 3.7. These dye molecules have been coupled to molecular catalysts or semiconducting materials. Alternatively, semiconducting materials themselves can facilitate the primary photo-physical steps, provided that they possess a suitable band structure.44-45 The use of charge-transfer transitions in relatively simple, purely inorganic transition-metal compounds represents another promising route that recently came into focus.39 Also other types of new inorganic materials, e.g. quantum dots, may replace dye molecules as photosensitizers.

While research on artificial photosynthesis typically is aiming at the direct coupling of light reactions to the catalytic processes, electro-catalytic systems are of interest as well (Figure 3.1). Here, solar energy is first converted into electricity, e.g., by photovoltaic solar cells, and then used, in a second step, for the electro-catalysis of water oxidation and proton reduction. Again, for any large scale use of such systems it is essential that only non-rare elements are used and that the system operates efficiently under largely fluctuating irradiation conditions.

### 3.4.2. Water oxidation

New catalysts for water oxidation are the topic of a number of current research projects. Many of these have adopted a biomimetic approach,
aiming at copying the very efficient natural catalyst for reaction (1), the “Water Oxidizing Complex” (WOC) of PS II.44 This enzyme is able to catalyze water oxidation at high turnover frequency and little energy loss. Moreover, in PS II this is achieved with a catalyst composed of Mn, Ca and O₂, all inexpensive and earth-abundant elements (Figure 3.3). 4

\[
2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- \quad (1)
\]

In recent years, progress has been made especially for two classes of WOC-mimics: oxido-bridged di-nuclear metal complexes and metal oxides. For homogeneous H₂O oxidation catalysis, a large number of complexes containing two (or more) closely linked Mn centers has been synthesized and studied in great detail. Important knowledge about both the architecture and the properties of the WOC could be gained in this way.44,45 However, catalysis of reaction (1) in homogeneous solution could not be reached using such Mn compounds, but only by similarly constructed di-ruthenium (Ru₂) complexes. In some cases, these Ru compounds reached very high turnover frequencies and good stability for H₂O oxidation, but the high price and low abundance of Ru leaves doubts whether such compounds will ever become affordable components of artificial photosynthetic systems.

Alternatively, heterogeneous catalysts in the form of oxides could model the active site of PS II. Specific Mn and Co oxides showed promising catalytic performances and were successfully used both as catalysts in light-driven systems (Catox in the left half of Figure 3.7) and for electro-catalytic H₂O oxidation. Reaction rates are still slow and a convincing link of the catalysts to photoreactions is so far lacking. If it were possible in the future to improve the catalytic rates of these materials, such oxides would have the potential to play a key role in solar fuel production, as they are easily prepared from both affordable and abundant raw materials. Their discovery thus marks a significant step forward, represents a real milestone in the field of artificial photosynthesis and indicates a potentially rewarding research direction.44 The device constructed by Nocera’s group consisting of earth-abundant metals and a cobalt-borate catalyst allows the solar-driven water-splitting reaction at efficiencies of 4.7 % for a wired configuration and 2.5 % for a wireless configuration when illuminated,41 which can compete with the basic functional elements of natural photosynthesis.

In conclusion, homogeneous (molecular) and heterogeneous (solid state) approaches are currently being pursued for the development of H₂O-oxidation catalysts. There is no clear dividing line between molecular and solid-state catalysts. The catalytically active oxides formed from first-row transition metals are highly amorphous and exhibit molecular properties. Also recently discovered all-inorganic metal complexes built up from a larger number of metal centers may be considered as an “in-between” with respect to both concepts. Key challenges for all approaches are first-and foremost to increase the catalytic rates and catalyst stability. For the natural catalyst, nature has developed repair mechanisms to replace the protein subunit D₁ containing the WOC within the PS II enzyme (see Chapter 3.3). Given the very high oxidation potentials needed for water oxidation, it is likely that in long-term applications, also any artificial catalyst will need a mode of “healing” (or self-repair) after oxidative modifications.

### 3.4.3. Hydrogen formation

The reversible inter-conversion of protons and H₂ is a two-electron process, which also requires catalysts to make it practically useful.

\[
\text{H}_2 \rightleftharpoons 2 \text{H}^+ + 2 \text{e}^- \quad (2)
\]

Available technological devices, such as proton exchange membrane (PEM) electrolyzers and fuel cells, integrate rare and expensive metals such as Pt for catalysis. Except for Ni electrodes used in alkaline electrolyzers (a technology associated with strong corrosion)46 only few noble-metal-free H₂-evolving systems are known. One of which is molybdenum disulfide, operating under pH 0 conditions with an overpotential of 0.1 – 0.2 V.40 Interestingly, this catalyst has a structure close to that found in the H₂-evolving metalloenzyme, nitrogenase.

Again, inspiration for the development of catalysts for reaction (2) comes from nature
where a family of enzymes, the hydrogenases, catalyzes this reaction at active sites containing Fe and Ni centers (Figure 3.4). Starting from the detailed structural information on hydrogenases, a number of chemists succeeded in synthesizing bio-inspired complexes that imitate the active sites of hydrogenases. When assayed in non-aqueous solvents, some of these compounds have been shown to display remarkable catalytic properties for both, the electro-reduction of protons to H$_2$ or the electro-oxidation of H$_2$. Alternatively, Co and Ni complexes coordinated with imine or oxime ligands also proved to be efficient and robust catalysts for H$_2$-evolution at low overpotentials. Such catalysts have been successfully coupled with photosensitizers to generate light-driven H$_2$-evolving systems (they act as Cat$_{red}$ in the right half of Figure 3.7).

It was an important step forward when recently bio-inspired Ni complexes bearing anchor groups where immobilized onto carbon nanotubes (Figure 3.8). Carbon nanotubes were chosen for their outstanding electron conductivity and also because of their large surface area, optimal for high catalyst loading. Deposition of a thin film of these electro-active Ni-functionalized carbon nanotubes onto a carbon substrate generated an inexpensive, stable, air-resistant cathode material with remarkable performance especially under the strongly acidic conditions required for the expanding proton exchange membrane technology. In this system, H$_2$ evolves from aqueous sulfuric acid solution at very low overvoltages and exceptional stability of the catalyst (> 100,000 turnovers). Interestingly, this Pt-free catalyst is also very efficient for the reverse reaction, H$_2$ oxidation under the same conditions with current densities similar to those observed for previously described hydrogenase-based materials (1-5 mA cm$^{-2}$). The latter property was completely unexpected from solution studies and shows how a modification of the distant environment of a metal complex, may also allow tuning of its catalytic properties. This has been the first report of a molecular-engineered and noble-metal-free electrode material that is capable of achieving H$_2$ evolution/oxidation with no or little overpotential. Key challenges now include the improvement of catalytic turnovers and development of new electrode materials for direct photocatalysis of H$_2$ production.

3.4.4. Perspectives
The concept of artificial photosynthesis offers a highly attractive perspective for sustainable production of molecular H$_2$ and also for fuels in general. For this concept to be implemented, the development of catalysts based on abundant, low-cost materials will be essential. Insufficient functionality and lack of robustness presently characterize molecular catalysts for homogeneous H$_2$O oxidation, especially the group of biomimetic Mn complexes. Degradation problems resulting from ligand oxidation may be solved by the development of new ligand systems or the employment of inorganic frameworks instead of organic ligands. Recently, there has been a wealth of new developments relating to heterogeneous water-oxidation catalysts composed of oxides of abundant transition metals (Co, Mn, Fe). These materials achieve catalysis without the need of organic ligands and are therefore highly promising candidates for the development of robust oxidation catalysts.
In the field of $\text{H}_2$-evolving catalysis, recently developed bio-inspired Fe and Ni complexes catalyze the reduction of protons at high rates. As catalyst performance could be increased substantially by the attachment of catalytic units to carbon nanotubes, well-designed nano-structures could generally result in desirable new properties of immobilized molecular catalysts. Metal oxides cannot easily be employed at the reducing potentials needed for proton reduction, but sulfides or other inorganic materials synthesized from abundant elements are of interest.

Today specific rates (per metal ion) for reactions electro-catalyzed by these new bio-inspired materials typically are by more than three orders of magnitude lower than those of the corresponding reactions in enzymes. However, taking into account the catalytic rate (or turnover frequency) per catalyst volume, comparable performance levels are within reach.

The development of functional components for artificial photosynthesis appears to be an especially promising concept for replacement of fossil fuels. However, all research and development activities in this area are at an early stage. The foundations for a technologically and economically viable solution are expected to arise from ongoing research on the biological systems, which still provide the basis for bio-inspired solutions. Therefore, most investigators in the field believe that currently any commitment to a specific direction of technological development might be premature; multiple alternatives are therefore currently being explored. This implies that the timeframe for large-scale implementation of technological systems is highly uncertain and as a consequence neither natural nor artificial photosynthesis can contribute to short-term solutions.
REFERENCES

**GLOSSARY**

<table>
<thead>
<tr>
<th>Acetone: an organic solvent (CH₃COCH₃) that is formed as a co-product with fermentative butanol formation.</th>
<th>Biobutanol is generated by microorganisms from the sugar-containing components of biomass via fermentation. It is more similar to gasoline than to ethanol.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arable land is land that can be used for growing crops.</td>
<td>Biodiesel is made from vegetable oils and animal fats by methanol-based transesterification. It can be used as a fuel for vehicles in its pure form, but it is usually used as a diesel additive. It is the most common biofuel in Europe.</td>
</tr>
<tr>
<td>Aerobic, in the presence of oxygen (O₂).</td>
<td>Biodiversity is the variety of life forms (plants, animals, microorganisms) within a given ecosystem.</td>
</tr>
<tr>
<td>Anaerobic, in the absence of oxygen (O₂).</td>
<td>Bioenergy is the energy released upon combustion of recently grown biomass (e.g. wood) or of biomass products (e.g. bioethanol, biobutanol or biogas). The term does not cover the energy released upon combustion of fossil fuels such as coal, oil or methane although fossil fuels also have their origin in ancient carbon fixation. Fossil fuels are not considered biofuels because they contain carbon that has been “out” of the carbon cycle for a very long time.</td>
</tr>
<tr>
<td>Anoxyogenic, without the formation of oxygen (O₂).</td>
<td>Bioethanol is an alcohol (CH₃CH₂OH) generated by microorganisms via fermentation from carbohydrate components of biomass or of biomass waste. Bioethanol can be used as a fuel for vehicles either in its pure form or as additive to gasoline.</td>
</tr>
<tr>
<td>Advanced biofuels are generated by aerobic microorganisms as part of their anabolism whereas biofuels such as bioethanol are generated as part of the energy metabolism of anaerobic microorganisms. Amongst them are isobutanol (2-methylpropanol) and isoprenes. In spite of beneficial properties, these “anabolic fuels” have the disadvantage that the energy recovered from them is less than 50% of the energy that was contained in the substrate from which they were synthesized.</td>
<td>Biofuels are fuels that are derived from biomass. They can be solid (wood chips), liquid (bioethanol and biodiesel), or gaseous (biogas). Although fossil fuels have their origin in ancient carbon fixation, they are not considered biofuels by the generally accepted definition because they contain carbon that has been “out” of the carbon cycle for a very long time.</td>
</tr>
<tr>
<td>Autotrophic, capable of synthesizing most cell components (carbohydrates, lipids, proteins, nucleic acids) from simple inorganic sources such as carbon dioxide, water, sulfate and nitrates.</td>
<td>Autotrophic respiration provides autotrophic plants with energy for maintenance and tissue construction in the dark and under light-limiting conditions and reduces gross primary productivity of photosynthesis on average by 50%.</td>
</tr>
<tr>
<td>Barrell: a volumetric unit (=159 L) by which petrol is traditionally quantified in the oil industry.</td>
<td>Billion: 10⁹</td>
</tr>
</tbody>
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**Glossary**

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- Arable land: land that can be used for growing crops.
- Aerobic: in the presence of oxygen (O₂).
- Anaerobic: in the absence of oxygen (O₂).
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- Advanced biofuels: are generated by aerobic microorganisms as part of their anabolism whereas biofuels such as bioethanol are generated as part of the energy metabolism of anaerobic microorganisms. Amongst them are isobutanol (2-methylpropanol) and isoprenes. In spite of beneficial properties, these “anabolic fuels” have the disadvantage that the energy recovered from them is less than 50% of the energy that was contained in the substrate from which they were synthesized.
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- Autotrophic respiration: provides autotrophic plants with energy for maintenance and tissue construction in the dark and under light-limiting conditions and reduces gross primary productivity of photosynthesis on average by 50%.
- Barrell: a volumetric unit (=159 L) by which petrol is traditionally quantified in the oil industry.
- Billion: 10⁹
**Biogas** is comprised of methane (approximately 60%) and carbon dioxide, produced by anaerobic digestion (absence of oxygen) of organic material by microorganisms. Biogas can be used as a transport fuel or, as a replacement for natural gas.

**Biome** is a large geographical area of distinctive plant and animal groups, which are adapted to that particular environment.

**Biomass** as a renewable energy source, is biological material from living, or recently living organisms. As an energy source, biomass can either be used directly, or converted into other energy products such as bioethanol.

**Biomimetics** is the examination of nature, its models, systems, processes, and elements to emulate or take inspiration from in order to solve human problems.

**Bioreactor** may refer to any manufactured or engineered devices that support growth of cells or processes that involve organisms or cell tissues.

**Butanol:** an alcohol composed of 4 carbon atoms \((\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})\) which can be formed by fermentation of sugars by specific bacteria (e.g., *Clostridium acetobutylicum*).

\(\text{CH}_4\), methane.

\(\text{CO}_2\), carbon dioxide.

**C3 plants** are plants in which \(\text{CO}_2\) is first fixed into a compound containing three carbon atoms (3-phosphoglycerate) before entering the Calvin cycle of photosynthesis. Most broadleaf plants (dikotyls) such as clover and sugar beet are C3 plants.

**C4 plants** are plants in which \(\text{CO}_2\) is first fixed into a compound containing four carbon atoms (oxaloacetate) before entering the Calvin cycle. Most grasses (monokotyls) such as maize and sugar cane are C4 plants.

**Cellulose** is a cell-wall component of plants. It is a polysaccharide consisting of a linear chain of several hundred to over ten thousand \(\beta (1\rightarrow4)\) linked D-glucose units. Cellulose is crystalline and resistant to hydrolysis.

**Carbon nanotubes** are nanometer-scale tube-like structures composed of carbon.

**Calorific value** of a fuel indicates the probability of the energy source reliably meeting fluctuating demands. Thus bioenergy can support grid stability by providing balancing and reserve power to an energy system with an increasing component of fluctuating renewable energy.

**Catalysis** is the change in rate of a chemical or biological reaction due to the participation of a substance called a catalyst. Unlike other reagents that participate in the reaction, a catalyst is not consumed by the reaction itself. Typical catalytic materials are transition metals often used to catalyze redox reactions (oxidation, hydrogenation). Examples are nickel, iron, manganese or "late transition metals", which include palladium, platinum, gold, ruthenium, and iridium. Biological catalysts, in contrast to synthetic catalysts, are enzymes composed of amino acids and often equipped with metal cofactors.

**Capacity credit** of a fuel indicates the probability of the energy source reliably meeting fluctuating demands. Thus bioenergy can support grid stability by providing balancing and reserve power to an energy system with an increasing component of fluctuating renewable energy.

**Distillation:** a process in which a mix of liquids is separated through preferred evaporation of single components at elevated temperatures, e.g. production of (nearly) pure ethanol from a fermentation broth. Requires substantial amounts of heat energy.

**Ecosystems** are systems of living organisms interacting with each other and with their physical environment.
**Electrochemistry** is a branch of chemistry that studies chemical reactions which take place in a solution at the interface of an electron conductor (a metal or a semiconductor) and an ionic conductor (the electrolyte), and which involve electron transfer between the electrode and the electrolyte or species in solution. The potential difference (voltage) between a half-reaction’s thermodynamically determined reduction potential and the potential at which the redox event is experimentally observed is expressed as the overpotential.

**Electrolysis** is a method of using an electric current to drive an otherwise non-spontaneous chemical reaction. An electrical potential is applied across a pair of electrodes (anode and cathode) immersed in the electrolyte. For instance electrolysis of water is the decomposition of water ($\text{H}_2\text{O}$) into oxygen ($\text{O}_2$) and hydrogen gas ($\text{H}_2$) due to an electric current being passed through the water.

**Energy crops** are plants grown to make biofuels, or to be burnt directly for their energy content to generate electricity or heat. Energy crops are generally categorized as woody or herbaceous (grassy).

**EROI**, energy return on investment.

**Energy return on investment** = energy output divided by fossil energy input.

**EU**, European Union.

**EU-25** countries are: Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Great Britain, Greece, Hungary, Ireland, Italy, Latvia, Lithuania, Luxemburg, Malta, Netherlands, Poland, Portugal, Slovakia, Slovenia, Spain and Sweden.

**Exa** = $10^{18}$.

**Ferredoxins** are iron-sulfur proteins that mediate electron transfer in a range of metabolic reactions including photosynthesis.

**Final energy** is the energy sold to the end-consumers after conversion of the primary energy to useful energy such as electricity, heat and fuels.

**First-generation bioethanol** is derived from the starch part of plants, second-generation bioethanol from the lingo-cellulosic parts of plants.

**Fischer-Tropsch-Synthesis** is a large scale technical process developed before 1925 by Franz Fischer and Hans Tropsch in Mülheim an der Ruhr, Germany, in which carbon monoxide ($\text{CO}$) and hydrogen ($\text{H}_2$) mixtures are converted to liquid hydrocarbons.

**Flex engines** are power units that can use ethanol and gasoline at all mixing ratios.

**Fossil fuels** include coal, petroleum, and natural gas. They are fuels that have been formed biogenically and abiogenically from biomass millions of years ago, their age sometimes exceeding 650 million years.

**Fuel cells** are devices that convert the chemical energy from a fuel into electricity through a chemical reaction with oxygen or another oxidizing agent. Hydrogen ($\text{H}_2$) is the most common fuel.

**Genetic engineering** is the direct modification of an organism’s genome using modern DNA technology.

**GHG**, greenhouse gas.

**GPP**, gross primary production.

**Gross primary production** is a measure of photosynthesis and is almost twice as high as the net primary production because approximately 50% of the photosynthesis products are respired by the plant for maintenance and growth in the dark and light-limiting conditions. It is generally given in g C m$^{-2}$ yr$^{-1}$, 1 g C corresponding to about 2 g biomass dry-weight.

**Greenhouse gas** is a gas (mainly $\text{CO}_2$, $\text{N}_2\text{O}$ or $\text{CH}_4$) in the atmosphere that absorbs and emits radiation within the thermal infrared range.
**Habitat** is an area that is inhabited by a particular species of animal, plant or other type of organism. It is the natural environment in which an organism lives, or the physical environment that surrounds (influences and is utilized by) a species population.

**Hydrogenase** is an enzyme that catalyzes the reversible oxidation of molecular hydrogen ($H_2$).

**HANPP**, human appropriation of net primary production.

**$H_2$**, hydrogen.

**$H_2O$**, water.

**Hemicelluloses** are cell-wall components of plants. They are polysaccharides composed of pentoses present along with cellulose in almost all plant cell walls. While cellulose is crystalline, strong, and resistant to hydrolysis, hemicellulose is easily hydrolyzed by dilute acid or base.

**Heterocysts** are differentiated cyanobacterial cells that carry out nitrogen fixation.

**IPCC, Intergovernmental Panel on Climate Change.**

**Jatropha** is a genus of approximately 175 succulent plants, shrubs and trees from the family Euphorbiaceae.

**J**, Joule.

**Joule** is a unit of energy. $1 \text{ J} = 0.239 \text{ cal}$; $1 \text{ cal} = 4.184 \text{ J}$; $1 \text{ Joule per second} = 1 \text{ Watt (W)}$.

**Jet fuel** is an aviation fuel designed for use in aircraft powered by gas-turbine engines. The most commonly used fuels for commercial aviation are Jet A and Jet A-1 which are produced to a standardized international specification. The only other jet fuel commonly used in civilian turbine-engine powered aviation is Jet B which is used for its enhanced cold-weather performance. Jet fuel is a mixture of a large number of different hydrocarbons. The range of their sizes (molecular weights or carbon numbers) is restricted by the requirements for the product, for example, the freezing point or smoke point.

**Land-use change**: An example of direct land-use change is the conversion of grassland to cropland for bioenergy production. Indirect land-use change (iLUC) occurs if cropland previously used for food crops is used for bioenergy crops and food production moves elsewhere. This may result in deforestation of other regions. The extent of iLUC depends on (i) changes in the food system (i.e. whether the lost food crop production is replaced or not – if not, however, this may result in more hunger), (ii) changes in the yields of food crops (e.g., if food crop production can be maintained through increased yields iLUC may be reduced or even absent, although in this case the additional emissions from land-use intensification must be taken into account) and (iii) the area required for bioenergy (and therefore the volume to be produced).

**Lignin** is a cell-wall component of plants. It is one of the most abundant organic polymers on Earth, exceeded only by cellulose, employing 30% of non-fossil organic carbon and constituting from a quarter to a third of the dry mass of wood.

**Lignocellulose** is composed of cellulose, hemicellulose, and lignin.

**Metabolic rate** is the amount of daily food energy expended by humans or animals. Food energy is the amount of energy obtained from food that is available through cellular respiration.

**Million**: $10^6$

**Miscanthus** is a genus of about 15 species of perennial grasses native to subtropical and tropical regions of Africa and southern Asia, with one species ($M. \text{ sinensis}$) extending north into temperate eastern Asia.

**Mycorrhiza** is a symbiotic association between a fungus and the roots of a vascular plant. In a mycorrhizal association, the fungus colonizes the host plant’s roots, either intracellularly as in arbuscular mycorrhiza, or extra-cellularly as in ectomycorrhiza.
N₂O: Dinitrogen oxide (nitrous oxide), laughing gas, a side product of microbial nitrate reduction (denitrification).

**NPP**, net primary production.

**Net primary production** is the amount of plant biomass (above- and belowground) that grows within a year in a given area that can be maximally harvested. It neglects emissions of volatile organic compounds and root exudates. It is generally given in g C m⁻² yr⁻¹ or for countries in million t C per year, 1 g C corresponding to about 2 g biomass dry-weight. The gross primary production (GPP), which is a measure of photosynthesis, is almost twice as high because approximately 50% of the photosynthesis products are respired by the plant for maintenance and growth when there is no light, or not enough light.

**Nitrogenases** are enzymes used by some microorganisms to fix atmospheric nitrogen gas (N₂) to form ammonia (NH₃).

**NPP₀**, NPP in the absence of human interventions such as deforestation, land use for infrastructure, fertilization, irrigation or soil sealing.

**O₂**, oxygen.

**Petrochemistry** is a branch of chemistry that studies the transformation of crude oil (petroleum) and natural gas into useful products or raw materials. These petrochemicals have become an essential part of the chemical industry today.

**Perennial** is a plant that lives for more than two years. The term is often used to differentiate a plant from shorter lived annuals and biennials.

**Photosynthesis** is a chemical process that converts carbon dioxide (CO₂) by reduction into organic compounds of biomass, especially sugars, using the energy of sunlight. The light-driven splitting of water (H₂O) to hydrogen (H₂) and oxygen (O₂) is a special case of photosynthesis.

**Photosystems** are functional and structural units of protein complexes involved in photosynthesis that together carry out the primary photochemistry of photosynthesis: the absorption of light and the transfer of energy and electrons. They are found in the thylakoid membranes of plants, algae and cyanobacteria. Two families of photosystems exist: type I (photosystem I) and type II (photosystem II). Type I photosystems use ferredoxin-like iron-sulfur cluster proteins as terminal electron. Photosystem II uses photons of light to energize electrons that are then transferred through a variety of coenzymes and cofactors to reduce plastoquinone to plastoquinol. The energized electrons are replaced by oxidizing water to form hydrogen ions (protons) and molecular oxygen.

**Photosensitizer** is a light-absorbing substance that initiates a photochemical or photophysical reaction in another substance (molecule), and is not consumed in the reaction.

**Photovoltaics** is a method of generating electrical power by converting solar radiation into direct current electricity using semiconductors that exhibit the photovoltaic effect.

**Photon** is an elementary particle, the quantum of light and all other forms of electromagnetic radiation.

**Primary energy** is the energy contained in natural resources, before undergoing any conversions or transformations. In the case of biomass, coal and oil it is the energy of combustion. In the case of non-combustible energy sources, including nuclear energy and all non-combustible regenerative energies, primary energy is the secondary energy that they produce (e.g. electricity).

**Proton exchange membrane (PEM)** is a semipermeable membrane to conduct protons while being impermeable to gases such as oxygen or hydrogen. This is the essential function when incorporated into a proton exchange membrane fuel cell or of a proton exchange membrane electrolyzer: separation of reactants and transport of protons.
PV, photovoltaics.

**Pyrolysis** is a thermochemical decomposition of organic material at elevated temperatures without the participation of oxygen.

**Renewable diesel** is derived from fats and oils by catalytic hydrogenation. It is distinct from biodiesel which is derived from fats and oils via transesterification.

**Renewable fuels** are fuels produced from renewable resources such as bioenergy and water or wind turbine electricity.

**Renewable wastes** are all agricultural and forestry wastes (manure, crop and wood residues etc.), food wastes and e.g. scrap paper.

**Respiration** is the process in which nutrients are converted into useful energy by oxidation with oxygen \((O_2)\) in a cell. Anaerobic respiration is respiration without oxygen \((O_2)\).

**Second-generation bioethanol** is derived from the lingo-cellulose part of plants, first-generation bioethanol from the starch parts of plants.

**Semiconductor** is a non-metallic material with electrical conductivity.

**Solar thermal collectors** are a designed to collect heat by absorbing sunlight. The term is applied to solar hot water panels, but may also be used to denote more complex installations such as solar parabolic, solar trough and solar towers or simpler installations such as solar air heat.

**SRREN, Special Report on Renewable Energy sources and climate change mitigation.**

**Switchgrass** is a perennial warm season bunchgrass native to North America, where it occurs naturally from 55°N latitude in Canada southwards into the United States and Mexico. Switchgrass is one of the dominant species of the central North American tallgrass prairie and can be found in remnant prairies, in native grass pastures, and naturalized along roadsides.

**Syngas = synthesis gas**

**Synthesis gas** is a mixture of carbon monoxide and hydrogen. Examples of production methods include steam reforming of natural gas or liquid hydrocarbons and the gasification of coal or biomass and the steam reforming of methane and other hydrocarbons.

**Synthetic diesel**: A mix of hydrocarbons produced from synthesis gas by e.g. Fischer-Tropsch synthesis. It is chemically very similar to refined conventional fossil fuel.

\(1\,\text{tonne} = 10^3\,\text{kg}\).

**Transesterification** is a reaction that is catalyzed by an acid or a base, to replace in an ester compound one alcohol by another alcohol, e.g. glycerol by methanol. The process is used in biodiesel production.

**Triticale** is a hybrid of wheat (**Triticum**) and rye (**Secale**) first bred in laboratories during the late 19th century. The grain was originally bred in Scotland and Sweden. Commercially available triticale is almost always a second generation hybrid, i.e., a cross between two kinds of primary (first cross) triticales.

\(1\,\text{year} = \text{yr}\).

**W, watt** = 1 J per second.

**Wind turbines** are devices that convert kinetic energy from the wind into mechanical energy. If the mechanical energy is used to produce electricity, the device may also be called a wind generator or wind charger. Wind is the movement of air across the Earth’s surface. Most winds are produced by differences in air pressure between one place and another. Differences in air pressure and the pressure gradient force are caused by the unequal heating (in time and space) of the Earth’s surface by solar radiation.
SCIENTISTS INVOLVED

Coordinators
Prof. Dr. Bärbel Friedrich ML
Institut für Biologie/Mikrobiologie, Humboldt-Universität Berlin
Prof. Dr. Bernhard Schink ML
Lehrstuhl für mikrobielle Ökologie, Limnologie und allgemeine Mikrobiologie, Universität Konstanz
Prof. Dr. Rudolf K. Thauer ML
Max-Planck-Institut für terrestrische Mikrobiologie, Marburg

Scientists involved in writing the report
Prof. Dr. Fraser A. Armstrong
Department of Inorganic Chemistry, University Oxford, Great Britain
Dr. Vincent Artero
Institute de Recherches en Technologies et Sciences pour the Vivant, Université Joseph Fourier, Grenoble, France
Priv. Doz. Dr. Nicolaus Dahmen
Institut für Katalyseforschung und -Technologie, Karlsruher Institut für Technologie (KIT)
Prof. Dr. Holger Dau
Fachbereich Physik, Freie Universität Berlin
Prof. Dr. Eckhard Dinjus
Institut für Katalyseforschung und -Technologie, Karlsruher Institut für Technologie (KIT)
Prof. Dr. Peter Dürre
Institut für Mikrobiologie und Biotechnologie, Universität Ulm
Prof. Dr. Bärbel Friedrich ML
Institut für Biologie/Mikrobiologie, Humboldt-Universität Berlin
Prof. Dr. Helmut Haberl
Institut für Soziale Ökologie (SEC), Alpen-Adria Universität Klagenfurt, Wien, Graz, Österreich
Prof. Dr. Thomas Happe
AG Photobiotechnologie, Ruhr-Universität Bochum
Prof. Dr. Christian Körner ML
Institut für Botanik, Universität Basel, Schweiz
Prof. Dr. Gerd Kohlhepp
Geografisches Institut, Eberhard-Karls-Universität Tübingen
Prof. Dr. Katharina Kohse-Höinghaus ML
Fakultät für Chemie, Universität Bielefeld
Dr. Philipp Kurz
Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel
Dr. Christian Lauk
Institut für Soziale Ökologie (SEC), Alpen-Adria Universität Klagenfurt, Wien, Graz, Österreich
Prof. Dr. Wolfgang Lubitz
Max-Planck-Institut für chemische Energiewandlung, Mülheim
Prof. Dr. Matthias Rögner
Lehrstuhl für Biochemie der Pflanzen, Ruhr-Universität Bochum
PD. Dr. Thomas Senn
Institut für Lebensmittelwissenschaft und Biotechnologie, Universität Hohenheim
Prof. Dr. Victor Smetacek
Alfred-Wegener-Institut für Polar-und Meeresforschung, Bremerhaven
Prof. Dr. Bernhard Schink ML
Lehrstuhl für mikrobielle Ökologie, Limnologie und allgemeine Mikrobiologie, Universität Konstanz
Dr. Ulrike Schmid-Staiger
Fraunhofer-Institut für Grenzflächen- und Verfahrenstechnik, Stuttgart
Prof. Dr. Ernst-Detlef Schulze ML
Max-Planck-Institut für Biogeochemie, Jena
Scientists Involved

Prof. Dr. Rudolf K. Thauer ML
Max-Planck-Institut für terrestrische Mikrobiologie, Marburg

Prof. Dr. Peter Weiland
Johann Heinrich von Thünen-Institut, Braunschweig

Dr. Karen Wilson
Cardiff School of Chemistry, Cardiff University, Wales, Great Britain

Scientists, who were interviewed to specific points

Prof. D. Thomas Bley
Institut für Lebensmittel- und Bioverfahrenstechnik der TU Dresden

Prof. Dr. Christian Barth
Deutsches Institut für Ernährungsforschung, Golm

Prof. Dr. Detlev Drenckhahn ML
Institut für Anatomie und Zellbiologie, Julius-Maximilians-Universität Würzburg

Prof. Dr. Ian Donnison
Institute for Biological, Environmental and Rural Sciences, Aberystwyth University, Wales, Great Britain

Prof. Dr. Ottmar Edenhofer und Kollegen
Potsdam-Institut für Klimafolgenforschung, Potsdam

Prof. Dr. Maarten Koornneef
Max-Planck-Institut für Pflanzenzüchtung, Köln

Dr. Adam Powell
Centre for Sustainable Aquaculture Research, Swansea University, Wales, Great Britain

Dr. Robin Shields
Centre for Sustainable Aquaculture Research, Swansea University, Wales, Great Britain

Prof. Dr. Mark Stitt ML
Max-Planck-Institut für molekulare Pflanzenphysiologie, Golm

These scientists are thanked for taking their time to read individual chapters and for raising many critical questions on numerous points, which helped balance the recommendations.

Scientific administration

Dr. Christian Anton
Nationale Akademie der Wissenschaften Leopoldina

Dr. Henning Steinicke
Nationale Akademie der Wissenschaften Leopoldina

External Reviewers

Prof. Dr. Nikolaus Amrhein ML
Group for Plant Biochemistry und Physiology, Eidgenössische Technische Hochschule (ETH) Zürich

Prof. Dr. Georg Fuchs ML
Institut für Biologie II, Mikrobiologie, Albert-Ludwigs-Universität Freiburg

Prof. Dr. Wolfgang Junge
Abteilung Biophysik, Universität Osnabrück

Prof. Dr. Bernt Krebs ML
Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster

Prof. Dr. Hermann Sahm
Institut für Biotechnologie, Forschungszentrum Jülich

Prof. Dr. Hans Joachim Schellnhuber ML
Potsdam-Institut für Klimafolgenforschung, Potsdam

Prof. Dr. Ferdi Schüth ML
Max-Planck-Institut für Kohlenforschung, Mülheim

Prof. Dr. Stefan Tangermann
Department für Agrarökonomie und urbane Entwicklung, Georg-August-Universität Göttingen, Akademie der Wissenschaften zu Göttingen

The reviewers are thanked for their many valuable suggestions, most of which were followed. The final text is, however, in the responsibility of the scientists who wrote the report.
Thursday, October 14, 2010

2.30 pm – 3.00 pm
Welcome Address
Bärbel Friedrich ML (Alfried Krupp Wissenschaftskolleg Greifswald)

Introduction
Rudolf K. Thauer ML (Member of the Presidium of the Leopoldina)

1. Availability of biomass as energy source
Chair: Rudolf K. Thauer ML (Marburg)

3.00 pm – 3.35 pm
Terrestrial Biomass carbon and its use
Christian Körner ML (Basel)

3.35 pm – 4.10 pm
Aboveground net primary production and greenhouse gas inventory
Ernst-Detlef Schulze ML (Jena)

4.10 pm – 4.30 pm
Human appropriation of net primary production
Christian Lauk and Helmut Haberl, Wien

4.30 pm – 5.00 pm
Coffee break

5.00 pm – 5.30 pm
Microalgae- an alternate energy source in future?
Rainer Buchholz (Erlangen)

5.30 pm – 6.00 pm
Use of microalgae for the production of energy carriers
Ulrike Schmid-Staiger (Stuttgart)

6.00 pm – 6.30 pm
Eco- and energy balances of biofuel production
Thomas Senn (Hohenheim)

6.30 pm – 7.00 pm
General Discussion

7.00 pm – 8.30 pm
Dinner

8.30 pm – 9.15 pm
Net primary production of marine micro algae
Victor Smetacek (Bremerhaven)

Friday, October 15, 2010

2. Conversion of biomass into fuels
Chair: Bernhard Schink ML (Konstanz)

8.30 am – 9.00 am
Practical experience with large-scale ethanol production in a tropical country
Joao Jornada (Rio de Janero, Brazil)

9.00 am – 9.30 am
Socio-economic and ecological implications of large-scale production of energy crops in Brazil. A case study on ethanol
Gerd Kohlhepp (Tübingen)

9.30 am – 10.00 am
Butanol fermentation – The scientific perspective
Peter Dürre (Ulm)

10.00 am – 10.30 am
Butanol fermentation – The industrial perspective
Ulrich Kettling (München)

10.30 am – 11.00 am
Coffee break

11.00 am – 11.30 am
Biotechnology of anaerobic processes: industry perspectives
Thomas Schäfer (Copenhagen)
Friday, October 15, 2010 continued

11.30 am – 12.00 pm
Biogas production from agricultural feedstocks: bottlenecks and necessary process improvements
Peter Weiland (Braunschweig)

12.00 pm – 12.30 pm
Conversion of algal biomass to biodiesel – efficiency and economic and environmental implications
Karen Wilson (Cardiff) / Durham

12.30 pm – 1.00 pm
Biofuels versus hydrocarbons – new chemistry towards new pollutants
Katharina Kohse-Höinghaus ML (Bielefeld)

1.00 pm – 1.30 pm
General Discussion

1.30 pm – 3.00 pm
Lunch

4.30 pm – 5.00 pm
Coffee break

5.00 pm – 5.30 pm
Chemical catalysts for a water splitting system
Holger Dau (Berlin)

5.00 pm – 5.30 pm
Model compounds of the FeFe hydrogenase active site
Leif Hammarström (Uppsala)

6.00 pm – 6.30 pm
Nobel metal-free catalytic nanomaterials for H₂ production and uptake
Vincent Artero (Grenoble)

6.30 pm – 7.00 pm
General Discussion

7.00 pm – 8.30 pm
Dinner

3. Biological and bio-inspired solar H₂ production
Chair: Bärbel Friedrich ML (Berlin/Greifswald)

3.00 pm – 3.30 pm
Biological catalysts involved in biosolar hydrogducation
Wolfgang Lubitz (Mülheim)

3.30 pm – 4.00 pm
A cyanobacterium design cell for the production of H₂
Matthias Rögner (Bochum)

4.00 pm – 4.30 pm
Enhancement of hydrogen production with green algae
Thomas Happe (Bochum)

Saturday, October 16, 2010
Writing of the report by a working group
SUPPLEMENT TO CHAPTER 1


**Die Nettoprimärproduktion der Pflanzen als Teil der Kohlenstoffumsetzungen im Ökosystem**

Die Nettoprimärproduktion (NPP) bezeichnet in erster Näherung die Menge an Biomasse, die in einem Jahr pro Bodenfläche wächst.7 Diese enge Definition ist aber nicht korrekt, denn die Photosynthese versorgt nicht nur den eigenen Organismus mit Kohlenhydraten, sondern sie liefert Zucker auch an die Mykorrhiza. Zucker werden als pflanzliche Schleime ausgeschieden, und ein Teil der Zucker und der Biomasse wird durch saugende und fressende Insekten entnommen, ohne dass dies bei der Bestimmung der NPP als Biomassezuwachs berücksichtigt wird. Die Bestimmung dieser Verluste ist mit großer Unsicherheit behaftet, liegt aber je nach Ökosystem zwischen 10 und 50%. Wegen der Schwierigkeiten, die Gesamt-NPP zu bestimmen, taucht dieser Begriff in den schematischen Darstellungen des Kohlenstoff-(C)-Kreislaufs des IPCC nicht auf.8 NPP bleibt damit ein Begriff, der vor allem im Zusammenhang mit Landnutzung durch den Menschen Verwendung findet. Die „Ernte“ nutzt einen je nach Pflanzenart unterschiedlichen Teil der NPP. Bei Feldfrüchten ist dies der sogenannte „Ernte-Index“, der selten 50% übersteigt, d.h. der Kornertrag kann 50% der oberirdischen Biomasse erreichen. Im allgemeinen liegt der Ernte Index aber bei 30 bis 40%. 9


Da die Diskussion über die Nachhaltigkeit der Bioenergie sehr davon abhängt, ob man das Ökosystem als Ganzes oder nur die Pflanzenbedeckung betrachtet, wird in Abbildung 1 der Kohlenstoff-Fluss durch ein Ökosystem und die dabei gängigen Definitionen wiedergegeben.
Ausgangspunkt ist die sogenannte Bruttoprimärproduktion (GPP = Gross Primary Production) als Maß für die Photosynthese. Der Begriff wurde eingeführt, da bis heute nicht geklärt ist, ob die mitochondriale Atmung, mit der alle Organismen ihren heterotrophen Betriebsstoffwechsel bestreiten, bei Photosynthese weiterläuft. Hierzu gibt es widersprüchliche Befunde. Bei der Berechnung der GPP wird also angenommen, dass die Atmung entsprechend der Dunkelatmung auch bei Photosynthese in den Blättern weiterläuft, d.h. die GPP könnte höher sein als die apparente Photosynthese. Die Pflanze verbraucht einen Teil der erzeugten Zucker für die Erhaltung der eigenen Struktur (Betriebsatmung) und für die Synthese neuer Strukturen (Wachstumsatmung). Der verbleibende Rest entspräche in erster Näherung der Nettoprimärproduktion (NPP).


Sofern die Bioenergie dazu dienen soll, dem Klimawandel Einhalt zu bieten, darf die Frage der Nachhaltigkeit der Nutzung von NPP nicht losgelöst von NGB betrachtet werden. Häufig wird in der CO₂-Diskussion NPP nicht nur wegen der möglichen Nutzung anstelle fossiler Energieträger (Substitution) genannt, sondern auch als Maß für die Kohlenstoffspeicherung (Sequestrierung) angesehen, was grundsätzlich falsch ist, wenn man die maßgeblichen zeitlichen und räumlichen Skalen betrachtet. Da dies eine der häufigsten Missdeutungen der Waldfunktion im CO₂-Kontext ist, sei folgendes Beispiel genannt: Nimmt man der Einfachheit halber eine hundertjährige Lebensspanne (bis zum Tod oder bis zur Ernte) von Bäumen an und setzt den maximalen Vorrat an Kohlenstoff (Biomasse) gleich 100%, so kann man NPP (im Wesentlichen das Wachstum der Bäume) verdoppeln, ohne dass sich am Vorrat etwas ändert, wenn die Bäume wieder bis zu 100% Vorrat stehen bleiben (zwei Ernten von 100% in 100 Jahren statt einer; Abbildung 2). Der Kohlenstoff rezykliert einfach doppelt so schnell durch das Ökosystem. Optimiert man nun NPP weiter und erntet in raschen Zyklus lange bevor der Zuwachs den ursprünglichen Wert von 100% Vorrat erreicht (intensive Plantagenwirtschaft), so reduziert sich der Vorrat in der Landschaft sogar deutlich. Diese Vorratsänderung muss unabhängig von dem Umsatz nach

Abbildung 1: Kohlenstoff-Fluss durch ein Ökosystem. Nach oben gerichtete Pfeile beschreiben Emissionen, nach unten gerichtete Pfeile beschreiben C-Speicherung (nach 5).


Abbildung 2: Wachstumsgeschwindigkeit und Vorrat an Biomasse-Kohlenstoff in der Landschaft an einem Beispiel für Bäume, die traditionell nach 100 Jahren geerntet werden. Solange immer derselbe maximale Vorrat (100%) erreicht wird, ist es bedeutungslos, wie rasch die Bäume wachsen und wie oft sie in den 100 Jahren geerntet werden. Dieser Fall tritt aber selten ein. Im allgemeinen führen rasche Erntezyklen zu einer Reduktion des maximalen Vorrates (nach 11).


Die flächenbezogenen Kohlenstoffbilanzen bewirtschafteter Ökosysteme

Supplement: Nettprimärproduktion und Bioenergie

a) The carbon flow and trace gas emissions in ecosystems [average (± st.dev.)]

<table>
<thead>
<tr>
<th></th>
<th>Autotrophic Respiration</th>
<th>Harvest</th>
<th>Manure</th>
<th>Heterotrophic Respiration</th>
<th>DOC/DIC</th>
<th>other GHGs (CH₄, N₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gross Primary Productivity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Net Primary Productivity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil Inputs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Net Biome Productivity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Net Biome Productivity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Net Greenhouse Gas Balance</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂ Soil</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NGB Soil</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total NGB</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

b) Forests [g C m⁻² yr⁻¹]

<table>
<thead>
<tr>
<th></th>
<th>589 (± 88)</th>
<th>63 (± 11)</th>
<th>0</th>
<th>368 (± 107)</th>
<th>7 (± 3)</th>
<th>1 (± 1)</th>
<th>-74 (± 22)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1107 (± 55)</td>
<td>-518 (± 67)</td>
<td>-400 (± 80)</td>
<td>-55</td>
<td>-20 (± 12)</td>
<td>-19 (± 11)</td>
<td>-74 (± 22)</td>
<td></td>
</tr>
</tbody>
</table>

c) Grasslands [g C m⁻² yr⁻¹]

<table>
<thead>
<tr>
<th></th>
<th>593 (± 297)</th>
<th>217 (± 43)</th>
<th>40</th>
<th>508 (± 152)</th>
<th>7 (± 3,5)</th>
<th>43 (± 14)</th>
<th>-14 (± 18)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1343 (± 269)</td>
<td>-750 (± 150)</td>
<td>0</td>
<td>-573 (± 172)</td>
<td>-57 (± 34)</td>
<td>-14 (± 18)</td>
<td>-14 (± 18)</td>
<td></td>
</tr>
</tbody>
</table>

d) Croplands [g C m⁻² yr⁻¹]

<table>
<thead>
<tr>
<th></th>
<th>570 (± 171)</th>
<th>257 (± 23)</th>
<th>26</th>
<th>319 (± 89)</th>
<th>3 (± 1)</th>
<th>7 (± 3)</th>
<th>30 (± 9)</th>
<th>40 (± 40)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1120 (± 224)</td>
<td>-550 (± 50)</td>
<td>0</td>
<td>-319 (± 64)</td>
<td>-319 (± 64)</td>
<td>-319 (± 64)</td>
<td>-319 (± 64)</td>
<td>40 (± 40)</td>
<td></td>
</tr>
</tbody>
</table>


Die Kohlenstoffbilanz Europas

Letztlich entscheidet die anteilige Fläche der Landnutzungen über die C-Bilanz eines Landes. In Tabelle 1 werden einige Kenngrößen der kontinentalen und regionalen C-Bilanz zusammengefasst. Tabelle 1 verdeutlicht, dass die zu erntende Energiemenge sehr gering ist im Vergleich zur eingestrahlten Sonnenenergie. NPP enthält nur 0.6% der Sonnenenergie. Die Nettoernte (die Ernte unter Berücksichtigung der betrieblichen Energiekosten) beträgt nur 0.2% der Sonnenenergie. Vergleicht man dies mit der Leistung
Eine Solarzelle (bis zu 30% Energieausbeute), die das gesamte Spektrum der eingestrahlten Sonnenenergie nutzt, so verbietet sich die direkte Nutzung von Biomasse als Energiequelle. Die gleiche Energiemenge wäre technisch auf einem Hundertstel der Fläche zu gewinnen.

Die NGB des Kontinents Europa ist eine geringe Senke, aber die EU-25 ist eine Nettoproduktion. Diese Ergebnisse beruhen auf Messungen der \( \text{CO}_2 \)-Konzentrationen in der Atmosphäre und anschließender inverser Modellierung der Senken und Quellen.

Für Deutschland können im Augenblick die C-Flüsse nur aus europaweiten Messungen abgeleitet werden, wobei die Schwierigkeit darin besteht, dass die Flussgrößen nicht gleichförmig über Europa verteilt sind. Die flächenanteilige Interpolation der EU-25 – Daten führt zu einer Unterschätzung der Flüsse über Deutschland, da Deutschland die stärkste Emissions-Quelle über Europa ist. Die Extrapolation der Ökosystemdaten über die anteilige Flächennutzung (Forst 11 Mio. ha, Agrarland 15 Mio. ha, Grasland und Feuchtgebiete 8 Mio. ha, Siedlungen 3 Mio. ha) führt zu höheren Werten als die flächenbezogene Interpolation. Am genauesten ist die Integration der Emissionskarten, die durch inverse Modellierung der gemessenen \( \text{CO}_2 \)-Konzentrationen in der Atmosphäre erzeugt wurden. Hier zeigt sich für die Methan- und Lachgasemissionen und die NGB, dass die Extrapolation aus europäischen Daten die tatsächliche Emission stark unterschätzt. Deutschland erzeugt 35% der biogenen Treibhausgase und 76% der NGB-Emissionen.

Im Augenblick ist unklar, wie hoch der Ernteentzug sein kann, ohne dass Ökosysteme nachhaltig geschädigt werden. Sofern die Ernte den oberirdischen Kohlenstoff entzieht, kommt es zum Humusabbau. Dieses „Experiment“ wird zurzeit in der Landwirtschaft durchgeführt, d.h. landwirtschaftliche Böden verlieren pro Jahr 2.6% des Bodenkohlenstoff (siehe oben) und das ist nicht nachhaltig. Vermutlich könnte man unter hohem Energieaufwand auch ohne Bodenkohlenstoff und ohne Bodenorganismen landwirtschaftliche Früchte erzeugen. Solch eine Landwirtschaft wäre aber voraussehbar sehr riskant und setzt energieaufwändige Infrastruktur voraus.

Die geographische Verteilung der einzelnen Flusskomponenten ist sehr unterschiedlich (Abbildung 4). Die Gesamtemissionen (biogene Emissionen und fossile Brennstoffe) erreichen über Deutschland ein Maximum.

**Auswirkungen einer Bioenergiwirtschaft**

**Die Situation in der Landwirtschaft**
Die Landwirtschaft hatte in der Vergangenheit die primäre Aufgabe, für die Ernährungssicherheit der Menschheit zu sorgen (CAP: Common Agricultural Policy). Für die Erreichung dieses Ziels werden auch Emissionen in Kauf genommen, die z.B. mit der Düngung verbunden sind. In neuer Zeit wird aber die landwirtschaftliche Fläche nicht mehr allein für die Erzeugung von Lebensmitteln verwendet, sondern für die Erzeugung von Rohstoffen eingesetzt, aus denen industrielle Produkte hergestellt werden (Biodiesel, Kosmetika aus pflanzlichen Ölen, Einkaufstüten aus Stärke). Die direkte energetische Nutzung von Biomasse (Bioenergie) gehört ebenfalls in diese Kategorie. In Deutschland dienen im Augenblick 17% der landwirtschaftlichen

Abbildung 4: Kohlenstoff und Spurengasflüsse über Europa. (a) Gesamtemission, inklusiver der Verbrennung fossiler Brennstoffe, (b) terrestrische Senken, (c) biogene Methanquellen, (d) biogene Lachgasquellen, (e) Gesamtbilanz (nach 5).


Geht man in der Agrarwirtschaft von einer Ernte von 257 g C m⁻² Jahr⁻¹ aus (Abbildung 3), dann wäre unter Einbeziehung des Einsatzes von fossilen Brennstoffen als Gestehungskosten, der assoziierten Spurengasemissionen und der Rückführung von C in Form von organischem Dünger der Nettoertrag nur etwa 160 g C m⁻² Jahr⁻¹. Würde man auf der Gesamtfläche der Landwirtschaft die Bewertung extensivieren, z.B. durch 20% weniger Düngemittelzusatz auf der gesamten Fläche, dann würde sich der Nettoertrag wegen der verringerter Emission sonstiger Spurengase wie z.B. N₂O und der verringerter Betriebskosten trotz verringerter Gesamternte sogar erhöhen.


In der Summe aller Effekte kann man nicht behaupten, dass die Erzeugung von Energie aus Produkten der Landwirtschaft in Bezug

**Die Situation in der Forstwirtschaft**


Der Preisanstieg im Brennholz und Industrieholz beruhte aber nicht allein auf dem Bedarf an Bioenergieholz sondern an dem weltweit gestiegenen Bedarf an Papier. Dies zeigt, dass die Bioenergiewirtschaft von anderen Wirtschaftsaktivitäten abhängt, die das gleiche Holzprodukt benötigen, so dass die Wirtschaftlichkeit von Bioenergieanlagen auf so hohem Preisniveau nur durch Subventionen möglich ist. Offensichtlich ist die Waldfläche von Deutschland zu klein, um alle drei Marktsegmente (Sägewindeholz, Industrieholz einschließlich Paletten und Papier, Bioenergieholz) zu bedienen. Würde man den gesamten jährlichen Holzeinschlag für die Energiegewinnung einsetzen, würde dies nur 4.7% des derzeitigen fossilen Energiebedarfs ausgleichen. Dies zeigt die begrenzten Möglichkeiten dieses Energiepfades, wobei ein Ausgleich für die stoffliche Nutzung von Holz dann durch zu-nehmende Importe (Leakage) gedeckt werden müsste.


**Der Virtuelle Fußabdruck land- und forstwirtschaftlicher Produktion**


<table>
<thead>
<tr>
<th>Agrarland EU-25 (gC m⁻² Jh⁻¹)</th>
<th>Grünländ EU-25 (gC m⁻² Jh⁻¹)</th>
<th>Wald EU-25 (gC m⁻² Jh⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nettprimärproduktion</td>
<td>550</td>
<td>750</td>
</tr>
<tr>
<td>Ernte a</td>
<td>-257</td>
<td>-217</td>
</tr>
<tr>
<td>Dünger, Emtereste a</td>
<td>26 bis 47</td>
<td>40</td>
</tr>
<tr>
<td>Verkaufte Produkte a</td>
<td>-221</td>
<td>-177</td>
</tr>
<tr>
<td>Fossile Brennstoffe für Erzeugung b</td>
<td>-26 bis -32</td>
<td>-15</td>
</tr>
<tr>
<td>CH₄ &amp; N₂O Emission der Böden c</td>
<td>-30 bis -33</td>
<td>-43</td>
</tr>
<tr>
<td>GHG Emission der Stalltierhaltung d</td>
<td>-85</td>
<td>-85</td>
</tr>
<tr>
<td>Fossile Brennstoffe der Verarbeitung a</td>
<td>-20</td>
<td>-10</td>
</tr>
<tr>
<td>Heterotrophe Atmung der Bodenorganismen a</td>
<td>-319</td>
<td>-508</td>
</tr>
<tr>
<td>Bilanz ohne fossile Brennstoffe für Arbeiter</td>
<td>-156</td>
<td>-88</td>
</tr>
</tbody>
</table>

Nach Tabelle 2 ist die Ernte in der Landwirtschaft am höchsten und in der Forstwirtschaft am niedrigsten. Ein Teil der Ernte wird als organischer Dünger zurückgeführt, bzw. verbleibt als Zweige und Laubwerk im Wald. Unterirdische Ernterückstände (Wurzeln und Stoppeln) wurden nicht berücksichtigt. Angerechnet werden die operativen Kohlenstoff-Kosten für fossile Brennstoffe, um das Produkt anzubauen und zu ernten, und die kohlenstoffäquivalenten Emissionen, die in der Grünlandwirtschaft am höchsten und in der Forstwirtschaft am niedrigsten sind. Diese „Produktionskosten“ addieren sich zu 26 (Forst) bis zu 45% (Grünland) der gernten Biomasse.

Im virtuellen Fußabdruck sind weitere Aufwendungen zu berücksichtigen. Insbesondere die C-Verluste durch Atmung bei der Viehhaltung im Stall und der Bedarf an fossilen Brennstoffen in der Produktionskette. In der Landwirtschaft handelt es sich bei dem Energiebedarf um die gesamte Nahrungsmitteleinheit und Bioenergie. Die hohen Produktionskosten in der Holzindustrie ergeben sich vor allem aus der Zellstoffindustrie, die aber zu einem überwiegenden Teil auf Holzimporten beruht. Im Jahr 2007 waren für Deutschland die Rundholzimporte und die Papierholzimporte größer (131.6 Mio. m³) als die Inlandproduktion (76.7 Mio. m³). Um nur die Energie der Inlandproduktion zu berücksichtigen, müsste der Wert für Produktionsenergie in der Forstwirtschaft auf etwa 37% sinken, und damit würde die Gesamtbilanz positiv werden (Netto-C-Abgabe, siehe Tabelle 2). Für eine entsprechende Anrechnung der Importe fehlen in der Landwirtschaft die Daten. Die Verluste im Bodenkohlenstoff bei der Agrarwirtschaft wurden nicht berücksichtigt.

In der Gesamtbilanz liegen die Gesamt-C-Verluste von der Ernte bis hin zur Erzeugung der Produkte zwischen 70% (Forstwirtschaft Inland) und 97% (Weidewirtschaft). Damit liegt die Gesamtbilanz unter Berücksichtigung aller Fehler und Ungenaugkeiten, die hier nicht diskutiert wurden, und unter Berücksichtigung, dass der fossile Brennstoffbedarf der Arbeitskräfte und der Mechanisierungsgrad nicht berücksichtigt wurde, für Land- und Forstwirtschaft nahe Null, d.h. es gibt kaum Spielraum für weitere holzverarbeitende industrielle Aktivitäten, bzw. Energiegewinne für andere Wirtschaftszweige. Diese Analyse wird durch den WBGU bestätigt, der eine negative Treibhausgasbilanz für Biomethan, Bioethanol, Pflanzenöl und Bio-diesel ausweist.
Schlussfolgerung


Rein rechnerisch ist die Produktionsfläche von Deutschland nicht ausreichend, um signifikante Einsparungen in der Nutzung an fossilen Brennstoffen zu erreichen. Die derzeitigen Umwidmungen der Flächen in der Landwirtschaft sind nur möglich durch Futtermittelimporte aus dem Ausland. Die Nutzung von Holz für Bioenergie hat zu einer starken Verzerrung im Preisgefüge von Holzprodukten und zu nicht-nachhaltigen Nutzungsformen (Vollbaumereignis) geführt, was wiederum technische Maßnahmen der Düngung erforderlich macht, um den Nährstoffhaushalt auszugleichen. Diese Maßnahmen haben wegen des Abbaus von Humus erhöhte Emissionen zur Folge.

LITERATUR


Angesichts dieser vielfältigen Effekte besteht die Notwendigkeit, die Intensität der Landnutzung durch Indikatoren abzubilden, die in der Lage sind, einzelne dieser Veränderungen räumlich verortet und im Zeitverlauf abzubilden und zu quantifizieren. Einer dieser Indikatoren ist die „menschliche Aneignung von Nettoprimärproduktion“ (abgekürzt HANPP für „human appropriation of net primary production“). HANPP ist ein Indikator für die Beeinflussung der Biomasseflüsse in Ökosystemen durch menschliche Nutzung. Auch wenn es wissenschaftlich wünschenswert wäre, NPP weiter zu fassen (siehe das Supplement von Schulze und Körner), bezieht sich das HANPP-Konzept auf Biomasseflüsse. Gründe dafür sind die bessere Messbarkeit, aber auch die unmittelbare Bedeutung von Biomasse für Menschen und Ökosysteme.

**Definition von HANPP**

HANPP bezeichnet die Differenz zwischen der NPP der potentiellen Vegetation, also der Vegetation, die an einem bestimmten Standort auf Grund von Standortfaktoren wie Boden und heutigem Klima in Abwesenheit menschlicher Nutzung zu erwarten wäre, und dem Anteil der NPP der gegenwärtig vorherrschenden Vegetation, der nach der menschlichen Ernte im Ökosystem verbleibt.

Die folgenden Formulierungen der Definition von HANPP, die in diesem Aufsatz verwendet wird (siehe Abbildung 1), sind äquivalent:

\[
\text{HANPP} = \text{NPP}_0 - \text{NPP}_t = \text{NPP}_h - \text{NPP}_{\text{act}}
\]

Unterschiedliche Definitionen von HANPP führen zu stark abweichenden Ergebnissen. So beträgt die globale terrestrische HANPP nach dieser Definition etwa ein Viertel der NPP (bzw. knapp 30% bezogen auf die oberirdische NPP; vgl. Ref. 7). Berechnet man die globale HANPP hingegen auf Basis der umfassendsten Definition von Vitousek et al. unter Verwendung der gleichen Datenbasis, so erhält man einen Wert von 37%, d.h. fast exakt den gleichen Wert, den Vitousek et al. bereits vor über 20 Jahren errechnet haben. Der wichtigste Unter-
schied besteht darin, dass Vitousek et al. in dieser umfassenden Definition die gesamte NPP von stark anthropogen beeinflussten Ökosystemen als ‚angeeignet‘ betrachten, während die in Abbildung 1 dargestellte Definition lediglich die tatsächlich geernteten oder von Menschen zerstörten Pflanzenanteile (z.B. Wurzeln von Bäumen, anthropogen verursachte Feuer) umfasst.

Methoden zur Berechnung von HANPP
Wie im Supplement 1 von Schulze und Körner im Detail ausgeführt, bestehen erhebliche Unsicherheiten bei der Ermittlung der NPP, sowohl auf Grund von definitorischen Unschärfen, als auch aus Gründen der Methodik und Datenlage, insbesondere wenn die NPP für größere Gebiete ermittelt werden soll. Im Bewusstsein entsprechender Unsicherheiten zeilen die im Folgenden diskutierten Ergebnisse für Europa darauf ab, den menschlichen Einfluss auf die Biomasseflüsse möglichst genau zu erfassen. Die Methoden werden im Folgenden kurz zusammengefasst:

• Bestehende Datenquellen unterschiedlichen Typs (Statistik, Fernerkundung, Vegetationsmodellierung, Daten aus standortspezifischen, empirischen Studien zur NPP) werden bestmöglich verknüpft. Dabei werden vor allem die Veränderungen durch menschliche Eingriffe so genau wie möglich erfasst; Fehlerquellen durch inkonsistente Datenquellen (z.B. Verwendung unterschiedlicher Modelle für NPP0 und NPPact) werden so weit wie möglich vermieden.
• Die Methoden zielen darauf ab, ein Gesamtbild zu erhalten, welches in möglichst viele Richtungen konsistent ist (z.B. entlang des Biomasseflusses vom Pflanzenwachstum bis zum Endkonsum der Biomasse sowie zwischen verschiedenen räumlichen Einheiten, d.h. von Pixels bis zur globalen Ebene). Die globale HANPP-Datenbasis, welche im Artikel von Haberl et al. dokumentiert ist (und unter http://www.uni-klu.ac.at/socce/inhalt/1191.htm heruntergeladen werden kann), beruht auf drei großen Klassen an Daten:
  • Daten zur globalen Landnutzung. Hierfür wurde ein eigener Datensatz erstellt, welcher umfassenden Konsistenzbedingungen genügt. Die Ackerbau- und Forstwirtschaftsdaten sind auf nationaler Ebene mit FAO-Daten sowie mit den großen globalen Forst-Assessments (FRA, TBFRA) konsistent. Die fünf Landnutzungsklassen sind auf Ebene einzelner Rasterzellen (Auflösung: 5min, ca. 10x10 km am Äquator) flächenreu, d.h. die Summe der Fläche der fünf Klassen ergibt die Fläche des gesamten Pixels. Der Datensatz wurde umfangreich statistisch mit anderen Landnutzungs- und Landbedeckungsdatensätzen verglichen.
  • Einer Datenbasis für globale soziökonomische Biomasseflüsse (inklusive Futtermittelbilanzen der Nutztiere) auf nationalstaatlicher Ebene (ca. 140 Länder), welche thermodynamischen Bilanzgleichungen genügt. Diese Datenbank beruht auf FAO-Daten und Futtermittelbilanzen und verfolgt Biomasseflüsse von der Ernte bis zur Ebene von Rohprodukten.
• NPP-Daten aus dem Dynamischen Globalen Vegetationsmodell (DGVM) LPJ. Zusätzlich wurden zahlreiche weitere Datengrößen herangezogen, etwa Daten über Bewässerung, Bodenqualität und NPP-Daten aus dem IBP (z.B. Ref. 12,13 und die online verfügbaren ORNL Daten).


<table>
<thead>
<tr>
<th>Land</th>
<th>Infrastruktur</th>
<th>Ackerland</th>
<th>Gras- und Weideland</th>
<th>Forste</th>
<th>Wildnisgebiete/ unproduktiv</th>
<th>Fläche insgesamt [1000 km²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Belgien, Luxemburg,</td>
<td>9%</td>
<td>37%</td>
<td>41%</td>
<td>12%</td>
<td>1%</td>
<td>111</td>
</tr>
<tr>
<td>Niederlande, Dänemark</td>
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<tr>
<td>Deutschland</td>
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<td>24%</td>
<td>30%</td>
<td>0%</td>
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</tr>
<tr>
<td>Estland, Lettland, Litauen</td>
<td>3%</td>
<td>34%</td>
<td>20%</td>
<td>42%</td>
<td>0%</td>
<td>171</td>
</tr>
<tr>
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<td>2%</td>
<td>7%</td>
<td>17%</td>
<td>69%</td>
<td>5%</td>
<td>315</td>
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<tr>
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<td>28%</td>
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<td>0%</td>
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</tr>
<tr>
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<td>27%</td>
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<td>139</td>
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<tr>
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<td>56%</td>
<td>10%</td>
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<td>19%</td>
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<tr>
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<td>6%</td>
<td>35%</td>
<td>23%</td>
<td>36%</td>
<td>0%</td>
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<tr>
<td>Polen</td>
<td>6%</td>
<td>46%</td>
<td>19%</td>
<td>29%</td>
<td>0%</td>
<td>310</td>
</tr>
<tr>
<td>Schweden</td>
<td>2%</td>
<td>6%</td>
<td>18%</td>
<td>69%</td>
<td>5%</td>
<td>431</td>
</tr>
<tr>
<td>Spanien und Portugal</td>
<td>4%</td>
<td>35%</td>
<td>30%</td>
<td>30%</td>
<td>0%</td>
<td>598</td>
</tr>
<tr>
<td>Summe</td>
<td>6%</td>
<td>29%</td>
<td>27%</td>
<td>36%</td>
<td>1%</td>
<td>3920</td>
</tr>
</tbody>
</table>

### Landnutzung in Europa

HANPP in Europa

Abbildung 3: Menschliche Aneignung von Nettoprimärproduktion und einige ihrer Komponenten in der EU-25 im Jahr 2000. Links oben die NPP der potenziellen natürlichen Vegetation laut LPJ-Berechnung, rechts oben der Verbleib von NPP im Ökosystem nach der Ernte. Unten links die Veränderung der Produktivität durch Landnutzung ($\Delta NPP_{LC}$); rot: Verminderung, grün/blau Erhöhung der NPP), unten rechts die HANPP. Quelle: verändert nach Ref. 7

<table>
<thead>
<tr>
<th></th>
<th>aNPP₀</th>
<th>∆aNPPₗₓc</th>
<th>aNPPₘₓₜ</th>
<th>aNPPₙₚₜ</th>
<th>aNPPₜ</th>
<th>aHANPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mio. t C/a]</td>
<td>[%]</td>
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<td>68</td>
</tr>
<tr>
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<td>60</td>
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<td>49</td>
<td>16</td>
<td>33</td>
<td>27</td>
</tr>
<tr>
<td>Finnland</td>
<td>94</td>
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<td>Deutschland</td>
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<td>76</td>
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<td>13</td>
</tr>
<tr>
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<td>103</td>
<td>-19</td>
<td>122</td>
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<td>68</td>
</tr>
<tr>
<td>Italien</td>
<td>94</td>
<td>-2</td>
<td>96</td>
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<td>52</td>
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<tr>
<td>Polen</td>
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<td>102</td>
<td>55</td>
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<td>70</td>
</tr>
<tr>
<td>Spanien und Portugal</td>
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<td>13</td>
<td>156</td>
<td>61</td>
<td>94</td>
<td>74</td>
</tr>
<tr>
<td>Schweden</td>
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<td>27</td>
<td>95</td>
<td>32</td>
</tr>
<tr>
<td><strong>Summe</strong></td>
<td><strong>1.296</strong></td>
<td><strong>-45</strong></td>
<td><strong>1.341</strong></td>
<td><strong>697</strong></td>
<td><strong>644</strong></td>
<td><strong>653</strong></td>
</tr>
</tbody>
</table>

Wie Tabelle 2 zeigt, beträgt die Aneignung oberirdischer NPP in der EU-25 etwa 50% der aNPP₀, wobei die Bandbreite von 25% in Schweden bis zu 69% in der Ländergruppe Belgien, Luxemburg, Niederlande und Dänemark reicht. Insgesamt wird derzeit auf dem Territorium der EU-25 Biomasse mit einem Kohlenstoffgehalt von knapp 700 Mio. tC/a geerntet, während etwas weniger als 650 Mio. tC/a an oberirdischer Biomasseproduktion im Ökosystem verbleiben. Das entspricht unter der Annahme von 50% Kohlenstoffgehalt an der Trockensubstanz und einem durchschnittlichen Brennwert von 18.5 MJ/kg Trockensubstanz etwa einer Energiemenge von 24 EJ/a, die derzeit in den europäischen Ökosystemen verbleibt.

**Unsicherheiten auf Grund von Flächen- und Erntedaten: Fallbeispiel Deutschland**

Deutschland liegt in der global-HANPP-Studie mit einer oberirdischen HANPP von 59% deutlich über dem europäischen Durchschnitt von 50% (siehe Tabelle 2). Lediglich die Ländergruppen Belgien, Luxemburg, Niederlande, Dänemark sowie Polen weisen höhere Werte auf. Bei einer differenzierten Betrachtung fällt auf, dass in Deutschland die aNPPₘₓₜ höher ist als die aNPP₀, d.h. die ∆aNPPₗₓc ist negativ. Das bedeutet, dass die oberirdische Produktivität der Vegetation in Deutschland auf Grund der intensiven landwirtschaftlichen Nutzung trotz eines erheblichen Flächenanteils von Infrastrukturflächen im Durchschnitt über dem natürlichen Niveau liegt. Dies deutet auf eine weit fortgeschrittene Intensivierung der Landnutzung hin, bei der unter anderem durch synthetische Düngemittel und andere landwirtschaftliche Inputs die Biomasseproduktion der Agrarökosysteme über jene der potentiellen natürlichen Vegetation angehoben wird.

Grundlage dieser Werte bilden, wie oben erläutert, verschiedene globale Datenquellen. Für eine Betrachtung auf globaler Ebene sind gewisse regionale Unschärfe unvermeidlich, bei einer auf ein bestimmtes Land fokussierten Betrachtung stellt sich jedoch die Frage nach der Zuverlässigkeit der Datenquellen. Deshalb werden im Folgenden wesentliche Daten, auf denen die global-HANPP-Studie beruht, für den Fall Deutschland anhand weiterer, hauptsächlich auf nationaler Ebene veröffentlichter Datenquellen überprüft.

Die für die räumliche Verteilung der HANPP relevanten Daten über die landwirtschaftlich genutzten Flächen werden in Deutschland unabhängig voneinander durch Bodennutzungshaupterhebung und Flächenerhebung berichtet. Zusammenfassend werden die der


Wesentliche Grundlage für die Berechnung der NPPₙ in der global-HANPP-Studie bildet außerdem die jährlich direkt durch den Menschen und indirekt durch Beweidung entzogene Biomasse. Die Berechnung in der

global-HANPP-Studie beruht diesbezüglich hauptsächlich auf von der FAO berichteten Erntedaten sowie im Fall der durch die Beweidung entnommenen Biomasse auf Futtermittelbilanzen der FAO sowie eigenen Berechnungen der Futtermittelbilanz der Nutztiere.\(^8\) Diese Futtermittelbilanzen ermöglichen es, die jährlichen Flüsse der durch Beweidung entnommenen Biomasse abzuschätzen, welche in den Erntestatistiken nicht berichtet oder unterschätzt werden.

Abbildung 5 vergleicht die der global-HANPP-Studie zugrunde liegenden Angaben der FAO über Erntedaten für Holz sowie Ackerfrüchte und Raufutter mit den entsprechenden Daten aus dem Ernte- und Betriebsbericht des deutschen Bundesamts für Statistik. Die Vergleichsdaten für die Holzentnahme in Abbildung 5a zeigen, dass die FAO-Daten für den Holzeinschlag, die auf der deutschen Holzeinschlagsstatistik beruhen, den tatsächlichen Holzeinschlag deutlich unterschätzen. Verschiedene Vergleichsdaten legen nahe, dass diese Unterschätzung bei 23% bis 46% liegen könnte. Diese Vergleichsdaten beruhen einerseits auf der Abschätzung des Holzeinschlags auf Basis der Holzverwendung für verschiedene Zwecke in Kombination mit Außenhandelsbilanzen (Ref. 18,19, modifiziert nach Ref. 20), sowie andererseits einem Vergleich mit der Holznutzung aus der Bundeswaldinventur, die für die alten Bundesländer für den Zeitraum 1987 bis 2002 einen Holzeinschlag ermittelt, der um 46% höher liegt als der für den selben Zeitraum durch die Holzeinschlagsstatistik ermittelte entsprechende Wert.\(^20\)


Die HANPP-Berechnung versucht, diese Unterschätzung zu vermeiden, indem die durch Wiederkäuer genutzte Biomasse über Futtermittelbilanzen abgeschätzt wird und kommt so zu höher liegenden Werten.

Insgesamt zeigt somit eine Analyse der Datengrundlagen, dass die global-HANPP-Studie für das Fallbeispiel Deutschland recht zuverlässige Aussagen trifft. Vermutlich dürfte der in dieser Studie für Deutschland errechnete HANPP-Wert eher zu niedrig als zu hoch ein-

Abbildung 5: Vergleich der in der global-HANPP-Studie verwendeten Daten zur Biomasseernte mit alternativen Datenquellen. (a) Daten zur Holzernte, (b) Daten zu Ackerbauprodukten und Raufutter. TM, Trockenmasse. Quellen: siehe Text.
zuschätzen sein. Eine Unterschätzung betrifft dabei die durch die Holzentnahme geerntete NPP, für die die deutsche Holzeinschlagsstatistik und damit die darauf beruhenden FAO-Statistik zu niedrige Werte verzeichnet\textsuperscript{20}. Berücksichtigt man dies, dürfte die oberirdische HANPP von Deutschland um 2-5\% über dem in Tabelle 2 angegebenen Wert liegen, wobei dies im Wesentlichen die Waldgebiete betreffen würde (siehe Abbildung 2).

**Unsicherheiten bezüglich der NPP-Daten**

Eine weitere Unsicherheit bezüglich der zitierten Ergebnisse zur HANPP in Europa ergibt sich aus den verwendeten Daten zur NPP. Wie bereits einleitend erwähnt, bestehen nicht nur definitorische Unscharfen hinsichtlich des Begriffs der NPP, sondern auch Unsicherheiten auf Grund von Methoden und Datengrundlagen. Für größere Räume kann NPP nicht gemessen, sondern nur mit Hilfe von Modellen berechnet werden. Diese Modelle sind zwar an Hand gemessener Daten kalibriert, ihre Ergebnisse sind dennoch aus vielen Gründen unsicher und können nur als Annäherung betrachtet werden. Um die Größenordnung der Unsicherheiten abschätzen zu können, vergleichen wir hier zwei Berechnungen der potentiellen NPP (NPP\textsubscript{o}) auf dem Territorium der EU-25:

- Der im Folgenden als „SEDAC-Daten“ bezeichnete Datensatz wurde mit dem Carnegie Ames Stanford Approach (CASA) erstellt\textsuperscript{21,22}.
- Der Datensatz der global-HANPP-Studie („gHANPP“) wurde mit dem LPJ-Modell berechnet\textsuperscript{7}.

Wie Tabelle 3 zeigt, liegt die NPP\textsubscript{o} laut SEDAC-Datensatz für das Territorium der gesamten EU-25 um etwa 11\% unter dem LPJ-Ergebnis, wobei die Abweichungen in einzelnen Ländern teilweise deutlich größer sind. Interessanter Weise liegen die LPJ-Ergebnisse für Zentral-, Ost- und Nordeuropäische Länder zum Teil erheblich über den SEDAC-Daten, wohingegen sie für West- und Südeuropa tendenziell eher niedriger liegen.

Im Zuge einer Berechnung der HANPP werden Vegetationsmodelle nicht nur zur Berechnung der NPP\textsubscript{o} herangezogen, sondern auch für die Berechnung von Teilen der NPP\textsubscript{act} (z.B. Wälder, Wildnisgebiete). Andere Teile der NPP\textsubscript{act} werden aus der Ernte mit Hilfe von Erntefaktoren hochgerechnet, diese sind daher von dieser Art der Modellunsicherheit nicht betroffen. Sollte LPJ die NPP\textsubscript{o} zu hoch eingeschätzt haben, so würde nicht nur die NPP\textsubscript{o} sinken, sondern auch die NPP\textsubscript{act}, letztere aber weniger stark, weil es am z.B. am Ackerland zu keiner Reduktion der NPP\textsubscript{act}-Schätzung käme.

### Tabelle 3: Vergleich zweier Datensätze zur potentiellen NPP (NPP\textsubscript{o}) auf dem Territorium der EU-25

<table>
<thead>
<tr>
<th>Fläche</th>
<th>NPP\textsubscript{SEDAC}</th>
<th>NPP\textsubscript{gHANPP}</th>
<th>SEDAC/gHANPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1000 km²]</td>
<td>[gC/m²/a]</td>
<td>[gC/m²/a]</td>
<td>[%]</td>
</tr>
<tr>
<td>Belgien, Luxemburg, Niederlande, Dänemark</td>
<td>111</td>
<td>577</td>
<td>612</td>
</tr>
<tr>
<td>Österreich, Tschechien, Slowenien, Slowakei, Ungarn</td>
<td>323</td>
<td>579</td>
<td>636</td>
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<tr>
<td>Estland, Lettland, Litauen</td>
<td>171</td>
<td>455</td>
<td>599</td>
</tr>
<tr>
<td>Finnland</td>
<td>315</td>
<td>305</td>
<td>513</td>
</tr>
<tr>
<td>Frankreich</td>
<td>547</td>
<td>713</td>
<td>655</td>
</tr>
<tr>
<td>Deutschland</td>
<td>357</td>
<td>577</td>
<td>619</td>
</tr>
<tr>
<td>Griechenland, Malta, Zypern</td>
<td>139</td>
<td>511</td>
<td>448</td>
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<tr>
<td>Großbritannien und Irland</td>
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<td>554</td>
</tr>
<tr>
<td>Italien</td>
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<td>621</td>
<td>555</td>
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<tr>
<td>Polen</td>
<td>310</td>
<td>474</td>
<td>639</td>
</tr>
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<td>Spanien und Portugal</td>
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<td>460</td>
<td>543</td>
</tr>
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<td>Schweden</td>
<td>431</td>
<td>345</td>
<td>514</td>
</tr>
<tr>
<td>Summe</td>
<td>3.920</td>
<td>516</td>
<td>578</td>
</tr>
</tbody>
</table>

Datenquellen: siehe Text.
Die NPPₜ wird hingegen aus Produktions- und Verbrauchsdaten ermittelt, welche auf grundlegend anderen Quellen beruhen, etwa Daten der Landwirtschaftsstatistik, Forstinventuren usw. Sinkt die Schätzung für die NPPₜ, so erhöht sich ceteris paribus bei gleich bleibender NPPₜ (die von der Modellunsicherheit der Vegetationsmodelle praktisch nicht betroffen ist) die HANPP. Der in der globalen HANPP-Studie verwendete Modellsatz (LPJ) führt daher tendenziell zu einer Unterschätzung der HANPP und einer Überschätzung der NPPₜ, also des Verbleibs von Biomasse in den Ökosystemen. Würde man also die SEDAC-Daten hinsichtlich der NPP, für realistischer halten als jene der global-HANPP-Studie, so wäre etwa in Deutschland die HANPP etwas höher als derzeit angenommen, während sie etwa in Frankreich und Italien etwas niedriger sein könnte als laut global-HANPP-Studie.

**Bioenergiepotentiale in Europa**


Die Studie zeigt, dass unter der Annahme der geschilderten Agrar-Intensivierung, insbesondere im Hinblick auf die Grünländer, substantielle Bioenergiepotentiale auf dem Territorium der EU-25 lukrieren werden könnten. Erhebliche Potentiale bestehen vor allem in den osteuropäischen Ländern, weil dort die Nutztierdichten der Raufutterverzehrer sehr niedrig sind, woraus sich beträchtliche Flächenpotentiale ergeben. Zu beachten ist, dass das Potential bei größerem Bevölkerungswachstum, einer Verstärkung des Trends zur Ernährung mit tierischen Produkten, gerin-

<table>
<thead>
<tr>
<th>Land</th>
<th>Energiepflanzenfläche [1000 km²]</th>
<th>Produktivität [gC/m²/yr]</th>
<th>Energiepotential [PJ/a]</th>
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<tr>
<td>Belgien, Luxemburg, Niederlande, Dänemark</td>
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<td>393</td>
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<td>364</td>
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<td>394</td>
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<tr>
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<td>238</td>
<td>32</td>
</tr>
<tr>
<td>Großbritannien und Irland</td>
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</tr>
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<td>Polen</td>
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</tr>
<tr>
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<td>319</td>
<td>3 698</td>
</tr>
</tbody>
</table>

Tabelle 5: Vergleich der Flächenpotentiale für Bioenergieplantagen in der EU-25 in verschiedenen Studien.

<table>
<thead>
<tr>
<th>Land</th>
<th>Ref. 27¹</th>
<th>Ref. 28²</th>
<th>Ref. 29³</th>
<th>Ref. 30,31⁴</th>
<th>Ref. 23</th>
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<tr>
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<tr>
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<td>26</td>
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<td>Griechenland, Malta, Zypern</td>
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<td>0</td>
<td>3</td>
<td>12</td>
<td>4</td>
</tr>
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<td>16</td>
<td>17</td>
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<tr>
<td>Italien</td>
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<td>15</td>
<td>22</td>
<td>16</td>
<td>12</td>
</tr>
<tr>
<td>Österr., Tschechien, Slowenien, Slowakei, Ungarn</td>
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<td>76</td>
<td>14</td>
<td>63</td>
<td>66</td>
</tr>
<tr>
<td>Polen</td>
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<td>91</td>
<td>45</td>
<td>85</td>
<td>87</td>
</tr>
<tr>
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<td>11</td>
<td>2</td>
<td>3</td>
<td>3</td>
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<tr>
<td>Spanien und Portugal</td>
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<td>181</td>
<td>26</td>
<td>18</td>
<td>23</td>
</tr>
<tr>
<td>Summe</td>
<td>576</td>
<td>627</td>
<td>193</td>
<td>337</td>
<td>305</td>
</tr>
</tbody>
</table>


Tabelle 5 vergleicht die Annahmen über Flächenpotentiale in der EU-25 für Energiepflanzenplantagen in verschiedenen Studien der letzten Jahre. Diese potentiell verfügbaren Flächen liegen im Bereich von 193,000-627,000 km², das entspricht 5-16% der gesamten landwirtschaftlich genutzten Fläche der EU-25. Wenn in einer Studie mehrere Szenarien entwickelt wurden, wurde das Szenario angegeben, das in seinen Annahmen am ehesten mit dem oben beschriebenen Szenario von Erb et al.²³ vergleichbar ist.

Die Unterschiede der Flächenpotentiale ergeben sich insbesondere durch (1) die angenommene Entwicklung der europäischen Außenhandelsbilanz für Nahrungsmittel, (2) die Entwicklung der Flächenerträge bei Nahrungsmitteln und (3) die Entscheidung, inwieweit durch die Intensivierung von Wiesen und Weiden frei werdende Flächen für den Anbau von Energiepflanzen genutzt werden.


Die vollen ökologischen Konsequenzen einer Umwandlung von 5-16% der europäischen Agrarflächen in Energiepflanzenplantagen sind beim derzeitigen Forschungsstand schwer abzuschätzen. Auch wenn Plantagen mehrjähriger Gräser, Kurzumtriebswälder und andere Lignozellulose-Energiepflanzen vermutlich ökologisch weniger belastend sein dürften als die meisten Nahrungspflanzen (Getreide, Mais etc.), sind...
alleine aufgrund des erheblichen Flächenbedarfs substantielle Effekte zu erwarten. Auch die Frage, wie die Treibhausgasbilanz eines derartig massiven Ausbaus der Bioenergieproduktion aussehen würde, ist noch zu klären.36,37

Energiepotentiale von 3-9 EJ/a sind zudem erheblich weniger eindrucksvoll, wenn man sie mit dem derzeitigen technischen Primärenergieeinsatz (d.h. ohne Ernährung von Menschen und Nutztieren) der EU-25 von etwa 70 EJ/a vergleicht38 – mehr als 4-13% des gegenwärtigen Primärenergieeinsatzes der EU-25 können durch Energiepflanzenplantagen auf dem Territorium der EU-25 wohl kaum bereitgestellt werden.

Außenhandel mit Biomasse


<table>
<thead>
<tr>
<th>HANPP auf der Landesfläche</th>
<th>eHANPP aufgrund des Biomassekonsums</th>
<th>eHANPP des Außenhandels</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mio. tC/a]</td>
<td>[Mio. tC/a]</td>
<td>[Mio. tC/a]</td>
</tr>
<tr>
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</tr>
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<td>Estland, Lettland, Litauen</td>
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</tr>
<tr>
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<td>38</td>
<td>30</td>
</tr>
<tr>
<td>Frankreich</td>
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<tr>
<td>Deutschland</td>
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<td>192</td>
</tr>
<tr>
<td>Griechenland, Malta, Zypern</td>
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<td>38</td>
</tr>
<tr>
<td>Großbritannien und Irland</td>
<td>91</td>
<td>161</td>
</tr>
<tr>
<td>Italien</td>
<td>84</td>
<td>168</td>
</tr>
<tr>
<td>Polen</td>
<td>114</td>
<td>126</td>
</tr>
<tr>
<td>Spanien und Portugal</td>
<td>137</td>
<td>227</td>
</tr>
<tr>
<td>Schweden</td>
<td>46</td>
<td>41</td>
</tr>
<tr>
<td>Summe</td>
<td>1.024</td>
<td>1.529</td>
</tr>
</tbody>
</table>
Eine Methode, mit deren Hilfe die Vorleistungen des Außenhandels mit Biomasse sichtbar gemacht werden können, ist die sogenannte „embodied HANPP“. Bei einer Berechnung der embodied HANPP (kurz: eHANPP) werden alle Verluste an Biomasse in der Vorleistungskette sowie die ΔNPP aufgrund der für die Biomasseproduktion nötigen Landnutzung den jeweils betrachteten Produkten zugerechnet, ähnlich wie beim *virtual water*-Ansatz (Abbildung 7).

Der eHANPP-Ansatz ermöglicht es, die HANPP, welche durch den Biomassekonsum einer definierten Bevölkerungsgruppe, etwa den EinwohnerInnen eines Landes, verursacht wird, zu ermitteln. Dies entspricht dem Ansatz der HANPP-Berechnung von Imhoff et al.²² Daten über die globale eHANPP, die mit Hilfe eines relativ simplen first-order Ansatzes ermittelt wurden⁶, liegen für das Jahr 2000 vor.⁴² Die Daten für die EU-25 werden in Abbildung 8 und Tabelle 6 dargestellt.


Zu beachten ist, dass die hier verwendeten Daten auf Grund der Methode, mit der sie ermittelt wurden, nur eingeschränkt belastbar sind. Nötig wäre es, diese Rechnung auf Basis

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**Abbildung 8: Analyse der embodied HANPP der EU-25 im Jahr 2000.**

(a) Konsum an embodied HANPP pro Flächeneinheit. (b) Differenz zwischen HANPP und Konsum an embodied HANPP je Rasterzelle (Smin). (c) Verhältnis zwischen HANPP und embodied HANPP der 25 EU-Länder. Quelle: verändert nach Ref. 42

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¹ Auf Grund der Verfügbarkeit der globalen HANPP-Datenbasis ist die Genauigkeit dieser Rechnung allerdings erheblich größer als jene von Imhoff et al., die auf einem noch viel größeren Faktoren-Ansatz beruht und keine globale Bilanzgleichung enthält, welche zumindest global Konsistenz herstellt.
bilateraler Handelsmatrizen und einer feineren Untergliederung der Produkte durchzuführen, was allerdings einen erheblichen Arbeitsaufwand für die Datenarbeit erfordern würde. Es ist aber davon auszugehen, dass die Daten mindestens Tendenzaussagen ermöglichen, da die globale Bilanz geschlossen wurde und somit zwar regionale Verzerrungen möglich sind, die globale Summe aber korrekt ist (siehe Ref. 42).

Abbildung 8 zeigt, dass das räumliche Muster des Konsums an embodied HANPP im Wesentlichen der Bevölkerungsdichte folgt, anders als die HANPP (vgl. Abbildung 3). Dies ergibt sich daraus, dass für die Erstellung von Abbildung 8a die Populationsdichte mit dem jeweils national durchschnittlichen Wert für den Konsum an eHANPP pro Kopf und Jahr multipliziert wurde. Abbildung 8b zeigt, dass innerhalb Europas große Regionen vorhanden sind, in welchen die HANPP die eHANPP übersteigt (diese sind blau gefärbt). Diese Regionen sind Netto-Lieferanten an Produkten, während die rot gefärbten Regionen, in denen die eHANPP die HANPP je Rasterzelle übersteigt, Netto-Konsumenten sind. Abbildung 8c zeigt das Verhältnis von eHANPP zu HANPP im nationalen Durchschnitt und bestätigt das in Tabelle 6 dargestellte Resultat, dass die EU-25 insgesamt ein starker Nettoimporteur ist.

**Schlussfolgerungen**

Europa nimmt schon jetzt weltweit erheblich mehr Produktivleistungen von Ökosystemen in Anspruch, als es in der Lage ist, auf seinem eigenen Territorium zu mobilisieren. Ein Großteil dieser massiven Nettoimporte an Ökosystemleistungen wird durch das Ernährungssystem verursacht.


LITERATUR

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