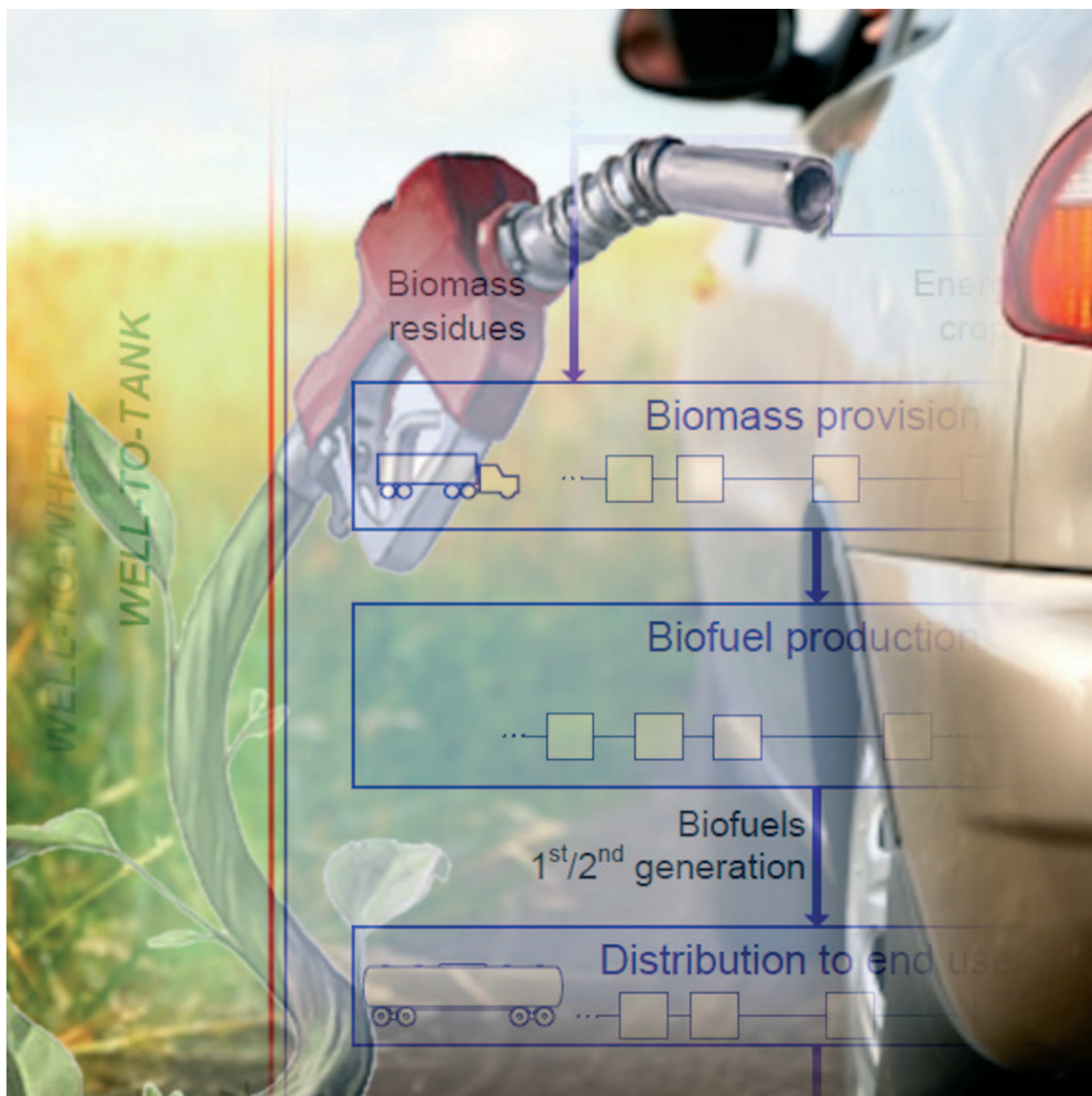# Next-Generation Biofuels: Survey of Emerging Technologies and Sustainability Issues

Sergey Zinoviev,[a] Franziska Müller-Langer,[b] Piyali Das,[a, c] Nicolás Bertero,[a, d] Paolo Fornasiero,[a, e] Martin Kaltschmitt,[b, f] Gabriele Centi,[a, g] and Stanislav Miertus*[a]

Next-generation biofuels, such as cellulosic bioethanol, biomethane from waste, synthetic biofuels obtained via gasification of biomass, biohydrogen, and others, are currently at the center of the attention of technologists and policy makers in search of the more sustainable biofuel of tomorrow. To set realistic targets for future biofuel options, it is important to assess their sustainability according to technical, economical, and environmental measures. With this aim, the review presents a comprehensive overview of the chemistry basis and of the technology related aspects of next generation biofuel production, as well as it addresses related economic issues and environmental implications. Opportunities and limits are discussed in terms of technical applicability of existing and emerging technology options to bio-waste feedstock, and further development forecasts are made based on the existing social-economic and market situation, feedstock potentials, and other global aspects. As the latter ones are concerned, the emphasis is placed on the opportunities and challenges of developing countries in adoption of this new industry.

1. Introduction

Decreasing reserves of fossil fuels, together with their impact on the environment in terms of greenhouse gas emissions, the geopolitical issues related to the market fluctuation of the oil prices, and the presence of fossil fuel resources only in certain areas have accelerated the need to explore renewable sources of energy.[1] While most current renewable energy options (e.g., wind, solar, and tidal energy, hydro-, and geo-energy) are suitable for the production of electrical energy, more than a half of the current energy consumption is based on liquid fuels. Thus, there is a need to exploit carbon-neutral energy resources, such as biofuels, that is, fuels produced from renewable biofeedstocks or biomass.[2–3]

Biofuels can be produced virtually from any source of biomass, including various crops and agricultural wastes, which are available in all countries. The latter aspect is particulary important for developing countries and countries with economies in transition, because it offers opportunities for an integrated development of agriculture and a sustainable chemical industry. Therefore, biofuels can become a synergetic driving force for energy security and industrialization, leading to improvements of the social and economical situation of people that live in less-developed regions, especially in rural areas.[4] However, the chaotic development of biofuels has shown how unsustainable practices can be detrimental to society and the environment.[5–10] Competition with food and the generally low ecocompatibility of technologies for the production of "first generation" biofuels (sugar- or vegetable oils-based) has fostered the need of a new generation of biofuels, which are to be produced from other types of biomass as well as through the use of more-sustainable technologies. These "next-generation" biofuels will be based on agricultural and other lignocellulosic (e.g., forestry) waste, waste oils, algae biomass, byproducts of other biobased industries (e.g., glycerol from biodiesel production by transesterification), and similar sources.[11, 12] Such feed resources will not compete with, but instead foster, food production, allowing the development of integrated agro-energy districts for a better rural economy.

We use the term "next"-generation, instead of the commonly used terminology of "second-," "third-," or other generations in order to avoid confusion and to underline the key difference between all these new biofuels and the first-generation ones: the use of non-edible biofeedstocks.

Although such feedstocks are, in principle, available in all countries, each country or even region will have its own specific type of biomass available to the production of biofuels. In addition, it is often necessary to use multiple biomass feedstocks at a single site, because the amount of a single type of biomass available within a reasonable distance might not be sufficient to operate a plant at full capacity during the entire year. Thus, there is a need to select preferred biofuel production routes and technologies, taking into account country-specific conditions. This aspect is even more relevant for developing countries, which have the tendency to import technologies from industrialized countries. Because these choices depend on many factors, one must assess different production technology options in terms of, for example, technical, economical, and environmental aspects; the three components of sustainability. While many reviews and books on biofuels analyse some

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of these aspects,[13–22] few have attempted to give a comprehensive, integrated picture.[23]

In addition, the development of biofuels requires multidisciplinary competences, from chemistry and biology to process development, agriculture, policy making, and more. Because of the pervasiveness of energy issues in today's world, policy makers should actively participate in the decision-making process on selection of development strategies for next-generation biofuels. Therefore, it is important to present, in a comprehensive way, key parameters that can be employed as criteria for this decision-making processes related to next-generation biofuels.

This Review adopts a comprehensive approach suitable for a larger, and not only specialized, audience. Some background and basis necessary for understanding technical aspects and related development history of production pathways are outlined together with other key aspects, such as opportunities and limits of the different routes, whilst many specialized reviews or books address specialized issues in a more detailed and extensive manner.

The review specifically addresses next-generation biofuels and not the first-generation ones. Attention is focused on the production technologies, that is, those that employ chemical treatment to convert biomass into end products. Most of these technologies, approaches, or methodologies are still at concept, research, or pilot scale-up phases, so the term "technology" is used in a general way.

Sergey Zinoviev obtained his PhD (2002) in chemistry and catalysis from the N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences. In 2001–2006 he held postdoctoral and fellowship positions at the Interuniversity Consortium "Chemistry for the Environment" in Venice and at ICS-UNIDO in Trieste, Italy. Since 2007 he is the associate scientific officer of the Area of Chemistry of ICS-UNIDO. His fields of expertise include applications of green techniques in organic chemistry, chemistry and technology for destruction of organic pollutants, and for production of biofuels and chemicals from biomass. He is a co-author of over 30 scientific papers and 2 books.

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Nicolás Bertero obtained his PhD in Chemical Engineering in 2007 (Universidad Nacional del Litoral, Santa Fe, Argentina). After his postdoctoral fellowship in the Area of Chemistry at the ICS-UNIDO and University of Trieste (Italy, 2009), he joined the CONICET (Argentina) as a Researcher in 2010. His work has been mainly focused on the utilization of heterogeneous catalysts in fine chemical synthesis, environmental applications and biofuels.

Prof. Dr. Martin Kaltschmitt studied petroleum engineering and obtained his PhD in the field of renewable energy. Today he is heading the Institute of Environmental Technology and Energy Economics at Hamburg University of Technology as well as the German Biomass Research Centre in Leipzig. He has published 10 books and more than 100 articles. In addition, he made more than 200 contributions to conferences and congresses worldwide. He is member of several committees within the field of renewable sources of energy.

Paolo Fornasiero completed his PhD in 1996. After one year as a postdoctoral fellow at the University of Reading (UK, 1997), he joined the University of Trieste (Italy) as an Assistant Professor in 1998. In 2006, he was appointed Associated Professor of Inorganic Chemistry at the same University. Since 2008, he is the scientific director of the CNR-ICCOM Trieste research unit. He is a co-author of more than 100 articles and 7 book chapters. His scientific interests are focused on technological applications of materials science and environmental heterogeneous catalysis.

Gabriele Centi is a full professor of Industrial Chemistry (University Messina, Italy). He was the President of EFCATS, and is Coordinator of the EU Network of Excellence IDECAT. He is also the Director of the Section Energy and Environment of INSTM and Scientific Coordinator of the Italian Technology Platform of Sustainable Chemistry. He is a Chairman of the Editorial Board for ChemSusChem, and Chief Editor of the Book Series Studies in Surface Science and Catalysis. He has published over 285 scientific papers, 8 books, and several special issues of journals.

Stanislav Miertus graduated from the Slovak Technological University (STU, Bratislava, Slovakia) in 1971 and obtained his PhD from the same insitute in 1975. He was Professor at the Faculty of Chemistry at STU from 1981–1990. In 1990 he moved to Trieste (Italy) where he acted as a Visiting Professor at the University of Trieste, and from 1998 onwards as the Area Chief of ICS-UNIDO. He has coordinated programmes on catalysis and sustainable chemistry, biofuels and bio-based products, and environmentally degradable plastics, among other topics. He has published more than 200 scientific papers and 20 books.

Specifically, the following next-generation biofuels are discussed: advanced biodiesel or hydrogenated vegetable oils (HVO); five synthetic biofuels, namely Fischer–Tropsch (FT) diesel, methanol, dimethylether (DME), substitute (or synthetic) natural gas (SNG), methyl-*tert*-butyl-ether (MTBE); biomethane (via biogas); ethanol (from lignocellulose); and hydrogen. Most of the options reviewed here refer to processes or approaches that are relatively new to the chemical industry, and many of them still require extensive research before mature commercial technologies can appear. Some core processes such as FT synthesis (FTS) or methanol synthesis are very efficient but rely on complex technological solutions and may require adaptation in order to be applied to the biobased feedstocks while others like biogas are based on simple technology and are highly relevant in developing countries because of the ease of operation and economy.

Following the technical overview, where only qualitative assessment will be made, the Review presents the results of economical and environmental assessments of the above mentioned biofuel options. These assessments are based on the general indicators of the overall value chain of biofuels, such as production costs, well-to-wheel costs, and greenhouse gas (GHG) emissions. To complete the picture, some projections and outlooks are made concerning the basis of demand and feedstock potentials, current investments, and the maturity of the technologies. Thus, this paper will provide the reader with a comprehensive interdisciplinary summary of the state-of-the-art of the rapidly emerging field of next-generation biofuels, giving at the same time insights into the sustainability, opportunities, and limits of specific processes, and the field in general.

2. Technical Overview of Production Technologies

2.1. General aspects

The conversion or treatment technologies for biofuel production are basically divided into physicochemical, thermochemical, and biochemical treatment, as shown in Scheme 1. Whilst the physicochemical approach serves mainly as pretreatment and does not involve any chemical transformation of the matter, the chemical conversion of biomass changes its chemical structure by treatment with heat, chemicals, catalysts, or combinations thereof. Thus, there are three main approaches for the chemical conversion of biomass for next-generation biofuels, namely: (1) thermochemical, (2) biochemical, and (3) chemical (chemically catalytic). If the primary step is not final, further chemical treatment steps are employed, which are usually chemically catalytic or biochemical.

The thermochemical approach consists of pyrolytic treatment processes of biomass to produce solid, liquid, or gaseous products that can be subsequently upgraded to fuels (synthetic biofuels). Depending on the reaction conditions, different types of pyrolysis, gasification, and torrefaction are used to produce gaseous, liquid, or solid fuels. These primary treatment methods produce intermediates that should be first purified, often in multiple steps, and then be further upgraded to fuels through catalytic treatments, for example, hydroprocessing, cracking, steam reforming, methanation, FTS, or other methods. In principle, all types of biomass can be treated thermochemically.

There are two main options for the biochemical treatment of primary biomass: (1) enzymatic hydrolysis of cellulose and
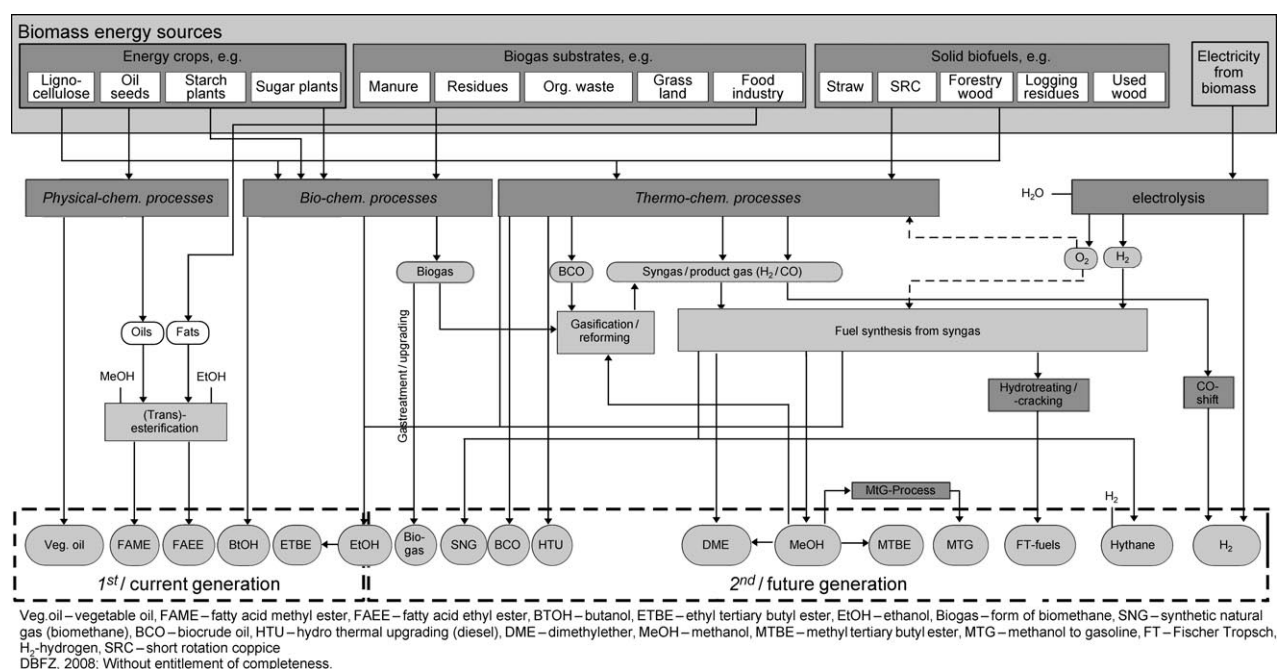
Scheme 1. A spectrum of biofuels and their production pathways.

hemicellulose, and (2) biogas production by anaerobic bacteria. While the latter can be directly applied to process soluble organic matter, the former is designed to treat lignocellulosic materials. However, because of the low rate of direct enzymatic hydrolysis of lignocellulose, a physicochemical pretreatment of lignocellulosic biomass is necessary. Lignin is not converted by enzymes and can be combusted, but its conversion by using new advanced biochemical methods is gaining attention.[24] Following the hydrolysis of cellulose and hemicellulose to hexoses and pentoses, further enzymatic transformation (fermentation) produces mainly alcohols. For example, bioethanol is produced via fermentation of C5–C6 sugars. Using different enzymes, other products (e.g., butanol) can be also synthesized.

With the chemical or chemical-catalytic approach, the cellulosic biomass undergoes catalytic hydrolysis with acids. The acid is used either in aqueous solution (e.g., diluted sulphuric acid; a commercial method) or as a heterogeneous phase (e.g., solid catalysts and ionic liquids) to lower the impact on the environment.[25,26] Another example of primary chemical-catalytic treatment is the transesterification of triglycerides, which is not detailed here because it is a common technology for the production of first-generation biodiesel; however, in the case of transesterification of waste oils or algae oils the so-obtained biodiesel can be classified as a next-generation biofuel. Chemical-catalytic routes are then also necessary for conversion of the intermediates (platform molecules) formed in the primary treatment steps to synthetic fuels and biohydrogen.

2.2. Primary thermochemical biomass treatment

2.2.1. Pyrolysis and cracking

Pyrolysis is the conversion of organic substances of complex structure (e.g., biomass) to smaller molecules, whereby cleavage of chemical bonds occurs by heating in the absence of oxygen.[27–29] Pyrolysis of vegetable feedstock normally produces mixtures of solid char, oxygenated liquid products (pyrolysis oil or bio-oil), and gases of different composition depending on the feedstock, temperature regime, reaction time, and other parameters.

Among different pyrolytic techniques (see Figure 1), flash or fast pyrolysis employing medium temperatures (up to 50 °C) and short reaction times (less than 2 s), is usually considered suitable for fuel production, as it affords higher yields of oily products. The process is well studied,[27,30,31] applicable to virtually any biomass,[32] and is commercially available. Clean Solutions, Pyrovac, Dynamotive, Ensyn, BTG, Changing World Technologies, Fortum, and ROI are among the main technology providers. Even though flash pyrolysis is mostly preferable for the production of higher-value chemicals, bio-oil is often regarded as a possible intermediate for fuel production.[33]

The pyrolysis oils should be upgraded to produce light hydrocarbon fuels, for example by cracking/hydrotreating. Crack-
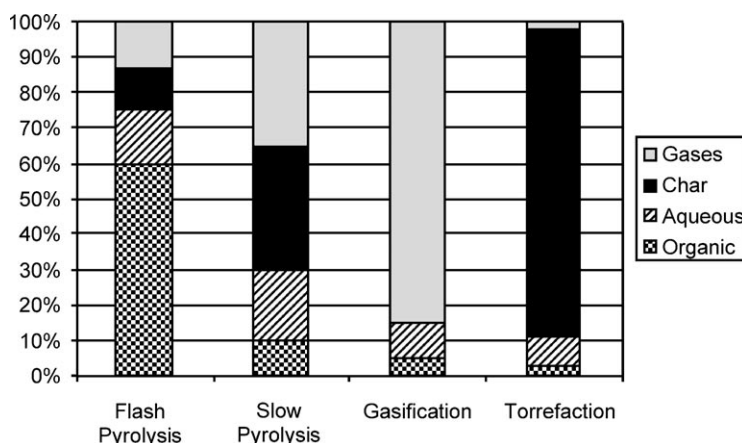

Figure 1. Indicative product composition ratios (mass %) of different pyrolytic treatment methods of lignocellulosic biomass.

ing is often performed in the presence of a catalyst, typically zeolites.[34–38] Catalytic hydrocracking is carried out in the presence of H_2 and bifunctional catalysts at 400 to 500 C and yields a heavier hydrocarbon fraction similar to conventional diesel.[39–42] Hydrocracking is a well-known process in the petroleum industry, and has recently also been applied to bio-oil and to vegetable oils.[41,43–45]

An interesting alternative pyrolytic process to convert cellulosic biomass into fuels is hydrothermal treatment or hydrothermal upgrading (HTU).[46] The thermal treatment is carried out in an aqueous medium under elevated pressures (sub-critical water) and yields bio-oil of good quality, because large amounts of oxygen are removed as CO_2 and water during the treatment. A similar treatment may be also applied to the liquefaction of rice straw to bio-oil with sub- and supercritical mixtures (ethanol/water and 2-propanol/water).[47] Temperatures of 350 to 450 °C and high pressures (6 to 18 MPa) are required. Bio-oil yields of around 40 % can be obtained. The lighter fractions of this biocrude are then upgraded to HTU diesel via a catalytic hydrodeoxygenation (HDO) process,[48] which is intrinsically similar to hydrotreatment. Intense research and developments (R&D) efforts have recently been dedicated to the hydrotreatment of bio-oils.[49–54]

Bio-oil can also be further processed by other thermochemical methods, such as gasification (see Section 2.2.2)[55,56] or by steam reforming, to produce synthesis gas (bio-syngas), which can be further upgraded to hydrogen or synthetic fuels. Steam reforming of bio-oil[57] or its fractions[58–64] requires temperatures of over 600 °C and the presence of a metal catalyst. The aqueous bio-oil fraction can also be converted to fuels by hydrolysis and fermentation.[65,66]

2.2.2. Gasification

Gasification is a thermochemical process similar to pyrolysis, and involves thermal treatment of biomass at a limited amount of oxygen or air at temperatures over 750 °C. The heat of reaction necessary for the conversion of biomass (from py-

rolysis and cracking to drying and reduction) is provided by the partial combustion of biomass (see Scheme 2).

Usually, gasification of biomass yields over 80 % of gas (see Table 1 for the composition),[67,68] which can, for example, be
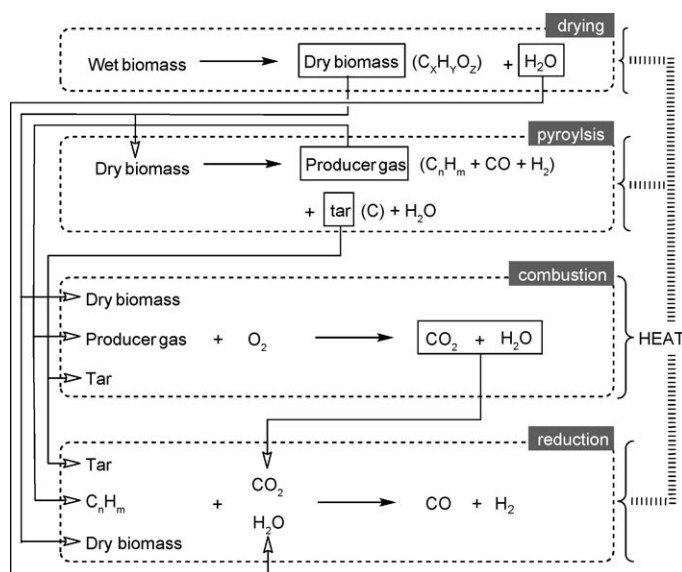
Scheme 2. Schematic of chemical and physicochemical processes that occur during the gasification of biomass, and their relationships.

Table 1. Composition of gas produced from wood and charcoal co-current gasifiers operated on low- to medium-moisture-content fuels, using air as oxidant and ambient pressure. Adapted from Refs. [67,68].

Component	Wood gas [% vol]	Charcoal gas [% vol]
Nitrogen	50–60	55–65
Carbon monoxide	14–25	28–32
Carbon dioxide	9–15	1–3
Hydrogen	10–20	4–10
Methane	2–6	0–2
Heating value [$MJ\,Nm^{-3}$]	3.3–7.2	4.5–5.6

cleaned and then directly used as a fuel (e.g., in heat and power generators) or be upgraded to a CO/H_2 synthesis gas mixture. Similar to the synthesis gas obtained via methane or coal gasification, bio-syngas is a valuable intermediate feedstock for the chemical industry because it can be converted into a range of useful products, such as biofuels and biohydrogen (Scheme 3 presents some pathways),[69] using various catalytic processes. These are described in more detail in the following chapters.

Because of this versatility of bio-syngas, gasification is usually preferred to flash pyrolysis for biomass treatment. Many companies have commercialized biomass gasification processes, for example, FERCO, Skive, BSC (Brightstar Synfuel), BGT, and Carbona. Intensive research, development, and deployment (R&D&D) in the specific field of biomass gasification

also takes place worldwide.[70–76] However, the upgrading of produced gas to bio-syngas suitable for synthetic and fuel applications requires several complex processes, namely: (1) removal of char particulate matter, inert gases (CO_2 and N_2), and traces of alkali metals, halides, sulphur, and nitrogen compounds, which can be poisonous to catalysts; and (2) adjustment of the CO/H_2 ratio via water–gas shift (WGS) reaction (increasing the H_2 content in the gas mixture via the reaction of water with CO).[77]

Flash pyrolysis can be a useful pretreatment step prior to gasification, because it allows both better yields and quality of produced gas and easier transport of bio-oil rather than of raw biomass to a centralized gasification unit.

2.3. Synthetic biofuels

As mentioned above, FT diesel, biomethanol, bioDME, bio-MTBE, and bioSNG are produced from bio-syngas.[78] Thus, the pretreatment process to obtain bio-syngas through biomass gasification is basically the same for different biofuels discussed in this section. The difference lies in the operating conditions and catalysts applied in the downstream bio-syngas conversion steps.[71]
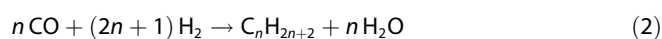
2.3.1. Fischer–Tropsch fuels

FT synthesis has been known for almost one century. First commercialized in Germany and in the US in the 1940s, a number of large scale CTL (coal to liquid) plants have been installed worldwide. Starting from the 1990s, there has been renewed interest in FT synthesis with the introduction of GTL (gas to liquid) plants in Malaysia, South Africa, and Qatar (under construction) that use syngas from natural gas. However, commercial experience with FT synthesis starting from bio-based syngas is at a very early stage.

The FT reaction yields a mixture of straight-chain alkenes and alkanes as major products, including CH_4, C_2H_4, C_2H_6, LPG (C3 to C4), gasoline (C5 to C12), diesel fuel (C13 to C22), and waxes (C23 to C33). Oxygenated compounds such as alcohols, aldehydes, acids, and ketones are produced as minor products.
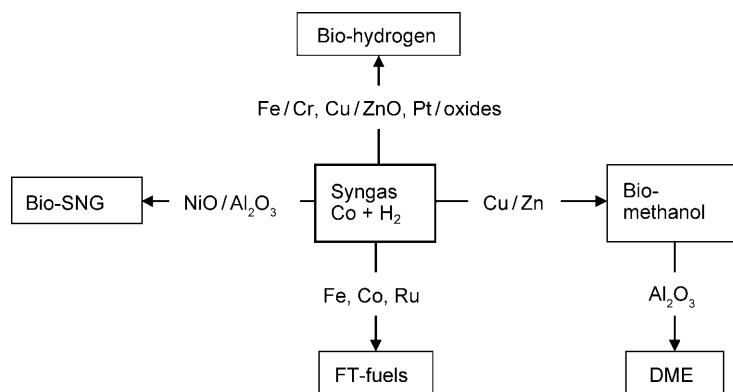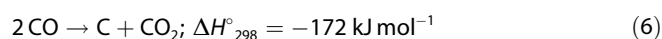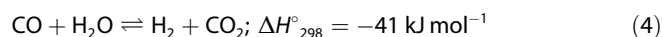

Scheme 3. Examples of syngas based catalytic processes for biofuel production. Adapted from Ref. [69].

Apart from being sulphur- and nitrogen-free, the high selectivity for linear hydrocarbons of the FT process has generated considerable interest for producing high-grade diesel in recent years.[79–88] The reaction follows a chain-growth mechanism.[89–94] Selectivity is controlled by the ability of a specific catalyst to facilitate chain propagation, versus chain termination, reactions.

$$CO + 2H_2 \rightarrow -CH_2- + H_2O; \Delta H^{\circ}_{227} = -165 \text{ kJ mol}^{-1} \quad (1)$$

$$n\,CO + (2n+1)\,H_2 \rightarrow C_nH_{2n+2} + n\,H_2O \quad (2)$$

$$n\,CO + 2n\,H_2 \rightarrow C_nH_{2n} + n\,H_2O \quad (3)$$

The required H_2/CO ratio for Co-based catalyst is 2.15, while in case of Fe-based catalyst a lower value 1.7 is preferred because H_2 is produced in situ by the strong WGS activity of Fe [Equation (4)].[79] Therefore, the net FT reaction for an Fe-catalyzed process is given by Equation (5). Due to the high exothermicity of the FT reactions, an efficient removal of the excess heat is necessary to obtain optimum product selectivity and long catalyst lifetimes, which otherwise leads to a high degree of carbon deposits over the catalyst surface, which causes catalyst deactivation via the Boudouard reaction [Equation (6)].

$$CO + H_2O \rightleftharpoons H_2 + CO_2; \Delta H^{\circ}_{298} = -41 \text{ kJ mol}^{-1} \quad (4)$$

$$2CO + H_2 \rightarrow -CH_2- + CO_2; \Delta H^{\circ}_{298} = -204 \text{ kJ mol}^{-1} \quad (5)$$

$$2CO \rightarrow C + CO_2; \Delta H^{\circ}_{298} = -172 \text{ kJ mol}^{-1} \quad (6)$$

Typically FT synthesis is performed at a temperature in the range of 200–350 °C and a pressure in the range of 1.5–4.0 MPa, using catalysts based on group VIII transition metal oxides (Ru > Fe > Ni > Co > Rh > Pd > Pt, in order of kinetic performance).[95] Co-based catalysts are the preferred choice for FT diesel synthesis because of their high hydrocarbon selectivity and good yield of straight-chain alkanes. However, the product selectivity is also a factor of reaction temperature, pressure, gas composition, and promoters.[96,97] Over the years several types of FT reactors have been developed for commercial applications. Among them, multitubular fixed-bed reactors, three-phase slurry, and fluidized- or circulating-bed reactors are the most common ones (Figure 2).[98–101]

The raw bio-syngas (gas produced from biomass gasification) consists of H_2, CO, CO_2, and CH_4, and is not suitable for direct FT conversions. The composition must be adjusted by CH_4 reforming, WGS reaction, and CO_2 removal. Steam reforming of bio-syngas with an additional natural gas feedstock is also considered as a viable option.[102–106] The Fe/Cu/K catalyst on Al_2O_3/SiO_2 support has recently demonstrated high FT activity on bio-syngas.[107] The key challenge of using bio-syngas is the clean-up step to separate tar, and other impurities prior to conversion steps.[108–111]

Only recently has FT synthesis based on bio-syngas gained importance. The first FT synthesis pilot plant using bio-syngas from woodchips and straw with a capacity of 1 MW (α-plant) was set up in 1998 by CHOREN in Freiberg (Germany). This
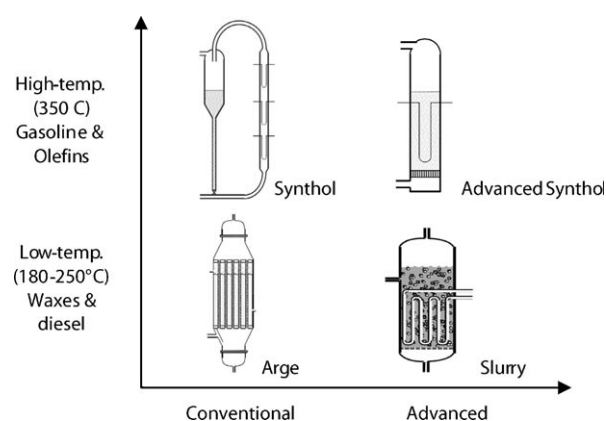

Figure 2. Sasol Fischer–Tropsch reactors. Adapted from Ref. [98].

plant is based on a patented gasification process called Carbo-V CHOREN,[112] involving three stages: (2) low-temperature gasification, (2) high-temperature gasification and (3) endothermic entrained-bed gasification.[112] In 2003–2005, in alliance with Shell, Daimler Chrysler AG, and Volkswagen AG, CHOREN started the construction of the world's first commercial 45 MW (biomass input) demonstration plant (β-plant) in Freiberg. The demonstration plant has a production capacity of 15.000 t of BTL fuel per year, and a large-scale plant of about 600 MW (biomass input; Σ-plant) is planned for the medium term.

By using the FT process it is possible to obtain diesel that has some advantages over conventional diesel, namely:[113] (1) a higher cetane number and, therefore, a much better ignition performance; (2) the absence of aromatics and sulphur, which significantly reduces pollutants in exhaust emissions; (3) no need for any adjustment to existing infrastructure or engine systems.

There are a few other R&D-scale BTL pilot/demonstration units in operation worldwide. For example, a 8 MW CHP (combined heat and power) demonstration plant in Güssing (Austria) has been in operation since 2005. The former IGCC (integrated gasification combined cycle) plant in Varnamo (Sweden) is under reconstruction to produce bioDME, biomethanol, and FT diesel.[115–118]
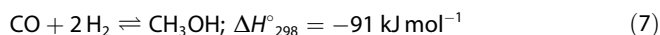
2.3.2. Biomethanol

Methanol (CH_3OH) is currently a large-scale chemical with global production of 80 Mt a^{-1}. It is an important intermediate for formaldehyde, DME, MTBE, acetic acid, olefins, and others. The interest is further increasing for its role as key intermediate in coal and CO_2 upgrading, as clean energy vector ("methanol economy"[119]), as fuel in direct methanol fuel cells (DMFC),[120] and as raw material in the production of FAME (fatty acid methyl esters) biodiesel.

Methanol is mainly produced by the catalytic conversion of the syngas obtained via catalytic steam reforming of natural gas.[121] Bio-syngas is not yet economically viable for industrial methanol production; however, there is an increasing interest in developing technologies for production of methanol from biomass. The net reaction of methanol synthesis is given in

Equation (7):

$$CO + 2H_2 \rightleftharpoons CH_3OH; \Delta H^\circ_{298} = -91 \text{ kJ mol}^{-1} \quad (7)$$

Methanol synthesis requires a stoichiometric ratio of slightly above 2, defined as $(H_2 - CO_2)/(CO + CO_2)$.[122] Methanol formation from syngas is 100 times faster in the presence of CO_2 compared to feeding CO/H_2 only.[123, 124] In the proposed mechanism, CO_2 is adsorbed onto the partially oxidized metal surface as a carbonate and is then hydrogenated to formate and further to methanol.[125] The net reaction of this process is shown in Equation (8):

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O; \Delta H^\circ_{298} = -49 \text{ kJ mol}^{-1} \quad (8)$$

Typically a CO_2 concentration of 4–8% is maintained in the syngas for maximum activity and selectivity, particularly when using Cu catalysts. The conventional methanol technology employs temperatures of 220 to 275 °C and pressures of 5 to 10 MPa in the presence of Cu catalysts. The presence of ZnO in the catalyst formulation prevents the agglomeration of Cu particles at the reaction temperature.[126, 127] Addition of K and Cs to Cu/ZnO improves methanol synthesis yields. Copper-zirconia based catalysts have been also reported to give high methanol yields in the presence of CO_2.[128]

The initial high-pressure (25 to 35 MPa) methanol process has now been replaced by low-pressure technology. The latter uses an adiabatic converter at 210 to 290 °C, 5 to 10 MPa, and a Cu/ZnO/Al$_2$O$_3$ catalyst (ICI-JM process) or an isothermal converter at 230 to 265 °C, 5 to 10 MPa, and a Cu/ZnO/Cr$_2$O$_3$ catalyst (Lurgi process).[121] Low-pressure technologies have also been developed and are marketed by Mitsubishi Gas Chemical Co. (240 °C, 8 to 10 MPa), and Haldor Topsøe (260 °C, 5 to 30 MPa).[121, 129–135] Liquid-three-phase slurry reactors (LPMEOH)[136, 137] similar to the FT slurry reactors are used for the latter cases. Most of these processes are able to process a low $H_2/(CO + CO_2)$ ratio syngas, and they are in principle suited to the use of bio-syngas as feed.

2.3.3. BioDME

DME (CH$_3$OCH$_3$) is a promising alternative to liquefied natural gas (LNG).[138–141] Its actual world production based on fossil fuels is about 3 to 4 Mt a^{-1}, but with an expected growth to 20 Mt a^{-1} by 2020. Many companies, such as KOGAS and PT Pertamina/Arrtu Mega Energie have announced large-scale DME plants, and Chemrec's pulp mill integrated bio-DME biorefinery demonstration plant in Piteå (Sweden) is expected to start production by the end of 2010.[142]

DME derives from methanol dehydration [Equation (9)][143] and can thus be produced from syngas or CO_2/H_2 in a single- or most often two-stage process from methanol [Equations (7) and (8)]. In the commercial DME production process, methanol is dehydrated to DME over a slightly acid catalyst such as γ-alumina (Al$_2$O$_3$) by a gas-phase exothermic reaction.

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O; \Delta H^\circ_{298} = -23 \text{ kJ mol}^{-1} \quad (9)$$

The conventional process includes vaporization of methanol and feeding it into the catalytic reactor under a pressure of 1–2 MPa and at temperatures of 220–250 °C (the temperature of reactor zone on the outlet is 300–350 °C). The resulting mixture containing DME, water, and unconverted methanol is fed to a distillation column after heat recovery and cooling.

Recently, direct synthesis of DME from syngas in single step (Equation 10) using bifunctional catalysts[144] and a slurry reactor (Liquid Phase DME process - LPDME) have been reported as an energy efficient alternative.[145, 146] This process operates at a pressure of 6 to 7 MPa and a temperature of 210 to 300 C. The ideal ratio of H_2 to CO for direct DME synthesis is one.[140, 141, 147]

$$3CO + 3H_2 \rightleftharpoons CH_3OCH_3 + CO_2 \quad (10)$$
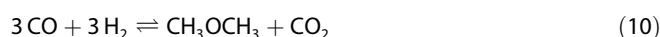
The first commercial DME plant (10 000 t a^{-1}) for fuel use was constructed by Lutianhua Group Inc. licensed under TOYO (Japan) in August 2003.[148] PR China plans to use DME as LPG substitute and several plants have been operating since 2003. In addition, there are several small- and medium-scale demonstration units in Japan and Korea for DME fuel production.

2.3.4. BioMTBE

MTBE [(CH$_3$)$_3$COCH$_3$)] is another derivative of methanol that is widely used as a gasoline additive, although its commercial production volume has been declining recently because of health and environmental issues.[149, 150] The process involves the reaction of isobutene with methanol in the presence of an acidic catalyst at 30 to 100 °C and 0.7 to 1.4 MPa in the liquid phase [Equation (11)].[151] When biomethanol is used, the obtained MTBE cannot be fully considered a renewable biofuel because isobutene is typically derived from oil.

$$i\text{-C}_4H_8 + CH_3OH \rightarrow (CH_3)_3COCH_3; \Delta H^\circ_{298} = -37 \text{ kJ mol}^{-1} \quad (11)$$
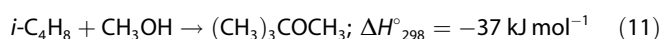
Solid acids such as zeolites (H-ZSM-5) and resins (Amberlyst-15)[152] are commonly used as catalysts. A molar excess of methanol is necessary to facilitate isobutene conversion and hinder the dimerization and oligomerization of isobutene.
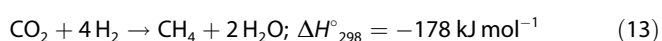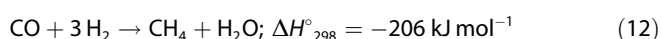
2.3.5. BioSNG

BioSNG is the synthetic equivalent of natural gas obtained from biomass, and can be used as fuel in vehicles and for heat and power generation. It is produced by methanation of bio-syngas, a process currently extensively studied at pilot scale. For example, a demonstration facility in Güssing (Austria) produces bioSNG (from woody biomass) at a capacity of ca. 10 m^{3}N h^{-1} (1 MW$_{SNG}$).[153] Commercial plants are expected to operate on a scale from 20 to a few 100 MW$_{SNG}$. The process is known in the coal industry, where SNG is made from coal through its gasification into syngas and successive methanation (e.g., the TREMP process by Haldor Topsøe).[154] Among

others, ECN has developed a system for the conversion of dry lignocellulosic biomass into natural gas quality gas.[155] A laboratory-scale system is available at ECN, and a 10 MW demo plant is planned to be operative from 2012.

SNG production occurs through the reaction shown in Equation (12). The reaction stoichiometry requires a H_2/CO molar ratio of 3, which can be reached through conditioning the WGS reaction (increasing the H_2 content in syngas by the reaction of CO with water). The CO_2 produced in the WGS reaction is converted to SNG via the reaction shown in Equation (13). Methanation is carried out over a commercial nickel oxide catalyst and involves temperatures of 300 to 350 C and 0.1 to 0.5 MPa pressure. Commercial-grade SNG requires post synthesis treatment of the crude SNG to remove water and CO_2 impurities. The methanation process is exothermic. Effective recovery of this heat can also produce additional power.[156]

$$CO + 3H_2 \rightarrow CH_4 + H_2O; \ \Delta H^{\circ}_{298} = -206 \ kJ \ mol^{-1} \quad (12)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O; \ \Delta H^{\circ}_{298} = -178 \ kJ \ mol^{-1} \quad (13)$$

The challenges for further development of bio-SNG production include: improvement of the primary gasification process, gas cleaning and conditioning, and more stable methanation catalysts. New biomass gasification technologies such as steam gasification or supercritical water gasification are currently studied to increase the content of hydrogen and methane, as well as to decrease that of nitrogen.[157]

2.4. Advanced biodiesel

Advanced biodiesel is an aromatic- and sulphur-free isoparaffin-rich diesel fuel with a high cetane blending value that is fully compatible with the oil-derived diesel.[158] It is produced by hydroprocessing of vegetable oils and animal fats.[159] The most-studied feedstocks are plant derived-oils, such as soybean, rapeseed, and palm oils, while non-edible oils, such as jatropha and algal oils, may become very important in the future, taking advantage of the process flexibility. Contrary to the conventional biodiesel by transesterification, hydrotreatment of triglycerides can operate with high concentrations of free fatty acids (FFAs), so waste oils, tallow, and greases can also be used as feedstocks. Depending on the specific contaminants, pretreatment of raw materials to remove solids and salts could be necessary.[160]

The aliphatic hydrocarbon chains of triglycerides and FFA are partially unsaturated and have a carbon number range and molecular weights similar to the molecules found in diesel fuels. The hydrotreatment of oils, generally described by the reaction in Equation (14), saturates these molecules and removes oxygen forming an alkane-rich product and propane (in the case of trigliceride).

$$\text{triglyceride}/\text{FFA} + H_2 \rightarrow \text{alkane} + \text{propane} + H_2O + CO_x \quad (14)$$
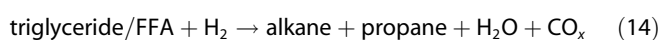
The first step is a skeletal isomerization, where branched chain fatty acids or alkyl esters of fatty acids are formed.[161]

This reaction takes place at a temperature between 220 to 300°C and under a pressure of 0.1 to 2 MPa using acidic catalysts, such as zeolites (faujasite, mordenite) or silico–alumino phosphates. The products are both saturated and unsaturated branched chain fatty acids, and esters of fatty acids. These products can be optionally prehydrogenated (at 150 to 250°C and 1 to 10 MPa using a Pd-, Pt-, or Ni-based catalyst and/or silica support) in order to remove unsaturation and to avoid coke formation.

The next step is deoxygenation, carried out by decarboxylation/decarbonilation or hydrodeoxygenation. In this step a Pt, Ni or Pd catalyst supported on carbon is used and the reaction conditions may vary with feedstock. This reaction takes place in liquid phase at temperatures between 250–350°C and between 0.1–5 MPa of pressure (inert gas/hydrogen mixture) to avoid vaporization. The product is a mixture of hydrocarbons, preferably branched alkanes boiling in the diesel range (180 to 350°C). The three-carbon backbone yields propane, which can be easily recovered and used as LPG.

Several companies worldwide have been developing and commercializing advanced biodiesel, such as ENI and UOP (green diesel),[162–164] Neste Oil (NExBTL),[165–166] and Petrobras (H-Bio process).[167, 168] Neste Oil has launched a 170 000 t a⁻¹ plant at Porvoo (Finland) refinery in 2007 and is building other plants with capacities of up to 800 000 t a⁻¹ in Singapore, Austria, and The Netherlands. Petrobras has started the H-Bio project in 2006 and, by the end of 2010, is expecting to have built 11 refineries in order to process 1.6 Mt a⁻¹ of vegetable oil for producing diesel.

2.5. Biohydrogen

Renewable hydrogen from low-value waste biomass has some potential to become a cost competitive next-generation biofuel. Currently, a number of processes are studied for conversion of biomass to hydrogen,[1, 61, 169–176] divided mainly in thermochemical (reforming and WGS reactions) and biological approaches.
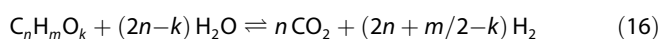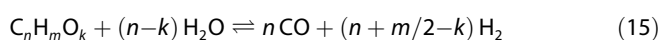
2.5.1. Thermochemical hydrogen production

Thermochemical methodologies for biohydrogen production often rely on the previously described primary processes of pyrolysis and gasification to yield, respectively: (1) gaseous or liquid hydrocarbons and oxygenates (pyrolysis gases or oils), or (2) mixtures of hydrogen with carbon oxides (producer gas). In both cases, the resulting products are mixtures of different proportions of hydrogen and carbon oxides, alkanes, alkenes, and other compounds which have to be further treated in order to increase hydrogen content and to remove impurities [pressure swing absorption (PSA), and other purification techniques]. In the case of bio-syngas, already rich in hydrogen and with a low content of hydrocarbons, the H_2/CO ratio is adjusted by the WGS reaction [Equation (4)]. The reforming reaction can be used to convert oxygenated compounds and low-molecular-weight hydrocarbons to hydrogen and carbon oxides. In addition to the products of primary thermochemical

methods of biomass treatment, a number of other biobased molecules, such as vegetable oils, their derivatives (glycerol and fatty acids), sugars, and alcohols, can also be reformed to hydrogen.

Four main different reforming technology processes are nowadays under consideration for the conversion of biomass-derived feedstock: catalytic steam reforming (CSR), catalytic partial oxidation (CPO), autothermal reforming (ATR) and aqueous phase reforming (APR).

CSR is the classical reforming technology developed to transform fossil hydrocarbons, especially methane, into hydrogen. Recently, it has been adapted to treat oxygenated compounds [$C_nH_mO_k$; see Equations (15) and (16)]. In the latter case, the WGS reaction is integrated into the overall process stoichiometry. In most reforming systems, WGS reaction occurs simultaneously with the reforming reaction boosting the H_2 yield.

$$C_nH_mO_k + (n-k)\,H_2O \rightleftharpoons n\,CO + (n+m/2-k)\,H_2 \qquad (15)$$

$$C_nH_mO_k + (2n-k)\,H_2O \rightleftharpoons n\,CO_2 + (2n+m/2-k)\,H_2 \qquad (16)$$

Process conditions similar to those used for steam reforming of natural gas (fixed-bed reactors, temperatures 800–900 °C, Ni catalysts) have been demonstrated to be inadequate for biomass liquids.[71,177–179] Research efforts focus on improving the efficiency of catalysts for reforming and WGS reactions by using different promoters like CeO_2[180–183] or alternative reaction conditions.

Reforming of hydrocarbons and oxygenated hydrocarbons strongly depends on the thermodynamics of both reforming and the WGS reactions. Reforming reactions of these compounds are strongly endothermic (e.g., $\Delta H^\circ_{298} = 90$, 173, and 245 kJ mol^{-1} for methanol, ethylene glycol, and glycerol, respectively). Ideally, they must be carried out at high temperatures, low pressures, and high steam-to-hydrocarbon ratios to achieve higher conversions. The WGS reaction is a mildly exothermic reversible chemical reaction ($\Delta H^\circ_{298} = -41$ kJ mol^{-1}), and thus low temperatures are needed to achieve high conversion. The best experimental conditions are based on a trade-off between reforming and the WGS reaction.

Reforming of biomass derivatives, such as methanol, ethylene glycol, glycerol, and sorbitol is thermodynamically more favourable at lower temperatures with respect to hydrocarbons with a similar number of carbon atoms.[184] In this sense, the reforming process is more compatible with the WGS reaction than the reforming of hydrocarbons. On the other hand, working at lower temperatures has a drawback of the further reaction of CO and CO_2 with H_2, leading to alkanes by methanation or FTS.[185]

In addition to the thermodynamic issues, the CSR is complicated due to the homogeneous (gas phase) thermal decomposition of oxygenated hydrocarbons and cracking reactions [Equation (17)] over the acidic sites of the catalytic support, as these processes lower selectivity and deactivate the catalyst.

$$C_nH_mO_k \rightarrow C_xH_yO_z + (H_2,\ CO,\ CO_2,\ CH_4,\ldots) + coke \qquad (17)$$
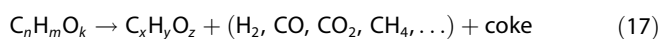
Coke formation on the catalyst surface is increased in the case of reforming of oxygenated organic molecules due to a high degree of instauration and aromaticity, as well as high molecular weight. For this reason, the reforming of biomass derived compounds requires suitable conditions to minimize the formation, or to facilitate the removal by steam gasification, of the coke deposits from the catalyst surface.

Catalytic partial oxidation (CPO) has been pointed out as an attractive alternative to the CSR process. In CPO, the fuel reacts with a lower quantity of oxidizer (O_2) lower than required by process stoichiometry for the complete combustion:[186]

$$C_nH_mO_k + (n-k/2)\,O_2 \rightarrow n\,CO_2 + (m/2)\,H_2 \qquad (18)$$
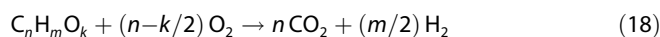
In the case of the most common oxygenated hydrocarbons the values for the enthalpy of this reaction are: $\Delta H^\circ_{298} = -193$, -393, and -603 kJ mol^{-1} for $n = 1$, 2, and 3 (i.e., methanol, ethylene glycol, and glycerol). This reaction provides sufficient heat to maintain a temperature in the reactor, capable of achieving equilibrium product concentrations even at times as short as milliseconds.[187]

The advantages of CPO over the conventional CSR are the smaller size of the reactor, absence of coking problem, and easier recovery of CO_2. However, safety issues are present, particularly in the premixing region, due to inflammation and explosion risks. In addition, long-term catalyst stability is still a critical aspect. Hydrogen production from light alcohols via CPO has been extensively studied recently,[188–190] while information on CPO of more complex oxygenated molecules is scarce in literature.

Autothermal reforming (ATR) is a combination of CPO and CSR technologies to realize a thermally self-sustaining process where hydrocarbons (or oxygenated hydrocarbons), steam and oxygen are all reactants [Equation (19)] and which is generally faster than CPO.

$$2\,C_nH_mO_k + (2n-k)\,H_2O + (n-k/2)\,O_2 \rightarrow 2n\,CO_2 + (2n+m-k)\,H_2 \qquad (19)$$
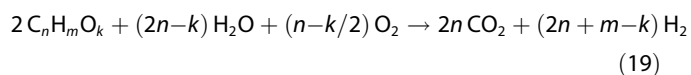
Typical values for the enthalpy of the reaction are $\Delta H^\circ_{298} = -72$, -160, and -240 kJ mol^{-1} for methanol, ethylene glycol, and glycerol, though other exothermic reactions may simultaneously occur. The severe operation conditions in the ATR necessitate catalysts with good mechanical properties and which are stable at high temperatures (650 to 900 °C) and at a high steam partial pressure. Potentially, ATR has a superior performance with respect to conventional CSR plants in terms of reduced size and weight, lower costs, faster starting time, and improved transient time. The design of novel ATR reactors and catalysts holds promises for efficient reforming of oxygenates such as methanol and ethanol. Up to now, still few studies are present in literature.[62,191,192]

Aqueous phase reforming (APR) is a flexible process to produce H_2 from biomass-derived oxygenates, such as sugars, ethylene glycol, glycerol, and alcohols, in a single step process

using supported metals and metal alloys as heterogeneous catalysts.[193, 194] The APR of oxygenated hydrocarbons has several advantages over the CSR, namely:[184]

(1) no need of reagent vaporization, which is critical for oxygenated hydrocarbons with a low vapour pressure, for example, sorbitol;

(2) relatively low temperatures and high pressures, favouring the WGS reaction, hence affording a product with low CO content (<1000 ppm) which is suitable for fuel cell applications;[195]

(3) low temperatures, minimizing undesirable decomposition reactions, for example, cracking;

(4) high pressures, allowing easy hydrogen purification (e.g., using membranes or PSA) and sequestration of CO_2.

On the other hand, there are also a number of disadvantages such as: (1) significantly longer reaction times and hence lower productivity and higher capital costs, (2) high-pressure environment and diluted feed solution add energy cost per unit of hydrogen production, (3) use of costly noble-metal-based catalysts, and (4) environmental impact of aqueous effluents.

The nature of the oxygenated hydrocarbon strongly affects the H_2 vs. alkanes selectivity, favoring H_2 in the order glucose $<$ sorbitol $<$ glycerol $<$ ethylene glycol $<$ methanol, while the alkane formation follows the opposite trend.[194]

The WGS reaction [Equation (4)] plays a critical role in most syngas-based catalytic syntheses of biofuels,[196] such as FT and methanol syntheses, but is especially important in the hydrogen production processes via reforming and cleaning of H_2 streams from CO. WGS is usually performed in two stages,[197–201] where the high-temperature shift (HTS) stage, which favours the kinetics and converts the bulk of CO, is followed by the low-temperature shift (LTS) stage, which takes advantage of the thermodynamic equilibrium. The sequential configuration of HTS and LTS reduces the CO concentration to less than 1%.[202] Several types of WGS catalysts are commercially available and widely applied in practice,[203] such as Fe_3O_4 doped with Cr_2O_3 (HTS catalysts operating at 350 to 500 °C and at sulphur content of <20 ppm), Cu supported over ZnO and Al_2O_3 (LTS catalysts operating at 185 to 275 °C and at sulphur content of <0.1 ppm), and sulphided Co and Mo (CoMoS; sour shift catalysts operating at 250 to 500 °C and sulphur content of >1000 ppm).

Most commercial and scale-up initiatives on CSR and ATR nowadays are limited to the reforming of natural gas. Virent Energy Systems Inc. was the first company to invest in pilot-plant experimentation of the APR technology. By altering conditions and catalysts, the Virent BioForming process can be tailored to produce different biofuels. Notwithstanding the increasing R&D effort on biomass reforming, particularly for APR of oxygenated hydrocarbons, no commercial technologies have been designed so far for WGS to work simultaneously with APR, even in the case of the most active traditional Pt-based reforming catalyst.[204]

If the desired product is pure hydrogen (e.g., for fuel cell applications), an additional separation/purification step is normally required. The selection of the appropriate hydrogen purifica-

tion technology is based on final application and the downstream impact of impurities such as CO and N_2.[205–207] Hydrogen produced from biomass contains different gaseous impurities such as O_2, CO, CO_2, CH_4 and moisture. The main H_2 purification technologies can be grouped into four categories, namely (1) chemical absorption,[208] (2) physical adsorption,[209–211] (3) membranes,[212–217] and (4) cryogenic processes.[218–220]

2.5.2. Biochemical hydrogen production

Biochemical technologies for biohydrogen production[172–175,221–223] started to receive attention after the oil crisis in 1970s.[157] Notwithstanding the steadily increasing interest and R&D on solar fuels, no commercial applications exist so far.[224,225] The biochemical technologies of hydrogen production can be classified into five groups: (1) direct biophotolysis, (2) indirect biophotolysis, (3) biological WGS reaction, (4) photo-fermentation ,and (5) dark fermentation.[226] All of these processes are controlled by hydrogen-producing enzymes, such as hydrogenase and nitrogenase.

In the direct biophotolysis the solar energy converts directly water into hydrogen via the photosynthetic reaction [Equation (20)].[227] This process operates at ambient partial pressure of oxygen which is 3 orders of magnitude higher than the hydrogenase toleration limit. Thus, sensitivity of the enzyme to oxygen remains the key issue.[228] The H_2 production rate in biophotolysis is in the order of 0.07 mmol h^{-1} L^{-1}.[229]

$$H_2O + hv \text{ (solar energy)} \rightarrow 2\,H_2 + O_2 \qquad (20)$$
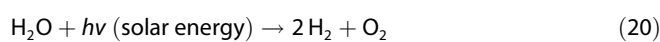
The cyanobacteria used in the indirect biophotolysis possess the unique characteristics of using CO_2 from the air as a carbon source and the solar energy as an energy source to produce biomass [Equation (21)] that is subsequently used for hydrogen production [Equation (22)].[226] This method affords a H_2 production rate of 0.35 mmol h^{-1} L^{-1}, which is comparable to the rate achieved by green algae.[230]

$$6\,H_2O + 6\,CO_2 + hv \text{ (solar energy)} \rightarrow C_6H_{12}O_6 + 6\,O_2 \qquad (21)$$

$$C_6H_{12}O_6 + 6\,H_2O + hv \text{ (solar energy)} \rightarrow 12\,H_2 + 6\,CO_2 \qquad (22)$$

The biological WGS reaction is related with photo-heterotrophic bacteria that can survive in the dark by using CO as the unique carbon source to generate ATP by coupling the oxidation of CO to the reduction of H$^+$ to H_2. Research on the biological WGS reaction for hydrogen production is still at the laboratory scale, and limited information is available,[231,232] although it was reported already several years ago by Uffen that two strains of photosynthetic bacteria are able to shift CO and H_2O into H_2 and CO_2.[233]

Photosynthetic bacteria evolve molecular hydrogen by using nitrogenase under nitrogen-deficient conditions starting from organic acids (acetic and butyric acids) and light energy.[218] These bacteria are not able to split water, but under anaerobic conditions they are able to use simple organic acids as electron donors [Equation (23)]. In the absence of nitrogen, a nitro-
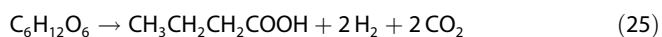
genase enzyme can reduce protons into H_2 gas using extra energy in the form of ATP. The H_2 production rates reported for this method are of the order of 145–160 mmol h^{-1} L^{-1}.[218]

$$CH_3COOH + 2H_2O + h\nu \text{ (solar energy)} \rightarrow 4H_2 + 2CO_2 \quad (23)$$
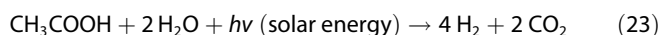
H_2 can also be produced by anaerobic bacteria or green algae grown in the dark on carbohydrate-rich substrates that may be derived from cellulosic biomass.[234] This process is mainly driven by the anaerobic metabolism of pyruvate, formed during the catabolism of various substrates. The products of dark fermentation are mostly H_2 and CO_2 with minor amounts of other gases (CH_4, H_2S). Using glucose as a model substrate, a maximum of 4 mol of H_2 is produced per mol of glucose giving acetic acid as by-product:

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 4H_2 + 2CO_2 \quad (24)$$
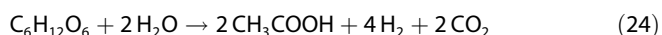
When the by-product is butyric acid, 2 mol of H_2 are produced:

$$C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH + 2H_2 + 2CO_2 \quad (25)$$

The amount of H_2 produced by dark fermentation strongly depends on the pH value, hydraulic retention time, and gas partial pressure. Solar radiation not being required in dark fermentation, the rate it is not affected by the weather conditions.[227]

For all the previous processes, batch (well-mixed) or continuous stirred-tank reactors are the most frequently used (on the laboratory scale), even if various types of reactors such as mixed reactor, packed-bed, fluidized-bed, sequencing-continuous reactor, trickling biofilter, and membrane bioreactors have been also reported.[219] Efficient mixing in the reactor for a good mass transfer between substrate and micro-organisms is a key factor for performance.[235,236] Several strategies have been adopted to overcome the problem of the cell washout when the reactor is operated at a high dilution rate, such as matrix entrapment,[237] self-flocculation of cells,[238] biofilm formation,[239] or cell granulation.[240] Recently, hollow-fibre membrane systems were developed for a complete retention of biomass.[236]

In general, hydrogen production rates by photoheterotrophic bacteria are higher when the cells are immobilized on a solid matrix than when the cells are "free-living." Continuous cultures of *Rhodopseudomonas capsulata* and *Rhodobacter spheroides* can produce 80–100 mL$_{H_2}$ L$_{culture}$$^{-1}$ h^{-1}.[241] Continuous cultures of *Rhodospirillum rubrum* were reported to produce H_2 at a rate of 180 mL$_{H_2}$ L$_{culture}$$^{-1}$ h^{-1}.[242] Cultures of *Rhodobacter sphaeroides* immobilized on porous glass were reported to produce H_2 at a rate of 1.3 mL$_{H_2}$ L$_{culture}$$^{-1}$ h^{-1}.[191] In the case of photofermentation processes, the efficiencies with solar or artificial radiation are very low because the majority of captured light is converted to heat.[243] The relatively high cost of transparent and H_2-impermeable materials, combined with the large surface area required for the photo-bioreactors, represent the issues for development of biohydrogen technologies.

2.6. Biomethane via biogas

Biogas, a mixture of 60–75% CH_4 and 40–25% CO_2, can be produced from a variety of organic compounds through a complex microbial process called anaerobic digestion (AD), and can be upgraded by further steps to biomethane.[244–247] Compared to other technologies, fermentor technology is simple in design and in operation, feedstock-flexible, and nondemanding in terms of consumables and infrastructure. A wide range of waste biomass, such as kitchen waste, sewage sludge, organic effluents from food and dairy industries, agricultural or crop residues (e.g., maize silage), municipal solid waste, livestock manure, and others can be processed. The main applications of biogas include CHP generation and cooking applications. The effluent byproduct (sludge), which is rich in nutrients such as ammonia, phosphorus, potassium, and other trace elements, has a potential use as fertilizer and soil conditioner. The renewed interest in this technology is driven by the need for an affordable fuel in less-developed regions.[248–253] Currently, about 25 million households worldwide receive energy for lighting and cooking from household-scale biogas plants, China and India being the leaders; a few thousand medium- and large-scale industrial biogas plants are also operating in these countries.[254]

The kinetics of the AD process are expressed in terms of hydraulic retention time (HRT), which equals the volume of reactor tank to the influent flow rate (*V/Q*). This is a measure of average retention time of the organic mass inside the digester tank for complete conversion. Three types of temperature conditions are maintained in industrial biogas generation.

(1) Thermophylic system: This operates in a high temperature range (50–70 °C), leading to a rapid break down of organic matter with a short HRT of 3–5 days to produce biogas. While these systems are more sensitive to the N_2 levels of substrate and temperature variations, they are more effective in pathogen removal.

(2) Mesophylic system: This needs longer retention times (15–20 days or more) and a moderate temperature range (35–40 °C) for the substrate to decompose. However, this system is more robust in terms of temperature variation and is most commonly used.
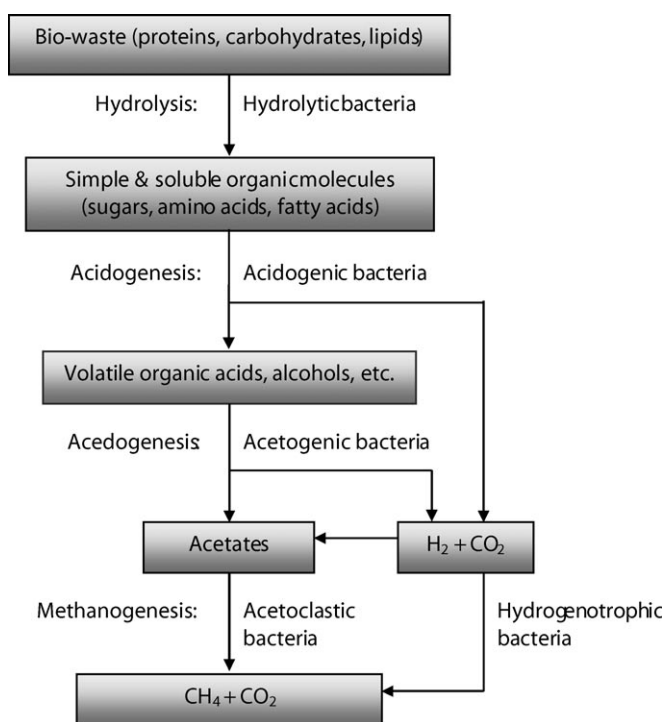
(3) Psychrophylic system: This type operates more specifically in low-temperature conditions (15–25 °C). Very high retention times (months) are required to achieve a high gas conversion efficiency and a high degree of pathogen removal.

Most of the commercial processes in Europe relied on mesophilic systems, while thermophilic technologies became available more recently.[255] Studies have shown that the average biogas yield in thermophilic process exceeds that of psychrophilic and mesophilic processes, by 144% and 41% respectively.[256]

AD proceeds through series of decomposition phases: hydrolysis, acidogenesis, acetogenesis, methanogenesis,[257,258] as shown in Scheme 4.[259]

Stage I. Hydrolysis: Organic materials, which are primarily composed of complex carbohydrates, lipids, proteins, and inorganic materials, are solubilized by extracellular enzymes such
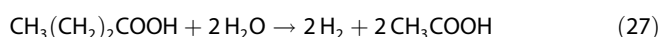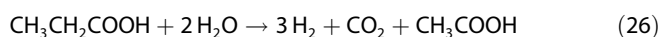
Scheme 4. Flow chart of the main processes of anaerobic digestion of biomass. Adapted from Ref. [259].

as cellulase, amylase, protease, and lipase into simpler molecules at this stage. For example, complex polysaccharides (cellulose) are broken down to dimeric and monomeric sugar (glucose), proteins are split into amino acids and peptides, and fats to fatty acids and glycerol.
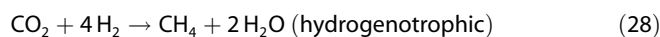
Stage II. Acidogenesis: At this stage, acid-producing fermentation bacteria, commonly named acidogens, convert the sugar monomers and other hydrolysates produced in the first stage into low-molecular-weight compounds, such as alcohols, acetic acid, and volatile fatty acids (VFA; e.g., propionic acids, butyric acids), amino acids, H_2, CO_2, H_2S, and CH_4 under anaerobic conditions. As example, the main reactions of glucose fermentation to acetic and butyric acids are described by Equations (24–25).

Stage III. Acetogenesis: At this stage VFA and other intermediates produced in Stage II are digested by acetogens to largely produce acetic acid, CO_2, and H_2. In the cases of above mentioned propionic and butyric acids the stoichiometry is described by the following reaction equations:

$$CH_3CH_2COOH + 2H_2O \rightarrow 3H_2 + CO_2 + CH_3COOH \tag{26}$$

$$CH_3(CH_2)_2COOH + 2H_2O \rightarrow 2H_2 + 2CH_3COOH \tag{27}$$

Stage IV. Methanogenesis: At this terminal stage acetates and other intermediates are metabolized by methanogenic bacteria or methanogens to form biogas via hydrogenotrophic or acetoclastic pathways [Equations (28–29)]. Methanogens are obligatory anaerobic and very sensitive to pH, temperature, and other environmental parameters. In contrast to the acidogens, the methanogens belong to group of bacteria with a heterogeneous morphology and the main difference lies in the makeup of the cell walls of the bacteria. Methanogens and acidogens act in a symbiotical way. Acidogens consume the dissolved oxygen in the organic media and thereby create ideal anaerobic conditions to facilitate the growth of methanogens. Methanogens, on the other hand, use the intermediate acids produced by acidogens to reduce the toxicity and pH of the medium.

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \text{ (hydrogenotrophic)} \tag{28}$$

$$CH_3COOH \rightarrow CH_4 + CO_2 \text{ (acetoclastic)} \tag{29}$$

Over the years several digesters models have been developed to treat heterogeneous substrates such as fruit, vegetable wastes, municipal solid waste (MSW), and others. These are one- and two-stage systems, depending on the separation of the acidogenic phase and methanogenic phase in the reactor. One-stage systems are one of two types: wet systems (total solid < 15%) and dry systems (total solid > 15%). About 90% of the full-scale plants in Europe are based on single-stage systems.[260] The most popular industrial designs under this category are: continuous stirred tank reactor, anaerobic sequencing batch reactor (ASBR), plug flow reactor, anaerobic filter (AF), and up-flow anaerobic sludge reactor (UASB). Dranco (Dry Anaerobic Composting), Kompogas, and Valorga single-stage processes have been demonstrated successfully at the industrial scale.[256, 261]

Owing to the different growth characteristics of hydrolytic and acidogenic-methanogenic microorganisms, two-stage digesters have been developed to independently optimize the conditions of each phase and to achieve very short HRTs.[262, 263] Two-phase digesters, also known as immobilized growth digesters, were initially employed for treatment of waste water and soluble substrates.[264, 265] Later, similar systems were developed for solid vegetable wastes.[264–267] Two-stage systems have resulted in superior conversion efficiency compared to the single-stage process.[262] The main features of these reactors are the bacterial sludge immobilization inside the reactor. The most significant two-stage anaerobic reactors developed are the following: up flow anaerobic sludge blanket (UASB),[268, 269] up flow and down flow anaerobic filters (UFAF, DFAF), anaerobic fluidized bed reactors (AFBR),[270, 271] and anaerobic attached film expanded bed reactor (AAFEB).[272–274] Many industrial processes are running based on these technologies.[275–282]

Subsequently to biogas production, the raw biomethane (biogas) is cleaned from CO_2 and H_2S by absorptive or adsorptive methods (e.g., water or amine scrubbing, pressure swing adsorption), dried, compressed, and injected into the natural gas grid. Successful commercial application has been demonstrated in, for example, Sweden, Germany, and Switzerland.

2.7. Lignocellulosic bioethanol

The commercial-scale production of ethanol from wood and waste biomass has taken place in different countries during the last century, for example, in the former Soviet Union, in Germany, and in Japan.[283] However, these traditional process-

es are mainly based on the acid hydrolysis of cellulose, which has a number of drawbacks: acid recovery, corrosion, and environmental pollution as well as with high temperatures in the case of diluted acid hydrolysis.[284–289] Novel commercial approaches for production of cellulosic ethanol from low-grade biomass have started recently, with a main focus on enzymatic hydrolysis and advanced lignocellulose pretreatments. Major attention is currently given to the development of efficient processes to work with agricultural crop residues, hardwood, softwood, cellulose wastes, herbaceous biomass, and MSW.[287,290]

Two major technological routes are followed for conversion of lignocelluloses to ethanol, namely, the HF process (hydrolysis and fermentation) and the TF process (thermochemical/gasification and fermentation).[291] Among these two, HF is the most commonly applied method, whereas the integration of biomass gasification with the fermentation process is relatively new.[292–296]

2.7.1. HF process

The conversion of lignocelluloses into ethanol is based on the following principal steps:

(1) Pretreatment of lignocellulose

(2) Hydrolysis/saccharification of the carbohydrate polymers to produce fermentable sugars such as hexose (C6 sugar) and pentose (C5 sugar)

(3) Fermentation of hexose and pentose to produce ethanol

2.7.1.1. Lignocellulose pretreatment

Lignocellulosic biomass has an inherently complex structure, in which cellulose and hemicellulose are encapsulated in lignin by hydrogen and covalent bonds, which makes the cellulose inaccessible for reaction with hydrolysis agents. Pretreatment is primarily aimed at removal of lignin and hemicellulose, reduction of cellulose crystallinity, and/or increase of porosity to facilitate downstream processes of cellulose hydrolysis conversion ethanol.[297] Several physical, physicochemical, chemical, and biological pretreatment processes have been developed.[290]

In physical methods, the biomass is mechanically processed in order to reduce cellulose crystallinity and/or increase the surface area of the material accessible to the reaction via a combination of processes such as chipping, grinding, milling. Although these processes are very helpful to facilitate the access of enzymes or chemical reagents to cellulose, they are often found unattractive because of their high energy and capital costs.[298]

Steam explosion is the most widely used physicochemical pretreatment method.[299,300] The biomass interacts with high-pressure steam at 180 to 230 °C for several minutes to achieve full or partial hydrolysis of the cellulosic component, and is then suddenly exposed to fast depressurization leading to the violent expansion of the water and steam in the bulk of the material. This phenomenon breaks down the fibre structure, separates, and partially solubilizes the lignocellulose compo-

nents. Addition of H_2SO_4, SO_2, or CO_2 in steam explosion has also been found effective for breaking the lignin encapsulation, limiting the formation of inhibitory toxic intermediates, and improving the hemicellulose removal.[301] The steam explosion method uses about half the energy than mechanical processing uses, but it is still quite energy intensive.[302] Other methods such as the ammonia fibre explosion (AFEX) process are, in principle, similar to steam explosion, but the yields are relatively lower.[290]

Thermo-hydrolysis or liquid hot water (LHW) treatment is another promising pretreatment method,[303–306] which can be comparable to dilute acid pretreatment. This method offers elevated recovery rates of pentoses and is eco-compatible because it does not use liquid acids.[307] However, it is also energy intensive.

Chemical pretreatment methods are based on the removal of lignin and hemicellulose via their reactions with different chemicals, such as ozone, diluted acids (H_2SO_4 and HCl), alkali, peroxides, and organic solvents. Dilute acid pretreatment is considered very efficient for the removal of hemicellulose into a mixture of monosaccharides, with mainly pentoses such as xylose as main product together with arabinose, glucose, and galactose.[308] Different to the cellulose hydrolysis discussed later, this technology uses temperatures below 200 °C. Higher-temperature (> 160 °C) continuous methods are generally employed for low solid loadings (5 to 10 %),[309] whereas the low-temperature (< 160 °C) batch process is used for high solid loadings (10 to 40 %).[310]

Ozone has been often used to degrade lignin and hemicellulose in many lignocellulose materials, such as rice straw,[311] bagasse, green hay, peanut, pine,[312] cotton straw[313] and popular sawdust.[314] Though this process is advantageous in terms of effective removal of lignin at room temperature and pressure conditions without affecting cellulose, quantitative use of ozone makes the process expensive.[290]

Alkaline pretreatment is the preferred choice for lignin removal from feedstocks with a high lignin content.[299] The method is carried at ambient pressure and temperatures up to 150 °C. Alkaline, earth alkaline metal, and ammonia hydroxides are used. The method affords efficient delignification (up to 90 %) with a lower degree of decomposition of sugars from cellulose and hemicellulose. Longer reaction times (on the order of hours or days) are required with respect to other pretreatment methods.

Organic solvents can be used to decompose and solubilize lignin and hemicellulose. For example, in the *Organosolv* process and in other similar processes, ethanol or methanol are used together with water and other reagents to give rise to low-molecular-weight lignins, oligomers and monomers of hemicellulose, and a solid cellulose fraction.[319–322] Many liquefaction methods are known,[319,320] which are based on the solvolysis of lignocellulosic components with ethylene glycols or phenol in the presence of catalysts and under influence of other conditions, for example, microwave radiation,[321] to yield a solid or aqueous liquid cellulose stream and an organic stream containing phenolic lignin derivatives. Most of these methods, however, are not cost competitive at present.

Biological pretreatment methods use micro-organisms such as brown, white, and soft rot fungi to produce lignin-degrading enzymes such as lignin peroxidase, Mn-dependent peroxidise, and laccase (monophenol oxidase).[322–327] This process is advantageous in terms of low energy requirement and needs mild environmental conditions. However, slow kinetics presently limits its application at industrial level.

2.7.1.2. Cellulose hydrolysis

Hydrolysis, also termed saccharification, is carried out to convert crystalline cellulose into glucose. Two technological routes, using acids or enzymes, are usually employed. Dilute or concentrated acids can be used in acid hydrolysis . Dilute acid hydrolysis is carried out in a single- or two-stage processes. In the single-stage process, 1.5% acid H_2SO_4 or HCl is used in a temperature range of 200–240 °C. This process also produces undesired degradation products such as HMF (hydroxylmethyl-furfural) and furfural, from glucose and xylose, respectively, which are potential inhibitors to the subsequent fermentation process. In the two-stage process, the first stage is operated under milder conditions (190 °C, 0.7% acid) to recover pentoses from hemicellulose (see the diluted acid pretreatment in the previous section), while in the second stage, the remaining cellulose undergoes harsher treatment (215 °C, 9.4% acid) to recover hexoses (glucose and cellobiose). This process results in a glucose yield of 50%.[308] The concentrated acid process, which uses 30 to 70% H_2SO_4, result in a higher degree of glucose recovery (90%). However, the high amount of acid used is a critical environmental constraint for the acid hydrolysis process. In few cases, high acid recovery (over 97%) has been reported using continuous ion exchange method.[308]

In enzymatic hydrolysis, cellulose is degraded by the highly specific cellulase enzymes. This process comprises three steps: adsorption of cellulase onto the surface of cellulose, biodegradation of cellulose to reducing-fermentable sugars, and desorption of cellulase.[290, 328] Cellulases are usually mixtures of several enzymes, where the following three enzymes mainly facilitate the cellulose hydrolysis process:[329]

(1) endoglucanase (*endo*-1,4-D-glucanohydrolase), which attacks regions of low crystallinity in the cellulose fibres and creates free chain ends;

(2) exoglucanase or cellobiohydrolase, which degrades the molecule further by removing cellobiose units from free chain ends;

(3) β-glucosidase, which hydrolyses cellobiose to glucose.[330]

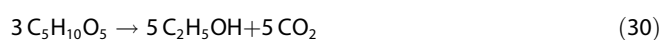In addition, various enzymes attack hemicellulose, such as glucuronidase, acetylesterase, xylanase, β-xylosidase, galactomannanase, and glucomannanase.[331] A large number of cellulase-producing bacteria, as well as fungi, have been reported.[329, 331, 332] However, commercial cellulase production is largely based on fungi due to higher rate of cellulase production by fungi compared to bacteria.[331] Presently, the economical production of cellulase enzymes is one of the key issues in the enzymatic hydrolysis process.[333] However, enzyme recycling has been found to be effective to increase the rate and yield of hydrolysis process and lower the enzyme cost to a large extent.[334, 335]

Enzymatic hydrolysis is conducted at mild conditions (pH 4.8 and temperatures of 45 to 50 °C) and does not produce inhibitory intermediates. However, enzymatic processes are relatively slower than acid hydrolysis,[331] although more ecocompatible. The hydrolysis rate decreases due to the irreversible adsorption of cellulase on cellulose.[336] To overcome this problem, the addition of surfactant has been used to modify the cellulose surface, minimizing the irreversible binding of cellulase to cellulose.

2.7.1.3. Sugar fermentation

C5 and C6 sugars are fermented to ethanol with microorganisms such as bacteria, yeast, or fungi according to the following reactions:

$$3\,C_5H_{10}O_5 \rightarrow 5\,C_2H_5OH + 5\,CO_2 \qquad (30)$$

$$C_6H_{12}O_6 \rightarrow 2\,C_2H_5OH + 2\,CO_2 \qquad (31)$$

The most commonly used microorganism for cellulosic sugars fermentation is *S-cerevisiae*, which ferments C6, but not C5 sugars. To overcome this problem and to improve the overall yield of ethanol two different methods are adopted. The first method uses genetically engineered recombinant strains that produce enzymes to efficiently co-ferment both C5 and C6 sugars.[337, 338] Genetic techniques are primarily used to clone the cellulase-coding sequences into bacteria, yeasts, fungi, and plants in order to create new cellulase production systems. The other method involves the separate fermentation of hexoses and pentoses using suitable microorganisms.

Several recombinant microorganisms have been successfully demonstrated. The hexose-fermenting yeast *Zymomonas mobilis* encoded with xylose-assimilating and pentose phosphate pathway enzymes,[338] the recombinant strain of *E. Coli* modified with genes from *Zymomonas mobilis*,[339] the metabolically engineered *S-cerevisiae* with insertion of the genes encoding XR (xylose reductase) and XDH (xylitol dehydrogenase) from xylose-metabolizing yeast such as *P-stipitis*,[340, 341] and the recombinant plasmid with XR gene from *S-cerevisiae* transferred into *Saccharomyces spp.*[342] are a few examples of using recombinant DNA technology.

A common technology employed for fermenting sugars is the sequential hydrolysis and fermentation (SHF) process, in which hydrolysis of cellulose and the fermentation of C5 and C6 sugars is performed separately. In the SHF process, the hydrolysis is rate-limited by the concentration of generated sugar, which inhibits the cellulase activity. Towards better efficiency, different approaches coupling hydrolysis and fermentation processes have evolved. These are simultaneous saccharification and fermentation (SSF),[343, 344] where the cellulose hydrolysis and C6 fermentation are carried out in one pot, and simultaneous saccharification and co-fermentation (SSCF),[345, 346] where the cellulose hydrolysis and C5 and C6 fermentation are performed in one pot.[308] The advantage of this coupling of processes is the immediate consumption of sugar to form eth-

anol, which leads to a lower enzyme requirement, less sterile conditions, a shorter process time, and a smaller reactor volume.

The world's first commercial cellulosic ethanol production plant from wood wastes, with an annual capacity 1.4×10^6 L began its operation in 2007 in Osaka (Japan) (Taisei Corp.).[347] The technology, licensed by US-based Cellunol, uses genetically engineered strains of *E. coli* to co-ferment C6 and C5 sugars. The development of alternative HF technologies is underway across the world, for example, in Canada by Logen Corp., in Spain by Abengoa Bioenergy New Technologies (ABNT), in Denmark by Dong Energy/Inbicon, in the Netherlands by Royal Nedalco, and in Italy by Mossi and Ghisolfi. In 2008, the world production of fuel ethanol was 67×10^9 L; an increase of 34% with respect to 2007.[348] Of this volume, about 15×10^6 L was cellulosic ethanol, but the production capacity has increased by a factor about 5 in 2009.

2.7.2. Thermochemical and fermentationprocess

The thermochemical and fermentation (TF) process is a low-temperature biological alternative to the high-temperature chemical catalytic synthesis of biofuels from syngas.[349] In this process, the bio-syngas produced by biomass gasification (process detailed in related section) is consumed by gas-fermenting bacteria such as *Clostridium ljungdahlii* to produce ethanol as major product and acetic acid or acetate as byproduct, at an optimal temperature of 37 °C. The reaction chemistry of the bio-syngas conversion step is as follows (1 kcal = 4.184 kJ):

$$6\,CO + 3\,H_2O \rightarrow CH_3CH_2OH + 4\,CO_2; \; \Delta G = -48.7 \; \text{kcal mol}^{-1} \tag{32}$$

$$6\,H_2 + 2\,CO_2 \rightarrow CH_3CH_2OH + 3\,H_2O; \; \Delta G = 28.7 \; \text{kcal mol}^{-1} \tag{33}$$

$$4\,CO + 2\,H_2O \rightarrow CH_3COOH + 2\,CO_2 \tag{34}$$

$$2\,CO_2 + 4\,H_2 \rightarrow CH_3COOH + 2\,H_2O \tag{35}$$

As seen above, the favourable change in free energy makes CO as a preferred substrate over H_2 and CO_2 for ethanol conversion. The relative product ratio is a function of pH of the reaction medium.[350] A pH range of 4–4.5 favors ethanol formation, while a pH range of 5–7 facilitates acetate formation.

The bio-syngas-fermenting microorganisms are anaerobes which follow an acetyl coenzyme A (Acetyl-CoA) pathway for acetogenesis.[351, 352] Ni/Fe-S CO dehydrogenase (CODH), the key enzyme employed by CO-utilizing anaerobic microorganisms, converts CO to CO_2.[351,353] Acetyl-CoA is synthesized from the resulting CO_2 in the CODH cycle of the Wood Ljungdahl pathway.[354] Acetyl-CoA is finally converted by the cell to metabolic products such as cell mass, acetate adenosine triphosphate (ATP), or ethanol and nicotinamide adenine dinucleotide hydrogen (NADH).[355] The detailed biochemistry of the acetogenesis process has been reviewed elsewhere.[356, 357] The Acetyl-CoA pathway indicates that acetate is the terminal electron acceptor when ATP is produced. ATP is required for cell growth; therefore, the acetate is formed under growth conditions. Under nongrowth conditions, ATP is consumed to maintain the cell function. When cells are not growing, NADH is formed and ethanol is the terminal electron acceptor.[355] Therefore, the nongrowth conditions induce bio-syngas fermentation to ethanol and, conversely, growth conditions produce acetate.

Based on the discovery of *Clostridium ljungdahlii*, the unique gas-fermenting bacteria,[350] BRI Energy Inc. is running a 1.5 tonne per day unit from various lignocelluloses such as wood, corn stover, tires, RDF, and MSW.[358] Later, a two stage reactor was developed in order to optimize conditions for cell growth and ethanol production, respectively.[359]

3. Economic assessment

Besides the analysis of technical aspects and environmental impact, the sustainability assessment of the next-generation biofuel options requires a consideration of the following economic aspects: capital investment, biofuels production costs and well-to-wheel (WTW) costs at local conditions.[360–365]

Typically, an economic assessment compares different cost alternatives in order to (1) identify relative advantages, (2) evaluate different options with regard to omission, and (3) determine important influencing factors. In particular, in order to assess biofuel production costs, dynamic partial models (e.g., based on annuity) can be favorably applied since the accuracy is higher compared to static partial models due to a periodic accounting. The specific cost parameters relevant to biofuel production as well as the basic approach based on the annuity model are presented in Figure 3.
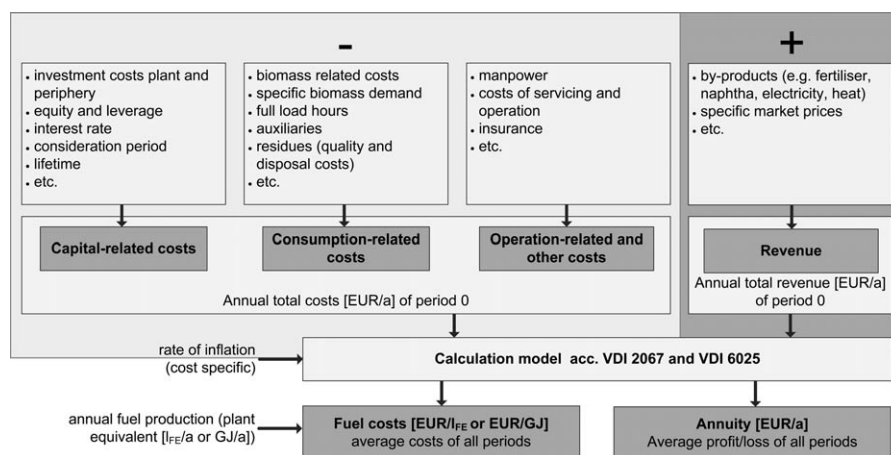

Figure 3. Model for cost calculation of biofuel production costs.

3.1. Capital investment requirements

Total capital investment (TCI) for biofuels production plants is an important aspect with regard to both financial risks and biofuel production costs. The calculation of TCI costs is based on an estimation (accuracy of ca. 20 to 30%) using the method of additional or overhead costs. According to this procedure, plant equipment costs have been determined by up- or downscaling (typical scale factor of ca. 0.7) of the existing costs for similar devices. Moreover, component-specific installation factors (e.g., 1.54 to 1.66) have to be taken into account.[366,367] Literature data are available for some components, while for others, for example, those currently in pilot stage, only rough estimations of technology developers are available. The investment cost figures given were calculated with references taken from literature dating from 2005 or before. An overview of rough estimations on TCI for future biofuel production plants is summarized in Table 2.[360–370] The range in the TCI costs reflects the spread of literature data and the influence of local conditions.

According to the economy of scale, specific TCI values typically decrease with the increase in plant capacity. However, there is a continuous cost increase in the engineering and construction industries, which cannot be reflected at all. The price development of chemical plants and machinery (that also refers to biofuel production plants) is commonly indexed by means of the so called Kölbel-Schulze methodology. According to this price index, the TCI for chemical plants has been increased by ca. 35% in the period from 2000 to 2007.

3.2. Biofuel production costs

The production costs of different next-generation biofuels, reported in Figure 4 (exemplary concepts projected for 2005), appear to vary in a wide range. Although there is a change in the actual costs (depending on local constraints or facilities) the relative scale has to be valid. Based on GJ fuel equivalent (FE), biomethane (SNG and biogas) appears to be the most favorable option. The sensitivity analyses show that besides the annual full-load hours of the plant, feedstock costs and capital requirements are strongly important. It is expected that production costs will moderately increase in the future due to the rising energy prices. The latter will affect biofeedstock prices in the case of the broad implementation of biofuel strategies. Based on the literature survey, the bandwidth of available production costs of biofuel options is presented in Figure 5.[118,371–378]

3.3. Well-to-wheel costs

For a market implementation, not only biofuels production costs, but also the total driving costs referred to as WTW are an important economic criterion.[378–381] The WTW costs are expressed per vehicle kilometer and comprise the costs of fuel distribution (i.e., via pipeline or tank) and the vehicles costs (i.e., of new private cars with combustion and hybrid engines, or fuel cells[365]). WTW costs for next-generation biofuels are summarized in Figure 6.

According to this analysis, the differences in production costs of some biofuels will be narrowed in terms of their related WTW costs. A similar cost range for different biofuels is primarily conditioned by vehicle use costs, except for fuel cell ve-

Table 2. Overview of TCI for selected biofuel options.[360-370]

| Biofuel option	Basic plant equipment	Typical (expected) plant size [MW$_{biofuel}$]	TCI [10^6 EUR]	Specific TCI [EUR kW$_{biofuel}$$^{-1}$]
Conventional options				
Biodiesel	Feedstock refinery, trans-/esterification, biodiesel washing, by-product cleaning and upgrading (e.g., glycerine, sulphates, methanol recovery), auxiliaries	4 to 190	0.9 to 65	190 to 340
Bioethanol	Feedstock pretreatment, hydrolysis/saccharification, fermentation, distillation/rectification, final upgrading, by-product treatment (e.g., DDGS, bagasse), auxiliaries	7 to 220	16 to 300	1360 to 2290
Future options				
HVO (NExBTL)	Feedstock refinery, hydrogenation, product separation, auxiliaries	150 to 1030	>100	390 to 470
Bioethanol	Feedstock pretreatment, hydrolysis/saccharification, fermentation, distillation/rectification, final upgrading, by-product treatment (e.g., lignin), auxiliaries	15 to 185	30 to 325	1800 to 2000
FT fuels	Feedstock pretreatment (e.g., mechanical, pyrolysis, torrefaction), gasification, gas cleaning and conditioning, FT synthesis, FT upgrading (e.g., hydrocracking), by-product treatment (e.g., naphtha), auxiliaries	>130 to 220	430 to 1000	2300 to 3480
Bio-MeOH	Feedstock pretreatment, gasification, gas cleaning and conditioning, methanol synthesis, product upgrading (e.g., separation), auxiliaries	126 to 270	232 to 330	1200 to 1800
DME	Feedstock pretreatment, gasification, gas cleaning and conditioning, DME synthesis, product upgrading (e.g., distillation), auxiliaries	130 to 340	290 to 350	1030 to 2200
Biomethane/ Bio-SNG	Feedstock pretreatment, gasification, gas cleaning and conditioning, methanation, final gas upgrading, auxiliaries	23 to 170	30 to 170	1000 to 2100
Biomethane/ Biogas	Feedstock pretreatment, digestion, final gas upgrading, auxiliaries	5 to 15	7.5 to 23	1500 to 3000
Biohydrogen	Feedstock pretreatment, gasification, gas cleaning and conditioning, final upgrading, auxiliaries	140 to 450	220 to 450	1000 to 1600
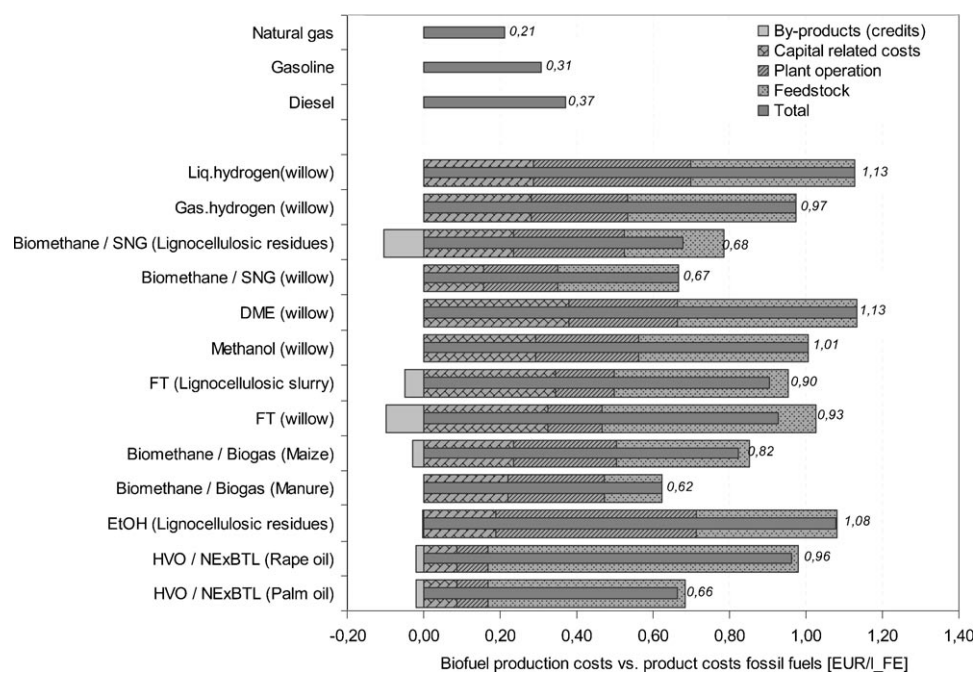
Figure 4. Exemplarily biofuel production costs vs. fossil fuels (European conditions, FE-fuel equivalent).[361, 362]
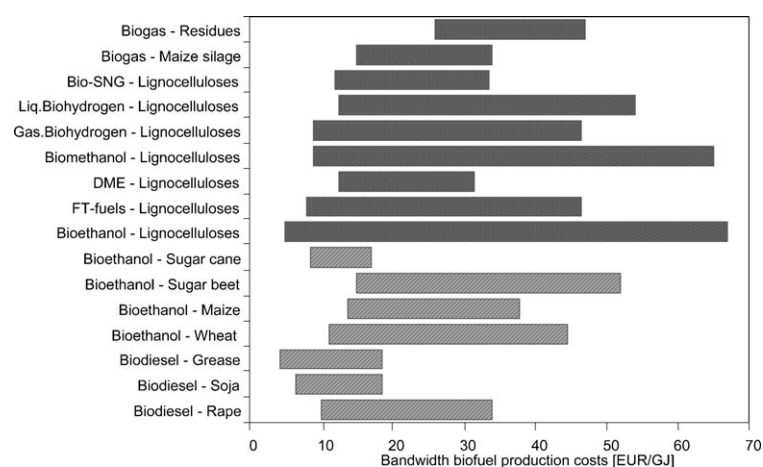

Figure 5. Biofuel production costs.[118, 371–378]

hicles. The costs for biofuel distribution play only a minor role. For a number of reasons (e.g., immature large-scale production), when compared to the conventional fossil fuels, such as diesel, next-generation biofuels are ca. 0.33 EUR km^{-1} more expensive in terms of WTW costs.
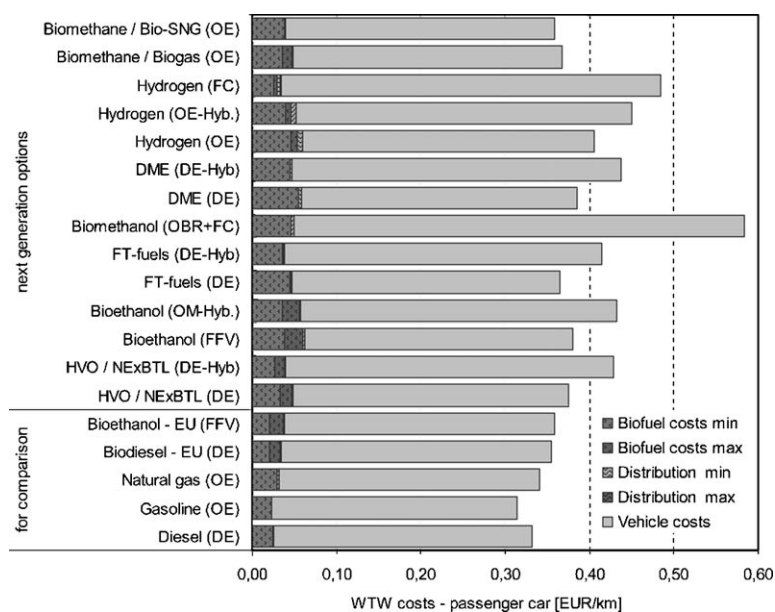
4. Environmental Assessment

An expanding biomass usage should also follow environmental criteria. Next to the impacts related to the environment through the biofuel production and usage itself, preserving diversity, conservation of ecosystems, avoiding negative impacts of fertilizer, avoiding water pollution, and avoiding soil erosion are basic sustainability criteria. The environmental impact of any product (e.g., biofuels) or services (e.g,. driven kilometers)

are often analyzed by life cycle analysis (LCA).[382–388] The basics of LCA and exemplary results are explained in Figures 7 and 8, respectively.
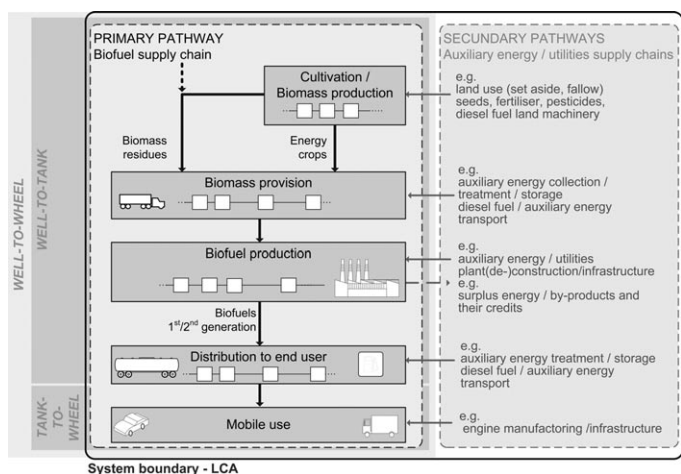
LCA is widely accepted to analyze the potential environmental impacts that are caused by products and services. The LCA method is defined within the international standards ISO 14040 and ISO 14044. An LCA considers the full life cycle of a product, from resource extraction to waste disposal (i.e., from cradle to grave). Its goal is to give an all-inclusive picture of the environmental impacts of products or systems, by taking into account all significant "upstream" and "downstream" impacts. The assessment should include the production or extraction of primary sources (energy crops or residues), the processing, transportation and distribution of the fuels, building of conversion and other plants, the usage of the fuel in motor engines, and waste disposal. Furthermore, byproducts should appropriately be considered along the life cycle of the production of the fuel. All impacts are dependent on the global or regional system where the production takes place or whose resources are used. Therefore, a detailed knowledge of the "surrounding" system is necessary to evaluate the environmental impacts of a product or system accordingly.

The global warming effect and the primary energy demand are considered key environmental impacts in most studies. Consolidated results of international studies for greenhouse gas (GHG) emissions for biofuels supply are shown in Figure 9 for the conventional biofuel option as well as the considered future biofuel options.[389–392]

The standardized method according to ISO is very flexible, to allow the assessment of all different types of biofuels under various circumstances and changing framework conditions. Considering additionally the fact that different LCA studies for biofuels are carried out under different assumptions made in the phase of goal and scope definitions (e.g., with regard to system boundaries, cut-off criteria, allocation of byproducts), the results vary significantly. As a consequence, results from different LCA studies are in most cases very difficult to compare. There are partly large bandwidths of results for each of the different biofuel options. While current biofuel options do not promise high GHG mitigation potential (in some biodiesel and bioethanol cases, the GHG values are even higher than for reference fossil fuels), results for advanced and future biofuels

Figure 6. WTW costs (passenger cars) of different biofuel options (DE: Diesel engine, OE: Otto engine, Hyb: hybrid engine, FFV: flexible fuel vehicle, OBR: onboard reformer, FC: fuel cell).[361]

Figure 7. System boundary for LCA process chain analysis.

have an effect on the in- or decrease of stored carbon; through changing of natural ecosystems (e.g., change of rain forests or grassland into agricultural land) an existing carbon (or CO_2) sink can get lost. The consideration of these effects within an LCA will typically give negative results, and thus a decreased potential for GHG mitigation.[393–395]

One consequence of the setting of the political frame conditions within recent years has been a significant increase in the use of biofuels. The overall goal of these activities is to reduce overall GHG emissions. Against this background, for example, the European Fuel Quality Directive (2009/30/EC) requires fuel suppliers to stepwise reduce the life cycle GHG emissions of the fuels they produce. This directive sets a mandatory reduction goal of at least 6% for 2020 compared to the average level of GHG emissions (in the European transport sector) in 2010. Since the fuel producers are free to choose how to achieve this goal, it is expected that the demand for biofuels with an outstanding GHG balance could increase. However, the discussion on expected positive environmental impact of this obligation is very controversial. This ongoing environmental debate has, among others, led to the introduction of sustainability requirements for biofuels defined within the European Renewable Energy Directive (2009/28/EC). This directive includes standards for a sustainable production of the biomass needed for the biofuel production as well as requirements for a mandatory minimum GHG mitigation. According to this, GHG saving targets, or at least a minimum GHG saving for all types of biofuels will be a mandatory requirement at national and/or European/global level in the future.

show the tendency to increasing GHG mitigation potentials. However, these results have been calculated for theoretical biofuel production concepts, since these options need to be demonstrated at commercial scale as a start.

The main parameters to have an influence on the total LCA results along the WTW chain are basically the production of biomass resources (especially for energy crops that require mineral fertilizer as well as when land-use change occurs) as well as the biofuel production process (especially for concepts with a high demand on external process energy based on the appropriate energy mix). Biomass transport to the biofuel production plant as well as biofuel distribution and its use are of less negative impact to the total WTW emissions.

It has to be noted that up to now the majority of studies do not include effects of land-use change. Change of land use can

5. Critical Discussion on the Potentials and Outlooks of Next-Generation Biofuels in the Context of Sustainability

5.1. Market status and projections

Currently about 13% of the global primary energy demand (in 2009 about 520 EJ, for example, 12.500 Mtoe) is covered by biomass, although it is mostly used for cooking and heating.[396,397] There is significant potential to expand biomass use by tapping the large volumes of unused residues and wastes. The technical potential for biomass is estimated as high as 1.500 EJa^{-1} by 2050, although most biomass supply scenarios taking into account sustainability constraints indicate an annual potential of between 200 and 500 EJa^{-1} (excluding aquatic biomass). Forestry and agricultural residues and other
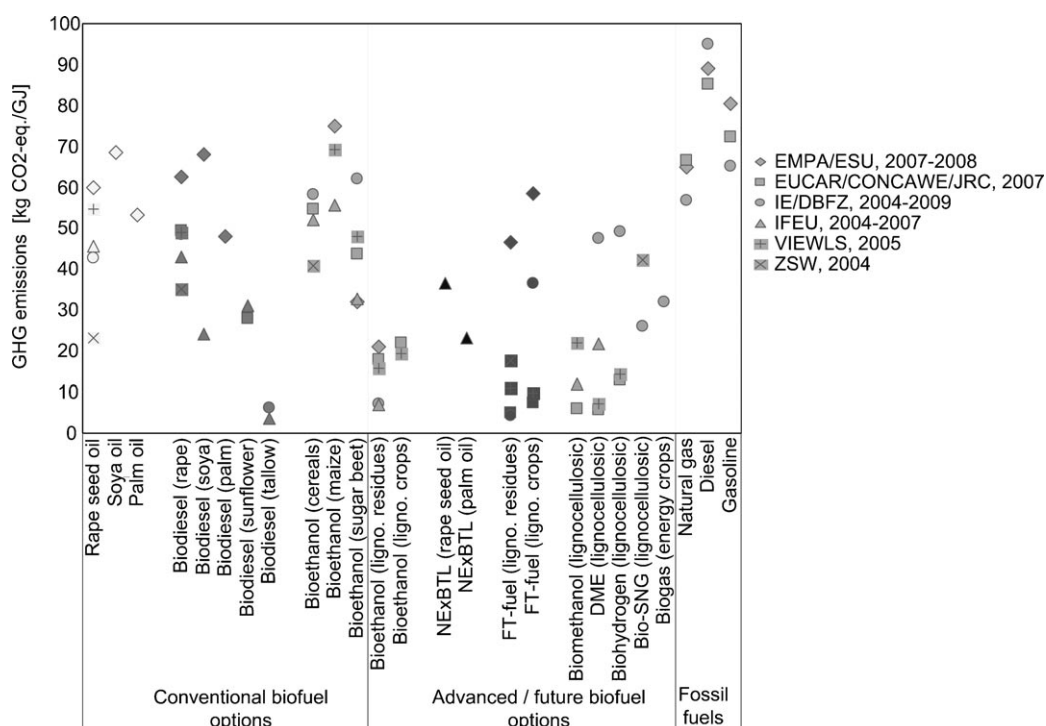
Figure 8. International results on global warming potentials (average values).[360,364,389–392]
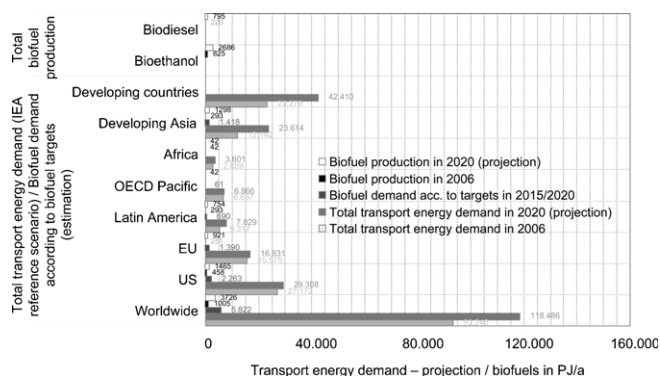

Figure 9. Biofuel demand to meet the defined targets in selected countries in 2015/2020.[400]

organic wastes (including municipal solid waste) would provide between 50 and 150 $EJ a^{-1}$, while the remainder would come from energy crops, surplus forest growth, and increased agricultural productivity.

Projected world primary energy demand by 2050 is expected to be in the range of 600 to 1000 $EJ a^{-1}$. Scenarios looking at the penetration of different low-carbon energy sources indicate that future demand for bioenergy could be up to 250 $EJ a^{-1}$. This projected demand falls well within the sustainable supply potential estimate, so it is reasonable to assume that biomass could sustainably contribute between one quarter and one third of the future global energy mix.[397]

Fuel ethanol production in 2008 was about 67×10^9 L, doubling from about 30×10^9 L in 2004. Brazil and US contributed about 40% and 50%, respectively, to this world production.[396]

Other countries producing fuel ethanol include Australia, Canada, China, Colombia, Costa Rica, Cuba, the Dominican Republic, France, Germany, India, Jamaica, Malawi, Poland, South Africa, Spain, Sweden, Thailand, and Zambia. Global production and wholesale pricing of ethanol and biodiesel reached 34.8 billion USD in 2008 and is projected to grow to 105.4 billion USD by 2018.[398]

Biodiesel production increased six-fold, from 2×10^9 L in 2004 to at least 12×10^9 L in 2008.[396] The EU is responsible for about two-thirds of world biodiesel production, with Germany, France, Italy, and Spain being the top EU producers. Outside of Europe, top biodiesel producers include the United States, Argentina, Brazil, and Thailand.

Of about 120 billion USD invested in renewable energy worldwide in 2008 (around double the equivalent 2006 investment about 13% was on biofuels. Taking into account the increasing number of countries define declarations on bioenergy use (e. g. biomass action plans, biofuel directives) all over the world, and that over the next 25 years world demand for liquids fuels is projected to increase more rapidly in the transportation sector than in any other end-use sector,[396] it may be estimated a fast growing of the investments in biofuels. According to International Energy Agency (reference scenario),[396] the transportation share of total liquids consumption increases from 51% in 2006 to 56% in 2030. Biofuel demand on the average will increase by 6.8% per year, but projections indicate that biofuels will be about 4% of total projected world transport energy demand in 2030 (about 3200 Mtoe).[399] On the other hand, selected countries have set more challenging targets, for example, the EU aims to achieve a 15% share of biofuels in the transportation fuel mix already by 2020.

However, these scenarios will considerably depend on the political targets, which are the main drivers for the development of biomass usage for bioenergy and biofuel production. In view of the bioenergy use and energy crop production, various political sectors with different objectives interact. The demand on biofuels to meet specific biofuel targets are summarised in Figure 9.[400]

5.2. Environmental concerns

There are many other factors, in addition to the technoeconomic considerations, which will determine the optimal strategies for bioenergy and bio-economy development, in general, and next generation biofuels, in particular. Evaluation of the environmental impact, through the use of suitable methodologies, such as LCA, has to be integrated in the analysis of the different options. There are notable changes in terms of GHG emissions for different bioenergy routes (Figure 8). Although LCA provides a means to quantify these potential benefits and environmental impacts, existing methods limit direct comparison within and between different biofuel systems, because of inconsistencies in performance metrics, system boundaries, and underlying parameter values. There is a critical need for standardized life cycle methods, metrics, and tools to evaluate biofuel systems based on performance of feedstock production and biofuel conversion at regional or national scales. It is also necessary to estimate the net GHG mitigation of an individual biofuel production system to accommodate impending GHG intensity regulations and GHG emissions trading. Predicting the performance of emerging biofuel systems (e.g., switchgrass cellulosic ethanol) poses additional challenges for LCA, due to the lack of commercial-scale feedstock production and conversion systems.

The next-generation biofuels are often considered in a wider aspect, where not only waste-derived feedstocks, but also specially cultivated lignocellulosic crops are used for their production. A general critical issue, in this connection, is the unbalance of rates of vegetation growth (slow) and biofuels consumption (fast). A massive introduction of land-dependent biofuels in the market might affect the food production, on one side, and on the world ecobalance (e.g., effects of fertilizers, use of water) on the other side.

Thus, the implications of such next-generation biofuels might be similar to those of the traditional first-generation biofuels. Such biofuels will tend to have impacts on eutrophication, acidification, and ozone depletion. LCA is a useful tool but a harmonized set of impact indicators is lacking. For example, the impacts, such as water consumption and effects on biodiversity are rarely considered by LCA. Results of lifecycle GHG balances depend on the way in which land-conversion-related impacts are attributed. Therefore, LCA, as a product-oriented approach, needs to be complemented by other methods that consider a wider spatial approach and socioeconomic contexts in order to account for effects such as indirect land use change (iLUC). Land conversion for biofuel crops can lead to significant GHG emissions. Clearing the natural vegetation mobilizes the stocked carbon and may lead to a carbon debt,

which could render the overall GHG mitigation effect of biofuels questionable. In 2030, 10% biofuels worldwide could substitute fossil fuels emitting 0.84 Gt CO_2, but iLUC-induced additional emissions could be in the 0.75 to 1.83 Gt CO_2 range.[401] Land conversion for biofuel crops can also lead to significant loss of biodiversity. Use of invasive crop species as feedstocks and nutrient pollution through intensive agriculture may also have impact on biological diversity. On the other hand, the use of abandoned and degraded land could lead to beneficial effects for biodiversity.

Water consumption and water quality are among the most important limiting factors for biofuel development. An increased use of fertilizers for biofuel production leads to higher nitrogen and phosphorus losses to water bodies, and related eutrophication issues. Feedstock production for biofuels in water-scarce regions requires irrigation. This may compete with food production. Extreme weather events (inundation, droughts) due to climate change might increase uncertainty.

It is necessary to include all these aspects in the assessment of next-generation biofuels and of related conversion pathways for their production in order to build a sustainable bio-based economy. Literature data are often confined to techno-economic aspects and perhaps to some LCA considerations, which are usually limited to the analysis of GHG emissions, while a more complete sustainability assessment considering technological needs for the emerging next generation biofuels technologies is required as the next step of the global transition to this new sector of economics and of chemical industry.

5.3. Outlook and conclusions

Despite a rapid worldwide expansion of the biofuel industry, there is a lack of consensus about the potential of biofuels to decrease GHG emissions and about the preferable technologies for their production. It is necessary to critically analyse trends and drivers in bioenergy and in biofuels, from a point of sustainability of next generation biofuels which stems from conjunction of related technical, economical, and environmental aspects. Thus, the scope of this Review was to overview these aspects of the existing and emerging technologies in this field. However, the factors conditioning the development in this field are manifold and often depend on local constraints or incentives (including geopolitical). Outlooks in this field are difficult, because the main triggers for the increase in biofuel development are policy targets and blending quotas. In combination with high oil prices, they attracted large private sector investments. For this reason, the aim of this work was not to identify the preferable technology options, but rather to outline the critical aspects and elements for evaluation and to present a comprehensive picture of the state of the art of this rapidly developing field.

Considering the abundant resources of waste biomass in the world, bioenergy could in principle cover about a quarter of total energy demand, even though the forecasts for 2030 by International Energy Agency indicate a lower share.[396] The potential of bioenergy has to be assessed in light of the global trends: population growth, nutrition, and agricultural yields.

Global population is expected to grow by 36% between 2000 and 2030 (medium projection of UN/FAO). Average crop yields are expected to increase at about the same rate, but meat consumption is expected to increase by 22% per capita between 2000 and 2030, requiring more cropland for feed. The effects of climate change will put further pressure on yield improvements and availability of arable land. Therefore, feeding the world population will require the expansion of global cropland. Additional demand for nonfood biomass will be added on top of this. Hence, it is evident that on the medium term, an integrated production of energy and food and chemicals from crops (where energy is also produced from crop residuals) is the only sustainable solution.

This integrated production of multiple chemicals from biomass, either dedicated crops or waste, is at the basis of the biorefinery concept.[19] Its principle of not wasting a single stream of organic matter is a promising factor to improve both economies and environmental impact of the biomass-feedstock-based processes, although from a technological point of view such facilities are awaiting a major development. The most feasible solution today appears the introduction of biorefinery principles into already existing production processes, where at least a part of organic waste could be valorized into value-added chemicals. Such possibilities exist in both industrialized and developing countries, for example, valorization of glycerol from biodiesel production, lignocellulose from forestry waste, bagasse from sugar production, and others. As far as the next-generation biofuel technologies are concerned, such as syngas or biochemical technologies: these have a high potential for the production of multiple product streams with respect to the traditional biofuels. Therefore, future production facilities have to consider, where possible, the possibility of integration of side processes to enable production of chemicals and energy.

In 2009 liquid biofuels of the first generation provided 1.8% of the world's transportation fuels, with a strong upward trend mainly in the USA, EU, Brazil, and China. Due to more favourable climatic conditions, growth in production is expected to continue in tropical countries. As a result, international trade in bioethanol and biodiesel will grow significantly, which will consequently stimulate the agro-food production in developing regions, creating incentives for rural development.

Due to limited land and resources availability, medium- to long-term future biofuel targets of some countries can only be achieved in a sustainable manner by implementing next-generation biofuels in addition to the existing biofuels. From a techno-economical viewpoint, only implementation of a reasonable mix of promising biofuels into the energy system is meaningful under consideration of existing infrastructure of transportation fuel distribution and use.

The increase in the world energy consumption in the next 20 years will be mainly triggered by the increase of the transportation fuels demand in developing and transition economy countries.[348] However, the next-generation biofuel production technologies, which are preferable in terms of sustainability (Figure 9), require large plants and investments, whereas the technologies with lower FCI (full circle investments) are needed in developing countries. For this reason, the penetration of next-generation biofuels in these countries might be very slow. The transition to next-generation biofuels in the developing world will probably require a part of the funds for developing countries agreed in the recent UN Framework Convention on Climate Change (Copenhagen, Dec. 2009), to be used also to promote the in house development of technologies and establishment of related industrial production capacity.

On one hand, currently developed next-generation biofuel production technologies often do not have the necessary characteristics to couple high efficiency with a low capital investment. This would slow down introduction of new processes and, in turn, the effective sustainability of the biofuel market. Thus, it is necessary to reconsider the technologies currently under development and to design alternative pathways. Introduction of efficient catalysts and of microreactor technologies, as well as of more efficient separation technologies, based on membranes for example, are the key elements to enhance efficiency, environmental impact and, therefore, the economic viability of new generation biofuel processes in a long term.[402] To achieve these objectives it is first of all necessary to foster R&D in this sector. Taking these aspects into account, next-generation biofuels are cost intensive and, therefore, have to overcome implementation barriers to be competitive with other alternative fuels. On the other hand, one of the key issues for the implementation of promising and efficient technologies concerns their economics, that is, their set up and operational costs, feedstock transportation and infrastructure costs, and risk management aspects, which require substantial capital investments. Last but not least, there is a need for qualified human resources and proper social programmes to enable a smooth introduction of these technologies. The abovementioned aspects are especially relevant for developing countries, where a proper policy has to be adopted to favor the development of human and industrial capacity, formation of a public opinion, and an encouragement to invest in the development of next-generation biofuels as a key sector of a national economy.

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