Chapter 9
Biorefineries in the World

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Abstract This chapter intends to give a brief overview of current conventional and advanced biomass-based biorefineries in the World. While the conventional biorefineries use mature and commercial technology, the advanced biorefineries (e.g., lignocellulosic-based biofuel biorefineries, microalgae-based biorefineries) have different degrees of technology-readiness level and regardless the process technology, only a few of them have reached the commercial scale although the profitability remains a quest. The most representative's examples of biorefineries in the World are reviewed in this chapter with special emphasis on thermochemical- and biochemical-based biomass processing technologies for advanced biofuel biorefineries at pilot, demo or commercial stage. Few examples of product (non-energetic)-driven biorefineries are also discussed, such as pulp and paper biorefineries and lactic acid-producing biorefineries, mainly because only a limited number are in operation because their key technologies are still in the R&D, pilot or demo stage.

9.1 Introduction

Similarly, to an oil refinery, a biomass-based refinery or "biorefinery" is an industrial plant that produces a variety of products and as a result of the whole utilization of complex raw materials, namely the lignocellulosic biomass. Some of these biorefinery products, e.g., ethanol, butanol, lignin are more oxidized molecules than the hydrocarbons molecules obtained from fossil fuels (Cherubini and Stromman 2010).

Conversely to other more conventional uses of biomass (e.g., the use of wood in pulp and paper mills or the use of oleaginous seeds to biodiesel), a biorefinery industrial plant aims for a greater utilization of the biomass feedstock, for an enhanced mitigation of greenhouse gas (GHG) emissions, for producing fewer

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wastes and residues, and for greater energy efficiency and product income. Other advantages claimed for the biorefinery concept have already been cited in Chap. 1 (Biorefinery concept).

The simplest (i.e., less complex in terms of design) biorefineriesuse sugar-based crops (e.g., sugar beet, sugarcane), starch crops (e.g., cereals, grains, such as corn, cassava, or wheat) or oleaginous crops (e.g., rape, soy), called "first generation" feedstocks, as raw materials. These biorefineries are already maturely established, and the majority of the commercial facilities belonging to this category produce first-generation (1G) biofuels, i.e., biodiesel or bioethanol. In addition, traditional pulp and paper mills can also be categorized as conventional biorefineries, since they produce multiple products from biomass (wood).

Conversely, advanced biorefineries are usually related with the use of more sustainable nonfood crop feedstocks, in particular lignocellulosic residues from forestry, agricultural, agro-industrial, the organic fraction of urban wastes, cellulose wastes (e.g., paper and sludge) and dedicated energy crops. Indeed, lignocellulosic biomass residues represent a promising option as feedstock for bio-based production, under a biorefinery concept, considering their output/input energy ratio, their great availability both in tropical and temperate countries, their moderate cost (primarily related to their transport), and the fact that they do not compete for food and feed production (Kheshgi et al. 2000; Cardona and Sanchez 2007; Lynd et al. 1991; Sanchez and Cardona 2008).

A classical classification of biorefineries has been proposed by Kamm and Kamm (2004), Kamm et al. (2006). They consider four types of biorefineries: whole crop biorefinery (e.g., integrating the whole plant harvested for food and nonfood purposes), green biorefinery (e.g., grass and other immature green biomass as feedstocks), lignocellulosic feedstock biorefinery (e.g., forestry-based lignocellulosic feedstocks) and the two-platform concept, based on main types of technology involved (e.g., sugar platform and the thermochemical platform). This classification has several limitations, e.g., it does not consider the concept of multi-platform biorefineries neither the existence of current algae-based biorefineries.

A more recent classification of biorefineries has been postulated by IEA-Bioenergy Task 42 based on energy-driven (or biofuel-driven) biorefineries and product (non-energetic)-driven biorefineries (IEA-Bioenergy 2014). In the former, the main target is to produce large amounts of energetic products (biofuels, heat, and power) while the latter are mainly focused for production of bio-based products out of biomass while their by-products or residues can be used for energy purposes.

We shall review in this chapter many examples of biofuel-driven biorefineries some of which that have reached the commercial scale although the profitability remains a quest, but not many examples of product-driven biorefineries since only a limited number are in operation, mainly because some key technologies are still in the R&D, pilot or, demo stage.

9.2 Conventional Biorefineries

There are in the World many examples of the so-called conventional biorefineries since they use only a fraction (usually a minor part, in weight) of the raw material as input. These biorefineries are already maturely established, and the majority of the commercial facilities belonging to this category produce first-generation (1G) biofuels, i.e., biodiesel (fatty acid methyl ester) or bioethanol. Besides these above-mentioned energy-based biorefineries, other non-energetic-based biorefineries can be classified as conventional if they use sugar-based crops, starch crops or oleaginous crops, i.e., edible feedstocks. Since all general rules might have exception, traditional pulp and paper mills can also be categorized as conventional biorefineries, since they produce multiple products from biomass, i.e., wood (Ragauskas et al. 2006).

The next sections illustrate some of the most important examples of conventional biorefineries already in the World market.

9.2.1 First-Generation Biodiesel

Biodiesel (fatty acid methyl esters—FAME) is a biofuel that can be used as pure biodiesel fuel or blended with diesel, due to the similarity in their physical and fuel properties. The 1G biodiesel production process is defined as a conventional oleaginous biorefinery since it integrates the production of an energy-based product (biodiesel) and non-energetic based co-products (animal feedstock and glycerin).

Oleaginous crops are the most used raw material for biodiesel production. In Europe, rapeseed is the main feedstock, accounting for 55% of total biodiesel production in 2014 (EU Biofuels Annual 2015), while in the USA, Argentina, and Brazil soybean is the largest biodiesel feedstock. Palm oil from Indonesia and Malaysia has also an important market in this biofuel industry. Besides these prominent oil crops, many other sources such as sunflower, canola, jatropha, and oil-based residues (e.g., used cooking oil, animal fat) can be used for the same purpose.

Figure 9.1 presents a simplified diagram of a 1G biodiesel production process. Using oilseeds as starting raw material, the first processing step corresponds to the oil separation, by pressing (cold or hot) and/or by solvent extraction (usually hexane). Through this process, crude vegetable oil is obtained and meal extract/seed cake incurs as co-products. The latter are usually used for animal feedstock due to their protein content while the crude vegetable oil, mainly composed of triglycerides, is used to produce biodiesel.

Fatty acid methyl esters (biodiesel) are obtained through the esterification and transesterification reactions of free fatty acids and triglycerides, respectively. In the transesterification process, glycerides react with an alcohol (e.g., methanol) in the presence of a catalyst (e.g., an alkali such as sodium methylate) to deliver FAME

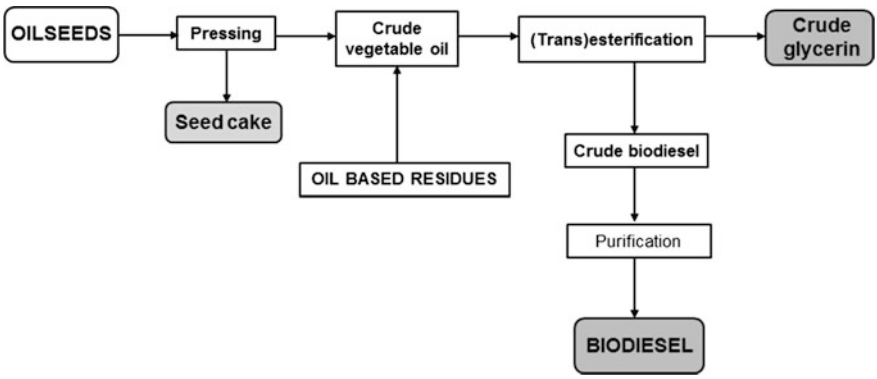

Fig. 9.1 Simplified flowsheet for biodiesel production from oilseeds and/or oil-based residues, co-producing crude glycerin and seed cake

and glycerin. Currently, this conversion process is used at a large scale to convert edible oils into FAME. For raw materials with high acidity, as nonedible oils and oil-based residues, a two-stage process is the most suitable approach to be used. In this case, the alkaline catalyzed transesterification is preceded by an acid catalyzed esterification that allows converting the free fatty acids (FFA) into FAME.

Crude glycerin from biodiesel production can be refined into a pure form and then be used in food, cosmetic and pharmaceutical industries. Nowadays, several applications for non-refined glycerin have been proposed, as anaerobic digestion, animal feeds, and thermochemical/biological conversions to value-added products. However, plants for the production of biodiesel are either stand-alone or integrated in oil mills, and are not yet connected to additional secondary refining of, e.g., crude glycerin into higher added value non-energetic based products shifting these first-generation biodiesel plants into more advanced biorefineries.

Biodiesel has been produced at an industrial scale in the EU since 1992, and nowadays there are approximately 250 plants with an installed production capacity of 23 million tons of biodiesel (European Biodiesel Board). These plants are mainly located in Germany, Italy, Austria, France, and Sweden. Table 9.1 presents the main 1G biodiesel producers in EU in 2014. The available data estimate that EU biodiesel consumption reached 11.1 Mtoe (12.9 million tons) in 2014 (Biofuels barometer, Eurobserv'er 2015).

Recent data from USA report a total of 166 biodiesel producers and an annual production capacity of 9.1 million tons (10.431 billion liters). The main 1G biodiesel producers in USA, with installed production capacity higher than 378 MM liters/year, are RBF Port Neches LLC in Texas (681.3 MM liters/year) and REG Grays Harbor LLC in Washington (378 MM liters/year). Otherwise, biodiesel production from the Midwest region (Petroleum Administration for Defense District 2) was about 71% of the United States total being Louis Dreyfus Agricultural Industries LLC in Indiana (341 MM liters/year) the largest plant (Biodiesel Magazine 2015).

Table 9.1 Main 1G biodiesel producers in EU in 2014[a] (biofuels barometer, Eurobserv'er 2015)

Company	No. of plants	Total production capacity (t/year)
Avril (formely Sofipetrol)	13	2,700,000
Neste Oil	3	1,180,000
ADM Biodiesel	3	975,000
Infinita (Musim Mas)	2	600,000
Marseglia Group (Ital Green oil and Ital Bi Oil)	2	560,000
Verbio AG	2	450,000
Eni	1	300,000
Petrotec	3	185,000

[a]Only units in Europe are considered

9.2.2 First-Generation Bioethanol

Nowadays the most common renewable fuel is 1G bioethanol, i.e., ethanol produced from sugar/starch crops, which is typically blended with petrol in most of the countries as low blends (e.g. E5, E10).

Sugar-based crops require minimal processing since the process only requires direct fermentation of sucrose (obtained via simple sugar extraction) into ethanol by *Saccharomyces* yeasts. Raw sugar is derived from both sugarcane and sugar beet.

Brazil and India are the World's two largest sugar producers, accounting together for over half the World's sugarcane production for the past 40 years (E4tech, RE-CORD and WUR 2015). Brazil is the largest producer of ethanol from sugarcane, which is the cheapest, and the World's second largest ethanol producer, behind the United States, and it is also a pioneer in using ethanol as a motor fuel (Sánchez and Cardona 2008). In 2013/14, Brazil produced 653.5 million tons of sugarcane, which yielded 37.7 million tons of sugar and 27.5 billion liters (7.3 billion gallons) of ethanol. Most of this production is absorbed by the domestic market where it is sold as either pure ethanol fuel or blended with gasoline. All common gasoline sold in Brazil includes superior blends with anhydrous bioethanol ranging from 18 to 27 %vol/vol, being currently 25% (Unica and ApexBrasil 2016). There are 391 ethanol plants operating in Brazil in 2016 (NovaCana 2016), being 126 dedicated to ethanol production and 252 producing both sugar and ethanol. There are 15 additional plants dedicated exclusively to sugar production (Ibeto et al. 2011).

Despite sugar beet is a demanding crop in terms of soil conditions, fertilizer and irrigation, in Europe 188.4 million tons of sugar beet were produced in 2012 (FAO 2014) and sugar beet has long been used to produce fuel ethanol, with France, Germany, Belgium, and Greece leading production (European Biofuels Technology Platform). Although North America has not processed beets for commercial ethanol, nonfood-grade "energy" beets have recently been used to produce commercial-quality ethanol. Following the closure of sugar plants, former sugar

beet farmers decided to produce "energy" beets for conversion to ethanol instead of table sugar. That ultimately led to the implementation in North America of the first demonstration plant (one million gallon-capacity) in California (Fresno County), operated by Mendota Bioenergy LLC, using the whole beet as feedstock for ethanol production (Renewable Energy World.com).

Starch processing also involves a fairly mature technology involving enzymatic hydrolysis—liquefaction and saccharification—to break the starch into its constituent sugar, producing a relatively clean glucose stream that is easily fermented to ethanol by *Saccharomyces* yeasts (Gray et al. 2006). There are two production processes: wet milling and dry milling. The main difference between the two lies in the initial treatment of the grain. In traditional dry milling, as shown in Fig. 9.2, the entire corn kernel or other starchy grain is first ground into flour, and processed without separating out the various component parts of the grain. The components of the kernel not intended for fermentation include the germ, fiber ,and protein, are concentrated in the distillers dried grains that are produced as co-products. These dried distillers grains with solubles (DDGS), a protein rich product, are used for animal feedstock. While dry milling is less capital intensive, it also yields less ethanol per bushel of corn than wet milling (Rajagopalan et al. 2005). In wet milling, the grain is soaked or "steeped" in water and dilute sulfurous acid for up to 48 h, to assist in separating the grain into its many component parts. Slurry processing separates the germ from the rest of the kernel, which is further processed to separate the fiber, starch, and gluten, as shown in Fig. 9.3. The fiber and corn gluten are sold as components of animal feedstock while the starch is fermented to ethanol, or commercialized as corn starch or corn syrup (Renewable Fuels Association 2005). Thereby, these ethanol plants shall be categorized as biorefineries since they produce multiple products from the sugar and starch components of biomass.

Starch processing for ethanol is dominated by USA using corn starch. Indeed, 40% of the USA corn harvest already is used for bioethanol production, mainly through dry-grind technology (E4tech, RE-CORD and WUR 2015). Europe leads on wheat, with modest production of barley and other coarse grains. Indeed, wheat is the main crop grown for bioethanol production in Europe, accounting for 0.7% of

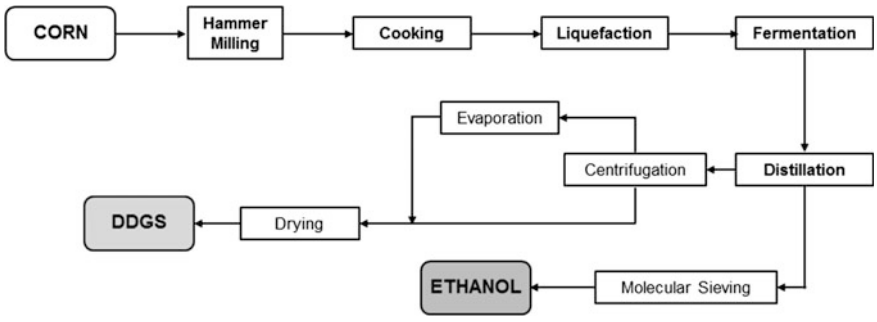

Fig. 9.2 Simplified flowsheet for ethanol production from corn via dry milling, co-producing dried distiller's grains with solubles (DDGS) (adapted from Renewable Fuels Association 2005)

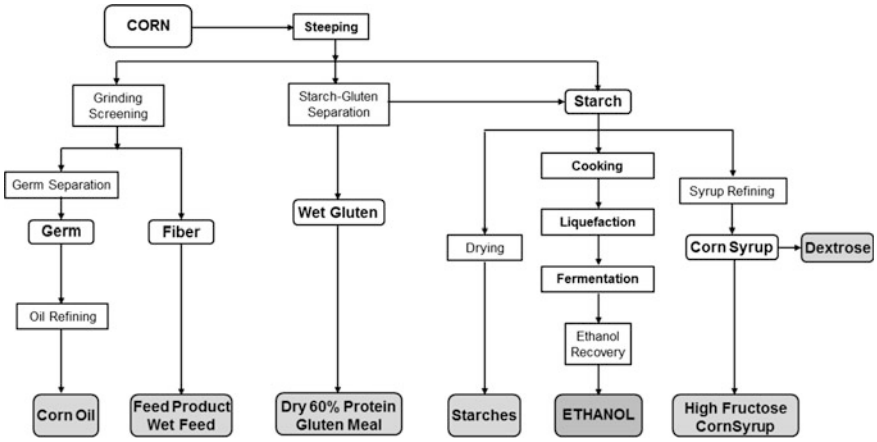

Fig. 9.3 Simplified flowsheet for ethanol production from corn via wet milling (adapted from Renewable Fuels Association 2005)

Table 9.2 Largest commercial producers of 1G bioethanol in the USA (according to data in Ethanol Producer Magazine 2016)

Company	No. of plants	Total capacity (million liters/year)
Archer Daniels Midland Co.	8	>5970
Big River Resources LLC	4	1475
Flint Hills Resources LLC	7	3050
Green Plains	14	4600
Marquis Energy LLC	2	1420
Pacific Ethanol	8	1950
Poet Biorefining	26	6315
Valero Renewable Fuels	11	4960

EU agricultural land and 2% of Europe's grain supply (European Biofuels Technology Platform). China is the global leader for rice production, along with significant production levels of wheat, coarse grains (corn), and sugarcane (E4tech, RE-CORD and WUR 2015).

There are 216 plants producing 59.5 billion liters of ethanol per year from sugar/starch in the United States. Seventy-four of the largest commercial 1G bioethanol facilities in operation in USA, belonging to 8 companies, produce 50% of this capacity (Table 9.2), using corn as raw material. Besides corn, sorghum is also used as a relevant starchy feedstock in the USA, and less than 0.2% of 1G ethanol produced in USA is obtained from wastes (e.g., beverage waste or wheat screenings).

In Canada, there are 17 plants producing 7.3 billion liters of 1G ethanol per year, with 54% of this capacity assured by two companies using corn as raw material, Green Field Ethanol (4 plants with a total yearly capacity of 2.49 billion

liters) and Suncor (one plant with a total yearly capacity of 1.5 billion liters). Besides corn, Canada is producing 1G ethanol from wheat, barley and waste beverage (Ethanol Producer Magazine 2016).

9.2.3 Other 1G Sugar Platform Bioproducts

Although bioethanol is the dominant sugar platform product, there are a few commercial biorefinery facilities producing other multiple sugar platform products, such as succinic acid, lactic acid, acetic acid, *n*-butanol, iso-butanol, 1,3-propanediol (PDO), or itaconic acid, from sugar or starch components of plant biomass (E4tech, RE-CORD and WUR 2015). Other primary bio-based products, i.e., made as a first step (by direct microbial fermentation) from sugars, such as 1,4-butanediol (BDO), farnesene, poly-hydroxyalkanoates (PHAs), are currently produced still at R&D, pilot, or demonstration scale. Indeed, in terms of bio-based markets volumes, bioethanol dominates (with 58 billions of dollars of sales per year), followed by *n*-butanol (1.1 billion USD/year), acetic acid (0.8 billion USD/year), and lactic acid (0.7 billion USD/year), with much smaller but still significant markets. Some of these established bio-based products already dominate global production, e.g., ethanol and lactic acid (E4tech, RE-CORD and WUR 2015).

For instance, worldwide demand for lactic acid is expanding, not only for the more conventional use in cosmetic, pharmaceutical, and food preservatives markets, with approx. 45% of market share, but also for industrial applications, mainly for polylactic acid (PLA) production.

PLA, or polylactide, is a biodegradable and recyclable thermoplastic polyester resin (Vaidya et al. 2005), suitable for packaging materials, insulation foam, automotive parts, and fibers (textile and nonwoven) (E4tech, RE-CORD and WUR 2015), and more recently, due do its biocompatibility, for biomedical applications (Vijayakumar et al. 2008). Packaging is likely to remain the key market for PLA, with the expected increase on demand for environmentally friendly starch-based plastics for this application. Indeed, most of PLA producers also manufacture lactic acid. The global annual demand for lactic acid (including PLA) is estimated at 472 ktons, and the global production capacity is estimated to be around 750 ktons per year, with a strong presence in China (E4tech, RE-CORD and WUR 2015).

Lactic acid can be manufactured either by chemical synthesis or by fermentative processes but the latter have been preferentially used in industrial production, accounting for approximately 90% of the total worldwide production (Hofvendahl and Hahn-Hägerdal 2000). The fermentative route allows the selective production of the desired L-lactic acid stereoisomer, with additional advantages in terms of energy efficiency and yield. Moreover, renewable carbon sources are used for microbial fermentation, and actually lactic acid is mostly produced from corn starch (in the USA), tapioca roots, chips or starch (in Asia), or sugarcane and sugar beets (in the rest of the World).

The largest global commercial producer of PLA is USA-based NatureWorks (former Cargill Dow), producing PLA resins under the Ingeo brand, with a commercial production plant in Nebraska (with an annual 150 ktonnes-capacity) and plans for a new plant in Thailand (E4tech, RE-CORD and WUR 2015). NatureWorks' Ingeo PLA is also foreseen to be used in filaments formulations for 3D printing. In short term, they plan the transition for the use of residual lignocellulosic biomass (e.g., corn stover, wood chips, switch grass, or straw) as inherently more sustainable feedstock, replacing the currently used corn starch (NatureWorks LLC website). The largest global lactic acid producer is Corbion Purac (Netherlands). The later produces lactic acid, lactic acid derivatives, and lactides (including lactide resins for high-performance PLA bioplastics), operating 5 production plants, in the USA, the Netherlands, Spain, Brazil, and Thailand (the largest plant, with an annual 100 ktonnes-capacity) (E4tech, RE-CORD and WUR 2015).

In Europe, there are other PLA (and lactic acid) producers, including Synbra Technology, which operates a commercial (annual 5 ktonnes-capacity) plant in Netherlands and a pilot production plant in Switzerland (annual 1 ktonnes-capacity). Cellulac announced the future conversion of a brewery in Ireland into a lactic acid and PLA plant with 2G feedstock. Besides Corbion Purac, Galactic and Jungbunzlauer are operating commercial lactic acid production plants in Europe.

Other PLA producers include the Chinese Zhejiang Hisun Biomaterial (with an annual 5.5 ktonnes-capacity to be expanded to 50 ktonnes; using cassava instead of corn). Other lactic acid producers include Henan Jindan Lactic Acid Technology (with an annual 100 ktonnes-capacity, the largest in Asia) (E4tech, RE-CORD and WUR 2015).

9.2.4 Pulp and Paper Mills

In fact, the existing technology in pulp production can already be denominated as a conventional biorefinery, as long as in addition to pulp a wide range of chemical by-products and energy are produced from biomass, i.e., wood, which is processed in a sustainable manner (Davenport 2008). The paper industry is based on the exploitation of a natural resource, renewable, and featuring carbon sequestration—the forest; it generates products with high carbon content, which gives it a sequestration status (proportional to the lifetime of the product); it generates products several times-recyclable, which allows to extend its lifetime; and it generates biodegradable products, which reduces the impact of its final disposal in the environment. In addition, a very significant and increasing energy amount (corresponding to 69% of its energy needs, in 2010, according to CELPA 2011) is obtained from biomass, e.g., wood wastes, bark and mainly from cooking liquor containing the lignin removed from wood during the manufacturing process (this

latter representing 85% of the total biofuels consumed in 2010) (Kheshgi et al. 2000).

The pulp and paper are ideal hosts for the combined production of heat and electricity called cogeneration because a large amount of steam is used for several purposes in production processes (Kheshgi et al. 2000). In fact, the proportion of electricity produced by cogeneration has reached high levels and the paper industry is currently the largest producer of electricity through cogeneration among all the industrial sectors of the European Union. The pulp and paper industry is, in fact, the largest user and producer of renewable energy in the European Union: it produces about 17% of the EU renewable energy and consumes about 13%.

Despite all these improvements in product and process efficiency that have been implemented in the pulp and paper industry, the core business of the majority of mills and infrastructures remains the same. However, this situation should change in the near future, since the pulp and paper industry is in a very favorable position to become the next generation of advanced biorefineries, taking advantage from its great experience on processing large streams of biomass (wood). Implementation of the modern and advanced biorefinery concept by pulp and paper manufacturers will benefit from biomass resource already collected, available, and centralized in one location, eliminating the need for implementation of new collection circuits (Ragauskas et al. 2006). Thereby, many of the companies are already evaluating its potential as a modern and advanced biorefinery, further extending the biorefinery concept, as reported in Sect. 9.6.4.

9.3 Thermochemical-Based Advanced Biorefineries

9.3.1 Introduction

Nowadays the main thermochemical processes for biofuel production are still gasification and pyrolysis. Pyrolysis of biomass produces gases, liquids, and solids (carbonaceous residue). The gases can be used as fuel and the major constituents are hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), nitrogen (N_2), and gaseous hydrocarbons. The liquids are used as raw material or as fuel either directly or after being converted into secondary fuels (more valuable). The proportion of the obtained products depends on the technology used, type of reactor and of operational conditions, such as the type of gas, pressure, temperature, reaction time, type of solvent and catalyst. The type and composition of the biomass is also of utmost importance. Currently the main purpose of pyrolysis is to obtain bio-liquids to be used as fuel or as raw material in the industry.

In Fig. 9.4 a simplified diagram of biomass pyrolysis' main products is presented.

The gasification process is more mature than pyrolysis. During gasification, biomass is converted into a gas, usually referred as syngas, whose major

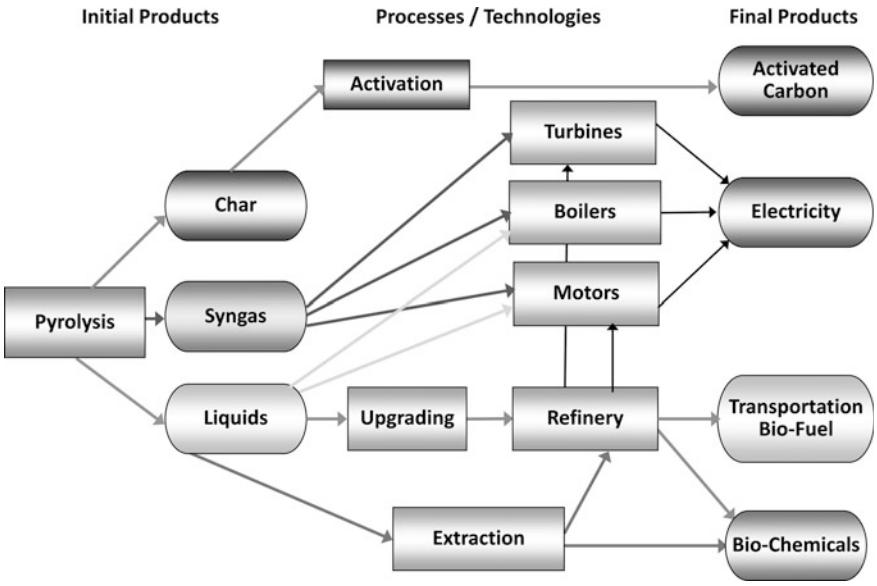

Fig. 9.4 Scheme of the main products of biomass pyrolysis

constituents are CO, H_2, and CO_2, methane (CH_4) and other gaseous hydrocarbons from C_2 to C_4, usually referred as (C_nH_m). Gasification may occur in the presence of different gasification agents, which determine the type of gas produced. The most common gasification agents are oxygen (or air) and steam, but CO_2 or mixtures of any of these components may also be used. The choice of the gasification agent depends on the application of gasification gas. The use of air leads to the production of a gas that is diluted with N_2, thus having a lower calorific value, not suitable for chemical synthesis. The use of oxygen solves the problem of N_2 dilution, but increases the operative costs because of the cost associated with oxygen production.

Gasification gas may be used in chemical synthesis to produce liquid or gaseous fuels. For such use, syngas cleaning and upgrading is required to reduce the contents in tar, alkali metal, and sulfur, N_2, and chlorine compounds. In addition, the H_2/CO ratio in the gasification gas must be between 1.5 and 3.0 depending on the chemical synthesis: Fischer–Tropsch, synthetic natural gas (SNG), alcohol syntheses (methanol, ethanol, and propanol) or synthesis of dimethyl ether (DME). As all these chemical syntheses are already well known, the main challenge is the production of syngas with the suitable gas composition to be further used in these processes (Rapagn et al. 2002; Lv et al. 2007).

Figure 9.5 shows the main products obtained from biomass gasification. Lately, research and development of thermochemical technologies has been focused on the production of alcohol mixtures and DME by chemical syntheses, instead of diesel like biofuels by Fischer-Tropsch synthesis, mainly due to economic reasons and absence of biomass supply chain at large scale and at competitive prices.

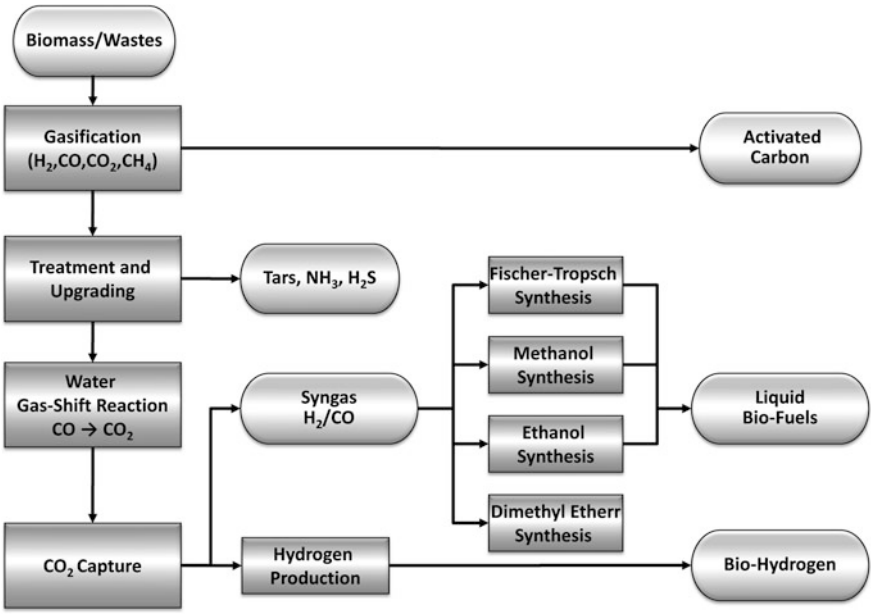

Fig. 9.5 Biomass gasification main products

The basis of a thermochemical-based biorefinery is the production of different biofuels and bio-chemicals using thermochemical processes, mainly gasification and pyrolysis. The main advantage is the production at regional or decentralized level, where biomass is available. Afterwards the high-energy bioproducts can be cost-effectively transported to existing centralized refinery facilities for further processing.

9.3.2 Most Relevant Thermochemical-Based Processes

A selection of the most important processes for biofuels production by thermochemical processes in biorefinery concept is presented (IEA Bioenergy 2014; Bacovsky et al. 2013). The criteria for the selection were the maturity of the process and the existence of demonstration or commercialization units. To facilitate the reading and comprehension of the main information available, the data are organized in the below format.

SNG demo

Process/Technology	SNG (synthetic natural gas)
Project owner	Biomassekraftwerk Güssing
Web page	http://www.eee-info.net

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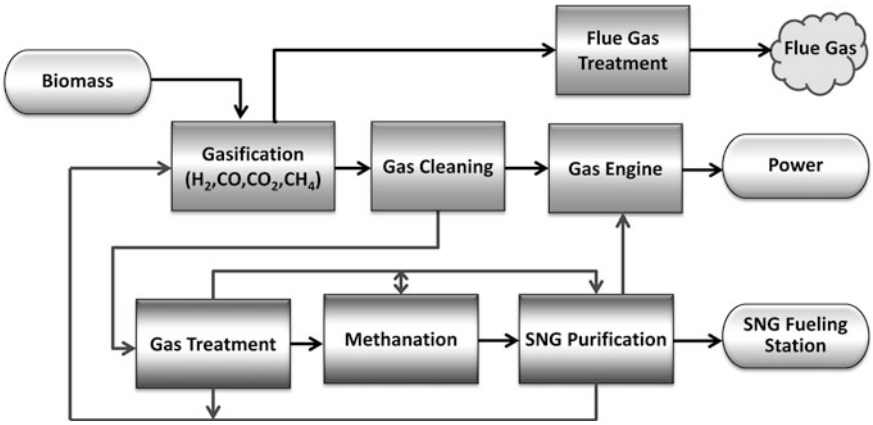

Fig. 9.6 Flow diagram of bioC Biomassekraftwerk Güssing

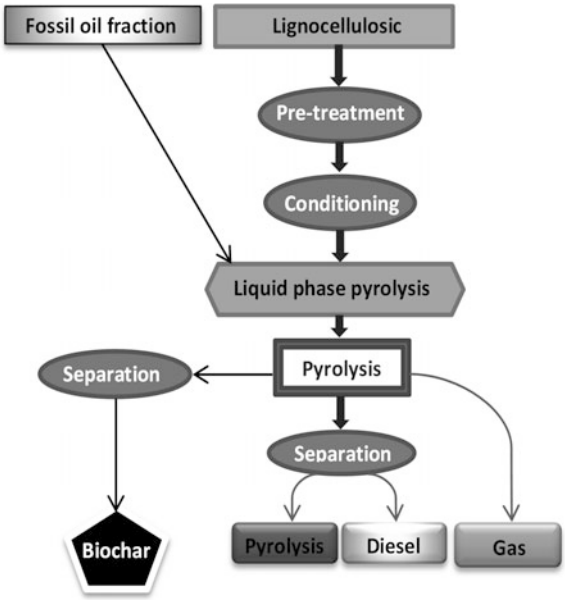

Fig. 9.7 Diagram block of bioCRACK process, Vienna

(continued)

Facility type	Demonstration
Operation	Since 2009
Feedstock	350 Nm^3/h of syngas
Outputs	576 t/year; 100 Nm^3/h of SNG
Status	Operation

(continued)

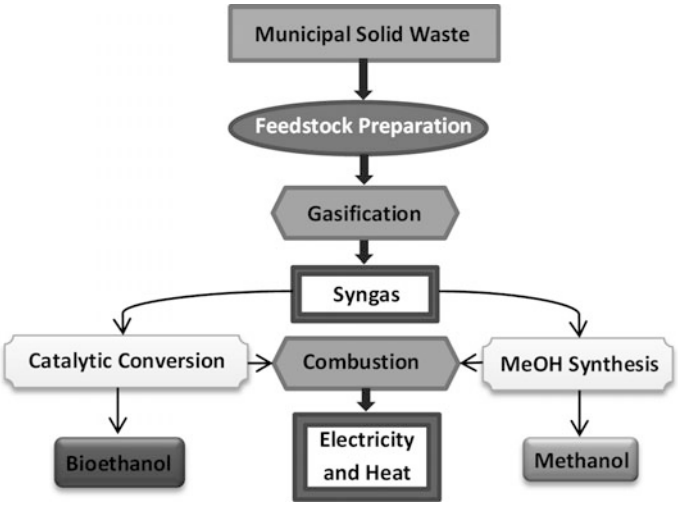

Fig. 9.8 Diagram of Enerkem process, Alberta

(continued)

Location	Güssing, Austria
Summary	The installation uses a gaseous stream from the existing gasifier in Güssing, which is purified before being introduced to the catalytic reactor for conversion to methane, which operates at a temperature between 300 and 360 °C and a pressure range from 1 to 10 bar (Fig. 9.6) This facility with 10 MW started in June 2009, after tests in a laboratory plant of 10 kW for a few years. The technology was developed in collaboration with Vienna University of Technology (TUV) The facility was originally owned by CTU—Conzepte Umwelt Technik AG and was subsequently acquired by Biomassekraftwerk Güssing (Bacovsky et al. 2013)

BDI bioCRACK pilot Plant

Process/Technology	A one-platform (pyrolysis-oil) refinery for the production of diesel fuel, pyrolysis-oil, and bio-char from solid biomass
Project owner	BDI—Bioenergy International AG
Web page	http://www.bdi-bioenergy.com/de-biomass_to_liquid-24.html
Facility type	Pilot plant
Operation	Since 2009
Feedstock	2.4 t/day Lignocellulosic biomass (wood chips, straw)
Outputs	5 t/a raw diesel fuel, pyrolysis-oil, char
Location	OMV refinery Schwechat/Vienna, Austria

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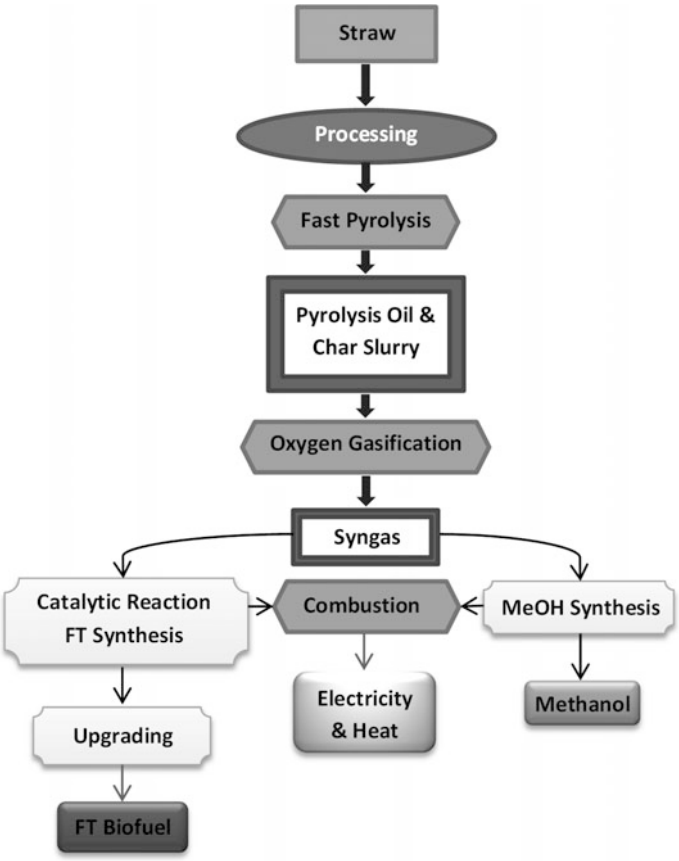

Fig. 9.9 Process block diagram of BIOLIQ plant, Karlsruhe

(continued)

Summary	This process uses the bioCRACK technology to produce mineral diesel blended with biofuels obtained from renewable sources which can be easily upgraded to EN590 quality, using current refinery units The bioCRACK process (Fig. 9.7) converts solid biomass like wood chips and straw directly into raw diesel fuel. The OMV refinery Schwechat was selected for the implementation of bioCRACK pilot plant that was the first worldwide to be implemented in a refinery (IEA Bioenergy 2014) This concept accomplishes two important tasks: production of diesel to meet the growing demand of liquid fuels and increase of biogenic share

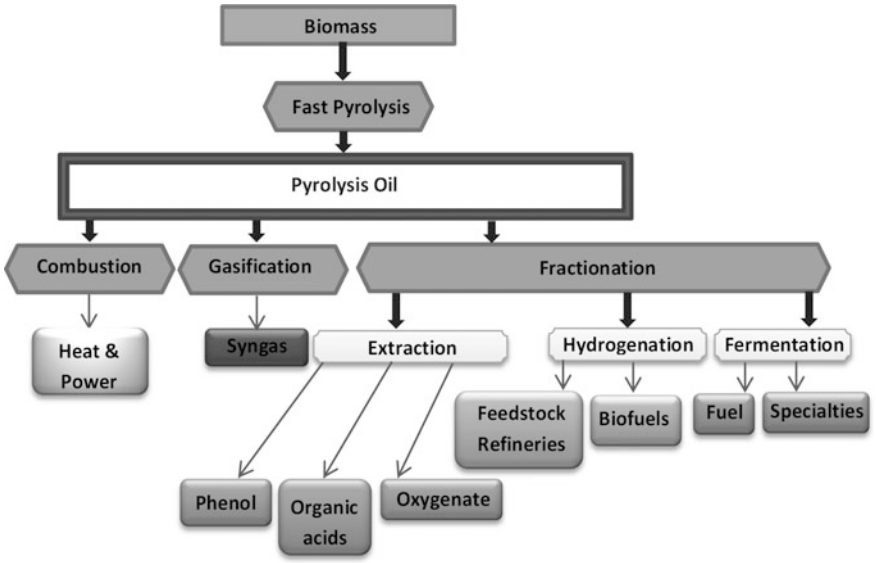

Fig. 9.10 Process block diagram of BTG plant, Hengelo

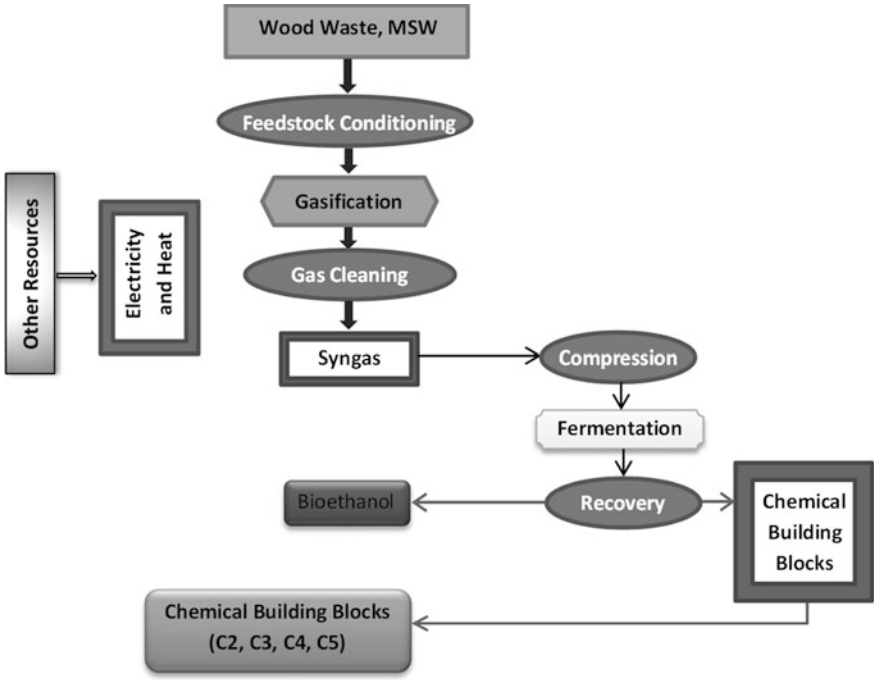

Fig. 9.11 Process block diagram of LanzaTech plant, Glenbrook

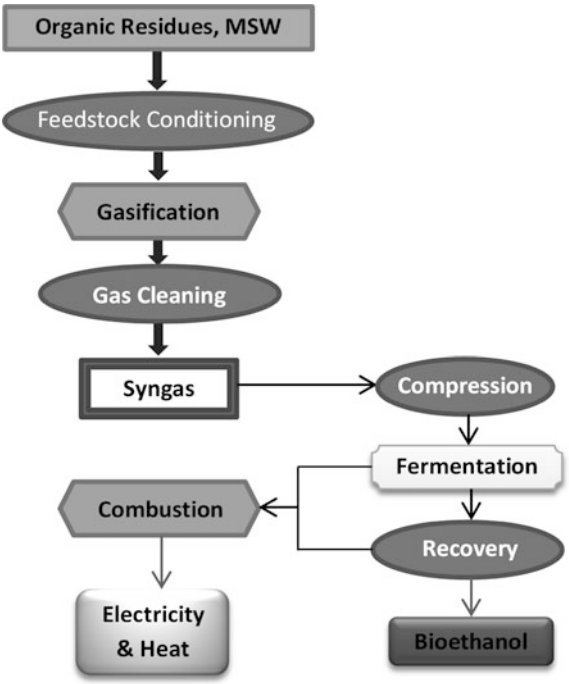

Fig. 9.12 Process block diagram of INEOS plant, Florida

Enerkem waste-to-biofuels facility (Alberta, Canada)

Process/Technology	1-platform (syngas) biorefinery producing biofuels, chemicals, and bioenergy from municipal solid waste
Project owner	Enerkem Alberta Biofuels L.P.
Web page	www.enerkem.com/www.edmontonbiofuels.ca
Facility type	Commercial Scale, under commissioning (Alberta) Demonstration (Westbury)
Operation	Since 2014 (Alberta) In operation since 2009 (syngas), 2010 (methanol), 2012 (ethanol) (Westbury)
Feedstock	100,000 dry tonnes of sorted MSW per year (Alberta) Decommissioned telephone poles and sorted municipal solid waste (Westbury)
Outputs	38×10^6 l/year of biofuels 5 million liters/year (methanol), syngas, ethanol
Location	Edmonton, Alberta (on the integrated waste management site of the City of Edmonton) Westbury facility (Canada)
Summary	Enerkem Alberta Biofuels made an agreement with the City of Edmonton to build, operate a plant and produce 38×10^6 l/year of next-generation biofuels, using around 100,000 of dry tonnes of nonrecyclable and noncompostable municipal solid waste, which will

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	be otherwise landfielded. This process includes feedstock preparation, gasification, syngas cleaning, and catalytic conversion to produce ethanol for transportation use and methanol for chemical applications. The plant started operation on June 4, 2014 and is the result of a fruitful collaboration with a municipality In Fig. 9.8, a diagram of Enerkem process is shown Enerkem Westbury demonstration facility is placed in a rural area and recycles used electricity and telephone poles and railway ties. It converts the non-usable parts of these poles and other waste materials into biofuels and green chemicals. It allowed the process scale-up to full commercial deployment, like the Enerkem Alberta Biofuels facility in Edmonton, Canada. Other important tasks include testing of unconventional feedstocks and raw materials, development of new products and training plant technicians and operators (IEA Bioenergy 2014)

BIOLIQ

Process/ Technology	A 3-platform (pyrolysis-oil, syngas, electricity, and heat) biorefinery producing customized BtL-fuels from (straw)
Project owner	Karlsruhe Institute of Technology (KIT)
Web page	http://www.bioliq.de/english/24.php
Facility type	Pilot Plant
Operation	Since 2008
Feedstock	500 kg/h of Residual biomass
Outputs	BioliqSynCrude®, Synthesis gas, BtL-fuels (Dimethyl ether, Gasoline)
Location	Karlsruhe, Baden-Württemberg
Summary	The Bioliq® pilot plant produces BTL (biomass to liquid) fuels from biomass wastes, mainly dry straw and wood. The integrating process chain also produces synthesis gas and chemicals (Fig. 9.9) The Karlsruhe BTL-concept combines decentralized production of BTL-fuels by rapid pyrolysis and central processing with final industrial-scale refinement. This process is based in energy densification, which increases its efficiency, save carbon dioxide by decreasing routes of transport to refineries and ensures the full exploitation of biomass that is transformed into material, and energy (IEA Bioenergy 2014)

BTG bioliquids refinery

Process/ Technology	1-platform (pyrolysis-oil) biorefinery for the production of chemicals, fuels, power, and heat from lignocellulosic biomass
Project owner	Empyro BV
Web page	www.btgworld.com; www.btg-btl.com
Facility type	Commercial Plant
Operation	Since 2015
Feedstock	5 t/h of wood residues
Outputs	Pyrolysis-oil, power, heat

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Location	Hengelo, the Netherlands
Summary	The pyrolysis facility of Empyro in AkzoNobel site in Hengelo, the Netherlands, was implemented in 2015. This pyrolysis-oil production facility was the first step of a full-scale biorefinery. It is planned that the production capacity will increase gradually till 20 million liters per year of pyrolysis-oil In Fig. 9.10 a process block diagram of BTG plant is shown The pyrolysis process used was created at the University of Twente and has been further developed for 20 years by BTG in Enschede, the Netherlands. Empyro BV was founded by BTG Bioliquids BV (owner of the technology) and Tree Power (long-term investor in renewables) and the main aim was to demonstrate BTG technology on a commercial-scale Pyrolysis plant processes 5t/h of biomass (wood chips) which is mixed with hot sand to be converted in a few seconds into 3.5 ton pyrolysis-oil, char and gas. Enough electricity will be produced for plant own use and steam will be supplied to the salt production of AkzoNobel, located near Empyro. The company FrieslandCampina will use the oil in its facilities located in Borculo to substitute annually 10 million cubic meters of natural gas (IEA Bioenergy 2014)

LanzaTech Plant

Process/ Technology	A 2-platform (syngas, chemical building blocks) biorefinery producing bioethanol and chemical building blocks from wood waste and MSW by syngas fermentation
Project owner	LanzaTech NZ Ltd
Web page	http://www.lanzatech.com/
Facility type	Pilot Plant (New Zealand) Mobile Plant (USA)
Operation	Since 2015 (New Zealand) Since 2014 (USA)
Feedstock	Wood waste and MSW (New Zealand) Woody biomass syngas produced from 125 t/day dry wood residues (USA)
Outputs	Fuel ethanol 250 l/day Ethanol, Chemicals (USA)
Location	BlueScope Steel mill, Glenbrook, New Zealand Soperton, Georgia USA
Summary	LanzaTech was founded in New Zealand in 2005 with the aim of developing and commercializing gas fermentation technologies to produce ethanol to be used as fuel, using carbon monoxide in low-hydrogen waste gases produced by the steel industry. Afterwards, LanzaTech decided to include syngas derived from waste woody biomass and municipal waste LanzaTech has used the pilot plant at the BlueScope Steel mill, Glenbrook, New Zealand to demonstrate its process using real waste gases. New organisms capable of producing a range of chemical building blocks from CO, CO_2, and H_2 have been developed LanzaTech has been developing other projects, two 378,000 l demonstration facilities, with Baosteel and Capital Steel in China and an

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	integrated biorefinery in the Soperton, Georgia, USA using forestry waste (Freedom Pines Biorefinery) (IEA Bioenergy 2014) In Fig. 9.11 a process block diagram of LanzaTech plant is presented

INEOS

Process/ Technology	A 2-platform (syngas, power and heat) Biorefinery producing bioethanol and power from vegetative, yard, and MSW by syngas fermentation
Project owner	INEOS New Planet BioEnergy
Web page	www.ineosbio.com
Facility type	Commercial scale
Operation	Since 2012
Feedstock	Vegetative, yard, and MSW
Outputs	Bioethanol, power
Location	Indian River County BioEnergy Center, Florida
Summary	INEOS Bio and its joint venture partner, New Planet Energy, have invested millions of dollars to build an innovative bioethanol facility in the Indian River County BioEnergy Center, near Vero Beach, Florida. The main objective is the production of eight million gallons per year of third-generation bioethanol from renewable biomass, such as: vegetative, yard, and municipal solid waste (MSW). The combination of gasification and fermentation processes to treat these wastes is used in this process Six megawatts (gross) of clean renewable power will also be produced to be used in the facility and the excess will be exported to the local community. Other objectives are the demonstration of key equipment at full commercial-scale The project started in February 2011 and construction was accomplished in the second quarter of 2012, with commissioning and start-up till the end of the year Figure 9.12 shows a process block diagram of INEOS plant (IEA Bioenergy 2014)

9.4 Biochemical-Based Advanced Biorefineries

In opposition to conventional first-generation biochemical-based technologies, which are well-established processes that are already operational on a commercial scale, most of advanced technologies, commonly referred to as second- or third-generation, are still in the research and development (R&D), pilot or demonstration stage. A few examples of advanced biorefineries, in particular biofuel plants, at commercial stage already exist although struggling to compete with the equivalent and cheaper first-generation plants. In this chapter, the terminology

"advanced" biorefineries includes production technologies based on the use of nonfood crops as feedstocks.

9.4.1 Biochemical-Based Advanced Lignocellulosic Biorefineries

Although there are many possible ways for the transformation of lignocellulosic biomass into biofuels and bioproducts, many products that are familiar today, including citric acid, ethanol, and lactic acid, are mainly fermentation-based (Zwart 2006). Indeed, carbohydrates can be converted through fermentation, by bacteria, fungi ,or yeast (genetically modified or not), into alcohols, organic acids, alkenes, lipids ,and other chemicals, under diverse process conditions (e.g., low/high pH, anaerobic/aerobic, nutrient rich/deprived). Monosaccharides and disaccharides are very widely converted whereas larger molecules such as oligosaccharides and polysaccharides (e.g., starch) are not easily metabolized by a wide range of organisms, and thus the latter are not included within the so-called "sugar platform". This terminology addresses any combination of C5 carbohydrates (pentoses, e.g., xylose, arabinose, ribose), C6 carbohydrates (hexoses, e.g., glucose, fructose, galactose), and/or C12 carbohydrates (e.g., saccharose, lactose, maltose) that exists within a pathway from biomass feedstock toward final biofuel or biochemical products (E4tech, RE-CORD and WUR 2015).

Thereby, under a "sugar platform" pathway, the achievement of carbon sources metabolically active from complex lignocellulosic substrates requires the prior degradation of its constituent polysaccharides, cellulose, and hemicellulose fractions, into their building blocks (Gírio et al. 2010). Therefore, there is a need of a mechanical comminution followed by a biomass pretreatment before application of an enzymatic process (van Wyk 2011), as shown in Fig. 9.13. The main purpose of any pretreatment is thus to free cellulose and hemicellulose fractions from the

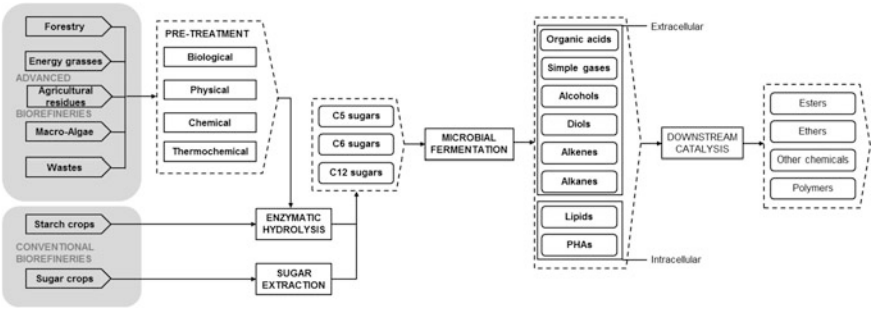

Fig. 9.13 Biochemical-based biorefineries—pathways via the sugar platform (adapted from E4tech, RE-CORD and WUR 2015)

lignin, reduce cellulose crystallinity, and increase the porosity of the material (Cheng and Timilsina 2011; Geddes et al. 2011; Zhang 2008).

Pretreatment has been recognized as the main bottleneck and one of the most expensive processing steps in cellulosic biomass-to-fermentable sugars conversion. In addition, improved bioprocesses through a better integration of the engineering and biology operation units (e.g., integration of pretreatment, enzymatic hydrolysis, fermentation and downstream processing technologies) should also be achieved to bring a bio-based process using lignocellulose feedstocks to commercial scale (e.g., Proethanol2G EU 7th FWP project website). Some of commercial lignocellulosic pretreatment technologies (e.g., PROESA™ Technology, Beta-Renewables, Italy; Liberty™ Technology, POET/DSM, USA; Abengoa, USA) are already available for the production of bioethanol and co-products from a wide variety of woody material, wastes, and other residues, contributing to the deployment of advanced biorefineries using raw materials other than readily available sugar and starch feedstocks. However, these advanced biorefineries are not yet mature but still under development.

These biochemical-based advanced bioethanol biorefineries in the World might be distinguished by the different technologies applied as pretreatment, which necessarily promotes a distinct biomass fractionation, as represented in Fig. 9.14 (E4tech, RE-CORD and WUR 2015).

The pretreatment technologies are grouped by process type, existing biological (microbial/fungi), physical, chemical, and thermochemical process options. Often, they differ according to the way how they extract/solubilize the lignin fraction during pretreatment or in a later stage in value chain (corresponding to the two distinct dashed arrows in Fig. 9.14). Indeed, lignin separation can be promoted by applying strong alkaline conditions (e.g., with sodium hydroxide and sodium sulphite with high temperature, such as used in kraft pulping), dilute and concentrated acids, organic solvents (as organosolv) or ionic liquids (Bacovsky et al. 2013).

Europe is leading research on lignin removal, with several companies conducting pilot/demo activities on this step, such as GreenValue, Switzerland or Borregaard Industries AS that owns and operates the World's most advanced biorefinery, producing advanced biochemicals (e.g., vanilla flavor vanillin), biomaterials (e.g. specialty celluloses) and bioethanol, using all the components of wood.

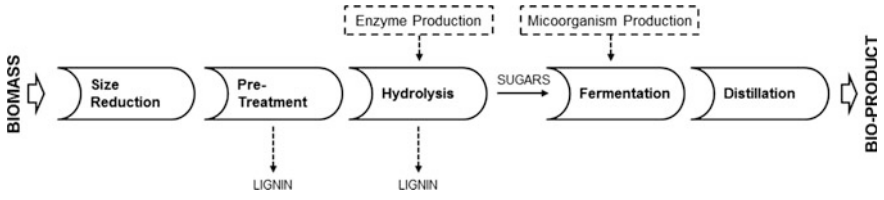

Fig. 9.14 Processing steps in a general biochemical-based lignocellulosic biorefinery (adapted from IEA-Bioenergy 2014)

The more mature pretreatment technologies include acid hydrolysis and hydrothermal (e.g., hot liquid water, steam explosion) pretreatments, the latter typically do not liberate lignin but solubilizes and hydrolyze hemicellulose component to different extents (Carvalheiro et al. 2004). Although steam explosion can be performed as uncatalyzed treatment (Glasser and Wright 1998), it is often applied as acid-catalyzed steam explosion (Sassner et al. 2008) or ammonia fibre explosion (AFEX) (Sendich et al. 2008). Wet oxidation treatment is also a form of hydrothermal treatment involving the use of oxygen and water at elevated temperatures and pressure, promoting the oxidation of lignin and its conversion into CO_2, H_2O, and carboxylic acids.

There are other emerging pretreatment technologies, such as supercritical (CO_2) pretreatment, ionic liquids and microbial (with fungi and bacteria) treatments (E4tech, RE-CORD and WUR 2015; Bacovsky et al. 2013), but these are still at research level, i.e., at a Technology Readiness Level (TRL) below 5, and thus commercial, or even demonstration or pilot processes are inexistent, and these will be out of the scope of this text.

Indeed, this chapter deals with projects involving the conversion of sugars to bioproducts (fuels, materials, or chemicals) via novel pathways, having commercialization as target following applied research and developments from pilot-scale (and above) within companies (not academia). Given this, once bioethanol is the sugar-based bioproduct at higher TRL in terms of commercialization, with first-of-a-kind commercial plants already operational, priority focus will be given to lignocellulosic bioethanol plants, rather than different fuels and chemicals.

Significant advances have been achieved in the past several years in all aspects of lignocellulose conversion into ethanol making it potentially competitive in economic terms, particularly for niche markets (Gray et al. 2006). Thus, whereas starch-based ethanol and sugarcane-based ethanol are now mature industries, companies such as Beta-Renewables/Biochemtex (Crescentino, Italy), Inbicon/Dong Energy (Kalundborg Denmark), Abengoa (Babilafuente, Spain), Clariant (Straubing, Germany) in Europe; Abengoa (Hugoton, Kansas), Blue Sugars Corporation (formerly KL Energy Corp.), BP Biofuels (formerly Verenium), Enchi Corporation (formerly Mascoma Corporation); Dupont (Nevada, Iowa) and POET-DSM (Emmetsburg, Iowa) in USA; Iogen Corporation in Canada; GranBio (Alagoas) and Raízen/Iogen (Piracicaba) in Brazil, are giving the first steps as major players to commercialize cellulosic ethanol. The existent pilot and demonstration plants will serve as platforms to identify bottlenecks and potential barriers to full commercialization of 2G bioethanol in the future.

Given this, a brief overview of the current worldwide most relevant (preferentially closest to commercial as possible) industrial activities on 2G bioethanol manufacturing, based on different pretreatment technologies, will be presented (Table 9.3). In addition, records containing more detailed process information were built for eight of these facilities, selected as the most representative (in terms of maturity) of each technological approach.

Table 9.3 Most relevant (commercial, demo or pilot) cellulosic ethanol production facilities in operation in the World

Project owner/Name	Location	Technology (pretreatment)	Typology	Raw material	Product(s) (total capacity)	Start-up link
POET/DSM Advanced Biofuels/ Project LIBERTY	Emmetsburg, Iowa, USA	Two-stage acid-catalyzed steam explosion	Commercial	Corncobs and corn stover	Ethanol (60,000 t/year), biogas and CHP (from lignin)	2014 http://www.projectliberty.com/
GranBio	São Miguel dos Campos, Alagoas, Brazil	PROESA™—uncatalyzed steam explosion	Commercial	Sugarcane straw	Ethanol (65,000 t/year) and 50 MWe (from lignin and bagasse)	2014 http://www.granbio.com.br/
Biochemtex/ Beta Renewables	Crescentino, Italy	PROESA™—uncatalyzed steam explosion	Commercial	Wheat straw (currently). Later on, Arundo donax.	Ethanol (60,000 t/year), biogas, 13 MW electricity and animal feed	2013 www.betarenewables.com/
Abengoa Bioenergy Biomass of Kansas	Hugoton, Kansas, USA	Sulfuric acid-catalyzed steam explosion	Commercial	Corn stover	Ethanol (75,000 t/year) and 18 MWe electricity	2015 http://www.abengoabioenergy.com/web/en/2g_hugoton_project/
Raízen Energia Participações S/A	Piracicaba, S. Paulo, Brazil	Iogen's Technology-acid-catalyzed steam explosion	Commercial	Sugarcane bagasse and straw	Ethanol (32,000 t/year) + electricity	2015 http://www.raizen.com/
Dupont	Nevada, Iowa, USA	Dilute ammonia hydrolysis with heat	Commercial	Corn stover	Ethanol (90,000 t/year) + CHP (from lignin)	2015 http://www.dupont.com/
Inbicon/DONG Energy	Kalundborg, Denmark	Autohydrolysis	Demonstration	Straw, corn stover, and bagasse	Ethanol (4300 t/year), C5 molasses (13,900 t/year) and lignin pellets (11,400 t/year)	2009 http://www.inbicon.com/en

(continued)

Table 9.3 (continued)

Project owner/Name	Location	Technology (pretreatment)	Typology	Raw material	Product(s) (total capacity)	Start-up link
Blue Sugars Corp. (former KL Energy) and Petrobras	Uton Wyoming, USA	Dilute-acid impregnation combined with thermal–mechanical	Demonstration	Sugarcane bagasse and other lignocellulosic biomass	Ethanol (4500 t/year) and lignin	2009 http://www.bluesugars.com/
Abengoa Bioenergía	Babilafuente Salamanca, Spain	Sulfuric acid-catalyzed steam explosion	Demonstration	Cereal straw (mostly barley and wheat)	Ethanol (4000 t/year)	2009 http://www.abengoa-bioenergy.com/web/es/
BP Biofuels/ Jennings Demonstration Facility	Jennings, Louisiana, USA	Dilute-acid impregnation combined with thermo-mechanical	Demonstration	Dedicated energy crops	Ethanol (4200 t/year)	2009 http://www.bp.com/en_br/brazil/o-que-fazemos/biocombustiveis.html
Borregaard AS/BALI Biorefinery Demo	Sarpsborg, Norway	BALI™ process—sulphite pretreatment (continuous technology, with patent applied in 2009)	Demonstration	Sugarcane bagasse, straw, wood, energy crops, other lignocellulosic biomass	Ethanol (110 t/year) or C5/C6 sugars (220 t/year) and lignin specialty chemicals (200 t/year)	2013 http://www.borregaard.com/
Biogasol APS/ BornBioFuel 2	Aakirkeby, Bornholm, Denmark	Carbofrac™—catalyzed "wet explosion"	Demonstration	Straw, various grasses and garden waste	Ethanol (4000 t/year), biogas, lignin and hydrogen	2015/2016 http://www.biogasol.com/
Iogen Corporation	Ottawa, Canada	Modified acid-catalyzed steam explosion	Demonstration	Cereals straw, corn stover,	Ethanol (1600 t/year)	2007

(continued)

Table 9.3 (continued)

Project owner/Name	Location	Technology (pretreatment)	Typology	Raw material	Product(s) (total capacity)	Start-up link
				sugarcane bagasse		http://www.iogen.ca/
Chempolis Ltd./Chempolis Biorefining Plant	Oulu, Finland	Formico™—organosolv with formic and acetic acids	Demonstration	Non-wood biomass—e.g., straw, reed, empty fruit branch, bagasse, corn and stalks	Ethanol (5000 t/year) and paper pulp from cellulose, various chemicals (e.g., acetic acid and furfural as chemical intermediates) from hemicellulose	2008 http://www.chempolis.com/
Clariant (former Süd-Chemie)	Straubing, München, Germany	Sunliquid™ process –with mechanical and thermal pretreatment	Pilot	Wheat straw and other agricultural residues	Ethanol (1000 t/year)	2012 http://www.sunliquid.com/
Enchi Corporation (former Mascoma Corp.)	Rome, New York, USA	CBP with little or no pretreatment —only mechanical disruption or hydrothermal	Pilot	Wood chips, switchgrass and other lignocellulosic biomass	Ethanol (500 t/year) and lignin	2003 http://www.enchicorp.com/
Abengoa Bioenergía	York, Nebraska, USA	Sulfuric acid-catalyzed steam explosion	Pilot	Corn stover	Ethanol (75 t/year)	2007 http://www.abengoa-bioenergy.com/web/es/
SP Plant (former SEKAB)/	Örnsköldsvik, Sweden	Two-stage Dilute-acid hydrolysis with/without SO_2 impregnation	Pilot	Softwood, sugarcane straw and bagasse	Ethanol (160 t/year), biogas and lignin	2005 http://www.sekab.com/biorefinery/demo-plant/

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Table 9.3 (continued)

Project owner/Name	Location	Technology (pretreatment)	Typology	Raw material	Product(s) (total capacity)	Start-up link
FUTUROL/ Procethol2G	Pomacle, France	Acetic acid and formic acid-based organosolv pretreatment	Pilot	Wheat and barley straw, corn stover, wood, sugarcane bagasse	Ethanol (700 t/year); C5 syrup (650 t/year); Lignin (750 t/year)	2011 www.projet-futurol.com
Weyland AS	Bergen, Norway	Concentrated acid hydrolysis	Pilot	Mostly wood (spruce and pine) and agricultural residues	Ethanol (158 t/year) and lignin	2010 http://www.weyland.no/
Virdia (former HCL Clean Tech)	Danville, VA, USA	CASE™ process (with concentrated HCl)	Pilot	Mostly softwood (pine) and hardwood (eucalyptus)	Cellulosic sugars and lignin	2012 http://biomaterials.storaenso.com/about-us/
Lignol Innovations Ltd.	Burnaby, BC, Canada	Alcell™ process—organosolv with ethanol (unique fractionation into cellulose, hemicellulose and lignin)	Pilot	Woody biomass—hardwood and softwood residues	Ethanol, pure lignin and other valuable co-products	2009 https://www.sdtc.ca/en/organizations/lignol-innovations-ltd
CIMV	Pomacle, Marne, France	Organosolv with formic acid and acetic acid	Pilot	Wheat straw	Paper pulp and glucose from cellulose, C5-sugars from hemicellulose, and lignin	2006 http://www.cimv.fr/

BETA-RENEWABLES

Process/ Technology	PROESA™—uncatalyzed steam explosion
Project owner	Biochemtex/Novozymes
Web page	http://www.betarenewables.com/
Facility type	Commercial
Operation	Since 2013
Feedstock	Started with wheat straw and they are planning to use energy crops (*Arundo donax* (giant reed), miscan-thus, and switch grass) in the future
Outputs	Ethanol (60,000 t/year) and biogas
Location	Crescentino, Italy
Summary	Beta Renewables is a joint venture established at the end of 2011 between Biochemtex, a company of the Mossi Ghisolfi Group, and the USA fund TPG (Texas Pacific Group), and Nozozymes, World leader in the enzymes industry that became a shareholder of the company in 2012. PROESA™ technology, basically consisting of an uncatalyzed steam explosion pretreatment followed by simultaneous saccharification and fermentation using a strain engineered to convert both C5 and C6 sugars to ethanol. PROESA has been already licensed to other World biofuel companies (e.g., GranBio, Brazil). Residual lignin is only used for power

POET/DSM (LIBERTY project)

Process/ Technology	Two-stage dilute-acid hydrolysis
Project owner	POET/DSM Advanced Biofuels
Web page	http://www.projectliberty.com/
Facility type	Commercial
Operation	Since 2013
Feedstock	Corncobs and corn stover
Outputs	Ethanol (75,000 t/year) and biogas
Location	Emmetsburg, Iowa, USA
Summary	POET-DSM Advanced Biofuels, is a joint venture between POET and Royal DSM. The new commercial cellulosic ethanol plant is based on dilute-acid or acid catalyzed steam explosion followed by enzymatic hydrolysis with enzymes provided by DSM. They plan to license this integrated technology package, converting corn crop residue to cellulosic bioethanol, to third parties and also to the other 26 existing corn ethanol plants in POET's network (Bacovsky et al. 2013)

ABENGOA

Process/ Technology	Steam explosion
Project owner	Abengoa USA
Web page	http://www.abengoa-bioenergy.com/web/es/
Facility type	Commercial

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Operation	Since 2015
Feedstock	Corncobs and corn stover
Outputs	Ethanol (75,000 t/year) and biogas
Location	Hugoton, Kansas, USA
Summary	This Spanish company did build an advanced biofuel plant at US benefiting from the generous governmental incentives for deployment advanced biofuel plants. It uses a steam explosion technology as biomass pretreatment and a property in-house enzyme production for enzymatic hydrolysis step

BIOFLEX

Process/ Technology	Two-stage steam explosion
Project owner	GranBio
Web page	http://www.granbio.com.br/
Facility type	Commercial
Operation	Since 2015
Feedstock	Sugarcane straw
Outputs	Ethanol (65,000 t/year) and 50 MWe electricity
Location	Alagoas, Brazil
Summary	Bioflex plant is a sugarcane straw-based 2G bioethanol plant and integrated in the same site of 1G ethanol and sugar plant. They bought the license to operate with PROESA™ Technology from the Italian Beta-renewables which is an uncatalyzed two-stage steam explosion technology. Besides ethanol, they co-produce 70 MWe, having a surplus of 50 MWe which they sells to the grid

Enchi Corporation

Process/ Technology	CBP with little or nopretreatment—only mechanical disruption or hydrothermal
Project owner	Enchi Corporation (former Mascoma Corp.)
Web page	http://www.enchicorp.com/
Facility type	Demonstration
Operation	Since 2003
Feedstock	Wood chips, switchgrass, and other lignocellulosic biomass
Outputs	Ethanol (500 t/year) and lignin
Location	Rome, New York, USA
Summary	Enchi Corporation (former Mascoma Corp.) combines enzyme production, hydrolysis and fermentation in a single step (consolidated bioprocessing or CBP). It uses thermophilic bacteria that are engineered to produce large amounts of the enzymes promoting cellulose hydrolysis and ferment the resulting sugars into ethanol (Bacovsky et al. 2013). Biomass is processed without external enzymes and with little or no pretreatment, thus avoiding the two main barriers to cost-effective processing today. Mascoma Corporation was a USA biofuel company founded in 2005 by Robert Johnsen (CEO), Lee Lynd and Charles Wyman, two professors from Dartmouth College, to produce cellulosic ethanol made from wood and switchgrass (Mascoma 2007). In November 2014, the yeast-related business assets including the Mascoma name were purchased by Lallemand, Inc. of

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	Montreal, Canada, and renamed Mascoma LLC which is now a subsidiary of Lallemand. The remaining business assets of the former Mascoma Corp., including the thermophilic bacteria technology and the pilot plant in Rome (NY) were renamed Enchi Corporation (Wikipedia 2016). Enchi Corporation, together with J.M. Longyear, under the joint venture Frontier Renewable Resources, is planning to build a commercial 2G ethanol facility (with 60,000 t-annual capacity) in Kincheloe (Michigan, USA) (Bacovsky et al. 2013)

INBICON

Process/ Technology	Autohydrolysis
Project owner	Inbicon (DONG Energy)
Web page	http://www.inbicon.com/
Facility type	Demonstration
Operation	Since 2009
Feedstock	Straw, corn stover, and bagasse
Outputs	Ethanol (4300 t/year), C5 molasses (13,900 t/year), and lignin pellets (11,400 t/year)
Location	Kalundborg, Denmark
Summary	DONG Energy is aiming to license their Inbicon technology and know-how to partners around the World to build commercial scale Inbicon Biomass Refineries. Inbicon's core technology consists of a three-stage continuous process: mechanical conditioning of the biomass; hydrothermal pretreatment (at 180–200 °C); followed by enzymatic hydrolysis at a high dry matter level (up to 30% of dry matter), providing continuous liquefaction. Hydrothermal pretreatment at Inbicon consists of an autohydrolysis by using compressed hot water processes with no added chemical catalyst. This pretreatment is economically and environmentally attractive, generating low levels of inhibitory products, with no significant effect on lignin and cellulose. However only solubilizes hemicellulose in oligomeric form (Carvalheiro et al. 2004) In Inbicon process—version 1—C5 sugars derived from hemicellulose, are separated into a liquid fraction that is further concentrated, and marketed as C5 molasses for biogas or animal feed. Since mid-2013, Inbicon did implement the version 2 technology using C5/C6 mixed sugar fermentation to ethanol. Thereby, in addition to ethanol, the demo plant only co-produces lignin pellets used as feedstock for power production (integrated with Asnæs power station in Kalundborg (Dong Energy power plant), allowing the highest possible energy efficiency

CLARIANT

Process/ Technology	Sunliquid™ process—with mechanical and thermal pretreatment
Project owner	Clariant
Web page	http://www.sunliquid.com/

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Facility type	Demonstration
Operation	Since 2012
Feedstock	Wheat straw and other agricultural residues
Outputs	Ethanol (1000 t/year)
Location	Straubing, München, Germany
Summary	Clariant (former Süd-Chemie) has developed the Sunliquid™ process for converting agricultural residues into biofuel, based on a mechanical and thermal pretreatment and an integrated process including enzyme production (using pretreated feedstock as substrate), optimized enzymes, simultaneous conversion of C5 and C6 into ethanol and innovative (based on adsorption technology) highly energy saving purification method (as alternative to conventional distillation) (Bacovsky et al. 2013). Based on this Sunliquid™ process, Clariant has been successfully operating a first pilot plant at its research facility [Clariant's Biotech & Renewables Center (BRC)] in Munich since 2009, producing up to two tons of ethanol per year. In July 2012, this Germany's largest plant to date started into operation in Straubing. Once designed for industrial plants with a production capacity of 50,000–150,000 t of cellulosic ethanol per year, Clariant intends to license out Sunliquid™ technology

IOGEN

Process/ Technology	Modified acid-catalyzed steam explosion
Project owner	Iogen Corporation
Web page	http://www.iogen.ca/
Facility type	Demonstration
Operation	Since 2007
Feedstock	Cereals (wheat, oat, or barley) straw, corn stover, sugarcane bagasse ,and other agricultural residues
Outputs	Ethanol (1600 t/year)
Location	Ottawa, Canada
Summary	Iogen's cellulosic ethanol process is based on separate hydrolysis and fermentation using a multi-stage hydrolysis process. The process involves C6 and C5 fermentation, and includes enzymes production once Iogen Corporation is also a manufacturer and marketer of enzyme products for application involving fiber modification or hydrolysis (e.g., for pulp and paper, grain processing, brewing, textile, and animal feed industries). In 2009, Iogen became the first cellulosic ethanol producer to sell its advanced biofuel at a retail service station (Bacovsky et al. 2013). For a one-month period, a 10% cellulosic ethanol blend was available for sale to the general consumers at an Ottawa Shell station. More than 60,000 liters of Iogen's cellulosic ethanol was sold (Iogen 2016). Iogen is seeking partners and licensees to commercialize its technology, and the Brazilian ethanol company Raízen Energia Participações S/A, the nation's leading manufacturer of sugarcane ethanol, is operating its commercial biomass-to-ethanol facility (adjacent to Raízen's Costa Pinto sugarcane mill) using Iogen Energy's advanced cellulosic biofuel technology

BornBioFuel 2

Process/ Technology	Carbofrac™—catalyzed 'wet explosion'
Project owner	Biogasol APS
Web page	http://www.biogasol.com/
Facility type	Demonstration
Operation	Since 2013
Feedstock	Straw, various grasses and garden waste
Outputs	Ethanol (4000 t/year), biogas, lignin, and hydrogen
Location	Aakirkeby, Bornholm, Denmark
Summary	BioGasol APS, company founded in 2006 as a spin-out of the Technical University of Denmark (DTU), combines wet oxidation with steam explosion as core technology. The process is called 'wet explosion' and the use of oxygen and pressure release at high temperature (170–200 °C) are combined, as a variant of conventional hydrothermal treatment. Additives such as acid, base, or solvents act as catalysts in the process, and dilute acid-catalyzed steam explosion pretreatment is BioGasol's reference process. All by-products are further converted to energy carriers (ethanol, hydrogen, methane and solid biofuel). The pretreatment technology developed, Carbofrac™, is licensed by the company, together with high-yield C5/C6 co-fermentation technology Pentoferm™ using the unique thermophilic Petocrobe™ (a recombinant derived from *Thermoanaerobacter italicus*) (Bacovsky et al. 2013)

DuPont cellulosic ethanol demonstration plant

Process/ Technology	Dilute ammonia hydrolysis
Project owner	DuPont
Web page	http://www.dupont.com/
Facility type	Demonstration
Operation	Since 2010
Feedstock	Corn stover, switchgrass, and sugarcane bagasse
Outputs	Ethanol (750 t/year), biogas, lignin and hydrogen
Location	Vonore, Tennessee, USA
Summary	DuPont Genencor Science, a joint venture between Danisco, Genencor and DuPont, is the only company applying alkaline processing for biomass pretreatment on industrial scale (Bacovsky et al. 2013). The developed conversion process, including novel enzymes and fermentation organisms, will be deployed at the first commercial DuPont Cellulosic Ethanol plant, which will be nearing operation in Nevada (Iowa) and it will produce ethanol from corn stover (corncobs, leaves, and stalks). DuPont offers cellulosic ethanol licenses to other companies, supplying enzymes and ethanologens for production at a licensed plant

9.4.2 Biochemical-Based Advanced Algae Biorefineries

Despite the intense effort in R&D in microalgae in recent years, not only in the food, cosmetic, and pharmaceutical fields but also in the production of conventional biofuels (biodiesel, bioethanol) and other more advanced than not even commercial phase (long-chain alcohols, hydrogen, hydrocarbons, and jet-fuel), the development and the transition to the desired scale of demonstration have not been so accelerated as expected in Europe (Gírio et al. 2013) and worldwide. The theoretical maximum productivity in oil from microalgae (354 m^3 ha^{-1} $year^{-1}$) is several orders of magnitude higher than the most productive terrestrial oleaginous culture so far (palm) but still very remote and unlikely from real values obtained according with the present state-of-the-art and technical knowledge. This gap is mainly due to technological barriers (Nurra et al. 2014; González et al. 2015; Jacob-Lopes et al. 2015) and problems of scale-up (Lopes da Silva and Reis 2015) that should be overcome at a short-term timeframe, in particular with regard to mild, simple, sustainable, and inexpensive methods of biomass pre-concentration and harvesting, cell disruption, and extraction of target components for a wide range of applications, in particular for bio-energy. The still high cost of producing microalgal biomass makes it unattractive for "high volume-low cost" applications as in the case of biofuels. The present costs of producing microalgal-based oils (for biodiesel FAME) are one order of magnitude higher than the FAME biodiesel made from vegetable oils (food). On the other hand, the concept of biorefinery applied to microalgal biomass which would lower production costs of biofuels through the integrated co-production of high value-added products to pay the technology is facing difficulties to be an expanded reality (Gao et al. 2012; Gírio et al. 2013; Hariskos and Posten 2014; Lopes da Silva and Reis 2015). As a result, it is not surprising that, to date, the number of demonstration facilities for the production of bioenergy vectors from micro and macro-algae, solar radiation and CO_2 as well as for upgrading to biofuels for use in carrier sector is limited worldwide and the available data are scarce. There have been some large-scale facilities for the production of microalgae in the Netherlands (AlgaePARC, Wageningen), southern Europe (Portugal and Spain), USA (Sapphire energy), Brazil (Solazyme), and India with operational flexibility that can take them to shift their conversion for bioenergy production if the conditions and markets are favorable. Among them is the greatest pilot installation that exists in Europe (Allmicroalgae, Portugal) which has 1200 m^2 of photobioreactors operation to a 1300 m^3 microalgae production volume, based in Leiria-Pataias, Portugal. This facility will allow accelerating and to implement the R&D necessary for the cultivation of microalgae in order to demonstrate the real potential as a sustainable and economically competitive technology for the production of advanced biofuels. In this sense, it is to be hoped that new flagship projects arise in a short-term timeframe. The use of microalgae coupled to wastewater treatment for energy emerges as a very promising possibility for its lower cost and the environmental benefits associated with. A selection of the most important processes about biofuels production by microalgae-based processes in the

frame of the biorefinery concept is presented next with special emphasis on selected cases in which the selection criteria was the maturity of the process and the existence of demonstration or commercialization units, if available (Petrick et al. 2013). The main information available is organized in table format for easy reading and understanding.

Allmicroalgae/AlgaFarm

Process/ Technology	Photoautotrophic microalgal production with CO_2 fixation
Project owner	Cecil/A4F
Web page	www.a4f.pt
Facility type	Demo/Commercial
Operation	Since 2013
Feedstock	CO_2, fertilizers
Outputs	Microalgal biomass (*Chlorella*), Pigments (possibility of reconversion to biofuels)
Location	Pataias, Portugal
Summary	The cement Portuguese company Secil and the biotech Portuguese company A4F, founded AlgaFarm, a joint venture to develop a process that initially used the combustion gases (CO_2) from the cement industry in the production of microalgae. The industrial-scale production unit resulted from the expansion of a pilot plant that has been in operation for two years. It is currently in commercial operation and produces *Chlorella vulgaris* directed for the food segment The AlgaFarm was designed with four main sectors: resources, production, processing, and management. Each sector covers several systems that together constitute the largest production facilities of microalgae Worldwide with closed photobioreactors, reaching 1300 m^3 of total volume of production The downstream processing of biomass includes harvesting through ultrafiltration to a biomass concentration between 5 and 10% on dry weight basis. The treatment includes pasteurization, spray drying ,and final packaging under protective atmosphere free from O_2. The AlgaFarm is currently a microalgae plant equipped with data acquisition system and fully automated control Allmicroalgae it is the new supplier of Allma Chlorella—and has unveiled plans for a significant new phase of investment in its production facilities Allmicroalgae is now selling Chlorella ingredients under the Allma brand, with production continuing at the existing Algafarm plant in Leiria, 100 km north of Lisbon. This site will be revamped—according to the company announcement—with new, state-of-the-art production technology that will boost output and increase quality levels

A4F

Process/ Technology	Direct Bioethanol production from autotrophic microalgae
Project owner	A4F
Web page	www.a4f.pt
Facility type	Pilot

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Operation	Since 2014
Feedstock	CO_2, fertilizers, microalgae
Outputs	Bioethanol (production culture volume: 3 m^3)
Location	Lisbon, Portugal
Summary	A4F AlgaFuel, S.A. is a spin-out from Necton S.A. company, dedicated to the development and implementation of bioengineering projects for the industrial production of microalgae. This unit is the first pilot unit of microalgae "GMO-compliance" in Europe, which allows the production and R&D of microalgae genetically recombined without risk of release into the environment

Algaenergy

Process/ Technology	Photoautotrophic microalgal production with CO_2 fixation
Project owner	Various companies among which are Repsol and Iberdrola
Web page	http://www.algaenergy.es
Facility type	Pilot
Operation	Since 2012
Feedstock	CO_2, fertilizers
Outputs	Microalgae, biodiesel (production culture volume: 40 m^3)
Location	Adolfo Suárez Airport, Barajas, Spain
Summary	The Spanish company AlgaEnergy, owned by various companies among which are Repsol and Iberdrola, leads the project named CO_2Algaefix which consists in carbon dioxide capture to the preindustrial scale on the basis of the development and initial experience obtained in the pilot installation

Buggypower S.L.

Process/ Technology	Photoautotrophic microalgal production with CO_2 fixation
Project owner	Partnership between Empresa de Electricidade da Madeira (EEM) and BioFuel Systems (http://www.biopetroleo.com/)
Web page	http://www.buggypower.eu
Facility type	Demo
Operation	Since 2011
Feedstock	CO_2, fertilizers
Outputs	Microalgae, biodiesel (culture volume capacity: 900 m^3 photobioreactors)
Location	Porto Santo, Portugal
Summary	Buggypower, has built and currently operates a facility for the production of biofuels with microalgae, on the island of Porto Santo, Madeira, Portugal. This innovative project has as main objective to replace the fuel from fossil resources, currently used in EEM thermal power station with biofuel produced by microalgae. When optimized this project, Porto Santo will become a fully sustainable island and "eco-friendly", in terms of energy supply and use

Kalundborg symbiosis

Process/ Technology	Mixotrophic microalgal production with wastewater treatment
Project owner	Public and private enterprises (industrial cluster)
Web page	www.symbiosis.dk/en
Facility type	Demo
Operation	Since 2013
Feedstock	Wastewater
Outputs	Microalgae; Treated wastewater (40 m^3 photobioreactors)
Location	Kalundborg, Dennmark
Summary	"Kalundborg Symbiosis" is an industrial ecosystem, where a residue or by-product of an industrial company is used as a resource by another company, in a closed loop. This industrial symbiosis is a local collaboration with several public and private companies that buy and sell their waste products one to each other, resulting in mutual benefits want to either environmental economic. The demo unit of microalgae is located within an industrial cluster and benefit from synergies, including energy efficiency

Bäckhammars Algbruk

Process/ Technology	Mixotrophic microalgal production for biodiesel with wastewater treatment
Project owner	SP Technical Research Institute of Sweden
Web page	Not available
Facility type	Pilot
Operation	Since 2014
Feedstock	Pulp and paper wastewater
Outputs	Biodiesel
Location	Bäckhammars, Sweden
Summary	The SP Technical Research Institute of Sweden leads a project named "Bäckhammars Algbruk" in partnership with 11 other partners such as Perstrop (expert in specialty chemicals). The project aims to study the use of microalgae in the production of biofuels

TNO-Valorie

Process/ Technology	Mixotrophic microalgal production for biodiesel with wastewater treatment
Project owner	GAIA consortium created by TNO (Netherlands Organization for Applied Scientific Research)
Web page	Not available
Facility type	Pilot
Operation	Since 2014
Feedstock	Microalgae
Outputs	Specialized compounds and biodiesel
Location	Mobile plant/factory, The Netherlands

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Summary	The project T-Valorie (VALORIE: "Versatile Algae on-site Raw Ingredient Extractor") aims at the construction of mobile factories used in the extraction, fractionation and specialized compounds and biodiesel production from microalgae. The objective is to adapt the mobile plant according to the type of raw material and existing technologies as well as the desired products. Another objective is to generate knowledge about the needs of downstream processing of biomass collected and business opportunities for the refined products so that the producers can assess the market value and the economic viability of the process. This project is owned by the industrial consortium called GAIA, created by TNO ("Netherlands Organization for Applied Scientific Research"). The consortium comprises the Algae Food and Fuel B.V., TNO, and a group of companies including Sabic, De Wit Oils and Van Varese Paint

AlgaePARC

Process/ Technology	Autotrophic microalgal production for biofuels and other products
Project owner	WUR (Wageningen University)
Web page	http://www.wageningenur.nl/en/Expertise-Services/Facilities/AlgaePARC.htm
Facility type	Pilot
Operation	Since 2011
Feedstock	CO_2
Outputs	Microalgae, other products (7 m^3 outdoors photobioreactors; 2 m^3 indoors photobioreactors
Location	Wageningen, The Netherlands
Summary	The AlgaePARC is a research facility located at the Wageningen University dedicated to the development of methods of outdoors sustainable production of microalgae with a competitive cost

Algenol biofuels

Process/ Technology	Autotrophic microalgal production for bioethanol and other products
Project owner	Algenol Biotech LLC
Web page	http://www.algenol.com
Facility type	Demo
Operation	Since 2013
Feedstock	CO_2, saltwater
Outputs	Ethanol, spent microalgae to biodiesel, gasoline ,and jet fuel (3 acre area with outdoor photobioreactors)
Location	Fort Myers, Florida, USA
Summary	Algenol is a global, industrial biotechnology company that is commercializing its patented algae technology platform for production of ethanol using proprietary algae, sunlight, carbon dioxide, and saltwater. Algenol takes advantage of enhancing a natural ability found in many

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	strains of cyanobacteria to produce ethanol by over expressing fermentation pathway enzymes channeling the majority of photosynthetically fixed carbon into ethanol production rather than routine cell maintenance. It is claimed that it is the only renewable fuel production process that can convert more than 85% of its CO_2 feedstock into fuel

BioProcess Algae, LLC

Process/ Technology	Autotrophic microalgal production for animal feeds, fish feeds, nutraceuticals, chemicals, and transportation fuels
Project owner	BioProcess Algae LLC [a joint venture between Clarcor (NYSE: CLC), BioHoldings, Ltd. and Green Plains Inc. (NASDQ: GPRE)]
Web page	http://www.bioprocessalgae.com
Facility type	Demo
Operation	Since 2009
Feedstock	Ethanol plant's CO_2 exhaust gas; (waste heat from the ethanol plant)
Outputs	Microalgae, animal feeds, fish feeds, nutraceuticals, chemicals and transportation fuels
Location	Shenandoah, Iowa, USA (shared with Green Plains Inc. ethanol plant)
Summary	BioProcess Algae, LLC designs, builds, and operates commercial scale bioreactors that enable efficient conversion of light and CO_2 into high-value microbial feedstock. The competitive advantage of BioProcess Algae cultivation technology involves the use of thin biofilms. The technology at the heart of BioProcess Algae cultivators is a unique high surface area, biofilm-based approach to enhance light penetration, productivity, harvest density, and gas transfer—all traditional bottlenecks to low-cost algae cultivation

Sapphire Energy, Inc.

Process/ Technology	Autotrophic microalgal production for omega-3 oils, high-value aquaculture and animal feed ingredients and renewable fuels
Project owner	Sapphire Energy, Inc
Web page	http://www.sapphireenergy.com/
Facility type	Demo
Operation	Since 2009
Feedstock	CO_2, non-potable water
Outputs	Microalgae, animal feeds, fish feeds, nutraceuticals, chemicals, and transportation fuels
Location	Las Cruces, New Mexico, USA (one million liter production ponds)
Facility type	Commercial (Algae Farm)
Operation	Planned to start by 2017
Feedstock	CO_2 (56 metric tons per day); non-potable water
Outputs	Microalgae (1600 tons of biomass per year), omega oils, high-value protein, fuels
Location	Columbus, New Mexico, USA (300 cultivated acres for cultivation)

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Summary	Sapphire's technology uses sunlight, CO_2, non-potable water, nonarable land, nutrients, and novel strains of algae in outdoor ponds to produce algae which then are converted into high-value oils, aquaculture and animal feeds, fuels, and other valuable products. The process is claimed to be economic, scalable, and sustainable as there are not competition for farmable land or fresh water, together with the absorption and reuse of CO_2 emissions. Sapphire claims to operate the largest algae-to-energy facility in the World. In the desert scrub outside of Columbus, New Mexico, Sapphire Energy is commissioning the most advanced, algae production facility in the World. Sapphire Energy's Algae Farm is expected to be the World's first commercial demonstration scale algae conversion farm, integrating the entire value chain of algae-based production, from cultivation, to production, to extraction

Solazyme

Process/ Technology	Heterotrophic microalgal production for oils and fuels
Project owner	Solazyme Inc. (a joint venture with Bunge Global Innovation LLC)
Web page	http://www.solazyme.com/
Facility type	Flagship/Commercial (625,000 L fermentation tanks)
Operation	Since 2014
Feedstock	Sugarcane bagasse
Outputs	Microalgae, oils, fuels, skin and personal care products, encapsulated lubricant (Encapso), bioplastics—total production: 100,000 metric ton renewable oils/year
Location	Orindiúva/Moema, São Paulo, Brazil
Summary	The oil production facility is the Solazyme Bunge Renewable Oils joint venture facility based in Orindiúva-Moema-SP, Brazil. The facility is capable of producing a range of oils and the same inputs are required for the different oils. The only difference is the type of algae strain that is grown in the fermentation tanks. The joint venture facility has a low carbon footprint due to the fact that waste sugarcane material (bagasse) provides all of the energy to power both the sugar mill and the oil production facility. The Brazilian facility can also feed excess energy back to the grid

9.5 Bio-thermo-chemical-based Lignocellulosic Advanced Biorefineries

Biomass gasification produces a gaseous mixture that is called synthesis gas or syngas whose main compounds are H_2, CO, CO_2, CH_4, and other gaseous hydrocarbons from C_2 to C_4. As aforementioned, syngas may have different applications, including its conversion into liquid fuels. Two procedures are possible for the

conversion of syngas produced from gasification of biomass into liquid fuels, the chemical catalytic conversion and fermentation. The chemical synthesis of ethanol and higher alcohols constitutes basically a reaction of CO hydrogenation conducted at high temperature and pressure and catalyzed by rhodium-, molybdenum-, copper-based, or modified Fischer–Tropsch catalysts (Lee et al. 2014). In this case, the challenge of finding highly selective, inexpensive, and robust catalysts, capable of preventing the need of a deep purification of the feed syngas currently still persists (Debabov 2013). Another option is syngas fermentation, which is subsequently addressed.

9.5.1 Syngas Fermentation

The fermentation of syngas explores the use of H_2, CO, and CO_2 as substrates for microbial metabolism, for the synthesis of biofuels (e.g., ethanol) and other carbon-based chemical building blocks. This process has the advantage of taking place at near ambient conditions of temperature and pressure, acting the microorganisms as highly specific biocatalysts more tolerant to gas contaminations than chemical catalysts (Kennes et al. 2016). There are also several advantages of ethanol production from syngas over up-to-date biochemical-based technologies of second-generation (2G) biomass conversion. One relates to the possibility of avoiding the complex pretreatments and the costly enzymes necessary for the saccharification of the biomass. Additionally, the gasification enables larger feedstock flexibility and a more complete utilization of the biomass, since it retrieves the chemical energy stored in all parts of the biomass, including in the more recalcitrant fractions (Daniell et al. 2012). This impacts directly in the biomass conversion and ethanol production yields.

9.5.2 Products from Microbial Gas Fermentation

Syngas can be metabolized by acetogenic anaerobic bacteria capable of growing autotrophically in $CO_2 + H_2$, CO, or the mixture of all these, by the Wood–Ljungdahl pathway. In this pathway, CO or CO_2 are reduced and condensed to form acetyl-CoA (Schiel-Bengelsdorf and Dürre 2012; Latif et al. 2014). Acetyl-CoA can be used for the synthesis of cell carbon or can serve as intermediate for the production of several naturally occurring acids and alcohols, e.g., acetate, ethanol, lactate, and 2,3-butanediol (Bertsch and Müller 2015; Kennes et al. 2016). The acetogens *Clostridium autoethanogenum*, *C. ljungdahlii*, *C. carboxidivorans*, *C. acetobutylicum* and *C. ragsdalei* have been object of the most intensive research applied to CO metabolism and syngas fermentation (Abrini et al. 1994; Abubackar et al. 2011; Cotter et al. 2009; Guo et al. 2010; Köpke et al. 2010; Kundiyana et al. 2011; Ramió-Pujol et al. 2015; Younesi et al. 2005). Specific strains of this group

have been used in large-scale industrial processes for syngas fermentation and are protected as industrial property. Genetic manipulation has habilitated these microorganisms to increase their tolerance to ethanol and to synthesize a portfolio of products, such as acetone, isopropanol, iso-butanol, terpenes, methyl ethyl ketone, 1-butanol, 2-butanol, propanal, propan-2-one, propan-1-ol and/or propan-2-ol, or its precursors, with potential application within the scope of a syngas fermentation-based biorefinery (Simpson et al. 2012a, b; Köpke and Liew 2012; Chen et al. 2013; Köpke et al. 2013; Gak et al. 2014). The potential of carboxydotrophic bacteria to act as biocatalyzers in the reduction of short-chain carboxylic acids into their corresponding alcohols, such as *n*-propanol, *n*-butanol, *n*-pentanol, *n*-hexanol, and iso-butanol, during syngas fermentation was also demonstrated (Perez et al. 2013).

The synthesis of biopolymers from syngas has been investigated under the frame of an EU collaborative project, SYNPOL, Biopolymers from Syngas Fermentation. This project focuses the optimization of the gasification and pyrolysis processes using biodegradable waste along with microbial strain improvement, particularly of the purple non-sulfur bacteria *Rhodospirillum rubrum*, for the synthesis of poly-hydroxyalkanoate (PHA) and poly-hydroxybutyrate (PHB) from syngas (Drzyzga et al. 2015; Dürre and Eikmanns 2015).

9.5.3 Syngas Composition and Mass Transfer Limitation

The overall fermentation yield is dependent of the syngas composition which, in turn, depends on the gasifier, the biomass type, and the gasification conditions (Liew et al. 2013; Munasinghe and Khanal 2011). A syngas where CO is uniquely used as carbon source whereas H_2 is used as energy source is more suitable for the overall carbon recovery (Bertsch and Müller 2015). In this case, the H_2 in the syngas is used to supply electrons for the reductive conversion of CO into acetyl-CoA, in a process catalyzed by a bifurcating hydrogenase. However, even low concentrations of CO may inhibit the enzyme activity. This shifts CO from carbon source to electron donor in a reaction catalyzed by CO dehydrogenase (CODH), and leads to carbon losses by the formation of CO_2, compromising the process efficiency and undermining the non-polluting aspect of syngas fermentation (Bertsch and Müller 2015). Data from the literature point to suitable H_2/CO ratios of less than 0.5 for air-blown updraft gasifiers, but between 0.5 and 1.0 for air-blown downdraft, air-blown fluidized bed, oxygen-blown, and indirectly heated gasifiers (Wilkins and Atiyeh 2011). Additionally, to maintain the culture stability and the efficiency of carbon conversion, the syngas should be free of other detrimental compounds, such as C_2H_2 or NO_X that inhibit hydrogenase activity, tars that were associated to cell dormancy, HCN that is toxic, and sulfur compounds that may affect cell function (Abubackar et al. 2011; Ahmed et al. 2006; Liew et al. 2013).

Gas–liquid mass transfer limitation is another technical hurdle in the process of syngas fermentation. This is due to the low solubility of CO and H_2 in liquid media, especially at the temperature range at which the fermentation process takes place and aggravated by the stoichiometry of carbon monoxide to ethanol synthesis (6CO: $1CH_3CH_2OH$) (Daniell et al. 2012). To overcome this problem, the bioreactor should be specifically designed and operated to favor the gas–liquid dispersion and solubility, so that microorganisms can have the maximum access to the gaseous substrate (Munasinghe and Khanal 2011).

9.5.4 Industrial Examples of Syngas Fermentation

Two major companies, INEOS Bio and Lanzatech, are currently using syngas fermentation at industrial scale for the production of ethanol, electricity and chemicals (Table 9.4) (Bacovsky et al. 2013). The diagram of Lanzatech and INEOS processes are shown in Sect. 9.3 (Figs. 9.11 and 9.12, respectively).

The activity of INEOS Bio is focused in the use of waste and nonfood crop biomass to produce carbon-neutral bioethanol and renewable energy (INEOS Bio 2012). Since 2012, the company is responsible for 10 patent applications with the aim to increase the yield and productivity of ethanol production by bacterial fermentation of gaseous substrates and improve the gasification process with CO_2 sequestration (Gaddy et al. 2012, 2014).

The process of ethanol production by syngas fermentation by INEOS Bio comprises (INEOS Bio 2012):

- Reception of biomass waste, which may include organic municipal solid waste, agricultural, vegetative ,and forestry residues and products, lignocellulosic energy crops, wood waste, and organic commercial and industrial wastes, for which remote or on-site mechanical, biological, and/or thermal pretreatment may be necessary;
- Biomass drying, using the heat that is recovered from gasification;
- Gasification by a two-step, oxygen-blown process to generate synthesis gas and avoid the formation of dioxins and furans;
- Cooling, cleaning, and compression of the syngas before entering the bioreactor;
- Addition of nutrients and fermentation of the syngas. Here, the bioethanol is synthesized in minutes, at low temperature and pressure and with high yield (maximum theoretical yield: 135 gallons of ethanol per dry ash-free ton of material) and selectivity;
- The liquid from the bioreactor is continuously removed, filtered, distilled, and dehydrated to obtain anhydrous bioethanol;
- Additionally, renewable power is generated by heat recovery from the hot syngas and by combustion of the off gas from the bioreactor.

Table 9.4 Biorefinery facilities based in syngas fermentation

Company, country	Input stream	Biorefinery type	Products	Output capacity	Facility type	Source
Lanzatech, NZ	Various	2-platform biorefinery (syngas, chemical building blocks)	Ethanol 2,3-BDOchemicals	Laboratorial scale	R&D	www.lanzatech.com Bacovsky et al. (2013), IEA Bioenergy (2014)
Lanzatech, NZ	Steel flue gas		Ethanol	90 t/year	Pilot	
Lanzatech, China (1st)	Steel flue gas		Ethanol	300 t/year	Demonstration	
Lanzatech, China (2nd)	Steel flue gas		Ethanol	300 t/year	Pilot	
Lanzatech, Taiwan	Steel flue gas		Ethanol	100 kg/day	Demonstration	
Lanzatech, USA	Woody biomass syngas (125 t/day dry wood residues)		Ethanol chemicals	15,000 t/year	Mobile pilot	
Lanzatech, India	Carbon monoxide containing gas from MSW		Ethanol	300 t/year	Planned	
INEOS Bio plant, USA	Syngas from vegetative yard waste, garden waste, clean woody construction and demolition debris	2-platform biorefinery (syngas, electricity and heat)	Ethanol electricity and heat	24,000 t/year	Commercial	www.ineosbio.com Bacovsky et al. (2013), IEA Bioenergy (2014)
INEOS Bio plant, UK	Syngas from vegetative yard waste, garden waste, clean woody construction and demolition debris		Ethanol electricity and heat	24,000 t/year	Project	

The core of Lanzatech activity in gas-to-liquid bioprocesses focuses mainly the carbon capture of industrial flue gases for the fermentative production of a myriad of low-carbon chemicals and fuels, including ethanol (www.lanzatech.com). The company is responsible for more than 40 patent applications in the past 6 years regarding genetic improvement of proprietary carboxydotrophic acetogenic strains and process optimization, for example to produce recombinant strains incorporating new biosynthesis pathways, to increase the bacterial tolerance to gas contaminants and ethanol, or to improve the carbon capture from the gas stream (Köpke and Liew 2012; Simpson et al. 2012a, b; Chen et al. 2013; Köpke et al. 2013; Schultz and Derek 2013).

The process of gas fermentation in Lanzatech consists of (www.lanzatech.com):

- Reception of the gas steams, from steel mills and processing plants, syngas generated from any biomass resource such as municipal biowaste, organic industrial waste, and agricultural waste, coal-derived syngas, and reformed natural gas;
- Feed of the gas into the bottom of the bioreactor to promote its dispersion by moving upward in the liquid medium. This contact is important to promote a better gas-to-liquid mass transfer, which is one of the major hurdles in the fermentation of gaseous substrates;
- Fermentation by Lanzatech proprietary microbial strains, which are tolerant to contaminants and admit a flexible H_2 content in the gas;
- Withdrawal of the fermentation product to a hybrid separation system, for products and co-products recovery and process water recycling;
- The separated products are used directly as fuel and chemicals or after conversion to common chemicals or drop-in fuels.

Other companies have demonstrated their interest in the process of microbial gas fermentation. Coskata Inc. is an American company with expertize in the production of cellulosic ethanol which in 2012 was seeking to expand its commercial activity to synthesis gas fermentation from diverse feedstock, such as woody biomass, agricultural residues, municipal wastes and natural gas (www.biofuelsdigest.com/bdigest/2014/03/25/coskata-biofuels-digests). The company is responsible for numerous patent applications in the past 5 year regarding the improvement of process efficiency by optimization of the reactor design and operation, protection from HCN and isolation of the novel ethanologenic species *Clostridium coskatii* (Hickey 2013; Hickey et al. 2014; Zahn and Saxena 2012).

Syngas Biofuels Energy Inc. is an American biotechnology company that has developed a "Reverse Global Warming" technology based in engineered biocatalysts for the manufacture of commodity chemicals and fuels from air CO_2 (www.syngasbiofuelsenergy.com). The company advertises the commercialization of scalable fermentation modules of 20,000 gallons for iso-butanol production, by continuous gas blend fermentation using a recombinant *Clostridium* (Gak et al. 2014).

9.6 Future Trends on Advanced Biorefineries

9.6.1 Lignocellulosic-Based Bioethanol Biorefineries

The shift from pilot- and demo-scale production of lignocellulosic ethanol to competitive full-scale production still requires further reduction of the production cost.

Most of the current 2G bioethanol demonstration facilities are only producing cellulosic ethanol, with the hemicellulose fraction (up to 40%) of feedstock being used for other purposes (e.g., animal feeding) (Ferreira 2011). Thereby, one promising strategy will be to integrate the production of ethanol into a biorefinery scheme in which the biomass components of lignin, hemicellulose and extractives are converted into co-value-added products, instead of energy application, in order to overcome the costs associated with pretreatment and enzymes for cellulose hydrolysis (Caesar 2008; Sammons et al. 2007).

Other approach is to integrate 1G plant with a 2G plant on a single site to optimize personnel, utilities, equipments, and other industrial synergies. An attractive option is to integrate cellulosic ethanol production with starch-based ethanol production to use the whole agricultural crop (Hahn-Hägerdal et al. 2006). For instance, in USA, POET/DSM has integrated ethanol production from corncobs into an existing grain ethanol plant and uses part of the collected biomass for power production (CHP integration). Also, cellulosic ethanol process co-produces biogas, which will meet a significant fraction of the adjacent grain ethanol plant's power needs (Bacovsky et al. 2013). The same did occur with GRANBIO plant in Alagoas-Brazil but using sugarcane and straw as 1G and 2G feedstock, respectively.

Moreover, lignocellulosic sugars obtained through enzymatic hydrolysis are diluted with C6 sugars and they are fermented together in the 1G plant (E4tech, RE-CORD and WUR 2015). ICM, Inc. has also co-located its pilot-scale cellulosic biorefinery—using corn fiber, switchgrass and energy sorghum—with the existing grain-to-ethanol facility at LifeLineFoods, LLC in St. Joseph, Missouri (USA) (IEA-Bioenergy 2014). Also, Green Field Specialty Alcohols Inc., Canada's largest producer of fuel ethanol and industrial alcohol, has installed its cellulosic ethanol pilot plant next to 1G corn ethanol facility in Chatham, Ontario. This company produces 2G ethanol, from agricultural crop residues, forestry residues and dedicated energy crops, by applying "Twin Screw Extruder Technology" which allows single-stage or two-stage continuous percolation/hot water/steam explosion pretreatment (IEA-Bioenergy 2014).

9.6.2 Feedstock-Flexible Biorefineries

Conceptually, biorefineries being flexible relatively to feedstock will also be advantageous once the risks associated with feedstock availability will be minimized (E4tech, RE-CORD and WUR 2015). Thereby, modern biorefinery processes should be based on fractionation and pretreatment approaches requiring only relatively small adjustments for application to several biomass feedstocks, allowing the plant to be fed with multiple different feedstocks.

9.6.3 Cluster-Based Biorefineries

Cluster-based biorefineries constituted by different value chains site plants aggregated as a cluster shall be more competitive, such as demonstrated by the successful implementation of the Chemical Cluster (five-site plants) in Stenungsund (Sweden)—Aga, AkzoNobel, Borealis, Ineos and Perstorp—developing a joint strategy of producing sustainable products (Five Clusters 2013). New technologies are being explored for integrating the production of biomass-derived fuels and other products, such as 1,3 propanediol, polylactic acid, and isosorbide, in a single facility (E4tech, RE-CORD and WUR 2015).

9.6.4 Integrated Pulp and Paper Biorefineries

The implementation of biorefinery concept is very attractive for pulp and paper manufacturers, providing high value-added products and pulp production in a closed loop. Manufacturers will continue to have as main objective to produce paper, but the producers have begun to explore how to use the waste streams and by-products—such as bark and wood wastes or the cooking liquor containing lignin and some hemicelluloses (glucomannans from softwood pulp and xylans from hardwood pulp), extractives, including resins and triglycerides, or even the ultimate sludge from their wastewater treatment—for the simultaneous production of biofuels and biochemicals (McElroy 2007; Muffler and Ulber 2008). These new products will be integrated with the existing product lines in the paper industry, while maintaining the properties of pulp and paper and introducing minor modifications in the plant, or alternatively may promote integration with other industries by identifying appropriate synergies (van Ree and Annevelink 2007).

Indeed, there are already some examples of pulpand paper mills that have already implemented this approach. For instance, the concept of the Austrian company Schweighofer Fiber (plans postponed) foresees integration of ethanol production into an existing pulp mill with production of ethanol and energy and recycling of chemicals from the sulphite spent liquor (SSL). Borregaard Industries

are successfully producing ethanol from SSL since 1938 (Bacovsky et al. 2013). In their Sarpsborg Biorefinery, spruce chips are treated with acidic calcium bisulfite cooking liquor, promoting hemicellulose hydrolysis to various sugars. After concentration of this SSL obtained, the sugars are fermented into ethanol (Bacovsky et al. 2013). Also, Oji Holdings Corporation (OJI), a Japan's paper manufacturer founded in 1873 that is the sixth largest paper manufacturing company in the World, with support from New Energy and Industrial Development Organization (NEDO), have developed a mechanochemical pulping process for conversion of cellulose to ethanol. This technology is being applied in a pilot plant producing ethanol (65 t-annual capacity) from eucalyptus wood, in Hiroshima (Japan) since 2011 (Bacovsky et al. 2013). The Canadian Alberta-Pacific Forest Industries Inc., one of the largest pulp companies in the World, in simultaneous with kraft pulp production, is manufacturing bio-methanol (4000 t/year) by separating and purifying it from its waste gas stream (steam stripper off-gas) in their commercial demo unit in Alberta (Canada) (Alpac 2016). This product is used for the on-site production of chlorine dioxide, used in pulp whitening operations and the surplus is available for sale to external industries. Domtar Corporation, one of the largest producers of kraft pulp in North America (with 9 pulp and paper mills and 1 paper mill, in USA and in Canada) (Domtar 2016) has created, in partnership with FPInnovations, CelluForce, a company that is producing nanocrystalline cellulose from a fraction of the mill's kraft pulp, based on new patented acid hydrolysis (IEA-Bioenergy 2014), in a demo plant located in Windsor (Québec, Canada) (CelluForce 2016). In addition to pulp, paper, heat, and power, several kraft pulping companies—such as Zellstoff Pöls (in Pöls, Austria) and Carter Holt Harvey Pulp & Paper in its Kinleith mill, New Zealand's largest pulp and paper mill located in the central North Island—are commercially co-producing tall oil and turpentine as attractive marketable intermediate chemicals recovered from black liquor (IEA-Bioenergy 2014).

9.6.5 Higher Added Value Products-Driven Biorefineries

So far biofuel-driven (or energy-driven) biorefineries have been discussed, i.e., with the main goal producing huge volumes of relatively low-value energy (or fuels) out of biomass (IEA-Bioenergy 2014).

There also some product-driven biorefineries, i.e., which have as the main goal produce smaller amounts of relatively higher value-added bio-based products out of biomass and primary (agro) and secondary (process) residues are used to produce energy (power/heat) for internal or external use. Currently, only limited product-driven lignocellulosic biorefineries are in operation, mainly because of the fact that some key technologies are still in the R&D, pilot and demo-phase. However, their potential is huge, and it is generally believed that a refocus will take place concerning optimal sustainable biomass use from mainly energy (fuel)

applications to chemical/material applications, and even to biorefineries that use biomass for both "Food" and "Non-food" applications (IEA-Bioenergy 2014).

For instance, in 2013, Cellulac Ltd. Galway (Ireland) announced plans to convert a brewery in Ireland—Great Northern Brewery, Dundalk, Co. Louth, the second largest brewery in Ireland—into a lactic acid and related products (PolyLactic Acid and Ethyl Lactate) plant using 2G feedstocks (together with lactose whey permeate). This company currently has a pilont plant in Postdam, Germany (E4tech, RE-CORD and WUR 2015; IEA-Bioenergy 2014).

Cobalt Technologies, in cooperation with Rhodia and Andritz, are building a demonstration plant in Brazil for the production of butanol from sugarcane bagasse. They combine dilute acid hydrolysis pretreatment with ABE-fermentation and claim that enzymatic hydrolysis is not necessary in their process (E4tech, RE-CORD and WUR 2015).

9.7 Concluding Remarks

A comprehensive overview of the current status of the biorefinery plants all over the World was presented, addressing the benefits, constraints and future challenges of these installations. In general terms, the rational use of the total fraction of the biomass, the broadening of the feedstock sources and the production of a vast product portfolio confer sustainability advantages to the biorefinery pathways and increase their breakthrough chances in the future.

Although it is still not evident that exists a clear winning technology (e.g., biochemical versus thermochemical) for biomass processing, namely lignocellulosic biomass, it rises from this chapter that some commercial cellulosic biofuel plants (biochemical-based) are already fully operational in Europe, USA and Brazil and are leading the current technologies for advanced biofuels in World.

References

Abrini J, Naveau H, Nyns EJ (1994) *Clostridium autoethanogenum*, sp. nov., an anaerobic bacterium that produces ethanol from carbon monoxide. Arch Microbiol 161(4):345–351. doi:10.1007/bf00303591

Abubackar HN, Veiga MC, Kennes C (2011) Biological conversion of carbon monoxide: rich syngas or waste gases to bioethanol. Biofuels, Bioprod Biorefin 5:93–114

Ahmed A, Cateni BG, Huhnke RL, Lewis RS (2006) Effects of biomass-generated producer gas constituents on cell growth, product distribution and hydrogenase activity of *Clostridium carboxidivorans* P7T. Biomass Bioenergy 30:665–672. doi:10.1016/j.biombioe.2006.01.007

Alberta Pacific Forest Industries Inc. (2016) https://alpac.ca. Accessed Feb 2016

Bacovsky D, Ludwiczek N, Ognissanto M, Wörgetter M (2013) Status of advanced biofuels demonstration facilities in 2012. IEA Bioenergy Task 39 Report 1–209

Bertsch J, Müller V (2015) Bioenergetic constraints for conversion of syngas to biofuels in acetogenic bacteria. Biotechnol Bioeng 8:210. doi:10.1186/s13068-015-0393-x
Biodiesel Magazine—The latest news and data about biodiesel, Dec 2015. http://www.biodieselmagazine.com/plants/listplants/. Accessed Feb 2016
Bioenergy2020+ (Renewable Energy Network Austria, Austrian Bio Energy Centre), FJ-BLT (Biomass-Logistics-Technology) IEA Bioenergy Task 39 'Commercializing 1st- and 2nd-Generation Liquid Biofuels from Biomass': Database on facilities for the production of liquid and gaseous biofuels for transport. http://demoplants.bioenergy2020.eu/. Accessed Feb 2016
Caesar B (2008) Industrial biotechnology: more than just ethanol. Factors driving industry growth. Ind Biotechnol 4:50–54
Cardona CA, Sanchez OJ (2007) Fuel ethanol production: process design trends and integration opportunities. Bioresour Technol 98:2415–2457
Carvalheiro F, Duarte LC, Medeiros R, Gírio FM (2004) Optimization of brewery's spent grain dilute-acid hydrolysis for the production of pentose-rich culture media. Appl Biochem Biotechnol 113–116:1059–1072
CelluForce (2016) www.celluforce.com. Accessed Feb 2016
CELPA—Portuguese Association of Paper Industry. www.celpa.pt. Accessed Oct 2011
Chen W, Liew FM, Köpke M (2013) Recombinant microorganisms and uses therefor. World Patent WO 2013/180584
Cheng JJ, Timilsina GR (2011) Status and barriers of advanced biofuel technologies: a review. Renew Energy 36:3541–3549
Cherubini F, Stromman AH (2010) Production of biofuels and biochemicals from lignocellulosic biomass: estimation of maximum theoretical yields and efficiencies using matrix agebra. Energy Fuels 24:2657–2666
Cotter JL, Chinn MS, Grunden AM (2009) Influence of process parameters on growth of *Clostridium ljungdahlii* and *Clostridium autoethanogenum* on synthesis gas. Enzyme Microb Technol 44(5):281–288. doi:10.1016/j.enzmictec.2008.11.002
Daniell J, Köpke M, Simpson S (2012) Commercial biomass syngas fermentation. Energies 5:5372–5417. doi:10.3390/en5125372
Davenport R (2008) Chemicals and polymers from biomass. Ind Biotechnol 4:59–63
Debabov VG (2013) Bioethanol from synthesis gas. Appl Biochem Microbiol 49(7):619–628. doi:10.1134/S000368381307003X
Domtar (2016) www.domtar.com. Accessed Feb 2016
Drzyzga O, Revelles O, Durante-Rodríguez G, Díaz E, García JL, Prieto A (2015) New challenges for syngas fermentation: towards production of biopolymers. J Chem Technol Biotechnol 90 (10):1735–1751. doi:10.1002/jctb.4721
Dürre P, Eikmanns BJ (2015) C1-Carbon sources for chemical and fuel production by microbial gas fermentation. Curr OpinBiotechnol 35:63–72. doi:10.1016/j.copbio.2015.03.008
E4tech, RE-CORD, WUR (2015) From the sugar platform to biofuels and biochemicals. Final report for the European Commission, contract No. ENER/C2/423-2012/SI2.673791
Ethanol Producer Magazine (2016) http://www.ethanolproducer.com/plants/listplants/US/Existing/Sugar-Starch/. Accessed Feb 2016
Eurobserv'er (2015) Biofuels barometer, http://www.eurobserv-er.org/biofuels-barometer-2015. Accessed Feb 2016
European Biodiesel Board. http://www.ebb-eu.org/stats.php. Accessed Jan 2016
European Biofuels Annual (2015) (GAIN Report Number: NL5028). Global Agriculture Information Network, USDA Foreign Agriculture Service
European Biofuels Technology Platform. Accelerating deployment of advanced biofuels in Europe. http://biofuelstp.eu/sugar_crops.html. Accessed Jan 2016
FAO (2014) FAO Statistics - Food and agriculture data. http://www.fao.org/faostat/en/#home. Accessed Feb 2016

Ferreira CSR (2011) Strategies to improve D-xylose and D-glucose co-fermentation for the production of second generation bioethanol. Master Thesis in Biotechnology, Instituto Superior Técnico, Lisboa, Portugal
Five Clusters (2013) Five clusters in west Sweden with strength and potential for the future. http://www.vgregion.se/upload/Regionutveckling/Publikationer/2013/Five_Clusters_2013.pdf
Gaddy JL, Arora DK, Ko C-W, Phillips JR, Basu R, Wilkstrom CV, Clausen EC (2012) Methods for increasing the production of ethanol from microbial fermentation. US Patent 2012/122173
Gaddy JL, Ko C-W, Phillips JR, Slape MS (2014) Methods for sequestering carbon dioxide into alcohols via gasification fermentation. US Patent 2014/45257
Gak E, Tyurin M, Kiriukhin M (2014) Genome tailoring powered production of isobutanol in continuous CO_2/H_2 blend fermentation using engineered acetogen biocatalyst. J Ind Microbiol Biotechnol 41:763–781. doi:10.1007/s10295-014-1416-5
Gao Y, Gregor C, Liang Y, Tang D, Tweed C (2012) Algae biodiesel—a feasibility report. Chem Central J 6(Suppl 1):S1. http://journal.chemistrycentral.com/content/6/S1/S1
Geddes CC, Nieves IU, Ingram LO (2011) Advances in ethanol production. Curr Opin Biotechnol 22:312–319
Gírio FM, Fonseca C, Carvalheiro F, Duarte LC, Marques S, Bogel-Łukasik R (2010) Hemicelluloses for fuel ethanol: a review. Biores Technol 101:4775–4800
Gírio F, Kurkela E, Kiel J, Lankhorst RK (2013) Report EERA-EIBI WORKSHOP "Longer term R&D needs and priorities on bioenergy: bioenergy beyond 2020", p 47
Glasser WG, Wright RS (1998) Steam-assisted biomass fractionation. II. Fractionation behavior of various biomass resources. Biomass Bioenergy 14:219–235
González LE, Díaz GC, Aranda DAG, Cruz YR (2015) Fortes MM biodiesel production based in microalgae: a biorefinery approach. Nat Sci 7:358–369. doi:10.4236/ns.2015.77039
Gray KA, Zhao LS, Emptage M (2006) Bioethanol Curr Opin Chem Biol 10:141–146
Guo Y, Xu J, Zhang Y, Xu H, Yuan Z, Li D (2010) Medium optimization for ethanol production with *Clostridium autoethanogenum* with carbon monoxide as sole carbon source. Bioresour Technol 101(22):8784–8789. doi:10.1016/j.biortech.2010.06.072
Hahn-Hägerdal B, Galbe M, Gorwa-Grauslund M, Lidén G, Zacchi G (2006) Bio-ethanol—the fuel of tomorrow from the residues of today. Trends Biotechnol 24:549–556
Hariskos J, Posten C (2014) Biorefinery of microalgae—opportunities and constraints for different production scenarios. Biotechnol J 9:739–752
Hickey R (2013) Processes for enhancing the performance of large-scale, stirred tank anaerobic fermentors and apparatus therefor. US Patent 2013/0078689
Hickey R, Jianxin D, Reeves A, Richard ET (2014) Processes for the anaerobic bioconversion of syngas to oxygenated organic compound with in situ protection from hydrogen cyanide. US Patent 2014/0273125
Hofvendahl K, Hahn-Hägerdal B (2000) Factors affecting the fermentative lactic acid production from renewable resources. Enzyme Microb Technol 26:87–107
Ibeto CN, Ofoefule AU, Agbo KE (2011) A Global overview of biomass potentials for bioethanol production: a renewable alternative fuel. Trends Appl Sci Res 6:410–425
IEA Bioenergy (2014) BIOREFINING—sustainable and synergetic processing of biomass into marketable food & feed ingredients, products (chemicals, materials) and energy (fuels, power, heat). IEA Bioenergy Task 42 Report 1–66
INEOS Bio, USA (2012) Process technology process description. http://www.ineos.com/globalassets/ineos-group/businesses/ineos-bio/technology/ineos-us-bio-process-description-brochure_april-2012.pdf. INEOS Process Technology Brochure
Iogen (2016) http://www.iogen.ca/cellulosic_ethanol/fuel_demo.html. Accessed Feb 2016
Jacob-Lopes E, Ramírez MLG, Queiroz MI, Zepka LQ (2015) In: Jacob-Lopes E, Zepka LQ (eds) Microalgal biorefineries. Biomass production and uses, pp 81–106. doi:10.5772/59969, ISBN 978-953-51-2181-7
Kamm B, Kamm M (2004) Principles of biorefineries. Appl Microbiol Biotechnol 64:137–145
Kamm B et al (2006) Biorefineries. In: Industrial processes and products. Wiley-VCH

Kennes D, Abubackar HN, Kennes C (2016) Bioethanol production from biomass: carbohydrate vs syngas fermentation. J Chem Technol Biotechnol 91:304–317. doi:10.1002/jctb.4842
Kheshgi HS, Prince RC, Marland G (2000) The potential of biomass fuels in the context of global climate change: focus on transportation fuels. Annu Rev Energy Environ 25:199–244
Köpke M, Liew F (2012) Production of butanol from carbon monoxide by a recombinant microorganism. World Patent WO 2012/053905
Köpke M, Held C, Hujer S, Liesegang H, Wiezer A, Wollherr A et al (2010) *Clostridium ljungdahlii* represents a microbial production platform based on syngas. Proc Natl Acad Sci USA 107(29):13087–13092. doi:10.1073/pnas.1004716107
Köpke M, Liew F, Mueller A (2013) Recombinant microorganisms and uses therefor. World Patent WO 2013/185123
Kundiyana DK, Wilkins MR, Maddipati P, Huhnke RL (2011) Effect of temperature, pH and buffer presence on ethanol production from synthesis gas by *Clostridium ragsdalei*. Bioresour Technol 102(10):5794–5799. doi:10.1016/j.biortech.2011.02.032
Latif H, Zeidan AA, Nielsen AT, Zengler K (2014) Trash to treasure: Production of biofuels and commodity chemicals via syngas fermenting microorganisms. Curr Opin Biotechnol 27:79–87. doi:10.1016/j.copbio.2013.12.001
Lee JH, Reddy KH, Jung JS, Yang EH, Moon DJ (2014) Role of support on higher alcohol synthesis from syngas. Appl Catal A 480:128–133. doi:10.1016/j.apcata.2014.04.026
Liew FM, Köpke M, Simpson SD (2013) Gas fermentation for commercial biofuels production. In: Liquid, gaseous and solid biofuels—Conversion techniques, pp 125–173. doi:10.5772/52164
Lopes da Silva T, Reis A (2015) Algal biorefinery: an integrated approach. In: Debabrata D (eds) Scale up problems for the large scale production of algae. Springer, Berlin, pp 155–186. doi:10.1007/978-3-319-22813-6_6
Lv P, Yuan Z, Wu C, Ma L, Chen Y, Tsubaki N (2007) Bio-syngas production from biomass catalytic gasification. EnergyConvers Manage 48:1132–1139. doi:10.1016/j.enconman.2006.10.014
Lynd LR, Cushman JH, Nichols RJ (1991) Wyman CE Fuel ethanol from cellulosic biomass. Science 251:1318–1323
Mascoma (2007) Mascoma buys Hoosier biofuels startup. Mass high tech. J N Engl Technol
McElroy AK (2007) Not so run of the mill. Biomass Mag 10:38–43
Muffler K, Ulber R (2008) Use of renewable raw materials in the chemical industry—Beyond sugar and starch. Chem Eng Technol 31:638–646
Munasinghe PC, Khanal SM (2011) Biomass-derived syngas fermentation into biofuels. Biofuels 101(13):79–98. doi:10.1016/B978-0-12-385099-7.00004-8
NatureWorks LLC. http://www.natureworksllc.com/#3. Accessed Jan 2016
NovaCana (2016) http://www.novacana.com/usinas-brasil/. Accessed Jan 2016
Nurra C, Torras C, Clavero E, Ríos S, Rey M, Lorente E, Farriol X, Salvadó J (2014) Biorefinery concept in a microalgae pilot plant. Culturing, dynamic filtration and steam explosion fractionation. Bioresour Technol 163:136–142. doi:10.1016/j.biortech.2014.04.009
Perez M, Richter H, Loftus SE, Angenent LT (2013) Biocatalytic reduction of short-chain carboxylic acids into their corresponding Alcohols with syngas fermentation. Biotechnol Bioeng 110(4):1066–1077. doi:10.1002/bit.24786
Petrick I, Dombrowski L, Kröger M, Beckert T, Kuchling T, Kureti S (2013) Algae biorefinery—Material and energy use of algae. DBFZ Report No. 16, p 164
Proethanol2G EU 7th FWP project. www.proethanol2g.org. Accessed Feb 2016
Ragauskas AJ, Nagy M, Kim DH, Eckert CA, Hallett JP, Liotta CL (2006) From wood to fuels. Integrating biofuels and pulp production. Ind Biotechnol 2:55–65
Rajagopalan S, Ponnampalam E, McCalla D, Stowers M (2005) Enhancing profitability of dry mill ethanol plants. Appl Biochem Biotechnol 120(1):37–50
Ramió-Pujol S, Ganigué R, Bañeras L, Colprim J (2015) How can alcohol production be improved in carboxydotrophic *Clostridia*? Process Biochem 50(7):1047–1055. doi:10.1016/j.procbio.2015.03.019

Rapagn S, Provendier H, Petit C, Kiennemann A (2002) Foscolo PU Development of catalysts suitable for hydrogen or syn-gas production from biomass gasi cation. Biomass Bioenergy 22:377–388

Renewable Energy World. http://www.renewableenergyworld.com/articles/print/volume-17/issue-2/bioenergy/ethanol-from-energy-beets-a-viable-option.html. Accessed Jan 2016

Renewable Fuels Association (2005) How ethanol is made? http://www.ethanolrfa.org/how-ethanol-is-made/. Accessed Feb 2016

Sammons N, Eden M, Yuan W, Cullinan H, Aksoy B (2007) A flexible framework for optimal biorefinery product allocation. Environ Prog 26:349–354

Sanchez OJ, Cardona CA (2008) Trends in biotechnological production of fuel ethanol from different feedstocks. Bioresour Technol 99:5270–5295

Sassner P, Martensson CG, Galbe M, Zacchi G (2008) Steam pretreatment of H_2SO_4 impregnated salix for the production of bioethanol. Bioresour Technol 99:137–145

Schiel-Bengelsdorf B, Dürre P (2012) Pathway engineering and synthetic biology using acetogens. FEBS Lett 586(15):2191–2198. doi:10.1016/j.febslet.2012.04.043

Schultz M, Derek G (2013) Improved carbon capture in fermentation. World Patent WO 2013/119866

Sendich E, Laser M, Kim S, Alizadeh H, Laureano-Perez L, Dale B, Lynd L (2008) Recent process improvements for the ammonia fiber expansion (AFEX) Process and resulting reductions in minimum ethanol selling price. Bioresour Technol 99:8429–8435

Simpson SD, Köpke M, Liew FM (2012a) Recombinant microorganisms with increased tolerance to ethanol. World Patent WO 2012/105853

Simpson SD, Köpke M, Liew FM, Chen WY (2012b) Recombinant microorganisms and uses therefor. World Patent WO 2012/115727

Unica (Brazilian Sugarcane Industry Association) and ApexBrasil (Brazilian Trade and Investment Promotion Agency) (2016) http://sugarcane.org/sugarcane-products/ethanol. Accessed Jan 2016

Vaidya AN, Pandey RA, Mudliar S, Kumar MS, Chakrabarti T, Devotta S (2005) Production and recovery of lactic acid for polylactide—An overview. Crit Rev Environ Sci Technol 35:429–467

van Ree R, Annevelink E (2007) Status report biorefinery. Agrotechnology and Food Science Group, Wagninger, NL

van Wyk JPH (2011) Biotechnology and the utilization of biowaste as a resource for bioproduct development. Trends Biotechnol 19:172–177

Vijayakumar J, Aravindan R, Viruthagiri T (2008) Recent trends in the production, purification and application of lactic acid. Chem Biochem Eng Q 22:245–264

Wikipedia (2016) Mascoma Corporation. https://en.wikipedia.org/wiki/Mascoma_Corporation. Accessed Feb 2016

Wilkins MR, Atiyeh HK (2011) Microbial production of ethanol from carbon monoxide. Curr Opin Biotechnol 22(3):326–330. doi:10.1016/j.copbio.2011.03.005

Younesi H, Najafpour G, Mohamed AR (2005) Ethanol and acetate production from synthesis gas via fermentation processes using anaerobic bacterium, *Clostridium ljungdahlii*. Biochem Eng J 27(2):110–119. doi:10.1016/j.bej.2005.08.015

Zahn JA, Saxena J (2012) Novel ethanologenic *Clostridium* species, *Clostridium coskatii*. US Patent 2012/0156747

Zhang YHP (2008) Reviving the carbohydrate economy via multi-product lignocellulose biorefineries. J Ind Microbiol Biotechnol 35:367–375

Zwart RWR (2006) Biorefinery the Worldwide Status at the Beginning of 2006—Including the highlights of the 1st international biorefinery workshop and an overview of markets and prices of biofuels and chemicals, Wageninger, NL

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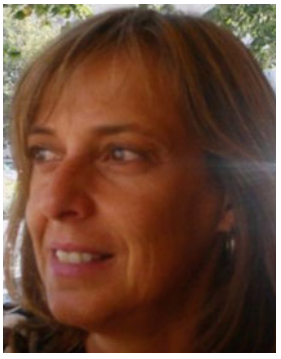
Susana Marques, Ph.D. is a Researcher at the Bioenergy Unit of the Portuguese National Laboratory of Energy and Geology (LNEG). She graduated in Chemical Engineering (1996) and obtained her Ph.D. in Biotechnology (2012) at Instituto Superior Técnico (IST, Lisboa). She has participated in more than 30 Portuguese and European Projects on lignocellulose bioconversion and co-authored 1 book chapter, 23 papers in International peer-reviewed journals, and more than 100 papers in International conferences. Her main focus of research has been the upgrading of lignocellulosic wastes and by-products into bio-based commercial products (e.g., bioethanol, lactic acid, and biopolymers), working on process intensification including enzymatic hydrolysis and fermentation, preferentially integrated with pretreatment and downstream processing. She was been awarded with *Honour Mention in the Green Project Awards 2009*—category of Research and Development—Project untitled "Upgrading of Wastes from the Pulp and Paper Industry under the Biorefinery Concept."

Filomena Pinto, Ph.D. has Ph.D. in Chemical Engineering, she is a Senior Researcher at Bioenergy Unit of LNEG, and an invited professor at FCUL—Faculty of Sciences of Lisbon. She has co-supervised several M.Sc. thesis (15 already finished) and Ph.D. thesis (5 already finished). Her main research areas cover: thermochemical conversion technologies (gasification, pyrolysis, liquefaction, and hydrothermal liquefaction) for coal, biomass and wastes, syngas cleaning and bio oil upgrading processes, emissions control from thermochemical processes, hydrogenation of oils and animal fats, and CO_2 capture. She is the author of 58 papers in international journals with referee, 41 papers in conference proceedings with referee, 19 chapters in books, and more than 145 papers in international conference proceedings.

Ana Cristina Oliveira, Ph.D. is a Senior Researcher at Bioenergy Unit of National Laboratory of Energy and Geology (LNEG), expert in liquid biofuels production, namely biodiesel, from different raw materials and technologies. She graduated in Chemistry at University of Lisbon (1986) and obtained her M. Sc. in Biotechnology/Biochemical Engineering (1990) and her Ph.D. in Biotechnology (2000) at Technical University of Lisbon (IST). Currently, in addition to her research activity, she is responsible for the liquid biofuels characterization group at LBA (Biofuels and Environment Laboratory) that is an accredited laboratory at LNEG. She also has been integrating the Sustainability Group of biofuels and bioliquids of LNEG's Bioenergy Unit. She is invited professor at Faculty of Sciences of University of Lisbon lecturing the course Energy from Biomass. She has supervised 20 M.Sc. students. She has participated in several national (coordinating 2 of them) and European projects and has published scientific papers in international peer-reviewed journals and in international conferences.

Paula Costa, Ph.D. is a Researcher at Bioenergy Unit of LNEG (National Laboratory of Energy and Geology) working mainly in the area of thermochemical conversion of wastes for alternative fuels production using pyrolysis, gasification, and hydrogenation processes. She obtained Ph.D. in Chemical Engineering at the Faculty of Science and Technology of the New University of Lisbon, titled "Production of liquid and gaseous hydrocarbons by plastic waste pyrolysis" in 2006. She is, also, an invited professor at FCUL (Faculdade de Ciências of the University of Lisbon)/UL (since 2008) and has supervised several MSc thesis (16 already finished). She co-authored 1 book chapter's, 13 papers in international journals, 6 papers in conference proceedings with referee, and more than 35 papers in international conference proceedings.

Alberto Reis, Ph.D. Chemical Engineer, Ph.D. in Biochemical Engineering, Researcher, and currently Deputy Head of the Bioenergy Unit within the National Laboratory of Energy and Geology (LNEG) in Lisbon, Portugal and Coordinator of the Biochemical Engineering Program at the same institution. Team member in six ongoing national and international projects in Bioenergy, and Coordinator of project SIMBIOALGA (New symbiotic approach for a truly sustainable integrated microalgae production directed to a biorefinery platform). Coordinator of the Iberian-Latin-American Thematic Network CYTED P711RT0095 "Iberian-Latin-American Society of Applied Algology SI3A" (162 researchers, 29 groups/institutions, 10 countries). Alberto Reis' scientific interests are in the areas of fermentation and photobioreactor technology, biological CO_2 fixation, and waste treatment. Author or co-author of 65 international peer-review papers.



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