

Chapter 9

Biomass for Energy: Energetic and Environmental Challenges of Biofuels

Jean Michel Most, Marie Thérèse Giudici-Orticoni, Marc Rousset, and Mireille Bruschi

Abstract Transportation is 94 % dependent on oil, represents around 20 % of global consumption of energy, and is responsible for 23 % of total emissions from fossil fuels. For several years, progress has been made to enhance the energy efficiency of the systems, but increasing the part of biofuel still seems irremediable both for environmental, economic, and energy independence reasons. Fuel production from biomass is clearly considered as an important substitute for liquid fossil fuels such as bioethanol for motor gasoline, biodiesel for diesel, jet fuel for biokerosene, and for gaseous fuels (hydrogen, natural gas for vehicles, biomethane, etc.). This chapter presents the main pathways for the production of biofuels, and classifies their degree of maturity:

- The first-generation processes that value the reserves of a plant (starch, sugar, oil) are now mature and industrially deployed.
- The second generation processes extend their resource to the whole plant tissues (agricultural, forest) or to organic waste, and are almost under scientific control but they still need more economic and energetic assessment before being commercially deployed.
- The last innovative pathway, the advanced or third biofuel generation, shows significant potential by using bioalgae or microorganisms capable of producing much more biomass oil convertible into biodiesel and gaseous fuels such as methane or hydrogen.

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List of Acronyms

ADEME	French Environment and Energy Management Agency
BtL	Biomass to liquid
CVO	Crude vegetable oils
Da	amu (atomic mass units)
DIREM	General Directorate for Energy and Raw Materials
DOE	US Department of Energy
E10	Gasoline with 10 % in volume of ethanol
E85	Gasoline with 85 % in volume of ethanol
ETBE	Ethyl tert-butyl ether
FAEE	Fatty acid ethyl ester
FAME	Fatty acid methyl ester
GHG	Greenhouse gases
GtL	Gas to liquid
HC	Hydrocarbon
IEA	International Energy Agency
MDa	1MDa = 10^6 Da
MJ	10^6 Joules
Mtoe	10^6 toe
NCV	Net calorific value
PAH	Polycyclic aromatic hydrocarbons
PCW	Plant cell wall
ppm	Part per million
PS II	Photosystem II (or water-plastoquinone oxidoreductase) is the first protein complex in light-dependent reactions .
TAG	Triacylglycerol
Toe	Ton of oil equivalent
v/v	Volume by volume

9.1 Introduction

Biomass potential is found in all living organisms on the continents and in the oceans; it is presently the main renewable energy resource on earth, providing 10 % of global primary energy demand (industrial combustion, transport, and traditional use, mainly wood for heating and cooking). This percentage has remained stable since the 1980s, and it should retain this value in the coming decades despite the increase in global energy demand. Consequently, biomass should clearly be considered in the energy mix for the years 2020–2050.

For decades, biomass conversion technologies have been developed to produce energy for transportation, agriculture, manufacturing, buildings, waste processing, and the like. In 2008, transport represented around 20 % of global energy consumption, corresponding to 2,300 Mtoe in comparison to a total of nearly 12,000 Mtoe. Transport currently is 94 % dependent on oil (IEA 2009a, p. 324), and is responsible for 23 % of global CO₂ emissions (IEA 2011, p. 9). Fuel production from biomass—bio fuels—could be an important substitute for liquid fossil fuels such as gasoline, diesel, kerosene, and jet fuel and for gaseous fuels (hydrogen, natural gas for vehicles, biomethane, etc.) simultaneously reducing the anthropogenic CO₂ emissions.

In 2008, 78 % of biomass energy was allocated for heating and cooking (IEA 2009b, p. 41). The new uses of biomass for electricity, heat, cogeneration, biofuels, and the like represented only 150 Mtoe, of which 46 Mtoe (2 % of fuel requirements, BP 2011, p. 39) dedicated to biofuels (ethanol for gasoline engines, biodiesel for diesel engines, etc.).

The projections (ADEME 2011), in the short and medium term, clearly cannot be strictly fixed and will depend on the energy options chosen for the future:

- For the “Blue Map” scenario, in 2050, the percentage of biomass could reach 3,500 Mtoe and biofuels could be around 750 Mtoe, which represents 27 % of energy consumption for transportation.
- For the same timeframe, the scenario trend (little change from the current energy policy) provides a more nuanced view: 1,900 Mtoe for the production of bioenergy and 160 Mtoe for biofuels (covering 4 % of demand).
- Finally, the “450 scenario” (see Chaps. 1 and 2), which proposes limiting the atmospheric concentration of CO₂ to 450 ppm, is a compromise and is already focused on the use of 280 Mtoe of biofuels by 2030.

It can be observed that, concerning aviation use, the impact is marginal inasmuch as the consumption of oil represents only 9 % of total hydrocarbons. The predicted increase in air traffic and the simultaneous decreasing supply of fossil fuels will induce a competitive use of biomass as BtL (second or third generation biofuel, biomass to liquid), natural gas, biogas, or even hydrogen if the limitations of its use related to the logistics and safety of its storage are solved.

Among the numerous reports available on biofuels (IEA 2009a, b; ADEME/DIREM 2002; ADEME 2011; DOE 2006, etc.), let us mention one of the last up-to-date reviews, an “advanced biofuels roadmap,” available on the Web (ADEME 2011), including the context, issues, and worldwide prospective visions on biofuels over a timescale to 2050.

Even if biofuels have engendered widespread enthusiasm in recent years, presuming to be a good solution for the growing demand for energy and reducing greenhouse gas emissions, an overall balance of advantages and disadvantages (real energy gain, CO₂ mitigation, land uses, water requirements, etc.) of their development must be prepared.

Presently, many organizational and technological locks subsist at all levels in the different processes of biomass fuel production. The earth’s surface, especially the area available for cultivation, is limited and it will be necessary, as the population

grows, to control the social problems linked to food security (competition between crops), to recycle agricultural waste and by-products, and to rationally exploit the forests. On this last point, let us evoke the controversial effects of deforestation, as the production of biofuels could increase the impacts on the environment (water, soil, or air) and on biodiversity.

We refer the reader here to Chap. 14 of this book, “The triple A issue: agriculture, alimentation needs, agro-fuels,¹” which deals with the following basic problem.

How relevant is it to build up agrofuel production in terms of a partial solution to energy self-sufficiency, in terms of the reduction of greenhouse gas (GHG) emissions, in terms of its impact on meeting humanity’s alimentation needs?

The present chapter is devoted more to scientific and technical considerations dealing with the state of the art of the different ways of producing biofuels from agriculture and with the main issues for research.

In the following paragraphs, an updated review is performed on the different processes for the production of:

- First-generation biofuels (the only currently operational ones) considering fermented sugars and oils, using the noblest part of the plant (seeds, grains, roots, etc.)
- Second-generation, based on the thermochemical processing of wood (lignocelluloses), implying the utilization of the whole plant (seeds and stems) as well as utilization of the wood and waste wood (lignocellulosic matter)
- Third generation, with, for instance, the development of biochemistry of algae

9.2 First-Generation Biofuels

First-generation biofuels, already present on the market and manufactured using mature technologies, only use part of the plant by processing the sugar or the starch that it contains or by extracting the oil from its seeds. The lignocellulosic part of the plant (stem, root) is generally not used for energy purposes (except for direct combustion). Two classical production pathways are currently being exploited: the ethanol pathway that leads to the production of ethyl tert-butyl ether (ETBE), shown in Fig. 9.1, and the diesel pathway that produces fatty acid methyl ester (FAME) or fatty acid ethyl ester (FAEE) fuel for diesel engines from processed vegetable oils. Figure 9.1 illustrates the main production steps of these two pathways.

9.2.1 Ethanol Pathway and ETBE (*Ethyl Tert-Butyl Ether*)

Three major families of alcohol-producing crops (see Fig. 9.1) are taken into account for the production of bioethanol:

¹*Agro-fuel*: Biomass from agricultural crops.

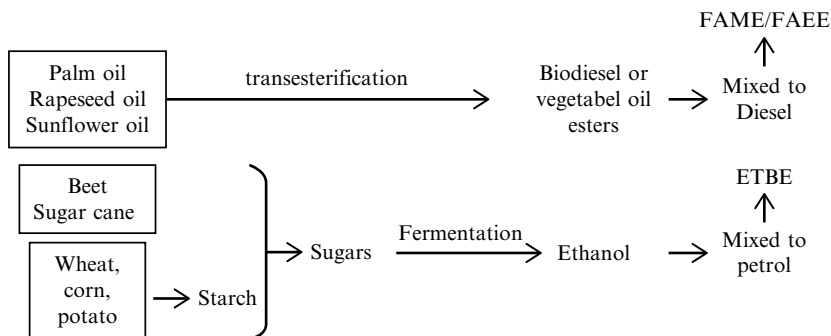
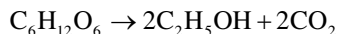


Fig. 9.1 Biofuel manufacturing principles diagram

- Sugar crops (beet, sugar cane, etc.), which contain sugars that are directly fermentable into ethanol.
- Cereal crops (corn, wheat, barley).
- Starchy crops and tubers (rich in fructans) such as potatoes, sweet potatoes, yams, manioc, and Jerusalem artichokes, among others, where sugars pre-exist in the form of starch. First of all, prior to fermentation, an hydrolysis of starch into sugar monomer must be carried out using enzymes.

The principle of alcoholic fermentation has been known for over 25 centuries. The sugars are converted into ethanol (C_2H_5OH) by the fermenting action of microorganisms, yeasts, and bacteria, in accordance with Gay Lussac's reaction:



Fermentation is influenced by the presence of ethanol and oxygen, by temperature, by minerals, and by the pH of the solution. The maximum efficiency of this reaction establishes that 100 kg of glucose will produce 48.4 kg of ethanol, which results in industrial efficiency of around 95 % of the theoretical efficiency of Guy Lussac's reaction (Ballerini 2006). This fermentation reaction is exothermic (1.2 MJ/kg of ethanol produced) and produces ethanol along with a release of gaseous CO_2 , which is a greenhouse gas.

To attain concentrations of more than 99.5 %, the ethanol needs to be purified. This is carried out industrially in two steps: a classic distillation to attain content close to that of azeotrope,² a second azeotropic distillation carried out with absolute ethanol at 99.8 % v/v; this step is generally performed with cyclohexane. With regard to the distillation step, energy savings are made by recovering the heat from the exothermic reactions.

²*Azeotrope*: A liquid mixture for which boiling occurs at a fixed temperature and composition.

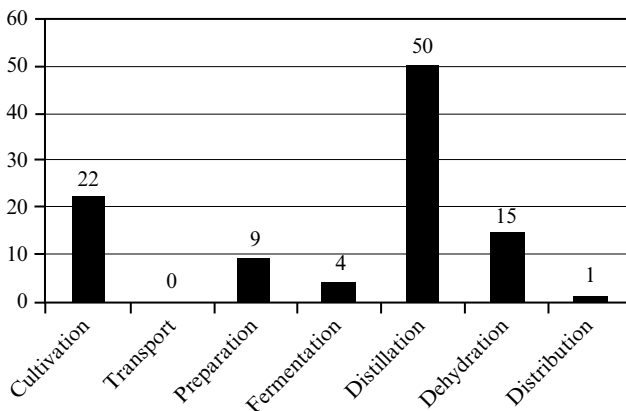


Fig. 9.2 Energy breakdown as a percentage based on wheat or beet ethanol production steps (After ADEME/DIREM 2002)

The production of bioethanol from cereals or starchy crops for manufacturing biofuel (ETBE) is initiated as soon as the agricultural resource is available. Examples of 6 m³ bioethanol production units exist on the market at a modest cost (large farm or village scale). The bioethanol obtained can be mixed directly up to 20 % with gasoline, using pumps, without changing engine settings. For an 85 % ethanol (referred to, in Europe, as E85), vehicles must be equipped with an ethanol-flex fuel system and the country is required to implement a distribution network for this E85 biofuel.

Processes can be used for recovering the effluents and by-products from ethanol production, for example, dry pulps may be used for animal feed, the residues recovered at the bottom of the distillation column may be spread as an amendment on farm land (subject to prior authorization), solid residues from grinding steps may be utilized as a fuel for thermal power plants. As an additional bioethanol outlet, hydrogen may be produced by reforming to be used in fuel cells.

Figure 9.2 shows the energy breakdown required for wheat ethanol production. This process mobilizes 0.49 MJ of nonrenewable energy per MJ supplied (i.e., 13.1 MJ of nonrenewable energy mobilized per kg supplied) and overall energy efficiency (energy restored/nonrenewable energy mobilized) is, as such, 2.05 (ADEME/DIREM 2002). In comparison, 1.15 MJ of nonrenewable energy must be mobilized to supply 1 MJ from petrol, with an efficiency of 0.87.

We can also see that 65 % of the energy required for producing bioethanol comes from the distillation and dehydration steps. In addition, free heat, from power plants and from the metallurgical industry may be utilized in such a process

Around 100 kg of ethanol is produced from 300 kg of dry starchy plant matter, which corresponds to one ton of potatoes, sweet potatoes, or starchy plants. By contrast, around 100 kg of ethanol can be produced from 200 kg of corn (dry matter).

If we wish to get a mixture of gasoline incorporating 10 % (in NCV, net calorific value³) of bioethanol, and if we take account of the ratio between the NCVs, then 1 t (≈ 0.6 toe) of ethanol needs to be incorporated in 6 t (≈ 6 toe) of gasoline. Knowing (see Table 9.1) that the ethanol net production is 1.25 toe/ha/year for wheat and 2.9 toe/ha/year for beets (even better for sugar cane ≈ 3.5 –4 toe/ha/year and less for starchy plants that comprise 70 % water), then the dedicated cultivation surface area for the production of 1 ton E10 (0.86 t gasoline and 0.14 t ethanol, containing 10 % bioethanol, according to the NCV criterion) will be 0.11 ha for wheat and 0.05 ha for beets. In intertropical regions, the use of sugar cane leads to slightly higher efficiency (≈ 10 %), therefore to a dedicated surface of around 0.045 ha.

9.2.2 *Crude Vegetable Oils and Vegetable Oil Esters (FAME, Fatty Acid Methyl Ester, FAEE; Fatty Acid Ethyl Ester)*

On a worldwide scale, soya oil represents the most important global production of crude vegetable oils (CVO), followed by palm oil, then rapeseed oil, sunflower oil, peanut oil, coconut oil (copra), and olive oil. The oils consist mainly of triglycerides, around 95–98 %. These latter are made up of an esterified glycerol molecule with three fatty acid molecules that may be either similar or different. Each oil has its own fatty acid composition, comprising between 6 and 21 carbon atoms.

There are three steps in the process for producing CVOs: trituration (seed crushing, cooking, and pressing), extraction (extraction of the oil contained in the oil cakes using solvent (n-hexane) at a temperature lower than 70 °C), and refining.

These CVOs are characterized by a molecular chain length that is longer than that of diesel, with high distribution and a significant number of unsaturations, a molecular weight of around 0.88 kg/mol and a density of more than 910 kg/m³. They are low-volatile oils and crack from 300 °C. The composition of the oil affects their viscosity, their resistance to cold, their ignition time, and their temporal stability. If used in an engine, the high viscosity that affects atomization, the low volatility that increases the ignition time, the deposits on the walls of the chamber, and the observed congealing problems at low temperature impair diesel engine running. Their dilution in lubrication oils should also be mentioned as this causes the engine to wear more quickly. All these drawbacks prove that direct use of such oils in modern engines will be increasingly critical.

Moreover, the use of these oils increases emissions of CO (+100 %), of unburned hydrocarbons HC (+400 %), which are frequently considered as carcinogenic particles (+90 to +400 %), of aldehydes and ketones (+30 to 330 %) and of polycyclic aromatic hydrocarbons PAH (+20 %); on the other hand, the formation of NO_x

³The *Net Calorific Value* (NCV) of a substance, is the amount of heat released during the combustion of 1 kg, the water produced being still considered as a vapor. The NCV of ethanol and of gasoline are, respectively, 26.8 and 42.7 MJ/kg, and their ratio is #0.6.

Table 9.1 Crop efficiency for producing agrofuels in temperate-region countries (first and second generations)

	Mass production (t/ha/year)	Energy gross production (toe/ha/year)	Energy net production (toe/ha/year) inputs deducted	Theoretically usable surface areas (nonaccumulable)	Industrial deadlines	Optimized provision cost (excluding taxes)
Wheat ethanol	~2.8 tons of ethanol/ha/year	~1.8	~1.25	~10 M ha (100 % foodstuffs)	Immediate	~0.5 €/l (NCV coefficient 0.64)
Beet ethanol	~6.5 tons of ethanol/ha/year	~4.1	~2.9	~1 M ha (including 50 % foodstuffs)	Immediate	~0.4 €/l (NCV coefficient 0.64)
FAME (rapeseed)	~1.5 tons of FAME/ha/year	~1.35	~1	~4 M ha (including 50 % foodstuffs)	Immediate	~0.5 €/l (NCV coefficient 0.9)
Cellulose ethanol by fermentation	~12 tons of DM/ha/year	~2	~1.5	~10 Equivalent M ha (agricultural and forest)	~2015	(NCV coefficient 0.64)
BtL–thermo–chemical autothermic (green diesel)	Idem	~2	~1.5	Idem	2010–2015	~0.7 €/l (NCV coefficient 1)
BtL–thermo–chemical allothermic (green diesel)	Idem	~4	~3.5	Idem	2020	~0.7 €/l (NCV coefficient 1)

Source: After Roy, 2008, Interministerial coordinator for biomass energy, personal communication

BtL Biomass to liquid; Autothermic and Allothermic: with or without external energy contribution (see Sect. 9.3.2); *DM* is for dry matter; *NCV* is for natural calorific value; *NCV* coefficient 0.64 means the *NCV* ratio ethanol/petrol is 0.64

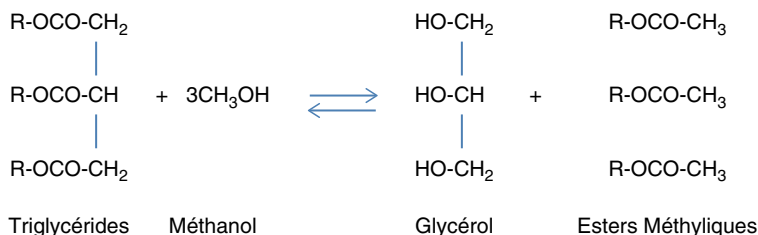


Fig. 9.3 The transesterification reactions

is reduced (-25%) as a result of the lower combustion temperature. If such oils could be used directly in tractors or power generators, their use in modern engines would come up against the same limitations as their use in automobile engines.

Direct CVO use in an engine (especially direct injection engines) is, therefore, limited and modifies engine performances. Only the few engines remaining that are fitted with a precombustion chamber and have an extremely low revolution speed (marine engines, old agricultural equipment, certain power generators) can use these oils. There seem to be fewer drawbacks but wall deposits are liable to form over the long term.

Once purified, crude vegetable oils are sometimes used as fuel for specific diesel engines, but the technology and the performance of new engines have requirements that can no longer accept these fuels. These oils are now transesterified with alcohol (generally methanol or ethanol) to produce fatty acid methyl ester (FAME) and fatty acid ethyl ester (FAEE). As such, this ester may be used in any diesel engine by mixing the diesel, of any concentration, even pure, which helps reduce the consumption of fossil fuels.

9.2.3 Processes for Producing FAME (Fatty Acid Methyl Ester) and FAEE (Fatty Acid Ethyl Esters)

When the CVOs are transesterified the triglycerides are transformed by the catalytic reactions of trans-esterification in a basic medium by methanol to form methyl esters and to form a subproduct: glycerol. One hundred kilograms of alcohol need to be added to a triglyceride cake to obtain one ton of biodiesel and 100 kg of glycerol that must be eliminated or utilized. This reaction requires the reagents to be slightly heated (see Fig. 9.3).

Transesterification may also be carried out using ethanol via a similar process; ethyl esters FAEE with similar properties to FAME are produced. Oil ester and glycerine is formed once the excess alcohol evaporates.

These esters are fatty acids used in human foodstuffs and animal feed and, they have a low impact on the environment. They are totally biodegradable which, unfortunately, results in their rapid oxidation; they are, as such, not very stable and it is compulsory to add additives for storing them.

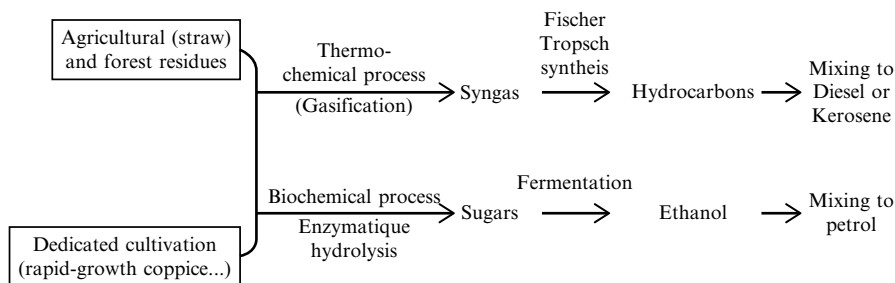


Fig. 9.4 Future production pathways for manufacturing second-generation biofuels

Direct FAME or FAEE use in diesel engines does not lead to the drawbacks related to CVO use. These esters are even beneficial for the lubrication of fuels with very low sulphur content. They are miscible with diesel (they may be used mixed with diesel or even pure) but their calorific value is slightly lower and leads to a 7 % higher consumption (Ballerini 2006).

FAEEs have a positive impact on the environment with, generally, a decrease in CO, HC, and particle emissions but with an increase in NO_x.

Similar to first-generation fuels, two pathways are used for utilizing this lignocellulosic resource: a thermochemical production pathway (dry) and a biological one (moist). The general principle is illustrated in Fig. 9.4.

9.3 Second-Generation Biofuels

This type of fuel is still in the research phase and has a number of aims: the utilization of the whole plant (seeds and stems) as well as the utilization of the wood and waste wood (lignocellulosic matter) and a reduction in the competition with food crops.

9.3.1 Lignocellulosic Biomass Resources

This resource comes from agricultural, forest, and wood transformation subproduct waste as well as from dedicated cultivation, whether it may be woody plants or herbaceous plants. Fuelwood represents half of the gross world production of this resource; the other half covers industrial uses (materials). Transforming wood generates a considerable quantity of waste recyclable in the form of energy or of raw material for trituration; dry agricultural and forest waste that also provides significant quantities of lignocellulosic biomass. Dedicated cultivation is an important source of lignocellulose (poplars, eucalyptus, willows, short rotation coppice and other herbaceous species, such as miscanthus) that is energetically utilizable.

The characteristics of the raw material influence the energy conversion process. For example, the concentration of inorganic matter disadvantages thermochemical conversion, the concentration of ash conditions the temperature of the reaction, as such, and the efficiency of the process, the concentration of sulphur and of nitrogen are responsible for the formation of pollutants that must be purified. The percentage of lignin, moisture, and its granulometry also play an important role. By contrast, in biochemical processes, it is the lignin that controls the conversion.

The lignocellulosic biomass resource is real or potential in different parts of the world, but the degree of mobilization of this resource depends greatly on the constraints of continuity of supply and of the land policy of the country, of standardization of the quality, and the cost of the cultivation (plantation, maintenance, exploitation, transport). This resource has two major interests, and this is one of the major challenges for the pathway: not to be in competition with food crops, a choice that might lead to the starvation of the world, and to make forest maintenance profitable (carbon storage protection).

Furthermore, these processes lead to clean synthetic fuels without aromatic molecules that are liable to affect health.

9.3.2 The Thermochemical Pathway

The thermochemical conversion of the lignocellulosic biomass will represent a major challenge to the world for 2020. It is currently referred to as BtL (biomass to liquid). Two main production pathways exist for producing energetically utilizable products: pyrolysis and gasification (Ballerini 2006).

9.3.2.1 Pyrolysis

Pyrolysis is thermochemical transformation of a solid fuel (coal, biomass, etc.) which is carried out in an inert medium (no oxygen). Two pyrolysis processes have been developed for biomass processing: a slow and a fast one.

In slow pyrolysis, the heating is performed at a slow rate (<50 °C/min) up to 600 °C and with a residence time of some hours. The result is essentially vegetal charcoal.

On the contrary, during fast pyrolysis the heating is performed at a much higher rate (100 °C/s) up to 500/550 °C and with much smaller residence times (on the order of 1 s). As a result of the action of heat and the lack of oxygen, lignocellulose constituents are pyrolyzed and may be converted here in three phases: the solid (vegetable coal), the condensable organic compounds (oils rich in oxygen), and the gases, where the main ones are CO₂, CO, H₂, and CH₄. By controlling process parameters, these reactions may be directed towards the preferential production of one of these three phases and efficiency may be maximized.

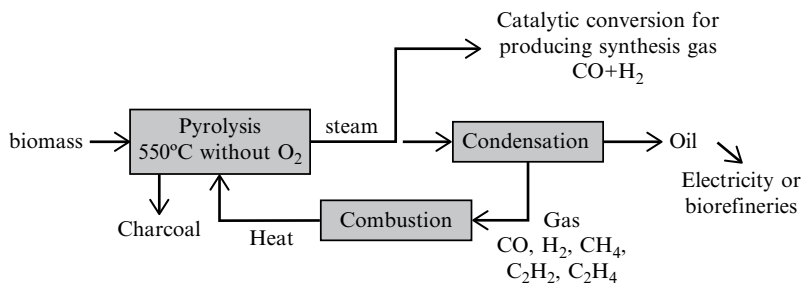


Fig. 9.5 Diagram of a fast pyrolysis principle

Fast pyrolysis is an homogenization stage and, as such, it is useful for preconditioning the biomass. This process has two advantages:

- To produce, from heterogeneous lignocellulosic composites (which are difficult to use or to transport in their common state) homogeneous and transportable solid or liquid intermediates such as charcoal and pyrolysis oils.
- As such, to decouple temporally biomass production and utilization. In this way, the production unit is established close to the resource so that raw material transportation costs are minimized; biofuel transformation is centralized and benefits from the scale effect on investment.

Another advantage of biomass pyrolysis concerns the versatility of the technology which, depending on operating conditions (heating speed, temperature, residence time in the reactor, and pressure), can direct the reaction to liquid, solid, or gas and thus recover or concentrate the undesired fractions in one of these phases.

Fluidized-bed, ablative, and vacuum processes generally adhere to the diagram displayed in Fig. 9.5. They generate gaseous compounds, which, following cooling and condensing, are recovered as a liquid phase, the noncondensable gases and the charcoal are recovered to be burned and to be used as auxiliary energy for pyrolysis. Pyrolysis oils contain several hundred chemical compounds in highly variable molecular proportions and weight. They are rather unstable (decomposition above 100 °C) and present a rather high acidity (risk of corrosion)

The technology is mature but still lacks opportunities. Pyrolysis oils may only be used in a few engines that are specially designed for electricity production but they must be excluded from use in a gas turbine or an automobile engine (oils cracking is difficult if they only spend a short time in the combustion chamber, which thus explains the high amount of unburned particles in the smoke and of destructive deposit of oils on the walls). The most promising operation concerns the gasification of oils and/or of charcoal to produce syngas which is then converted into methanol or hydrocarbon using the Fischer–Tropsch process (see the following section, “Gasification”). The gasifier could, thus, work with oils with similar characteristics but from different biomasses.

9.3.2.2 Gasification

Gasification is the thermochemical transformation of a solid fuel (coal, biomass, etc.) using a reactive gas (oxygen, water vapor, hydrogen, etc.) compared to pyrolysis, which is carried out in an inert medium. The aim is to convert the solid into a gaseous mixture, referred to as “syngas” or synthetic gas containing H_2 and CO with other minor species CO_2 , H_2O , CH_4 , in proportions that depend on the process used.

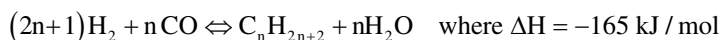
The gaseous mixture obtained may be used here for different applications:

- Engine combustion
- Heat and power cogeneration, with an improved efficiency compared to direct biomass combustion, given the increase in combustion temperature (efficiency up to 40 % of the biomass NCV)
- Biofuel synthesis, including liquid hydrocarbons including synthetic gasoline, kerosene, or diesel (because of their linear chains they must be mixed with fossil hydrocarbons to ignite the fuel correctly in the chamber).

With regard to combustion, syngas may contain methane and heavier compounds. But concerning biofuels synthesis, it is better to get a syngas with a maximum conversion into CO and H_2 , and more precisely a ratio H_2/CO , in volume, close to 2. The process is normally autothermic.⁴ But, to increase gasification efficiency, an allothermic⁵ process is preferable and the introduction of external hydrogen can favor the CO/H_2 ratio in syngas.

Lignocellulose gasification (syngas) or pyrolysis oils process must be followed by a Fischer–Tropsch synthesis so that the liquid fuel produced corresponds to a mixture of hydrocarbons such as gasoline, diesel, or kerosene.

The Fischer–Tropsch process consists in establishing the catalytic reaction, at a temperature of 220 °C, of syngas, with a H_2/CO ratio close to 2.05, so that saturated paraffin (C_nH_{2n+2}) may be produced, ranging from ethane to $C_{80}H_{162}$, with cobalt as the catalyst.



This reaction is highly exothermic and one of the technological barriers is the cooling of the multiple reactors. By controlling the temperature, the H_2/CO ratio, the gas flow rate (residence time), and the type of catalyst, the optimal hydrocarbon may be selected that has a large number of carbons (between C_{10} ⁶ and C_{20} , similar to diesel) and oil-refining chemistry is then applied. These Fischer–Tropsch units

⁴*Autothermic*: The reactions involved in the process are globally endothermic, but some of them are exothermic and can provide an internal energy contribution to the process. An endothermic reaction needs an external heat to be provided to the system. An exothermic reaction creates heat that must be evacuated to the external ambient.

⁵*Allothermic*: With contribution of external energy.

⁶ C_{10} and C_{20} : Hydrocarbon molecules with, respectively, 10 or 20 carbon atoms.

should be set up close to a refinery: the natural gas to liquid fuel (GtL) process is carried out in the same way as that of coal or of biomass to biofuels and such a pilot unit exists in the United Arab Emirates. Let us also mention that the diesel obtained has high qualities: no sulphur, no nitrogen, no metal, no aromatic compounds, and a good cetane index (70/75 compared to 50 for commercial diesel).

Biomass gasification using this thermochemical process still lacks maturity, as it is still better adapted to coal gasification than to that of the lignocellulosic biomass. In addition, a continual and significant flux of biomass and/or coal resource is required to be able to establish an installation big enough to ensure efficiency of 30–40 % (allothermic process).

Efficiency not only depends on the gasification technology, but also on the choices made for the overall integrated process, in upstream steps (using the biomass directly or products from slow or fast pyrolysis), as well as in downstream steps, particularly as regards developing subproducts using Fischer–Tropsch synthesis, such as gases and naphthas: gases may be burned and supply part of the energy required for the industrial unit to operate.

To retain some figures, carbon efficiency from autothermic processes is less than 30 %. A supply of external energy, for example, as electricity injected into the gasifier or during the high-temperature gas reforming step, or a supply of external mass hydrogen, may increase efficiency significantly up to 40/50 %.

9.3.3 The Biochemical Pathway

The use of biomass to supply renewable fuel for transportation was first integrated in our economy in the first-generation biofuels by converting the edible part of crop biomass (stored sugars or lipids) into ethanol or biodiesel (first generation). With first-generation biofuels coming under increasing criticism for driving up food prices and putting biodiversity at risk, politicians and scientists turned their gaze towards next-generation biofuels (advanced biofuels), the production of which use the nonedible part of biomass (lignocellulose; second-generation biofuels), and new energy crops (third-generation biofuels; for instance, H_2 , microalgae). However, the technologies behind these new forms of bioenergies are not yet mature owing to biological and technological barriers. Major efforts in R&D are therefore required to create innovative processes for the production of advanced biofuels. In the following pages we present an overview of the different biological energy alternatives that are currently the subject of intense research; we also identify the major obstacles that need to be overcome for each of them.

9.3.3.1 Recall of the Main Steps to Accomplish

Although the process for producing ethanol from the sucrose of sugary plants or from the starch of starchy plants is mature (first generation), the process of ethanol

production from lignocellulosic matter (second generation) comes up against two barriers: the hydrolysis of cellulose to fermentable sugars and the conversion of pentoses from hemicellulose to ethanol. As lignin cannot be fermented in ethanol, the lignocellulosic matrix must be preprocessed to make the cellulose and the hemicellulose hydrolyzable to obtain potential sources of fermentable sugars

9.3.3.2 An Enzymatic Approach to the Production of Biofuels from Lignocellulose

The production of second-generation fuels from lignocellulosic biomass displays many benefits (energetic, economic, and environmental) that are associated with the use of enzymes or microorganisms as catalysts.

The process includes an enzymatic saccharification (breakdown to C₅ and C₆ sugars⁷) of the pretreated plant biomass, performed by the enzymes of a cellulolytic fungus, *Trichoderma reesei*. This step accounts for approx. 50 % of the total cost of production, because a huge amount of enzyme (about 1 % of the mass of substrate) is needed, especially for the hydrolysis of the main polymer, cellulose. Use of microbes for fermentation is the most common method for converting sugars produced from biomass into liquid fuel. To develop commercially viable processes for cellulose bioconversion to ethanol, an organism is needed that uses all sugars (C₅ and C₆) produced from biomass saccharification, at rates and in high alcohol concentrations that match or surpass current yeast-based glucose fermentation.

Trichoderma reesei is the primary producer of cellulase and hemicellulase because it secretes high amounts of cellulase (100 g/L). Analysis of its genome revealed a surprising small set of genes encoding enzymes for the breakdown of plant cell wall polysaccharides thereby suggesting this cocktail could be improved by additional enzymes. Furthermore, it was recently reported that some proteins devoid of measurable activity can significantly improve the activity of plant cell wall (PCW) degrading enzymes or cocktails, thus showing that our understanding of the mechanisms underlying the enzymatic degradation of biomass is far from complete. In an effort to identify novel enzymes or synergistic factors that would efficiently boost the enzymatic cocktail of *T. reesei*, Henrissat's group has surveyed a large number of fungal and bacterial genomes to identify putative novel proteins involved in plant cell wall digestion (Weiner et al. 2008; Martinez et al. 2009; Yang et al. 2009; Ma et al. 2010). Another promising approach lies in the exploration of atypical cellulolytic systems in which the catalytic subunits are gathered in huge complexes of 1 MDa⁸ range called cellulosomes. Cellulosome engineering exhibits an important potential for biotechnological applications including biofuel production (Mingardon et al. 2007). Furthermore, anaerobic

⁷Hydrocarbon molecule with respectively five or six carbon atoms.

⁸1MDa = 1M Dalton = 10⁶ Da; 1 Da = 1 amu (atomic mass units).

bacteria represent a source of novel enzymes that can be mixed with fungal enzymes for improving the overall performance of the enzymatic cocktail. Another application is the introduction of an optimized cellulosome in a biofuel producer to establish a single-organism process enabling the direct conversion of biomass into biofuel.

9.4 Third-Generation Biofuels: Algae and Microorganisms

9.4.1 Using Microalgae for Biofuels

Microalgae are photosynthetic microorganisms that convert water and carbon dioxide in cell material using sunlight. Microalgae are receiving more and more attention as the search for sustainable and profitable biofuel feedstocks progresses. They exhibit several advantages, when compared to other biofuel crops such as wheat, corn, rapeseed, or sunflower. Microalgae show a very high surface productivity and they can be produced on noncultivable land surfaces, therefore not competing with food production by agriculture. Three different types of energy compounds can be produced by microalgae from which biofuels are made: lipids (transesterification will give biodiesel), starch (fermentation will give bioethanol), and biohydrogen (for reviews see Radakovits et al. 2010; Stephens et al. 2010; Larkum et al. 2011). When compared to major crops, microalgae show a very high productivity potential.

In spite of a high productivity potential, large-scale cultivation of microalgae shows relatively low sunlight conversion yields into biomass (from 0.5 to 3 %), much lower than the maximal photosynthetic conversion yield (~10 %). At a laboratory scale it is, however, possible to approach theoretical limits, but the existence of biological limitations considerably lowers the yields, especially when the metabolism is oriented towards the production of high-energy compounds. During growth in optimal conditions, the photosynthetic metabolism is oriented towards cellular growth and division. Cells accumulate high-energy compounds only in response to unfavorable conditions, such as nutrient deprivation (nitrogen, sulphur, etc.). This response allows optimizing survival and awaiting a return to better conditions. As a result, accumulation of lipids or starch relies on a phase of nutrient starvation which considerably lowers production yields.

9.4.1.1 Lipids for Biodiesel

The most abundant microalgae studied for biodiesel production are *Cyanophyceae* *Synechocystis* (blue green algae, Fig. 9.6), *Chlorophyceae* (green algae), *Bacillariophyceae* (diatoms), and *Chrysophyceae* (golden-brown algae). Some unicellular microalgae, such as *Chorella* or diatoms, accumulate triglycerides in response to



Fig. 9.6 Examples of microalgae: *Cyanophyceae Synechocystis* (with permission Y. Tsukii)

Table 9.2 Comparison of lipid productivity of major crops and microalgae

Plant source	Seed oil content (% oil by wt in biomass)	Oil yield (L oil/ha year)	Land use (m ² year/kg biodiesel)	Biodiesel productivity (kg biodiesel/ ha year)
Soybean	18	636	18	562
Jatropha C.	28	741	15	656
Camelina S.	42	915	12	809
Rapeseed	41	974	12	862
Sunflower	40	1,070	11	946
Palm oil	36	5,366	2	4,747
Microalgae (low oil content)	30	58,700	0.2	51,927
Microalgae (medium oil content)	50	97,800	0.1	86,515
Microalgae (high oil content)	70	136,900	0.1	121,104

nutrient shortage (nitrogen for most microalgae, silicium in the case of diatoms). Lipid accumulation can reach up to 60 % dry weight in some algal species. Table 9.2 presents the lipid production yield of main crops and microalgae. Lipid accumulation by algae is of considerable biotechnological interest in the perspective of producing renewable biodiesel.

However, at present there is a major discrepancy between predicted hydrocarbon yields based on laboratory experiments and the measured hydrocarbon yields of large-scale algae production systems. Algae possess a variety of lipid types ranging from the less commercially useful membrane-bound polar lipids to large

droplets of unbound triacylglycerols, which are of prime interest as a biofuel source. Identifying those algal species capable of producing large stores of readily extractable neutral lipid droplets is the first step in the development of algal biofuels as an economically viable fuel source. On the other hand, the lipid content may vary according to the growth conditions. This means that it is theoretically possible to improve the lipid content in cells by adapting growth parameters but also by modifying the metabolic pathways responsible for lipid production. Several research programs around the world are currently devoted to exploring biodiversity to discover the best organism able to reach both a high growth rate and high lipid content. Global studies such as proteomic and transcriptomic are also being conducted in order to better understand the whole metabolic processes leading to lipid accumulation, and to identify the main enzymes as potential targets for metabolic engineering. Photobioreactors have allowed the production of such lipids at the lab scale (Pruvost et al. 2009).

9.4.1.2 Starch for Bioethanol

Carbohydrates are produced by microalgae mainly under nitrogen starvation conditions. They can be transformed by a subsequent fermentation step into a variety of biofuels, including ethanol, butanol, H₂, lipids, and/or methane. Glucans⁹ are stored in microalgae in a variety of ways. The phyla *Chlorophyta*, *Dinophyta*, *Glaucoephyta*, and *Rhodophyta* store glucans in linear α -1,4 and branched α -1,6 glycosidic linkages. In *Phaeophyceae* and *Bacillariophyceae*, water-soluble granules of laminarin and chrysolaminarin are synthesized, which are made up of β -1,3 linkages with branching at the C-2 and C-6 positions of glucose. In green algae, starch is synthesized and stored within the chloroplast, whereas it is stored in the cytoplasm in *Dinophyta*, *Glaucoephyta*, and *Rhodophyta* and in the periplastidial space in *Cryptophyceae*.

Most microalgae do not contain lignin because they do not require the mechanical support that lignin provides. The fact that microalgae produce fermentable carbohydrates without containing lignin makes them an attractive feedstock for bioethanol production. This is especially true when the superior productivity of microalgae is taken into account. Table 9.3 illustrates the differences in productivity of three terrestrial crops and three microalgae. The microalgae exhibit considerably higher productivity. It is clear that they have the potential to produce more fermentable carbohydrates annually per hectare than terrestrial feedstock, despite containing a lower percentage of fermentable carbohydrates, because of their high rates of productivity. Table 9.3 also shows that the terrestrial feedstock produces a considerable amount of lignin annually, which inhibits their efficient conversion to bioethanol.

⁹Glucans are polysaccharides of D-glucose monomers, linked by glucosidic bonds.

Table 9.3 Comparison of lipid productivity of major crops and microalgae

Feedstock	Biomass productivity (dry T/ha · year)	Fermentable carbohydrate (%)	Lignin (%)	Fermentable carbohydrate productivity (T/ha · year)	Lignin productivity (T/ha · year)
Corn	7	80	15	5.6	1.05
Switchgrass	3.6–1.5	76	12	2.8–11.5	0.4–1.8
Woody biomass	10–22	70–85	25–35	7–18.7	4–7.7
<i>Chlorella</i>	127.8–262.8	33.4	0	42.7–87.8	0
<i>Tatraselmis</i>	38–139.4	11–47	0	4.2–65.5	0
<i>Anthrospira</i>	27–70	15–50	0	4.1–35	0



Fig. 9.7 Large-scale cultivation of microalgae in open ponds: Earthrise Farms, California (Aerial photo of Earthrise Nutritional Spirulina ponds with photoshop of microscopic spirulina algae in ponds by Robert Henrikson (2010), with permission)

9.4.1.3 Algae Cultivation, Harvest, and Extraction

Microalgal productivity depends on the culture system used. It is relatively low for open-pond systems (Fig. 9.7), and can be much higher for closed photobioreactors which allow better control of culture parameters and contamination with other species. Cultivating photosynthetic microorganisms in closed photobioreactors limits the environmental cost by recycling water and nutrients. Microalgae may also use industrial or urban waste as sources of CO₂, nitrogen, or phosphate. Considering the low productivity of the open-pond system and the high costs of closed photobioreactors, industrial applications of microalgae are presently limited. In this context, production of biofuel from microalgae can only be considered as a side product of an economically viable production. After separation of high-value compounds, residual

biomass can be used for energy production through lipid extraction, hydrogen, or ethanol production from fermentation. It is estimated that productivity of microalgae actually obtained in production systems should be increased fivefold to meet the criteria of profitability.

It is believed that among the most costly downstream processing steps in fuel production using microalgae are the harvesting/dewatering steps and the extraction of fuel precursors from the biomass. Based on currently achievable productivities, most microalgae will not grow to a density higher than a few grams of biomass per liter of water. Although there are several possible low-cost solutions to concentrating the biomass, including settling and flocculation, these methods are slow and the resulting biomass may still require further dewatering. Alternative methods to concentrate algal biomass include centrifugation and filtration, which are faster, but are also typically much more expensive and energy intensive. In addition, many microalgal species have a very tough outer cell wall that makes extraction of fuel feedstock difficult, thereby requiring the use of harsh lysis conditions. The addition of all these steps dramatically raises the cost of the biofuel produced, meaning that the process is not economically viable.

One possible solution is to manipulate the biology of microalgal cells to allow for the secretion of fuels directly into the growth medium. There are, in fact, several pathways in nature that lead to secretion of hydrophobic compounds, including TAGs (triacylglycerol), free fatty acids, alkanes, wax esters, and soluble sugars. However, the introduction of metabolic pathways for the direct production of fuels faces many challenges. The product yields for pathways that lead to the accumulation of compounds that are not necessarily useful for the cell are unlikely to be economically viable without the comprehensive engineering of many aspects of microalgal metabolism. In addition, many types of fuel products have the potential to be toxic, and tolerant species of microalgae may have to be generated.

9.4.2 Biohydrogen Production by Microorganisms or Using Bacteria for Hydrogen Production

In the biosphere, H₂ (hydrogen) is generated by different metabolic processes in a wide range of microorganisms. It is also the energy source of many living species using hydrogenases as catalysts. The enzyme catalyzes the heterolytic splitting of H₂ ($H_2 = H^+ + H^-$). The most significant discoveries on the structure/function of hydrogenases have been exclusively carried out by European research groups (Brugna-Guiral et al. 2003; Liebgott et al. 2009; Dementin et al. 2006, 2008, 2009; Rousset and Cournac 2008; Fernandez et al. 2007; Pandelia et al. 2010a, b, 2011). Hydrogenases could potentially replace platine as a first-row transition element in fuel cells, with the advantages of specificity, biodisponibility, and biodegradability (Lojou et al. 2008; Luo et al. 2009; Ciaccafava et al. 2010, 2011; Armstrong et al. 2009).

9.4.2.1 Biophotoproduction by Algae

Some microalgae, such as *C. reinhardtii*, harbor an hydrogenase interacting with the photosynthetic electron transfer chain. This property allows these organisms to produce hydrogen using light as the sole energy source. When an anaerobic adapted culture of *C. reinhardtii* is placed in the light, hydrogen production is observed for a few minutes at very high efficiency (close to the maximal photosynthesis yield ~10 %). However, hydrogen photoproduction rapidly stops, the hydrogenase being sensitive to oxygen produced at PSII (Photosystem II). Melis et al. (2000) proposed an experimental protocol to overcome this main limitation. Sulphur deprivation triggers PSII degradation. This results in installation of anoxic conditions because O₂ consumption by respiration becomes higher than its production. However, the general cellular metabolism is also severely affected by sulphur starvation, therefore considerably lowering the productivity of the algal culture. Two main research pathways are currently being explored for biohydrogen production by microalgae. The first is to control PS II activity and starch accumulation in nutrient-replete conditions. The second is to study at the enzyme level the mechanisms of hydrogenase inhibition by O₂. Once understood, the basic mechanism of natural algae has been reproduced by artificial means (biomimeticism) and has led to the conception of photobioreactors (Fouchard et al. 2008; Shi et al. 2011).

9.4.2.2 Dark Fermentation by Bacteria

Dark hydrogen fermentation (or anaerobic digestion) is an attractive pathway to produce H₂. This metabolism is ubiquitous in nature under anaerobic conditions. The advantage of dark fermentation is that the H₂ production rate can be of a magnitude higher than those achieved by other means. Moreover, dark fermentation systems are relatively simple to construct and their functioning does not consume much energy. However, the amount of H₂ produced per molecule of fermented hexose (i.e., yield) is low. Instead of the expected 12 H₂ per hexose if 100 % conversion of hexose electron equivalents occurs, a yield of 2 H₂ per molecule of hexose is obtained (Nath and Das 2004) except in some thermophilic bacteria such as *Caldicellulosiruptor* that reach a molar yield close to 4 H₂ per hexose. Another advantage is that fermenting bacteria can utilize complex forms of organic substrate for H₂ production, that is, cellulose, food waste, and urban and industrial waste. These sources represented about 849 million tons worldwide in 2006. Pure cultures (i.e., containing a single microorganism species) have been intensively investigated in fermentation processes, including *B. coagulans*, *Thermoanaerobacterium* spp., *E. aerogenes*, and *C. butyricum*. In contrast, the use of mixed cultures (i.e., containing a mix of different microorganism species), which allows the degrading of more complex substrates, has received little attention. The major obstacle of mixed culture is the presence of three classes of microorganisms that establish close metabolic interactions, that is, H₂ producers, H₂ consumers (methanogenic bacteria producing methane), and metabolic competitors. The control of H₂ consuming

pathways constitutes the main challenge for improving the stability of the fermentation process in bioreactors treating agricultural waste. Various studies have enabled the identification of major strains present in the bacterial consortia that develop spontaneously in fermenting wastes; yet few of these studies were completed by a metabolic characterization of the organism. Moreover, uncertainties remain regarding the identity of minor species as well as their role in the control and resilience of the process.

9.5 Conclusion

In a context of increasing world energy demand, biomass conversion into energy can propose a contribution to the mitigation of GHG emission and to the limitation of climate change. It has the potential to make a significant contribution to the energy mix, particularly biofuels for transportation. But the development of biofuels still requires awareness with regard to the complexity of the global problem where both the scientific and technological issues, but also the environmental, social, and economic impacts must be considered. The processes from well-to-wheel must be discussed in terms of a positive energy balance, GHS emission reduction, biodiversity and forest protection, environment degradation limitation, water availability, and food.

This chapter is essentially oriented towards the scientific and technological issues of the three biofuel pathways. An interesting complement can be found in Chap. 14 which gives a more worldwide and geopolitical analysis of first-generation biofuel potential and risks (environmental impacts, energy efficiency, world hunger, etc.).

Our chapter proposed a scientific state of the art on the three generations of biofuels and, when available, on the manufacturing processes.

Technologies, such as the first biofuel generation, that value the reserves of plants (starch, sugar, oil), are already fully mature and industrially controlled and they have still a fair potential of deployment.

The second biofuel generation that turns to the whole plant tissues (agricultural, forest, or organic waste resources), are rather operational for dry processes (thermochemical transformation of lignocellulose), and research is still underway for wet processes (enzymatic biological transformation of lignocellulose in sugars, and fermentation). Although these processes are already scientifically and technologically almost validated, or on the way to being so, the economical cost remains high as regards fossil fuel, the energetic and environmental balance must still be validated, and the indirect impacts of the pathways assessed.

Finally, very innovative processes have been developed on the third biofuel generation that show significant potential by transforming lipids, starch, and biohydrogen, thanks to bioalgae or microorganisms, into biofuel, which is a completely new concept in comparison with other biofuel crops such as wheat, corn, rapeseed, or sunflower. Fundamental research studies are still to be developed to describe the rather complex involved biological processes. Additional locks subsist on the

cultivation, harvest, and extraction of algae to assess pathway productivity depending on the culture system and energy required for extracting a very low proportion of oil from a great water volume for producing biofuel.

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