

# Chapter 2

## Bioenergy and the Sustainable Revolution

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### 1 Introduction

In this chapter, we will discuss some unexpected consequences that renewable energy policies might present for technological development and present an overview about the main current approaches to produce Biofuels. The technological barriers and alternatives investigated to overcome them are also discussed. In the first section, we argue that such radical changes in the way we think and sustain our development might imply that we are facing a new revolution in our energy production system. We proceed to elucidate some principles that are likely to determine the ideal and actual scenario of renewable fuels, including how ethanol can succeed and how biotechnological approaches chosen to produce second generation ethanol imply coping with the high complexity of lignocellulosic material. We also discuss the principles of biodiesel production, the importance of this incipient biofuel might offer to the setting of ethanol industry. Finally, we discuss the advantages and main perspectives in the short-term developments expected by the promising area of thermochemistry to biofuel production.

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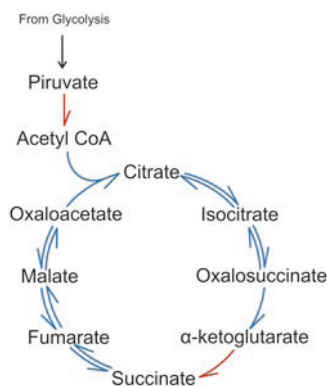
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## 2 Energy Revolution

### 2.1 Mitochondrial Revolution

Evolution does not always occur as a soft continuum of myriads of little adaptations. It sometimes jumps. Since the origin of life around four billion years ago, green–blue bacteria increased the amount of molecular oxygen ( $O_2$ ) in the atmosphere conspicuously. For most of the living organisms at that time (exclusively bacteria), oxygen was very dangerous. For some organisms it was (and still is) deadly. Thus, most bacteria lived only in oxygen-free environments. In the absence of oxygen, one of the main forms that heterotrophic organisms used to obtain energy was via the fermentation process. This process preserves part of the free energy content from a molecule of glucose in two adenosine-triphosphate (ATP) molecules, the standard energy fuel in catabolic processes. However, in this process, most of the chemical energy present in glucose is wasted as fermentation residues such as alcohol or lactic acid.

In the presence of oxygen, some organisms are able to accomplish cell respiration, a process in which glucose is completely oxidized to  $CO_2$  and 36 ATP are produced from every single glucose molecule!. About two billion years ago, micro-organisms undergoing selective pressure in an atmosphere that was becoming increasingly toxic with oxygen, developed the ability to tolerate and even obtain benefits from it. The last enzyme from the citric acid cycle to emerge and make possible respiration as we know it today was the  $\alpha$ -ketoglutarate complex. This is thought to have occurred by mutations of genes of the pyruvate dehydrogenase complex, an enzyme complex with a similar structure and role in the citric acid cycle in aerobic as well as in anaerobic organisms (Fig. 1).



**Fig. 1** Some anaerobic bacteria have the enzymes to produce several metabolic intermediates of the citric acid cycle. However, they cannot complete the cycle because they do not have the  $\alpha$ -ketoglutarate dehydrogenase, which converts  $\alpha$ -ketoglutarate into succinyl-CoA (red arrow in the cycle). This enzyme probably evolved from pyruvate dehydrogenase. Such complex performs a similar reaction converting pyruvate into acetyl-CoA (red arrow above). Both complexes exhibit three analogous enzymes and use the same cofactors (TPP, lipoate, FAD, NAD, and coenzyme A).

This highly efficient novel system for using energy from carbohydrates completely changed the biological scenario, making a whole new level of complexity in living organisms possible. From that time on, with more available energy, multicellularity became viable and many other types of organisms evolved. In other words, this energetic revolution was so powerful that today, most unicellular eukaryotes, all fungi, animals, and plants are dependent on mitochondrial machinery, the organelle responsible for accomplishing cell respiration.

## ***2.2 Modern Bioenergy: A Sustainable Revolution***

With the increase in population, which is expected to reach over nine billion people by the year 2050, the issue of availability of energy appears to be crucial. Humans are increasingly better at improving health and elongating life span. Furthermore, capitalism requires profit, continuous production of all types of products in order to survive. Therefore, over the next 40 years, humans will need to find a way to greatly increase efficiency of energy production.

The problem is that in the cycle of energy production that we are in, which is essentially based on fossil fuels, the excess of production of some useful or even essential molecules residues such as CO<sub>2</sub> turned them into pollutants. As a result, we discovered that we were poisoning the atmosphere and changing the climate (IPCC 2007). The environmental impacts are now regarded as fundamental for the survival of humans on this planet. As a consequence, the production of energy, food, and all products consumed by human societies will need to come out from sustainable ways of production.

As the evolutionary burst supported by the mitochondrial energetic efficiency, we also experienced successful development cycles based on the exploration of coal throughout the Industrial Revolution and still enjoy, sponsored by oil. We need to find a way to produce more energy in order to supply our development aims for the decades to come. However, we know that the consequences of this step can cause problems further into the future, our choices must be based on approaches capable of making the energy production system progressively sustainable. Although there are nuclear and geothermal nonbiological ways to obtain energy, the use of biomass to produce energy is certainly one of the more realist ways to increase energy production in short term, especially thanks to the advances obtained during the twentieth century in the areas of biochemistry and molecular biology. The production of energy from biomass is not new as humans have been burning wood for thousands of years. However, we are now reaching a point in which we can think and design, through synthetic biology, forms to improve plant photosynthesis and cell wall architecture to make cell wall carbohydrate more accessible to hydrolysis and available for fermentation. These two targets can possibly work to significantly increase energy production. This is because (1) improving photosynthesis efficiency can increase productivity of biomass, and (2) gaining access to the monosaccharides of the cell walls opens

the way to obtain energy from ca 70% of the plant body thus greatly increasing the production of energy in the form of biofuels as ethanol, for instance. Most chapters in this book are about the biochemical routes to obtain lignocellulosic ethanol. However, it is not (and cannot be) the only one to be adopted in biofuel production. Transesterification of plant fat acids are used to produce biodiesel and it is thought that the production of such hydrocarbons as well as a wide variety of other chemicals is also possible by chemical routes such as pyrolysis and gasification, as we discuss later in this chapter. Whatever the route, the development of technologies to efficiently use renewable sources of energy might imply a new age of social development without the ghosts of global warming and petroleum shortage. Although such technologies alone do not mean an energy revolution, they can be thought as a radical change in ways humans understand economy and development. Production and goods do not move in closed mechanical cycles as taught by classical economy. Rather, civilization is an opened thermodynamic system in which crude matter and energy are continuously appropriated from nature to produce humans goods and residues and entropy are unavoidably produced (Cechin 2008). Being part of nature, we need to learn how to cope with nature's limits to supply our demands and recycle our residues. Using bioenergy in a sustainable way is currently the most realistic form to harmonize our ambitions for economic growth with the planetary constrictions. It is certain that some day we will find the limits of using renewables as well, given our boundless obstinacy for progress. Meanwhile, however, we seem to be starting a promising cycle of sustainable technological growth based in renewable sources of energy: the sustainable revolution.

### 3 Choices for Renewable Fuels

According to the second law of thermodynamics, in a chemical reaction the products will conserve a fraction of the existent energy in its reactants. In general, the energy potential of the products is lower than the reactants that made them. In this way, the amount of energy conserved by a molecule is inversely proportional to the number of chemical reactions necessary to build it. In this sense, perhaps the cheapest renewable fuel that we can produce is the molecular hydrogen ( $H_2$ ). A source of energy (i.e., light, electricity, etc.) can be used to liberate hydrogen directly from water. As this process is direct (i.e., without many chemical steps) the efficiency of the conservation of the energy for the production of  $H_2$  is relatively high. That type of direct production can also be accomplished with other molecules, but considering the amount of water on the planet, in practice, any other molecules are far less abundant. Another advantage of using  $H_2$  is that its combustion produces no pollution, only water. However, although the production of  $H_2$  can be cheap and clean, its use is not easy.

$H_2$  is a highly explosive gas and must be transported under pressure, which considerably increases the cost of transport and risks of accidents. From this point of view, liquid fuels seem to be a more convenient option for use in vehicles.

When compared with  $H_2$ , liquid fuels can present a considerable difference in energy density, related to difference in the oxidation state of carbon. Alcohols such as methanol and ethanol are more oxidized than lipids in the form of biodiesel and in this way, alcohols release less energy during combustion per unit of mass. The complete combustion of one gram of ethanol liberates about 7 kcal of energy while one gram of lipids releases ca. 9 kcal. Because  $H_2$  is a gas, it presents an even smaller energy density. On the other hand, as discussed above, the fact that liquid fuels are more complex than  $H_2$  implies that they are less efficient in energy conservation.

The processes involved in the synthesis of liquid biofuels such as ethanol is indirect and imposes a higher cost to obtain it. Part of the energy present in the sugars used to produce ethanol, for instance, encloses energy that had to be used for agricultural processes, planting, irrigation, fertilization, harvesting, plant transportation, milling, and industrial processes such as fermentation by yeasts, distillation, and subsequently fuel distribution. Therefore, in order to rationally choose an ideal fuel and production technology, one must consider the energy efficiency throughout the whole chain of production, consumption. and renewability.

### 3.1 Biodiesel from Plant Sources

Following the wave of ethanol success, other kinds of biofuels are now being developed as well in scale production, as biodiesel. In Brazil, plants such as palm, soybean, and other edible cultures are being partially used to produce biodiesel. On the other hand, nonedible plants able to grow in marginal lands and climates as semiarid and cerrado (Brazilian savanna) have been studied in order to avoid competition with traditional agriculture and food production. They have been studied and selected by their seed and seed oil yields, oil profiles, and rusticity. Such characteristics are found in many *Euphorbiaceae* species as *Jatropha curcas*, sea almond (*Terminlia catappa*), neem (*Azadirachta indica*). *J. curcas* and other genera have been considered as plants with the strongest potential for biodiesel production in Brazil with financial support for farmers from cerrado regions and industrial plants being build.

Oleaginous plant seeds store oil in cell structures called oil bodies. Seedlings use their reserve compounds as a source of carbon and energy until being able to self sustain. The principal lipids stored by oleaginous are triglycerides. They exist in esters of a residue of glycerol, a trihydroxylic alcohol known commercially as glycerin, with fatty acids. Fatty acids are interesting as fuel because of their high energy content.

However, the viscosity of triglycerides can be too high for its direct use in diesel engines. Therefore, they must to be converted to ethyl or methyl esters of fat acids in order to be useful. The transesterification process includes substituting the glycerol by ethanol or methanol using a chemical catalysts such as  $H_2SO_4$ , NaOH, KOH, or  $NaOCH_3$ . The length of fatty acids also influences the viscosity and energy density of biodiesel. The longer the length of the aliphatic chain, the higher the energy density, but the lower the viscosity will be. On the other hand, fatty acids might

present unsaturations, i.e., some carbons of the aliphatic chain might be oxidized to form one or more double bonds. These unsaturations produce breaks in the linear geometry of saturated (nonoxidized) fatty acid, decreasing the spatial proximity among molecules and as a consequence increasing its viscosity. In this way, the kind of alcohol residue esterified to fatty acids, the length of aliphatic chain and the degree of unsaturation of fatty acid residues are features that imply a trade off among viscosity and energy density for biodiesel. Thus, the fatty acid profile of different plants strongly determines the choice of plant species for biodiesel production.

### 3.2 *Bioethanol*

Ethanol is an organic compound used as liquid fuel in light vehicles since the invention of internal combustion motors by Nikolaus Otto. Today, it is the first renewable fuel produced from plants such as sugarcane in Brazil and corn in the USA. Carbon dioxide produced by burning ethanol is assimilated by plants from the air. Thus, ethanol does not generate a net unbalance of greenhouse gases as do gasoline, diesel, and other petroleum derivatives.

Currently considered a traditional producer of sugarcane, Brazil inaugurated the industry of ethanol for fuel applications early in the twentieth century. In 1973, an unprecedented increase in the price of petroleum harnessed to Yom Kippur's war and the seizure of the USA and western Europe by Middle East petroleum producers. As a result, the Brazilian government decided to increase the production of ethanol throughout an extensive program of incentives.

Currently, Brazil has no pure gasoline in any gas station. Flex fuel engines afford the choice to drivers to use E25 to E100 gasohol (25–100% of ethanol). Strategic concerns about energy security and global warming has impelled other countries to develop their own production of ethanol and in spite of the greater productivity of sugarcane, 2,105 gallons per acre against 495 gallons per acre of corn ethanol, the US overcame Brazilian ethanol production in 2006 and are today the largest producer of ethanol in the world.

However, the current means of production are far from being able to supply ethanol to support potential demand to the whole world. In this sense, governments and researchers have been driving their attention to explore the wide energy availability of lignocellulosic biomass in order to produce more biofuels, and do so more efficiently and sustainably. Currently, most of the biomass from sugarcane and corn is wasted as residue or inefficiently burned to run the mills. However, such biomass is formed mainly by sugars such as cellulose and other related polysaccharides. The problem is that they are linked to each other in complex ways, forming an interwoven network of polymers, which are very difficult to disentangle. However, once broken into free sugars these polysaccharides might be fermented to produce ethanol.

Two thirds of the energy produced by sugarcane is in the lignocellulosic material. Besides being the most abundant biomolecules in nature, technologies able to hydrolyze holocellulose (cellulose and hemicelluloses) in its monosaccharides at a low cost, will

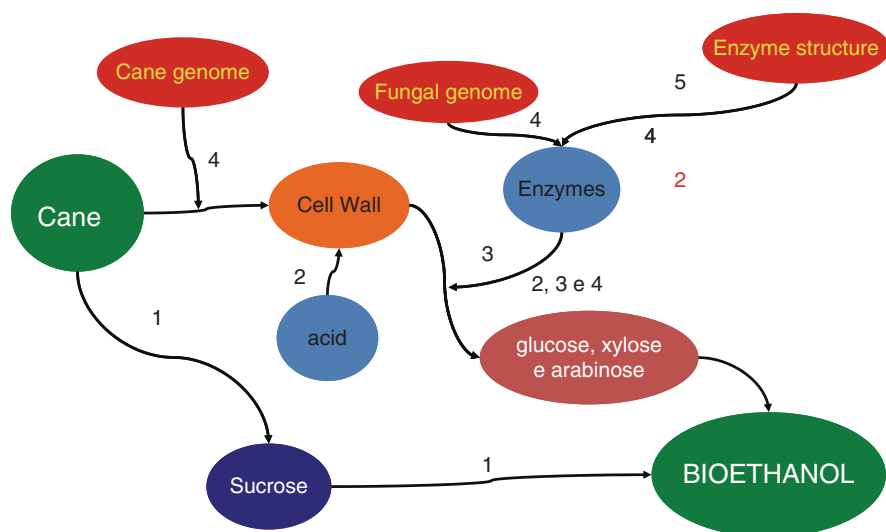
make possible the utilization of the most diverse plant residues for production of ethanol. Such technologies might, in theory, double bioethanol productivity, thus helping to avoid the expansion in the area needed to produce biofuels and consequently avoiding impacts on forests by indirect land use.

### 3.3 *Biochemical Conversion*

The biochemical approach toward saccharification of lignocellulose biomass is based on the principle that catalysts may decrease the activation energy and accelerate the velocity of the hydrolytic reaction. A small amount of a specific catalyst might accomplish a number of reactions virtually infinite. Due to the complexity of lignocellulosic material, a cocktail of enzymes will have to act in concerted fashion in order to carry out the hydrolysis of the great number of reactions necessary to release all monosaccharides present. It would need to cope with the lignin present in the mixture and also with the crystalline (water free) cellulose, which is resistant to most of the physical and chemical attacks (Socol et al. 2010).

In order to overcome these barriers, biomass has to be prepared beforehand and this process is called pretreatment. Several types of pretreatments have been made. They consist of methods able to increase the surface area of polysaccharidases available to enzyme attack. In thermo acid treatment, lignin is partially removed, exposing polysaccharides to enzyme hydrolysis. Alkali treatment may also be used to remove ester linkage between lignin along with pectic and hemicellulosic polysaccharides. Indeed, polysaccharides might be dissolved by strong alkali and hydrolyzed by mild acid treatments with sulfuric acid. However, once the glycosidic linkages are broken, the monosaccharides might be easily oxidized to furfurals and hydroxymethylfurfurals. The different degrees of susceptibility from  $\alpha$  and  $\beta$  linkages, as well as the pectin connection among fibers (middle lamella), results in oxidation of significant parcels of the carbohydrates. Pentoses, furfural derivatives, and phenylpropanoids from lignin will inhibit subsequent sugars' fermentation to ethanol by yeasts, reducing the efficiency of direct chemical hydrolysis. Ethanol at high temperature might be used to partially extract lignin and other soluble solids in organosolv<sup>®</sup> process developed by the Dedini Co (Ramires et al., 2010). These and other processes are used in the paper industry and have been adapted as pretreatments for ethanol production from lignocellulosic material. Other processes have been developed specifically for bioethanol technology. One of such processes is steam explosion, a method in which biomass is submitted to high pressure and left to expand fast in presence of vapor exposing the fibers to subsequent hydrolysis.

The biochemical route is in fact an application of modern techniques of cell and molecular biology (Buckeridge et al. 2010). The possibilities are many (Fig. 2). Bioenergy feedstock species can be genetically modified so that their cell walls become more accessible to enzyme hydrolysis during the industrial process. The microorganisms that will be used to produce the enzymes that will perform hydrolysis can be engineered, and the ones that will ferment the sugars, which in the case of



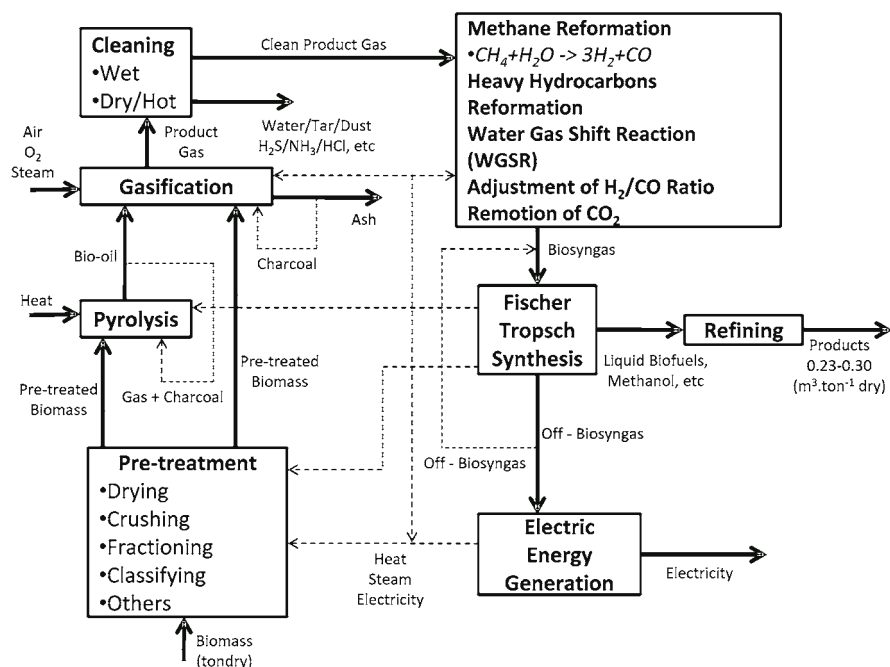
**Fig. 2** Strategies for the biochemical route to obtain cellulosic bioethanol from sugarcane. Numbers refer to phases that will need to be followed in time, in order to complete the process of cellulosic ethanol. Phase 1 is already completed, but must be improved; it is called first generation. Phase 2 refers to the use of acid hydrolysis couple with enzyme hydrolysis to produce fermentable sugars. During phase 3, enzyme cocktails will be available and enzymatic hydrolysis will be mastered in large scale. On phase 4, modified walls, better enzyme producing fungi, and modified enzyme structures could be used to improve the industrial process even more (from Buckeridge and Salatino, 2010)

grasses are pentoses, will need to have their metabolism adapted to use this kind of sugar. In the era of synthetic biology, the biochemical route will probably join other industrial processes in a revolution without precedents in biology, i.e., industrial processes strongly based on biological mechanisms.

### 3.4 Thermochemical Conversion

Synthesis gas generated from catalytic reform of fossil fuels (natural gas), or gasification of coal, is a versatile platform in conventional chemical and energy industries. By thermochemical processes, lignocellulosic biomass can be converted into biofuels and other derivatives (Fig. 3). The main advantages of such an approach do not cope directly with the natural complexity of biomass as in biochemical approaches and the low intensity of pretreatment involved. The cores of thermochemical conversion are the processes of pyrolysis and gasification. Pyrolysis is a heating procedure performed in complete absence of oxygen. It produces different phases depending basically on parameters such as temperature, pressure, time of reaction, and heating rate. Among the phases, one is an oil (bio-oil) that can be used to feed the gasification process. Gasification can be accomplished with a controlled amount of oxygen and is driven toward obtaining a product gas, also named synthesis





**Fig. 3** Steps in thermochemical production of biofuel. The main thermochemical processes are pyrolysis and gasification. Both pyrolysis and the gasification produce different phases depending basically on temperature and pressure, reaction time, process time, heating rate, etc. The bio-oil from pyrolysis can be used to feed the gasification process. The biofuel synthesis processes have several requirements in relation to reactor temperature and pressure, type of catalysts, H<sub>2</sub>/CO ratio in syngas, which can be adjusted by water gas shift reaction (WGS) or by membrane separation techniques, impurities content in the syngas such as CO<sub>2</sub>, dust, tar, H<sub>2</sub>S, NH<sub>3</sub>, HCl, CH<sub>4</sub>, halogen and alkali compounds, and type of downstream processes. There have been propositions of poly-generation where integrated processes are used to produce syngas to chemicals, biofuels and generation electricity in the same plant and from the same feedstock

gas or syngas (Fig. 3). Syngas can be converted by fermentation or catalytic synthesis in liquid and gaseous fuels such as gasoline, diesel, ethanol, methanol, methane, and hydrogen, among other energetic and nonenergetic products (Rezaian and Cheremisinoff 2005; Knoef et al. 2005).

Theoretically, a syngas is composed of equimolar amounts of hydrogen (H<sub>2</sub>) and carbon monoxide (CO), which goes through water gas shift reaction (WGS) and a further process to remove carbon dioxide (CO<sub>2</sub>). Synthesis gas produced by direct gasification of lignocellulose or bio-oil is composed of solid and liquid particles (dust and tar), halogen and alkali compounds with inorganic impurities being hydrogen sulfide (H<sub>2</sub>S), ammonium (NH<sub>3</sub>), hydrogen chloride (HCl), methane (CH<sub>4</sub>), and other light hydrocarbons (C<sub>2</sub>H<sub>6</sub>) which contaminate the catalysts used in downstream processes (Obando et al. 2010). There have been propositions of polygeneration in which integrated processes are used to produce syngas and generation of electricity in the same plant. Others consider the possibility to

integrate the biochemical with the thermochemical route by using by-products of the pretreatment processes.

### ***3.5 Comparison of Thermochemical and Biochemical Routes***

Thermochemical conversion is at a stage of development and evaluation on a pilot scale to improve the quality of the syngas as well as the capabilities needed to achieve economical viability. On the other hand, the biochemical route is presently at the precommercial stage of development due the great number of plants being implanted and already in operation. The current estimated costs of biofuel production by thermochemical route are around 0.5–0.6 US\$ per liter of equivalent fuel, while the estimated cost of biochemical conversion is 0.7–0.9 US\$ per liter of equivalent fuel. However, biochemical conversion must undergo a rapid cost reduction in the face of commercial plants being set until 2012, when costs are expected to reach about 0.3 US\$ per liter of equivalent fuel (Lora et al. 2007).

Biochemical conversion presents great challenges in bioengineering of enzymes and yeasts, detoxification of substrates (pretreatment), as well as the energetic optimization and integration of the processes. Of course both routes require several unitary operations as harvest, transport, storage and final arrangement of biomass such as drying, fractionating and classifying of particles, to name but a few. But there are differences. Pretreatment, for instance, has a high impact on the cost of biofuels in both routes. However, pretreatments are considered of lower intensity in thermochemical approaches, when compared with pretreatment intensities required to biochemical conversion. Biochemical approaches demand improvement of cellulose accessibility to enzymes that are capable of hydrolyzing polysaccharides. This confers a considerable impact on the energetic balance of bioconversion.

Both technological platforms require large scale plants to reach economic viability. However, reported data suggest facilities to process 100 ton/h of dry biomass to biochemical plants are feasible, while about 500 ton/h of dry matter is necessary in order for a thermochemical platform to become economically viable. In this last case, gasifiers of 150 ton/h of dry matter will be needed. This is currently a relevant technical and economical constriction for the thermochemical route. One promising study, although still on a laboratory scale, proposes the production of bio-oil by fast pyrolysis and successive gasification of bio-oil. If such technology becomes possible and safe, reactors able to process about 2 tons of biomass per hour could produce bio-oil in a decentralized way, centralizing the gasification an economically viable scale (Rocha 2008).

## **4 Concluding Remarks**

The availability of useful types of energy strongly determines the evolutionary potential in nature. Human technological development is also highly dependent on energy availability. In recent history, coal and petroleum played an important role

in industrial and postindustrial revolutions. The pressure against environmental imbalance caused by greenhouse gases emissions due to the use of fossil fuels implies a strong barrier against the maintenance of the rates of social and economical development on the basis of oil and coal as main sources of energy. On the other hand, the potential to produce energy from biomass and other renewable sources exceeds (several times) the world current demand. The development of technologies to extract energy from renewable sources (such as lignocelluloses) is the way to enter a new age of technological development.

Lignocellulose is the most abundant biological crude matter on the planet and is composed of high energy molecules. However, it is also a highly ordered cell structure which renders mechanical and biochemical resistance to plant tissues. Furthermore, cell walls present a relative high diversity among different plant species and might become progressively recalcitrant when it is (wrongly) disassembled. Nonetheless, several biological systems have coevolved with plant cell walls and optimized the biochemical conversion of cellulosic biomass using a similarly complex set of enzymes. We are now able to face this challenge using and advancing the knowledge about plant cell wall architecture. Because most species chosen as feedstocks for bioenergy are grasses, the primary focus of technological development will be the type II cell wall (i.e., the wall typical of grasses that is composed of arabinoxylans and mixed linkage glucans as main hemicelluloses). Although they represent just a small fraction of the plant species, grasses respond for ca. one-fifth of world green cover and more than four-fifths of food consumed by humanity, including forage and biofuel.

Some exciting synergy might be found between biodiesel and bioethanol production. Glycerol, a by-product of the biodiesel industry, might be fermented by yeast to produce ethanol. Ethanol, in turn, might be used to transesterify triglycerides and reduce viscosity. On the other hand, harvesters, tractors, and trucks used in the cultivation and transport of ethanol production and consumption chain today, all run on diesel engines, which negatively impacts sustainability of ethanol. Therefore, the emergence of large scale biodiesel industry might mean a snap point in sustainability of the whole chain of biofuel production.

There is an aspect toward the technological routes convergence. They offer opportunities for scientific development in areas such as development of new pyrolysis and gasification processes, catalysis applied to syngas production and purification, development of new pretreatments of biomass, enzymes and microorganism engineering, as well as energetic optimization and integration of the processes. All present potentials to be part of the solution and research in these areas must be put forward in order to guarantee that a better solution to the problem will be found in the shortest possible time and will be strongly based on high quality science.

It seems, therefore, that humanity is living one of these moments of revolution in which the system will jump to a superior level of organization that will make us capable of going far beyond where we have been during the last centuries.

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