Chapter 5

Advanced technologies in the sugarcane agroindustry

The range of products that can be made from sugarcane is not limited to those discussed in the previous chapter. This chapter presents innovative technologies for using sugarcane as an industrial and energy input. These technologies link the production of bioethanol to novel processes such as hydrolysis of lignocellulosic residues (Section 5.1) or gasification for fuels and electricity (Section 5.2) — which will increase the value of lignocellulosic materials — and the production of biodegradable plastics (Section 5.3). A review of the ways bioethanol can be used as a basic input in the petrochemical industry — or the alcohol-chemical industry as it will come to be known — is also included (Section 5.4) in this chapter, including reference to alcohol-chemical projects developed some decades ago and to renewed initiatives in the field in recent years. The chapter closes with a discussion of the potential of biorefineries (Section 5.5). It is argued that because the entire cane of the sugarcane plant — with its sugars and fibres — is a source of valued materials, sugar mills and bioethanol plants will increasingly be configured as "biorefineries," a concept that mimics the refineries of the oil industry, but using new inputs that are renewable and more environmentally friendly. Biorefineries will allow to transform sugarcane biomass into a wide range of products through integrated and interdependent processes.

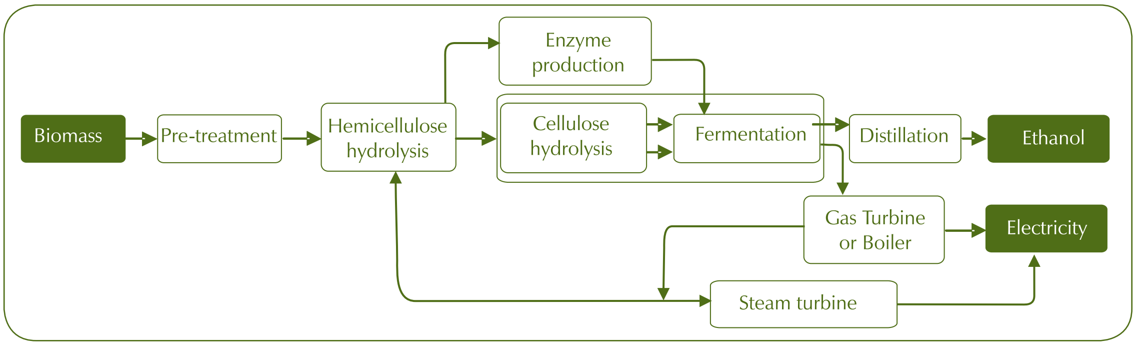
5.1 Hydrolysis of lignocellulosic residues

As discussed in Chapter 3, with the exception of sugarcane, the technologies commercially available for bioethanol production from starch and sugars, such as those derived from corn and sugar beet, involve modest energy and environmental gains. Furthermore, the use of these inputs offer limited economic benefits, when there are more profitable alternative markets (eg, food markets). On the other hand, despite its outstanding advantages as a bioethanol feedstock, sugarcane is not a viable option in all regions of the planet. Partially for those reasons, countries in the Northern Hemisphere have been searching intensely for technological approaches that would permit the production of biofuels that are attractive both from an economic and from an environmental perspective. Today, the prevailing view is that, in the future, in five to ten years, bioethanol production using hydrolysis of cellulosic materials will come to represent the realization of this long awaited alternative. Nevertheless, there are great obstacles to overcome and it is not easy to forecast how long such development will take.

Bioethanol has been produced through hydrolysis and fermentation of lignocellulosic materials since the end of 19th century, but it is only in the last 20 years that this technology has been proposed to serve the fuels market. The main research and development programs are being conducted in the United States and Europe, basically in experimental production scales. Their success could transform bioethanol into a viable biofuel that could be produced in almost all regions of the world, using available organic waste from various sources [Macedo (2005b)]. In fact, almost all biomass waste produced in agricultural and industrial activities — and even urban trash — contain substantial lignocellulosic material that can be converted into bioethanol through the new expected technologies.

Technologies for producing bioethanol from lignocellulosic materials involve the hydrolysis of biomass polysaccharides into fermentable sugars, and their subsequent fermentation to produce bioethanol. Hydrolysis uses complex and multiphase technologies based on acid or enzymatic routes, or both, in order to separate the sugars and remove the lignin. A simplified version of the generic sequence of this process is illustrated in Figure 19.

Figure 19 – **Schematic of the process of ethanol production by hydrolysis of biomass**



Source: Seabra (2008).

Unlike thermochemical processes, the composition and structure of the biomass employed have strong influence on the course and yield of the processes of hydrolysis and fermentation. Indeed, a considerable research effort should be exclusively focused on better understanding the formation of structural components of plants and how to modify them, to increase the yields from hydrolysis [DOE (2006)], as hydrolysis is really efficient only after the separation of the biomass fractions.

Lignocellulosic biomass is composed of polysaccharides (cellulose and hemicellulose) and lignin, a complex polymer of methoxy and phenylpropane groups that keep cells joined. The cellulosic fraction (40%-60% of dry matter) is a linear polymer of glucose-glucose dimers (cellobiose), rigid and difficult to break. Its hydrolysis produces glucose, a six-carbon sugar whose fermentation by *Saccharomyces cerevisiae* is well known. The hemicellulosic fraction (20%-40%), in general, is composed of a main chain of xylose (with β-1,4 bonds), with various branches of mannose, arabinose, galactose, glucuronic acid, etc. Hemicellulose is easier to hydrolyze than cellulose, but the fermentation of five-carbon (pentose) sugars is not as developed as the processes for glucose. The biochemical structure of the lignin fraction (10%-25%) is not related to simple sugar molecules, thus is not suited for bioethanol production using fermentation. The lignin fraction, however, still has an important role to play in the success of hydrolysis technology. Although it is possible to use lignin to produce several products, the focus of ongoing studies is the use of this material as a source of energy for such processes, which will ensure self-sufficiency and, perhaps generate surplus electric power which can be sold. Of course, this situation is attractive not only for the economic viability of the technology, but also from an environmental perspective, if it reduces dependence on external fossil energy resources.

In general, the first step consists of mechanical pre-treatment of the feedstock to clean and "crush" the material in order to break its cellular structure and make it more susceptible to subsequent chemical or biologic treatments. The next step, which is also considered pre-treatment, consists of lignin removal and hydrolysis of the hemicellulose. For this step there are several types of processes, with different yields and distinct effects on the biomass, which in turn have implications on the subsequent steps. Table 20 presents the most used methods.

Table 20 – Processes to pre-treatment biomass for hydrolysis

Process	Description	Reaction time	Xylose yield	Cost*
Physical				
Vapour explosion	Crushed biomass is treated with vapour (saturated, 160°-260°C) followed by a rapid decompression.	1-10 min	45%-65%	–
Thermohydrolysis	Uses hot water at high pressure (pressure above the saturation point) to hydrolyze the hemicellulose.	30 min	88%-98%	–
Chemical				
Acid hydrolysis	Uses concentrated or diluted sulphuric, hydrochloric or nitric acids,	2-10 min	75%-90%	+
Alkaline hydrolysis	Uses bases, like sodium or calcium hydroxides.	2 min	60%-75%	++
Organosolv	A mixture of an organic solvent (methanol, bioethanol and acetone, for example) and acid catalyst (H_2SO_4, HCl) is used to break internal bonds of lignin and hemicellulose.	40-60 min	70%-80%	
Biologic	Fungi (molds) are used to solubilize the lignin. Generally used in conjunction with other processes.			
Combined				
Catalyzed Vapour Explosion	Addition of H_2SO_4 (or SO_4) or CO_2 in the vapour explosion may increase the efficiency of enzymatic hydrolysis, reduce the production of inhibitor compounds, and promote a more complete removal of hemicellulose.	1-4 min	88%	–
Afex (ammonia fibre explosion)	Exposure to liquid ammonia at high temperature and pressure for a period of time, followed by a rapid decompression.		50%-90%	
CO_2 Explosion	Similar to the vapour explosion		75%	

Source: Based on Hamelinck, et al. (2005).

* The + symbol indicates advantageous effect (lower cost).

In the actual hydrolysis step, cellulose is converted into glucose, according to the following reaction, which may be catalyzed by a diluted acid, concentrated acid, or enzymes (cellulase):

$$n\ C_6H_{10}O_5 + n\ H2O \rightarrow n\ C_6H_{12}O_6 \qquad (3)$$

The acid hydrolysis (both the concentrated and diluted one) occurs in two stages, to exploit differences between hemicellulose and cellulose. The first stage involves the hydrolysis of hemicellulose, which follows the pre-treatment process described above. In the second stage, high temperatures are applied to optimize the hydrolysis of the cellulosic fraction [Dipardo (2000)]. Hydrolysis with diluted acid employs high temperatures and pressures. Reactions that take only seconds to a few minutes permit a continuous process. In contrast, processes that use concentrated acid are conducted under milder conditions, with longer reaction times [Graf and Koehler (2000)]. A comparison of the different hydrolysis processes is presented in Table 21.

***Table 21* – Comparison of different options for cellulose hydrolysis**

Process	Input	Temperature	Time	Saccharification
Diluted Acid	< 1% H_2SO_4	215° C	3 min	50%-70%
Concentrated Acid	30%-70% H_2SO_4	40° C	2-6 h	90%
Enzymatic	Cellulase	70° C	1.5 day	75%-95%

Source: Based on Hamelinck, et al. (2005).

In the enzymatic process, hydrolysis is catalyzed by enzymes that are generically referred to as cellulases. Cellulase, in fact, is an enzymatic complex composed of endoglucanases (that attack the cellulose chains to produce shorter polysaccharide chains), exoglucanases (that attack the non-reducer terminals of these short chains and remove the cellobiose) and β-glucosidases (that hydrolyze the cellobiose and other oligomers into the glucose) [Philippidis and Smith (1995)]. As in the acid processes, pre-treatment is required to expose the cellulose to the attack of enzymes.

As the enzymatic process is conducted in mild conditions (pH 4.8 and temperature between 45° and 50° C), the cost of processing is relatively low [Sun and Cheng (2002)]. Additionally, it allows larger yields and simultaneous saccharification and fermentation (SSF), and has lower maintenance costs (because there is virtually no corrosion). Because of its great potential for development and lower costs, many experts consider enzymatic hydrolysis as the key to cost-competitive bioethanol production over the long-term [Dipardo (2000) and Lynd, et al. (1996)].

Hydrolysis by diluted acid is currently at a more advanced stage in comparison to the others processes, but it has serious limitations in terms of yield (50%-70%). Hydrolysis with concentrated acid offers better yields and fewer problems in terms of the production of inhibitors, but the need to recover the acid and for equipment that is resistant to corrosion diminishes profitability of the process. Enzymatic hydrolysis, on the other hand, offers high yields (75%-85%) and further improvements are expected to get yields up to 85% to 95%. Furthermore, the non-use of acids may represent not only economic advantages (equipment with low operating cost and cheaper materials), but also environmental advantages (there is no production of residues). In most cases, these processes still are at early stages of development, with experiments conducted on reduced scales. In real systems with large volumes yields will be lower.

Regardless of the method, the fermentation of sugars from the hydrolysate into bioethanol basically follows the same principles as those observed in the production based on starch or sugars. In the case of hydrolysis, however, a good part of the hydrolysate is composed of five-carbon sugars, which cannot be fermented by wild lines of *S. cerevisiae*. Currently, most fermentation processes exclude this fraction of the sugars, or carry out the fermentation in two steps, significantly compromising profitability.

The expectation is that in the future these transformations could happen simultaneously in a smaller number of reactors, requiring, therefore, micro-organisms capable of fermenting both sugars with high yields. For this, researchers have turned to genetic engineering to insert pentose metabolic routes into yeast and other bioethanologenic microorganisms, as well as to improve the performance of micro-organisms that already have a capacity to ferment both sugars. Even though there have been successes in this area, fermentation of mixtures of biomass sugars still has not achieved commercial viability [Galbe and Zacchi (2002), Lynd, et al. (2005) and Gray, et al. (2006)]. In addition, it is important to consider harmful inhibitors of fermentation present in the hydrolysate (acids, furans, phenolic compounds, etc.), which should be removed when their concentrations are high, or which require the use of robust lines of resistant micro-organisms.

Within the context of enzymatic hydrolysis, the process with simultaneous saccharification and fermentation (SSF) — although not yet optimized — is viewed as a real option that could reduce substantially the problem of inhibition. One development in this process is the inclusion of co-fermentation of substrates with multiple sugars, which permits the conversion of pentoses and hexoses in the same reactor. Currently this approach — simultaneous saccharification and co-fermentation (SSCF) — is being pilot tested and will be a focus of development in the medium term. The endpoint of this technologic development could be the establishment of consolidated bioprocessing (CBP), in which the four biologic conversions employed in bioethanol production (enzymatic hydrolysis, saccharification, fermentation of hexoses, and fermentation of pentoses) occur in a single step. In this case, thermophilic micro-organisms would anaerobically produce enzymatic complexes with better cellulolytic activity than typical mold-derived enzymes and would ferment all the sugars released in the same reactor [Wyman (2007)].

In view of the long-term outlook for all these possibilities, some increase in bioethanol yield is expected, but the main outcome should be a reduction in the costs of production. A large prospective study carried out recently [Hamelinck, et al. (2005)], projected that enzymatic hydrolysis with diluted acid pre-treatment would be feasible on a commercial basis in the near future. In this scenario the process could recover approximately 35% of biomass energy in the form of bioethanol, and a total of 38% if surplus electricity is included. Bioethanol cost would be € 22 per GJ, assuming a biomass cost of € 3 per GJ and an investment of € 2100 per kW of bioethanol (using 2003 prices). In the long-term, using consolidated bioprocessing, the energy recovery with bioethanol could reach 47%, and a total of 52% counting surplus electricity. But the main expected advantage is a great reduction in the cost of producing bioethanol. The cost could drop to as low as € 9 per GJ, if the cost of biomass could be reduced to € 2 per GJ and investments requirements decline to € 900 per kW of bioethanol. In all estimates the energy considered always refers to the superior calorific power (SCP).

Table 22 summarizes the main results of studies concerning processes in development for bioethanol production by means of hydrolysis. It should be noted, however, that time frame forecasts in the last column should be taken cautiously, as they were generated at the time of the studies. Yields refer to the bioethanol produced per ton of dry biomass. The cost of biomass refers to its use as an input in bioethanol production and it is defined exogenously to such production process.

***Table 22* – Comparison of yield and cost estimates for bioethanol production by means of hydrolysis**

Reference	Process	Yield (litre/t)	Biomass cost	Ethanol cost	Availability
Hamelinck et al. (2005)	SSF with diluted acid pre-treatment	~300	3 €/GJ	0.98 €/litre	Short-term
	SSCF with vapour explosion pre-treatment	~340	2,5 €/GJ	0.58 €/litre	Medium-term
	CBP with thermohydrolysis	~400	2 €/GJ	0.39 €/litre	Long-term
Aden et al. (2002)	SSCF with diluted acid pre-treatment	374	33 US$/t	0.28 US$/litre (Minimum price)	Short-term
Wooley et al. (1999)	SSCF with diluted acid pre-treatment	283	44 US$/t	0.38 US$/litre	Short-term
	SSCF with diluted acid pre-treatment	413	28 US$/t	0.20 US$/litre	Long-term

Sources: Seabra (2008).

Regardless of the technological approach, it is important to note the great influence that biomass cost has on the final cost of bioethanol. In general, in estimates for countries in the Northern Hemisphere biomass cost represents approximately 40% of bioethanol costs and a large part of future reductions of biofuel prices depend on reductions of biomass costs. Therefore, high expectations are created when the situations in other regions are considered, especially those that can produce biomass at lower costs. One example is sugarcane biomass in Brazil. Sugarcane straw has a cost initially estimated at around US$ 1 per GJ [Hassuani, et al. (2005)], while bagasse — considered a residue — has no cost, in terms of what it takes to produce it; however, bagasse is indeed highly valued for electric power production, as discussed in the previous chapter.

In Brazil, hydrolysis technology also has been developed, with applied research already at a reasonably advanced stage. A process for producing bioethanol from bagasse (and eventually from straw) using an Organosolv treatment combined with diluted acid hydrolysis has been tested on a pilot scale for some years, as part of a project involving the Research Support Foundation of the State of São Paulo (Fapesp), the Sugarcane Technology Center (CTC), and Dedini S/A Indústrias de Base, a manufacturer of bioethanol plant equipment. The project has in operation an unit with an installed capacity to produce 5,000 litres of bioethanol per day, located next to a sugar and bioethanol plant; the objective is to determine process engineering parameters for the fabrication of large scale units [Dedini (2008)].

In the process, Dedini Rapid Hydrolysis (DHR – Dedini Hidrólisis Rápida) — a Dedini patented solvent (ethanol) — is used to break the cellulose-hemicellulose-lignin matrix, dissolving the lignin, hydrolyzing the hemicellulose, and exposing the cellulose to diluted sulphuric acid, which rapidly promotes (in 10 to 15 minutes) the hydrolysis of this fraction at temperatures of 170°C to 190°C and pressures of around 25 bar. It is a continuous process that has been uniformly and routinely operating since 2003. Although there are still aspects to fine-tune, complex challenges have been already overcome, such as how to continuously feed bagasse into high-pressure reactors, and the selection of materials which can be handled under demanding mechanical specifications in highly corrosive environments. Since the pentose fraction is not used in the process, yields are relatively low, on the order of 218 litres of bioethanol per ton of dry bagasse. However, it is expected that using this fraction of sugar will increase yields close to 360 litres per ton of bagasse [Rossell and Olivério (2004)].

More recently, Petrobras installed a reactor for enzymatic hydrolysis at *Cenpes,* its Research Center in Rio de Janeiro. And supported by the Ministry of Science and Technology, another pilot scale platform for enzymatic hydrolysis of bagasse is being implemented at the newly established Bioethanol Science and Technology Center in Campinas, São Paulo. This pilot reactor is the result of laboratory experiments that have involved about a hundred researchers from twenty research groups at universities and research centers throughout Brazil, many with international partners.

Dedini plant-pilot for producing bagasse-based ethanol.

In general, we can say that significant progress has been achieved in the development of hydrolysis technology; however, there are still important challenges to overcome for the implementation of commercially competitive units based on this technology. Given that resources are limited, it is essential to determine what critical issues need to be addressed for the consolidation of this technology. In recent years modified micro-organism were developed, and the main operations of industrial hydrolysis were modeled and optimized, but basically still on the limited scale of experimental reactors, in which it is easier to control temperature and contamination by other micro-organisms. Despite there is no consensus about the best technological approach for bioethanol production through these innovative routes, researchers around the world are nevertheless calling for the construction of the first commercial plants, which would permit to realize the expected rewards usually associated to *learning from experience* [Lynd, et al. (2005), Zacchi (2007), and Wyman (2007)].

5.2 Gasification for fuels and electricity production

Gasification is a process of thermochemical conversion of biomass carried out at high temperatures, in which solid or liquid organic substances are converted into gassy products, chiefly CO, H_2, CO_2 and water vapour, along with the formation of light hydrocarbons and other volatile and condensable compounds as secondary products [Grabowski (2004)]. The inorganic components of biomass are discharged in the form of ashes. The process can be carried out by means of a reaction of organic material with oxygen from the air or from vapour, or even with pure oxygen, using reactors at atmospheric pressure or pressurized. Heating of the gasifier can be done directly, by partial oxidation of the biomass, or indirectly, using heat exchange mechanisms. Fixed, fluidized, or entrained bed gasifiers may be used in the reactor. The choice of the gasification approach will depend on the biomass to be processed, the type of product sought, and the size of the plant.

The reactions that take place in a gasifier are extremely complex and the efficiency of the process depends on how properly they are carried-out. To give a simplified idea of the gasification process that follows the volatilization of the solid fuel, the following reactions occur simultaneously [Rauch (2002)]:

$$C + \tfrac{1}{2}\, O_2 \rightarrow CO \tag{4}$$

$$C + H_2O \rightarrow H_2 + CO \tag{5}$$

$$C + O_2 \rightarrow CO_2 \tag{6}$$

$$CO + H_2O \rightarrow CO_{2\,+}\, H_2 \tag{7}$$

$$C + CO_2 \rightarrow 2\, CO \tag{8}$$

Using gasification, an heterogeneous material such as a biomass can be transformed into a gaseous fuel suited to various applications; sometimes the gas must be properly cleaned to the specifications required by the particular use. Cleaning can occur at low temperatures, for example by filtering (at around 200°C) and washing for removal of particulates and condensable materials after cooling. Cleaning may be also carried out at medium-high temperatures (350°-400°C) for use in gas turbines and fuel cells. Hot cleaning is usually done using ceramic filters [Macedo, et al. (2006)].

Biomass gasification has been evolving since the 1940s, with the creation of different types of gasifiers, process arrangements and applications. Contemporary gasifiers range from small systems that supply gas for automotive internal combustion engines to small stationary units that produce combined heat and power (CHP). In addition, larger scale gasifiers have been developed to generate power with gas turbines, at thermal power ratings of 10 MW to 100 MW and, more recently, to produce clean gas for the synthesis of liquid fuels (methanol, Fischer-Tropsch liquids, bioethanol, DME, etc).

Many of the obstacles to the development of this technology were identified and partially resolved in the 1990s, including how to feed large quantities of loose biomass into pressurized reactors, the development of systems to clean the gas to meet required quality standards, and other specific requirements so that the gas can be used in gas turbines designed for gases with low calorific power or in synthesis reactors which convert them into liquids fuels. Fuels synthesis can benefit from the experience of the fossil fuel industry, but the high complexity of the processes involved will certainly require further development.

The expectation is that biomass gasification could lead to the production of both liquid biofuels, mainly for automotive use, and bioelectricity on a large scale, as described in the following paragraphs. The main factor driving this technological development is the desire to reduce greenhouse gases emissions and substitute the consumption of petroleum-derived products. Despite promising previous experience with several demonstration plants, research and development efforts have not been consistent over the years; therefore, it is expected that these technologies will only become mature commercial options in the medium to long term (ie, in a period probably longer than ten years). But for those developments to actually take place a major commitment to research and development is needed, as well as the definition and implementation of encouraging public policies.

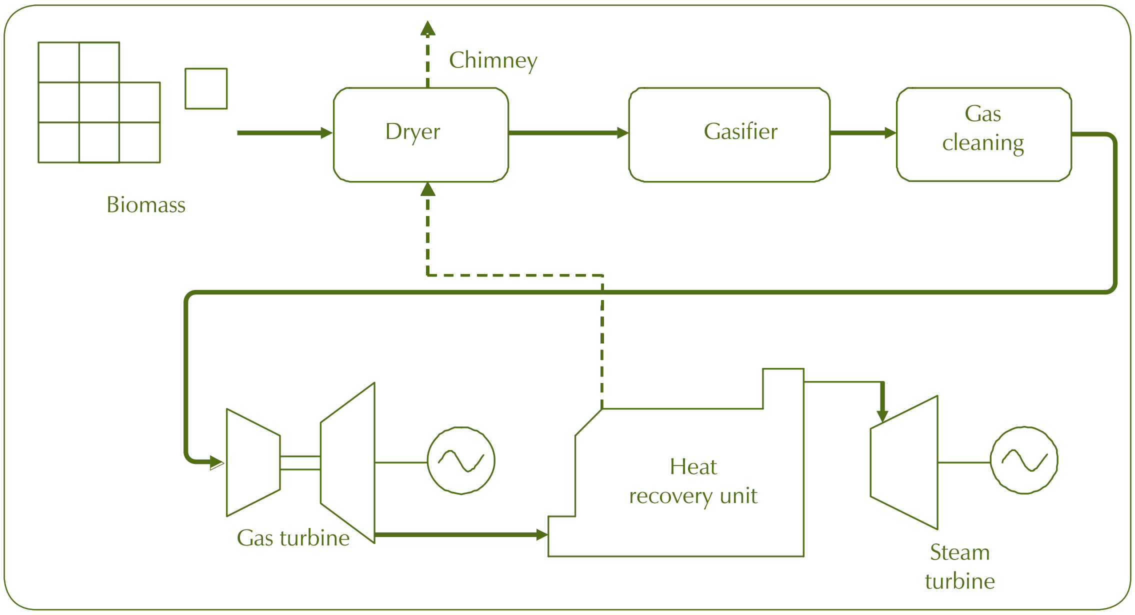
Gasification of biomass integrated with combined cycles (BIG/GT-CC technology)

Gasification is considered a critical technology to facilitate the efficient, clean and low cost conversion of biomass into bioelectricity. Gasification enables to implement the use of biomass in gas turbines, which have a thermal power cycle where working fluid operate at average temperatures considerably higher (above 1200°C) than in conventional steam cycles (below 600°C), reducing thermodynamic losses and maximizing performance. In this regard, it is expected that the biomass integrated gasification / gas turbine combined cycle (BIG/GT-CC) technology will become viable, creating a broad field for using solid biomass in the generation of electric power. In the case of gasifiers, smaller volumes of gas should be clean when compared with the direct combustion of biomass; and gas turbines associated with steam cycles (combined cycle) offer great efficiency in the generation of electricity with low capital costs.

The basic concept of BIG/GT-CC technology involves pre-treatment of biomass, followed by gasification, cooling and cleaning of the gas, and its combustion in a turbine. The hot gases that leave the gas turbine are transformed into steam using a heat recovery system, and steam is then used in a steam cycle to generate more electricity. Furthermore, after they are used to produce steam, the exhaust gases at low temperature can still be used in biomass drying, completing integration of the system [Faaij, et al. (1998)]. Figure 20 presents a basic schematic representation of a BIG/GT-CC system.

Given the basic concept of gasifying biomass and using the gas in gas turbines, there are three variations that may be used, which differ mainly in terms of how the gasifier is designed. One approach is based on circulating fluidized bed (CFB) technology, where the gasifier operates at atmospheric pressure with air injection to supply the oxygen that is needed for the gasification reactions. A Swedish company, Termiska Processer AB (TPS), with extensive experience in biomass gasification using this technology, proposes to insert a reactor in BIG/GT-CC systems immediately after the gasifier, for cracking of tar, a substance that hampers gas cleaning systems. The second approach is based on a gasifier with indirect heating and operating close to atmospheric pressure. The most relevant project on this gasification approach is conducted at the Battelle Columbus Laboratory (BCL), in Columbus, Ohio, and involves the use of sand to enable heating of organic material. The third approach involves CFB gasification technology, but operating at high pressures (20-30 bar, 900°-1000° C). Foster Wheeler (US) and Carbona (Finland) are two companies that have gained prominence with this technology [Consonni & Larson (1996) and Larson, et al. (2001)].

Figure 20 **– Schematic exhibition of a BIG/GT-CC system**



Source: Based on Larson, et al (2001).

In terms of yields, several studies have been carried out to estimate the efficiency and costs of bioelectricity, under the assumption that all technological problems have been resolved. However, the fact is that there are some significant obstacles to overcome, such as feeding and operation of high capacity pressurized gasifiers, gas cleaning with complete tar cracking, separation of alkali and particulates from the gas produced, modification of gas turbines for using gas with low caloric power obtaining a performance comparable to turbines that burn natural gas, and a significant reduction of capital costs through the learning effect. It is estimated that efficiency for generating electric power could be around 45%, for electric power costs in the range of US$ 40 to US$ 60 per MWh, as shown in Table 23, depending on the cost of biomass and the gasification technology used [Jin, et al. (2006)].

In the past 15 years there have been considerable research and development efforts in biomass gasification technologies associated with the use of gas turbines. Various projects were considered during this period; however, only one facility was actually built and operated for a significant time, in Värnamo, Sweden, using TPS technology. In Brazil there were plans for a BIG/GT-CC system generating 30-32 MW of electric power, in the interior of Bahia, using eucalyptus wood as fuel, but it was never built. The most plausible alternative —yet still highly unlikely— would be the use of BIG/GT-CC systems integrated with sugar mills and bioethanol plants, because the low cost of biomass would favour viability of the project. This alternative has been investigated since 1997 by the Copersucar Technology Center (now called the Sugarcane Technology Center) in partnership with TPS. At the moment, however, there is only speculation regarding the possibility of constructing a demonstration unit, in a future phase of the project [Hassuani, et al. (2005)].

Table 23 **– Comparison of yields and costs estimates of BIG/GT-CC systems**

Study	Gasification Technology	Efficiency Relative to PCI	Investment (US$/kW)	Biomass Cost (US$/GJ)	Electric Power Cost (US$/MWh)
Jin et al. (2006)	Atmospheric pressure with indirect heating	43.8%	968	3.0	55
	Pressurized with oxygen injection	45%	1,059	3.0	52
Faaij et al.* (1998)	Pressurized CBF	54%	1,950	4.0	80
Consonni & Larson (1996)	Atmospheric pressure with direct heating	41.9%	1,500	2.0	49

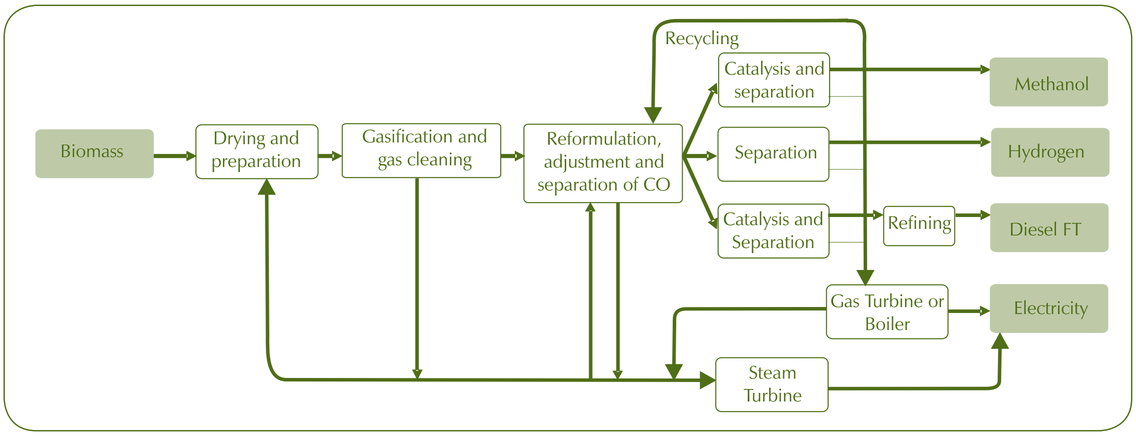
Source: Adapted from Seabra (2008).
* Original values in Dutch florins were converted at an exchange rate of US$ 1.00 = Dfl 2.00.

Synthesis fuels

Various biofuels, such as Fischer-Tropsch liquids (FT gas and FT diesel), hydrogen, methanol, ethanol, and dimethyl ether (DME) may be obtained out of synthesis gas (syngas) produced from biomass. In this process, biomass gasification generates synthesis gas, which must pass through cleaning and reforming processes and, if necessary, adjustment of its composition, so that it can be converted into fuel in a reactor. Given that not all the gas is converted into fuel, the unconverted portion can be re-circulated (to maximize fuel production), or it can simply be burned to generate electric power (in a BIG/GT-CC system, for example). The last option is known as *once-through* and it is considered the most economically viable approach when the electricity can be sold [Hamelinck, et al. (2001), Hamelinck, et al. (2003) and Larson, et al. (2005)]. Figure 21 presents a general diagram of the production of several fuels.

The scale of production is a determinant factor of the economic viability of liquid fuels produced using gasification technology, and a reason why the pressurized CFB gasification technology is favoured by some authors [Hamelinck, et al. (2003), Larson, et al. (2005) and Hamelinck, et al. (2001)]. The gasification process should be such that the gas produced is rich in CO and H_2, the two main reactants in liquid fuel production. Air injection should be avoided because it is not desirable that the gas produced is diluted in nitrogen.

Figure 21 – **General flowchart of methanol, hydrogen and diesel production through the biomass gasification (Fischer-Tropsch)**



Source: Adapted from Hamelinck (2004).

Because gas produced by gasification may contain considerable quantities of methane and other light hydrocarbons, one option is converting these compounds into CO and H_2 at high temperature and in the presence of a catalyst (generally nickel). Another important factor is the H_2/CO ratio, which should be adjusted for each type of biofuel, with less hydrogen in heavy fuels like diesel. This adjustment is done by the water-gas shift reaction, carried out in the presence of an iron-based catalyst [Van der Laan (1999)]:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (9)$$

The basic reactions involved in the production of each fuel are the following [Larson, et al. (2005)]:

For Fischer-Tropsch liquids: $CO + 2H_2 \Leftrightarrow CH_2 + H_2O$ (10)

For dimethyl ether (DME): $3CO + 3H_2 \Leftrightarrow CH_3OCH_3 + CO_2$ (11)

For methanol: $CO+2H_2 \Leftrightarrow CH_3OH$ (12)

There are three basic reactor designs: fixed bed (gas phase), fluidized bed (gas phase), and mud bed (liquid phase) [Larson, et al. (2005)]. The first design provides low conversions with only a single passage and it is still difficult to extract heat. The second design offers greater conversions, but it involves a more complex operation. The last is the one that offers the highest conversion rates for processes with simple passage.

Looking into the current state of this technology, significant development has been observed, especially in Europe, with the construction and operation of demonstration projects and even some commercial units. Based on the experience with biomass gasifiers and in the oil synthesis industry, in recent years some analyses have been conducted to evaluate the possibilities and costs of these biofuels in the future. In the case of FT liquids (gasoline and diesel), for example, if all technological problems were resolved, the overall efficiency could surpass 57%, considering the combined production of fuels (with an efficiency of 34%) and electricity (efficiency of 23%). The cost of biofuel would be around US$ 15 per GJ, given biomass costs of US$ 50 per ton and an investment of about US$ 1,770 per kW of fuel produced [Larson, et al. (2006)]. For the sake of comparison, conventional diesel costs around US$ 7 per GJ when the barrel of oil is at US$ 30 [Macedo (2005b)]. Table 24 presents some values from the literature, including yields and costs of liquid biofuels produced by means of synthesis processes associated with biomass gasifiers.

***Table 24* – Comparison of yields and costs for fuel production from synthesis gas**

Reference	Fuel	Yield (litre/ dry ton)	Investment	Biomass cost	Fuel cost
Phillips et al. (2007)	Ethanol	303	0.82 US$/litre/year	35 US$/t	0.26 US$/litre
Larson et al. (2006)	FT liquids	138	1,774 US$/kW$_{\text{comb, PCI}}$	50 US$/t	15.3 US$/GJ$_{\text{PCI}}$
	DME	468	1,274 US$/kW$_{\text{comb, PCI}}$	50 US$/t	13.8 US$/GJ$_{\text{PCI}}$
Hamelinck et al. (2002)	Methanol	280-630	930-2,200 US$/kW$_{\text{comb, PCS}}$	2 US$/GJ	8.6-12.2 US$/GJ$_{\text{PCS}}$

Source: Seabra (2008).

As previously stated, concerns about greenhouse gas emissions and oil costs are stimulating research into alternative ways of producing liquid fuels from biomass, reducing the use of fossil energy and even sequestering carbon emissions. A recent proposal [Williams, et al. (2005)] is the use of biomass gasification in conjunction with coal in a "hybrid" system, in which biomass would be used at a level that would significantly reduce greenhouse gases emissions of the thermal cycle.

Analyses of all innovative gasification bioenergy systems showed that assigning a value to their ability to mitigate climate change is essential to promote their economic viability, assuming the price of oil is US$ 30 a barrel. However, the recent increases in oil price, combined with renewed efforts to develop and demonstrate gasification technology, could lead to commercial systems in less time than originally predicted.

In addition to the hydrolysis and gasification approaches, which are reasonably well-known and have good prospects for economic viability improving in the medium term, other possibilities have emerged that could open new frontiers for the use of sugarcane in energy production, if their technical feasibility on commercial scales is confirmed. One of those possibilities, still being studied, is the production of butanol (C_4H_8O) — a widely-used industrial solvent currently manufactured in petrochemical plants — through biochemical processes that use lignocellulosic materials as inputs. Butanol can then be used as a gasoline additive in elevated concentrations without affecting mileage [DuPont (2008)]. Another approach that has been suggested is the production of biodiesel through biochemical processes that use sugars as the substrate. Projects to establish such industrial units have been proposed by the company responsible for such technology and its Brazilian partners [Amyris (2008)]. Such possibilities are certainly interesting and have a significant volume of applied technology; however, their economic feasibility has not been demonstrated and there is little knowledge of their performance and costs, both fixed and variable.

5.3 Using bioethanol as a petrochemical or alcohol-chemical input

Plastic materials — a generic term that designates a diversified family of artificial polymers — play an important role in our modern life, with a wide range of applications, whether replacing traditional materials like glass and wood, or creating new products (eg, packaging, coating and structural materials, among other possibilities). The main inputs to produce plastics in the petrochemical industry are natural gas and petroleum- naphtha. Production processes involve complex reactions that are usually grouped into three categories: a) first generation industries, which supply basic petrochemical products, such as ethene (or ethylene, C_2H_4), propene (or propylene, C_3H_6) and butadiene; b) second generation industries, which transform the basic petrochemicals into so-called final petrochemicals, such as polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polyesters and ethylene oxide; and c) third generation industries, in which the final products are chemically modified or built-in final consumer products, such as films, containers, and objects.

Bioethanol is an homogeneous and reactive substance that can be used as an input in various traditional petrochemical processes, which in this case could be called alcohol-chemical. The most important processes used in the transformation of bioethanol are classified as shown in Table 25. Prominent among them is ethane — produced by the dehydration of bioethanol — the precursor of a wide range of second generation products, such as polyethylene (PE), polypropylene (PP), and polyvinyl chloride (PVC). According to the equation for the dehydration of bioethanol, and assuming a conversion efficiency of 95%, 1.73 kg or 2.18 litres of bioethanol are consumed for each kilogram of ethane produced.

Based on the dehydrogenation of bioethanol into acetaldehyde, it is possible to generate another important class of intermediate butadiene and polybutadiene basic components of synthetic rubber used for various applications, including tires. Almost all products listed in Table 25 have widespread use in the industrial (paints, solvents and adhesives), agricultural (fertilizers and agrochemicals) and final use (for example, in textile fibres) sectors. Therefore, bioethanol can be considered an input for a wide range of traditional petrochemical products, by means of first and second generation conversion processes.

Table 25 – Basic processes of the alcohol-chemical industry

Processes	Main products	Typical application
Dehydration	Ethene Propene Ethylene-glycol	Plastic Resins Solvents Ethyl Ether Textile Fibres
Dehydrogenation Oxygenation	Acetaldehyde	Acetic Acid Acetates Dyes
Estherification	Acetates Acrylates	Solvents Textile Fibres Adhesives
Halogenation	Ethyl chloride	Cooling Fluids Medicine Products Plastic Resins
Ammonolysis	Diethylamin Monoethylamine	Insecticide Herbicide
Dehydrogenation Dehydration	Butadiene	Synthetic Rubbers

Source: Adapted from Schuchardt (2001).

The markets for these uses of bioethanol are important. Bioethanol demand by the Brazilian chemical and petrochemical industries could reach 7 million cubic meters [Apla (2006)], roughly one-third of the production in the 2006-2007 harvest. As the production of these sectors in Brazil represents only around 3% of global production, it is evident that there is large potential to expand the use of sugarcane bioethanol as a input on a global scale. Considering just that worldwide ethylene demand in 2005 was 105 million tons [CMAI (2005)], the use of bioethanol to replace 10% of other inputs would result in a demand of 23 billion litres, which is on the same order of magnitude as current Brazilian bioethanol production. With the basic technologies well understood, the critical factor for the development of this market is the relative price of bioethanol vis-à-vis other relevant inputs.

First steps of ethanol-chemical industry in Brazil

Projects to promote the use of ethanol to substitute fossil inputs in the Brazilian petrochemical industry were successfully implemented by Oxiteno and Coperbo, during the 1980s. These production routes were discontinued in 1985 because unfavourable prices, but there is renewed interest out of the recent increase in the cost of fossil inputs.

Oxiteno — the petrochemical branch of Grupo Ultrapar — used sugarcane bioethanol regularly as an input at its unit in Camaçari, Bahia, during the first half of 1980s, with an annual production of ethylene estimated at 230,000 tons. Today, the company is investing considerably on the development of technologies for petrochemical and alcohol-chemical processes, and has obtained several international patents, especially for the production of catalysts, which are essential components for converting ethanol into ethylene and other precursors. Furthermore, Oxiteno is working to develop the production of ethanol by hydrolysis of cellulose and to implement biorefineries, explicitly acknowledging its interest in supplying the inputs it needs for ethylene and ethylene-glycol production units [Inovação Unicamp (2006) and BNDES (2007)].

Coperbo — a Pernambuco Rubber Company — has an even longer history tying bioethanol to the production of chemical inputs. In September 1965, this company started the production of its butadiene unit in the city of Cabo, Pernambuco, to manufacture 27,500 tons per year of synthetic rubber based on ethanol. The objective was to meet the growing demand for this elastomer, which was only partially met by the domestic production of natural rubber. However, the approval by the Government of exports of molasses and imports of natural rubber created a shortage of ethanol to produce rubber, hampering the company's operations. In 1971 shareholder control of Coperbo was transferred to Petroquisa. This improved its financial situation and gave it a new impulse to increase its ethanol production, starting in 1975. The inclusion of acetic acid and vinyl acetate in its product line led to the creation of the National Alcohol-Chemical Company, which was later controlled by Union Carbide, a company that is currently managed by Dow Chemical [Jornal do Comércio (1999)]. No further details were obtained about its current industrial processes, but it is a fact that for several years this company produced ethanol-based butadiene, which was mainly used to manufacture tires on a commercial scale.

5.4 Biodegradable plastics production

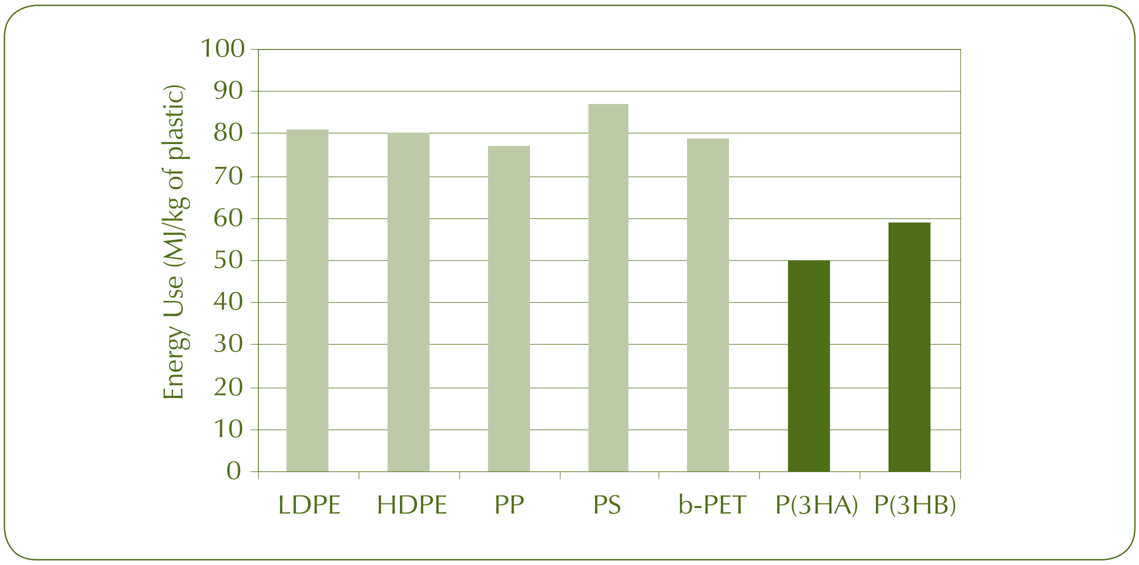
The global production of plastics was 230 million tons in 2004 and it is expected to increase to nearly 300 million tons en 2010 [Dröscher (2006)]. This enormous and growing market is a source of increasing environmental concern, because most plastic products are rapidly discarded and they have slow decay rates. Once used, less than 10% of plastics are recycled; the vast majority ends up in landfills [Waste-online (2008)], where complete decomposition can take from 100 to 500 years. The use of biodegradable plastics — besides increasing recycling — would be an effective solution to circumvent the problem.

Biodegradable plastics are polymers that, under appropriate environmental conditions, decompose completely in a short period of time due to microbial action. Bioplastics have an added important advantage: they are produced from renewable sources, like starches, sugars or fatty acids. One example of a bioplastic is polylactic acid (PLA), which is composed of lactic acid monomers obtained from microbial fermentation. Another possibility is to obtain the biopolymers directly from micro-organisms as in the case of polyhydroxybutyrate (PHB), polyhydroxyalkanoate (PHA) and their derivatives; in these cases the biopolymer is biosynthesized as energy reserve material of micro-organisms.

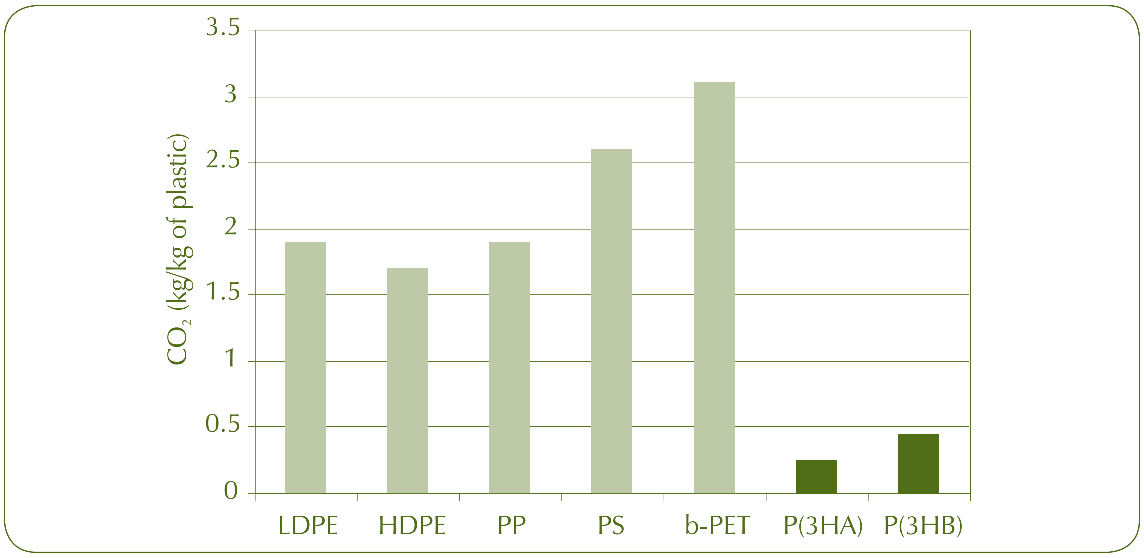
The first report about bioplastics was published in the 1920s, but the subject remained dormant until the 1970s, when the oil crisis revived research in alternative sources of materials and energy. Today, structures and biosynthetic routes and applications of many bioplastics are well understood, but there are still important limitations for large-scale production; for example, special growth conditions required for the synthesis of these compounds, the difficulty of synthesizing them through low cost precursors, and the high cost of their recovery. Even using recombinant micro-organisms capable of fermenting low cost sources of carbon (eg, molasses, sucrose, vegetable oils, and methane), these processes are still not competitive with the conventional production of synthetic plastics [Luengo, et al. (2003)].

Besides economic issues, it is also important to have a positive energy balance over the life cycle of these polymers, as they are intended to replace petrochemical materials. Normally, energy gains are small, since the energy supply, in general, is based on fossil fuels. In this case, once again the materials derived from sugarcane are favoured, thanks to the use of bagasse as an energy input in the process. Graph 15 presents a comparison between the energy consumed and greenhouse gases emitted in the production of 5 plastics of fossil origin — low density polyethylene (LDPEP), high density polyethylene (HDPE), polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (b-PET) — and two co-polymeric polyesters produced with biomass: P(3HA), based on soybean oil, and P(3HB), based on glucose [Akiyama, et al. (2003)].

Graph 15 – Energy use (a) and Emissions of Greenhouse Gases (b) in the production of various types of plastics



(a)



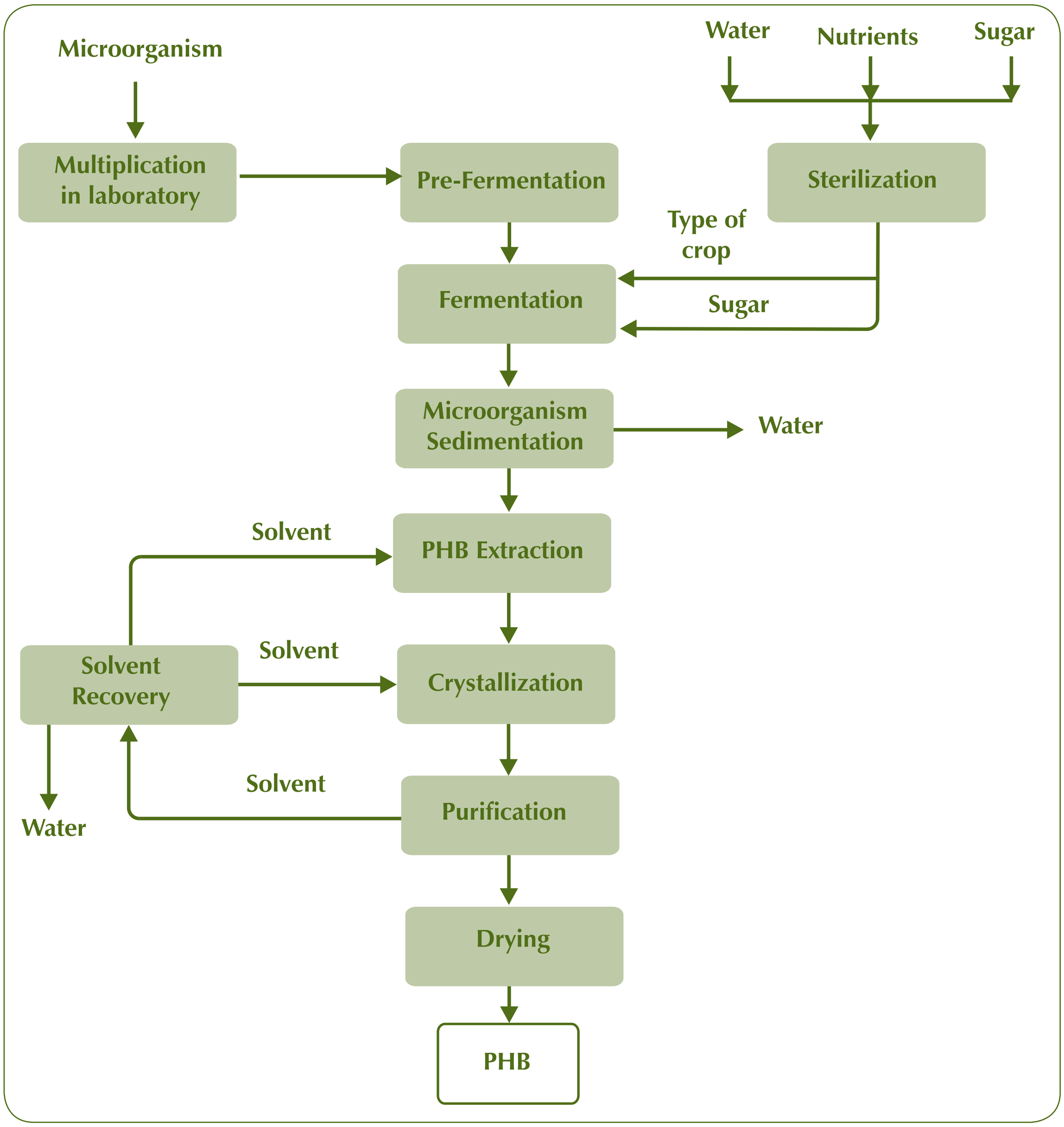
(b)

Source: Akiyama, et al. (2003).

In Brazil, there is already one PHB (polyhydroxybutyrate) production unit operating on a pilot basis with capacity to produce 60 tons per year. PHB Industrial S.A., in the city of Serrana, São Paulo, is attached to the *Usina da Pedra*, a sugar and bioethanol plant which supplies the sugar input and all the steam and electric power required by the plant. Industrial scale production is scheduled to start in 2008, beginning with 10,000 tons per year, destined mainly for the foreign market [Biocycle (2008)]. The production process is illustrated in Figure 22. Fermentation is carried out by micro-organisms cultivated anaerobically in a medium composed of sugarcane sugar and inorganic nutrients [Nonato, et al. (2001)]. Given this production design, it is estimated that only 10% of all the energy consumed in the life cycle of PHB comes from non-renewable sources, since bagasse provides the entire energy needed in the process [Seabra and Macedo (2006)]. Thus, it is reasonable to imagine considerably better performance in terms of non-renewable energy use and greenhouse gas emissions vs. polymers synthesized from other sources.

Pilot plant of PHB Industrial S.A. for biodegradable plastic production based on sugarcane sugar.

Figure 22 – Flowchart of PHB production from sugarcane sugar



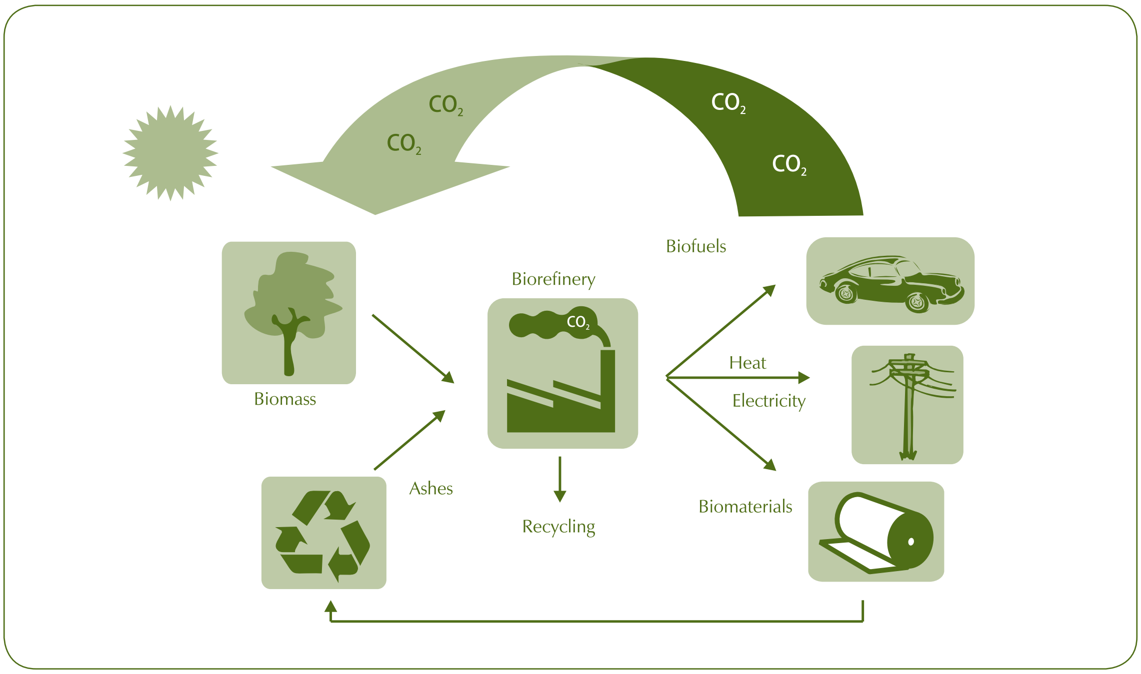
Source: Nonato (2007).

5.5 Biorefinery: multiple products and integral use of raw materials

A true biorefinery, as it is in the case of oil, can be defined as an integrated complex capable of producing various products — fuels, chemicals and power — using different types of biomass [Ondrey (2006)], in a model that would permit reaching greater efficiencies in thermodynamic, economic and environmental terms. Sugarcane bioethanol production can already be considered an example of a biorefinery, with its combined production of sugar, bioethanol and other chemical products, as well as power and heat generation from biomass residues [Macedo (2005b)].

Ragauskas, et al. (2006) provide a broad discussion of biorefineries and argue that they represent an optimized option for using biomass in the sustainable production of bioenergy, biofuels and biomaterials, both in the short and long term. Because of these attributes, large investments in development have been made in the past few years, both by governments and large private companies [Genencor (2004) and Ondrey (2006)]. Those investments create the expectation for competitive commercial plants in a not very distant future.

Figure 23 **– Complete integrated biomass-biofuel-biomaterial-bioenergy cycle**



Source: Adapted from Ragauskas, et al. (2006).

Some analyses of hypothetical "biorefineries" have contemplated the use of technologies that are expected to be "mature" in the future. Lynd et al. (2005) visualize the future self-sufficient production of power, Fischer-Tropsch fuels, and hydrogen, based on lignocellulosic materials, as well as scenarios involving the co-production of bioethanol-power, FT bioethanol-power-fuels, bioethanol-hydrogen or other combinations of products in conjunction with the production of protein. In the analysis, some scenarios demonstrate global energy efficiency on the order of 70% and economic competitiveness with conventional processes based on fossil fuels prices of the last few years.

A similar process of productive diversification and by-products valorization is taking place in forest-based industries. Analyses of the process envision the production of paper and cellulose, energy and a variety of chemical products, contributing to increase process efficiency, improve the benefit/cost ratio, and reduce environmental impacts [Karlsson (2007)]. The forest-based industry presents growth prospects which are similar to those in the sugarcane agroindustry, as well as interesting synergies between both industries in the development of technologies and markets.

Throughout this chapter it was possible to perceive the enormous potential associated with gasification technology as well as the possibilities of technologies for producing energy and different fuels. As a final point, and illustrating the potential of hydrolysis, it is important to bear in mind that when that technology becomes commercial and competitive, all biochemical sugar-processes for producing plastics, organic acids and solvents, among others, will no longer be restricted to the conventional sugar industry, but could be derived from any other source of biomass.