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MINI-REVIEW

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Integrated production of biodegradable plastic, sugar and ethanol

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Abstract Poly 3-hydroxybutyric acid (PHB) and related copolymers can be advantageously produced when integrated into a sugarcane mill. In this favorable scenario, the energy necessary for the production process is provided by biomass. Carbon dioxide emissions to the environment are photosynthetically assimilated by the sugarcane crop and wastes are recycled to the cane fields. The polymer can be produced at low cost considering the availability of a low-price carbon source and energy.

The sugar cane agroindustry in Brazil

In the 1970s, due to the gasoline crisis, Brazil implemented an audacious program for the use of ethanol as a fuel for motor vehicles. This program led to increased production in sugar mills, which were then combined with distilleries for the production of fuel ethanol in a very effective way.

Sugarcane mills located in the central-southern region of Brazil are large agroindustries that produce white sugar of various grades, hydrated and anhydrous ethanol for fuel purposes, and some by-products from sugar cane and ethanolic fermentation. These mills have the interesting characteristic of self-generating all the energy they require, thermal, mechanical and electrical, by burning sugarcane bagasse, a lignocellulosic residue obtained after the juice is extracted from sugar cane. Sugarcane contains 28% bagasse (at 50% moisture content), which is burned in medium (21 bar) to high-pressure boilers (60 bar) for steam production. Steam is expanded in turbines to provide the necessary mechanical and electrical power, and also, after expansion, the thermal requirements of the sugar mill. This energy is employed in sugar-processing operations, such as juice extraction, juice treatment, concentration and crystallization. Energy is also necessary during the fermentation and distillation procedures related to the production of hydrated and anhydrous ethanol. It is interesting to note that the net energy balance of a sugarcane mill is positive, even when including the ethanol distillery (Macedo and Nogueira 1985; Macedo and Koller 1996). Bagasse provides more energy than is necessary to drive sugar and ethanol production, a fact that renders sugarcane processing self-sufficient in energy.

Regarding effluents and wastes, it has been shown (Macedo 1996) that CO_2 emissions from the mill are balanced by the photosynthetic pathway of biomass production in cane crops. Furthermore, the use of ethanol or ethanol/gasoline blends as fuel for vehicles significantly reduces carbon dioxide emissions to the environment. Solid wastes remaining after juice treatment, which are rich in organic matter, phosphates, calcium and magnesium, are composted and applied to cane fields as fertilizer. Stillage resulting from ethanol distillation, with a high content of potassium salts, is sprayed on cane fields, supplying the cane crop with potassium, other minerals and organic nutrients. Stillage, as well as effluent water from washing operations and purges of water circuits, also serve as irrigation for cane crops.

These characteristics, added to the fact that low-cost, low-quality sugar can be produced and used as a carbon source in fermentation processes, greatly contribute to the integration of large-scale biotechnological enterprises into sugar mills. In this economic and environmentally favorable scenario, some of the difficulties in implementing new bioprocesses can be overcome, as suggested by the model proposed here.

A green cycle for simultaneous poly 3-hydroxybutyric acid, sugar and ethanol production

Biodegradable plastics have been the focus of intense discussion for a number of years, with one side strongly defending the idea, the other dismissing it as a mere curi-

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osity with no practical use. An important issue has been made clear by these discussions: biodegradability alone, although a prerequisite, is not enough for the success or failure of the new material. Initially, the product has to undergo a series of tests, now well-defined (DIN V-54.900, several ASTM standards grouped under ASTM D 6400–99, Narayan and Pettigrew 1999), that determine whether the claim of "biodegradable" truly applies. This means considering not only the initial attack of microorganisms on the material, but also the environmental impact of its disposal (De Wilde and Boelens 1998).

Once biodegradability has been demonstrated for the case material, its application has to be carefully chosen. It must be kept in mind that one quite interesting property of some conventional plastic resins is precisely their weather resistance. If the final product is expected to endure the weather (vehicle external parts, electric wire lining, protective paints, civil works, to name a few), biodegradability of course should be avoided. Clearly, then, biodegradability itself is advantageous only when it is implicitly demanded; thus conventional resins are still irreplaceable and different disposal procedures are necessary for each case.

For applications in which they would pose a sure advantage, biodegradable polymers have not yet replaced conventional plastics in any significant way. The main reason for this is economic: petroleum-based plastics can still be manufactured much more cost effectively (Braunegg et al. 1998). The closing of Monsanto's Biopol facilities clearly states that the willingness of the public to pay more for environmentally friendly products is limited.

To overcome the economic drawbacks, it is necessary to reduce the production costs of the resin or to increase its intrinsic value. The production of specialty products with high market values, for instance biodegradable and biocompatible resins for medical uses, may present a solution for small enterprises. Additionally, environmental legislation, making it compulsory to use a certain amount of biodegradable polymers, would contribute to the success of the product. The same applies to extra taxes on conventional non-biodegradable packaging materials. However, the development of a biodegradable plastic commodity market may only be feasible if a drastic reduction of the production cost is achieved.

Different approaches have been attempted or suggested with this objective in mind, such as mixing the polymer with cheaper materials (inorganics such as calcium chloride or carbonate, natural fibers and cellulose derivatives, starch, some conventional resins), optimization of synthesis, including engineering aspects of fermentation (Ackerman and Babel 1998; Grothe et al. 1999; Lee and Choi 1998; Naylor and Wood 1999), use of cheaper raw materials (Kim 2000), selection and genetic improvement of bacterial strains (see Da Silva and Gomes 1998; Renner et al. 1998; Vicente 1998a, b), production of transgenic plants (John and Keller 1996; Poirier et al. 1995), and optimization of the recovery and purification steps (Bueno Netto et al. 1993; Derenzo et al. 1993; Hahn et al. 1994; Holmes and Lim 1984, 1990). It is also most relevant for the concept of biodegradable plastics that its whole life cycle is environmentally sound, "from cradle to grave" (Gerngross 1999, 2000; Heyde 1998). If the process for obtaining the raw materials, producing a certain biodegradable material, collecting and finally disposing of it demands more energy or non-renewable resources than the more conventional materials, the advantages of biodegradability are very much impaired. With these considerations in mind, the model proposed here may well take biodegradables from a mere curiosity to a true commodity market.

This model for the integration of a poly 3-hydroxybutyric acid (PHB) production plant into the mill takes into account some important characteristics of the sugar agroindustry in Brazil, including the availability of energy, both thermal and electric, from renewable sources; effective residues- and waste-disposal management; availability of sugar at low prices and large quantities; availability of large-scale fermentation process technology. In response to the intensive thermal and electric energy demand of PHB production, the sugar mill provides a primary energy source, while simultaneously allowingfor effluent management according to environmental disposal regulations. The effluents remaining after PHB processing, mainly wasted culture media after biomass removal and effluent waters from the processing, can be sprayed on cane fields in the same way as distillery effluents. The biomass remaining after PHB recovery, which is rich in phosphate, calcium, nitrogen and micronutrients, can be composted and applied to the cane crops.

Another interesting aspect of the integration of the PHB plant into a sugar mill is the availability of natural solvents for PHB purification, which is a critical step in its production process. These solvents, by-products of ethanolic fermentation, help in solving one difficult problem in PHB production: purity vs environmental impact. Since the whole idea of the project is to produce an environmentally sound plastic resin, the use of chlorinated compounds in the purification step, which result in high-quality PHB (Hahn et al. 1994), should be avoided. One less aggressive process, which makes use of enzymes (Holmes and Lim 1984, 1990), has in our hands proved to be either quite expensive or lead to a material with lower purity. The use of naturally produced, biodegradable solvents could overcome these drawbacks: they allow for the production of a very pure PHB, while protecting the environmental aspect of the project.

Copersucar assembled, in 1995, a pilot-scale PHB production plant in one of its member mills. The goal of this pilot plant was to produce enough PHB to supply the market for tests and trials. Also, this pilot plant was intended as a training facility for future operators, and it is currently providing data for scale-up and economic evaluation of the process. Some data about the polymer produced at this pilot plant are presented in Table 1.

Table 1 Data from a pilot plant assembled inside a sugar mill intended for the production of 5 tons/month of PHB. The plant has been in operation since 1995. The values presented here for the fermentation step are similar to those observed by other authors (review by Braunegg et al. 1998). Also, the yield and purity attained following the extraction and purification steps closely resemble the values presented by Hahn et al. (1994), although their process made use of chlorinated compounds. Steam consumption is much higher than the value Gerngross (1999) adopted (2.78 kg/kg PHB), whereas electricity consumption is lower (5.32 kWh/kg PHB). This huge difference in steam consumption reflects the fact that the pilot plant was not optimized for energy recovery (no regenerative heat exchangers were used, for instance). Considering that the cost composition for the industrial plant takes into account the actual figures from the pilot plant, as presented here, a significant reduction in the "energy" item is to be expected with a careful energy balancing

Fermentation	
Biomass concentration	120–150 kg/m^3 (dry basis)
PHB content in biomass	65–70%
Productivity	1.44kgPHB/m^3 per h
PHB yield	3.1 kg sucrose/kg PHB
Extraction	
Yield	95%
PHB purity	>98%
PHB molecular weight	250,000–400,000
Energy	
Steam consumption	39.5 kg steam/kg PHB
Electric power	3.24 kWh per/PHB
Cost composition for PHB production (10.000 tons/year plant estimate)	
Raw material (sugar)	29%
Other chemicals	20%
Equipment depreciation	27%
Energy	11%
Others	13%

PHB production process

Poly 3-hydroxybutyric acid and related copolymers, such as poly 3-hydroxybutyric-*co*-3-hydroxyvaleric acid (PHB-V), are natural polyesters, synthesized by a wide range of organisms, particularly by some bacterial strains. They have very interesting properties such as being biocompatible and totally and rapidly biodegraded to carbon dioxide and water by a large number of microorganisms (Ohura et al. 1998). They can be compounded to thermoplastic resins that have physicochemical and mechanical properties similar to petrochemical-based polymers, e.g., polyethylene and polypropylene, and standard plastic-engineering molding procedures can be applied to them.

The homopolymer PHB is itself quite brittle, a fact that reduces the range of its applications. Nevertheless, nucleating agents, plasticizers and other additives allow PHB to be used in several processes, especially injection molding for pots, caps and other single, hard pieces. Other uses, such as molds for metal casting, prosthetics, paper and granule coating, composites (starch, cellulose) are under development. Copolymers such as PHB-V, middle chain length polyalkanoates (mcPHA), 4-OH-PHB and other polymer from the PHB family present very interesting properties and may be considered in our production model in the near future. At present, though, PHB is the material of choice due to economic and environmental reasons: it is produced directly from sugar by naturally occurring microorganisms and without any petrochemical-derived substrates. Sugar is, for this model, the cheapest, most appropriate substrate available.

The adopted PHB production process was developed by a joint venture between Copersucar, IPT (Technological Research Institute of São Paulo) and ICB (Biomedical Institute of University of São Paulo) (Bueno Netto et al. 1993; Derenzo et al. 1993). It comprises a fermentation step, in which strains of *Ralstonia eutropha* (Vicente 1998a, b) or *Bhurkolderia SP* (Da Silva and Gomes 1998) are aerobically grown to a high cell density in a well-balanced medium consisting of cane sugar and inorganic nutrients. Cell growth is then shifted to PHB synthesis by limiting nutrients others than the carbon source, which is continually fed as a high-concentration sugar syrup. After 45–50 h, the fed-batch fermentation process is stopped, with a final dry cell mass of 125–150 kg/m^3, containing nearly 65–70% PHB. The fermented medium is thermally inactivated in a heat exchanger, diluted with water, and flocculated. Separation and concentration procedures yield a cell sludge containing 25–30% solids which is then submitted to a multistage extraction process with medium-chain-length alcohols in continuous-stirred tank reactors. The extract is purified for cell debris removal and then cooled down to recover a PHB gel. Solvent from the gel is removed by mechanical and thermal concentration. The resulting PHB paste is mixed with water and distilled to remove the remaining solvent. PHB granules are then collected by a sieve, vacuum dried, compounded and extruded as pellets.

Mass and energy balance for PHB production at the sugar mill

The production of PHB integrated into a sugar and ethanol mill relies mostly on the capacity of the system to supply the necessary energy for running the processes, the availability of raw materials, and the ability of the system to process and use effluents without adverse impact to the environment. Figure 1 shows a mass and energy diagram for sugar, ethanol and PHB production from sugarcane.

In the south-central region of Brazil, an average sugar mill crushes 12,000 tons of sugarcane per day, during a milling season of 180 days. The amount of land required to produce sugarcane for such a mill is approximately 25,000 hectares. The juice obtained from crushing the sugarcane is used to produce both sugar and ethanol. It is into this type of mill, which will operate year round and produce 10,000 tons of PHB per year, that the integration of a PHB production unit is planned.

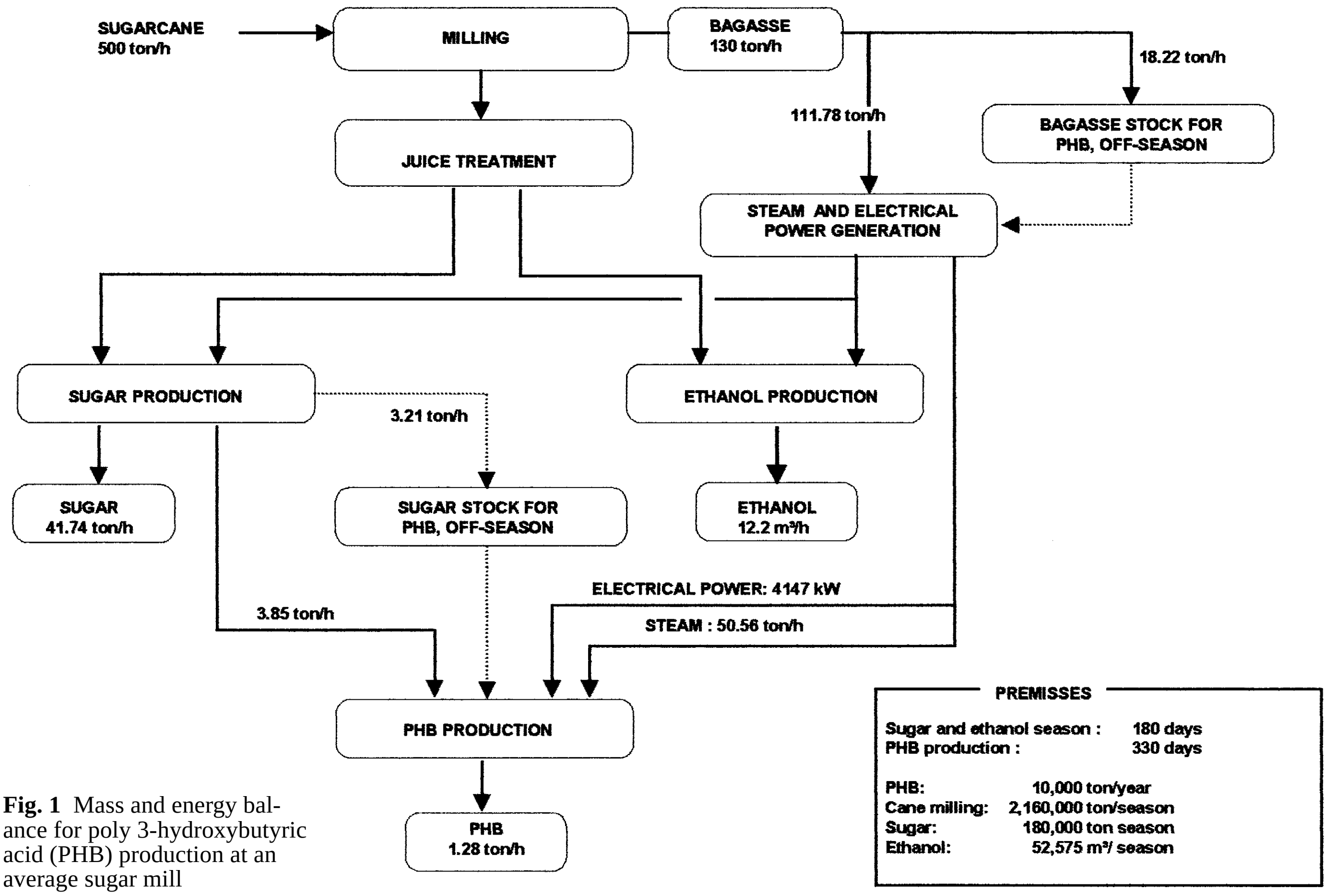

Fig. 1 Mass and energy balance for poly 3-hydroxybutyric acid (PHB) production at an average sugar mill

In order to attain the energy requirements, some changes have to be introduced in the mill. Medium-pressure boilers must be replaced by a larger, more efficient high-pressure boiler capable of generating superheated steam at 60 bar and 450 °C. High-efficiency, multistage turbo-generators need to be installed to increase electric power production. Low-pressure steam demand for heating has to be decreased to 350 kg of steam per ton of cane. This can be achieved if sugar-factory consumption is optimized by the use of heat regeneration, increased use of secondary steam in juice heaters and vacuum pans, and increasing the number of stages in multiple-effect juice evaporation. Similarly, increasing the alcoholic concentration in the fermented mashes and optimizing distillation towers can also reduce the steam demand of the ethanol plant.

Yields, investment and costs

The production of PHB requires 3 kg of sucrose per kg of final product. At present, the process demands a large quantity of steam (39.5 kg/kg PHB) and electrical energy (3,24 kWh/kg PHB), although these figures can be reduced in a short time. For a 10,000-ton PHB per year plant, the cost of equipment for the fermentation plant is estimated at US$15,000,000, the extraction and purification unit at US$15,000,000 and utilities at US$5,000,000. The cost of land, construction and buildings is estimated at US$900,000 for the fermentation plant, US$1,600,000 for the PHB-recovery facilities and US$600,000 for the utilities unit.

The PHB production cost is heavily dependent on sugar prices, which account for nearly 29% of the final cost (not considering taxes). Depreciation costs closely follow in terms of cost formulation, with thermal and electric energy representing another 11%. As a whole, the cost of PHB production has been estimated (Lee and Choi 1998) at US$2.65/kg PHB for a 100,000-tons-per-year plant, with the use of sucrose as substrate and fossil fuels. Other preliminary estimates (Bertrand 1992) for an autonomous unit using glucose as a substrate and fossil fuel showed a cost of US$5.85 per kg PHB for a plant of 30,000-tons-per-year capacity. It is worthwhile noting that Biopol (Monsanto), a PHB copolymer compounded resin, was sold at a price of US$10.00–20.00 per kg, depending on grade.

Our preliminary evaluation for a 10,000-tons-per-year plant points out that the production cost is heavily related to the market price of sugar. The price of bagasse, which is the primary energy source, is directly related to oil prices, and has a weight of approximately 5% on the PHB cost. Our pilot trials enable us to foresee that the production cost (without taxes) could very much approach the lower estimate (Lee and Choi 1998), depending on raw-material prices and fermentation and separation yields.

Conclusions

It is a fact, at the present state of technological development, that the bioprocess used for PHB production requires more energy than do those for most petrochemical plastic resins, as demonstrated by Gerngross (1999). Nevertheless, the integrated model we have proposed here makes extensive use of facilities, materials and surplus energy from the sugarcane industry that would otherwise be wasted or sold at subsistence prices. This integrated model also permits wastes from the PHB plant, either directly or after composting, to be returned to the cane fields, reducing the need for fertilizers, mainly nitrogen and phosphate. Since all the carbon involved (both as fuel or feedstock) comes from sugarcane, CO_2 emissions from the production plant also return to the fields by means of photosynthesis, which means that the net carbon balance is close to zero.

Large-scale production of PHB in sugarcane mills (in this case, 10,000 tons/year) presents a successful opportunity for expanding the sugar industry. The total amount of sugar diverted to PHB synthesis would account for a low percentage (17%) of the total sugar produced by the (average) mill where the plant is integrated. This fact assures that PHB production would not affect sugar stocks, nor would it have any significant impact on sugar prices. It is expected that the PHB production capacity could be increased approximately two to three times for the same mill, if the market for biodegradable resins increases. Expansion will be possible by optimizing the energy consumption in PHB production, by the use of cane leaves and wastes as a new source of primary fuel at the mill, and mainly by optimization steps at the power plant, the sugar factory and the distillery.

When considering the prospects for the near future, it must be mentioned that the annual production of sugar and ethanol in the south-central region of Brazil, from approximately 265 million tons of sugarcane, are 16.9 millions tons and 11.6 millions cubic meters, respectively. There exists a significant amount of available arable land, now occupied by low-grade pastures, that could be used for sugarcane production if market demand increased. This capacity could allow for the rapid growth of PHB production to cope with the market needs, should the demand for biodegradable resins match the projections.

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