
BIOETHANOL

Edited by **Marco Aurélio Pinheiro Lima**

Alexandra Pardo Policastro Natalense



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Preface

Nine billion. This is the estimated number of people who will inhabit our planet in 2050. In a few decades, we will have nearly a quarter more than humans circling the globe in search of food, shelter, clothing and other manufactured products. Among the new individuals, the United Nations (UN) estimates that 98% will live in developing countries, with the highest level of economic growth, which in turn will result in a considerable expansion in per capita consumption worldwide.

On the one hand we have a significant increase in energy demand and consumption, resulting from population and income growth, and on the other, there is a considerable uncertainty about the world's available supply of natural resources to support this development. Intergovernmental Panel on Climate Change (IPCC) recent reports have shown strong evidence of the impact of human activity on the climate of the planet. Estimates of the entity warn about a potential increase in global average temperature by up to 5 or 6°C by the end of this century. The raise in temperature itself would cause drastic changes in many ecosystems, but the reports also mention the intensification of extreme weather events such as hurricanes.

This apparently catastrophic scenario for the maintenance of the human species on Earth, opens up several possibilities for what is now called "green" or low carbon economy. We are talking about creating new businesses and industries geared to develop products and services with low consumption of natural resources and reduced emission of greenhouse gases. Within this category of business, biofuels is a highlight and the central theme of this book.

Biofuels are now the main alternative to automotive fossil fuels due to the fact that they are produced from renewable sources such as sugar cane, corn, cassava, oil seeds, agricultural waste, algae, etc.. Ethanol from sugar cane produced in large scale in Brazil, for example, illustrates the benefits of these products. Its production costs are low, which makes it competitive with oil derivatives. Each unit of fossil energy used in ethanol production is reversed in eight to nine units stored in the fuel. Finally, one of the most important qualities, each cubic meter of sugarcane bioethanol used as fuel reduces from 1.7 to 1.8 tonnes of CO₂ (equivalent) emitted into the atmosphere. Due to the flex-fuel engine technology, more than 90% of light vehicles produced in Brazil are now able to run on 100% fuel ethanol.

The successful history of Brazilian ethanol is undoubtedly the first successful case of production and use of a biofuel in large scale, but is far from being the last. From the beginning of the century, two main factors have made the world turn its attention to research on biofuels. The first, already mentioned, is the increasing debate on climate issues. The second is the raise in the price of the oil barrel. In 1970, before the first shock in the price of fossil fuel, a barrel costs about \$ 3. In 2008 the price was above \$ 120. These facts stimulated scientists around the world to focus their research on themes that could result in the diversification of the energy matrix in many countries.

The globalization of the research on biofuels may bring a number of advancements to the industry and has already awakened a wish the market: to also convert cellulose into ethanol. Materials not used in the production of biofuels, such as sugarcane bagasse, corn stover and forest residues can be a significant source of additional ethanol, provided that appropriate industrial technologies are developed. In the case of sugarcane ethanol for example, data from the Brazilian Bioethanol Science and Technology Laboratory (CTBE) indicate that the conversion of bagasse and straw would increase the current production of bioethanol in Brazil in about 50%.

However, the challenges to make this technological potential an industrial reality are numerous and need investment in research and development (R&D). There are technological barriers with respect to the initial treatment of the raw material, production of microorganisms that break down cellulose into fermentable sugars, the fermentation of five-carbon sugars (pentoses), among others.

The new global market of bioenergy that has been structured in recent years has yet another relevant route for exploration: the biorefinery. Similar to the oil industry, it uses different types of processes to transform the same raw material in different products used by many industrial sectors, such as food, pharmaceutical, chemical, etc.. Companies and research institutes have studied and developed processes that convert biomass into raw materials for their production chain, potentially replacing substances that were produced from petroleum. Thus, in most cases, the environmental benefits and the reduction of dependence on fossil fuels are evident. Some studies even indicate that the use of biomass within the biorefinery concept may improve the profitability of cellulosic ethanol technology (second generation) and favor the integration of this new technology with the current first generation process.

The first section of this book presents some results for first generation ethanol production, i. e., from starch and sugar raw materials, which include cassava, sorghum, and sugarcane. In the second section, the chapters present results on some of the efforts being made around the world in order to develop an efficient technology for producing second-generation ethanol from different types of lignocellulosic materials. While efficient ethanol production technologies are being developed, one can also start thinking about different uses for it. In addition to the more straightforward use as fuel, it is worth to study other applications. The chapter in the

third section points to the use of hydrogen in fuel cells, where this hydrogen could be produced from ethanol.

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Part 1

First Generation Bioethanol Production (Starch and Sugar Raw-Materials)

Cassava Bioethanol

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1. Introduction

1.1 Cassava

Cassava (*Manihot esculenta* Crantz) is a shrubby perennial crop in the Family of Euphorbiaceae. It is also named others, depending upon geographic regions such as yucca in Central America, mandioca or manioca in Brazil, tapioca in India and Malaysia and cassada or cassava in Africa and Southeast Asia. Cassava is mostly cultivated in tropics of Africa, Latin America and Asia, located in the equatorial belt, between 30° north and 30° south. The crop produces edible starch-reserving roots which have long been employed as an important staple food for millions of mankind as well as animal feed. Due to the fact of ease of plantation and low input requirement, cassava is mostly cultivated in marginal land by poor farmers and is sometimes named as the crop of the poor. In these planting areas, cassava plays an essential role not only as food security, but also income generation. In addition to a primary use for direct consumption and animal feed, starch-rich roots are good raw materials for industrial production of commercial tapioca starch, having excellent characteristics of high whiteness, odorless and tasteless and when cooked, yielding high paste viscosity, clarity and stability. The distinct attributes of extracted cassava starch, either as native or modified form, are very attractive for a broad range of food and non-food application including paper, textile, pharmaceutical, building materials and adhesives. Furthermore, cassava starch is extensively utilized for a production of sweeteners and derivatives including glucose syrup, fructose syrup, sugar alcohols (e.g. sorbitol, mannitol), and organic acids (e.g. lactic acid, citric acid). The application of cassava as renewable feedstock is now expanded to biorefinery, i.e. a facility that integrates processes and equipment to produce fuels, power, chemicals and materials from biomass (Fernando et al., 2006). With this regard, cassava is signified as a very important commercial crop that can have the value chain from low-valued farm produces to high-valued, commercialized products.

1.2 Cassava agronomy and plantation

Cassava is well recognized for its excellent tolerance to drought and capability to grow in impoverished soils. The plant can grow in all soil types even in infertile soil or acid soil (pH

4.2-4.5), but not in alkaline soil ($\text{pH} > 8$). Despite of that, cassava prefers loosen-structured soil such as light sandy loams and loamy sands for its root formation. As the drought – tolerant crop, cassava can be planted in the lands having the rainfall less than 1,000 mm or unpredictable rainfall. Rather than seeding, the plants are propagated vegetatively from stem cuttings or stakes, having 20-cm in length and at least 4 nodes. To ensure good propagation, good-quality stakes obtained from mature plants with 9-12 months old should be used. The appropriate time of planting is usually at an early period of rainy seasons when the soil has adequate moisture for stake germination. When planted, the stakes are pushed into the soil horizontally, vertically or slanted; depending on soil structure. For loosen and friable soil, the stakes are planted by pushing vertically (“standing”), or slanted approximately 10 cm in depth below the soil surface with the buds facing upward. This planting method gives higher root yields, better plant survival rates and is easy for plant cultivation and root harvest (Howeler, 2007). The horizontal planting is suited for heavy clay soils. Planting with 100 x 100 cm spacing (or 10,000 plants/hectare) is typical, however, less spacing (100 x 80 cm or 80 x 80 cm) and larger spacing (100 x 120 cm or 120 x 120 cm) are recommended for infertile sandy soil and fertile soil, respectively. At maturity stage with 8-18 months after planting, the plants with two big branches (i.e. dichotomous branching) or three branches (i.e. trichotomous branching) are 1-5 m in height with the starch-accumulating roots extending radially 1 m into the soil. Mature roots are different in shapes (as conical, conical-cylindrical, cylindrical and fusiforms), in sizes (ranging from 3 to 15 cm in diameter, as influenced by variety, age and growth conditions) and in peel colors (including white, dark brown and light brown). Although the roots can be harvested at any time between 6-18 months, it is typically to be harvested on average at 10-12 months after planting. Early or late harvesting may lower root yields and root starch contents. Still, the actual practice of farmers is depending on economic factors, i.e. market demand and root prices. Root harvesting can be accomplished manually by cutting the stem at a height of 40 - 60 cm above the ground and roots are then pulled out by using the iron or woody stalk with a fulcrum point in between the branches of the plant. Plant tops are cut into pieces for replanting, leaves are used for making animal fodder and roots are delivered to the market for direct consumption or to processing areas for subsequent conversion to primary products as flour, chips and starch.

1.3 Cassava production

Since 2004, the world production of cassava roots has been greater than 200 million tons and reaches 240 million tons in 2009 (Food and Agriculture Organization [FAO], 2011; Table 1). The major cassava producers are located in three continental regions which are Nigeria, Brazil and Thailand, accounting approximately for 20, 11 and 12% of total world production, respectively. In the last two decades, the world production of cassava continuously increases (Table 1), as primarily driven by the market demand, in particular an expansion of global starch market. The growth rate of root production in the last decade (2000-2009) is even greater than the previous one (1990-1999) due to markedly rising demand of cassava for bioethanol production in Asia especially in China and Thailand. Interestingly, the root productivity of cassava has been dramatically increased in some countries including Vietnam, India, Indonesia and Thailand by 8.46, 7.46, 6.22 and 5.85 tons/hectare in the past 10 years. The root productivity of India is the greatest (34.37 tons/hectare), followed by Thailand (22.68 tons/hectare) and Vietnam (16.82 tons/hectare) while the world average is

Region	Production (x 1,000 tons) ¹							
	1990-94 average	1995-99 average	2000-04 average	2005	2006	2007	2008	2009
<i>World</i>	160,769	163,220	187,540	207,332	222,879	226,312	232,463	240,989
<i>Africa</i>								
Angola	1,868	2,743	6,366	8,606 (4.15)	8,810 (3.95)	9,730 (4.30)	10,057 (4.33)	12,828 (5.32)
Congo	648	770	869	935 (0.45)	1,000 (0.45)	950 (0.45)	1,000 (0.43)	n.a.
Ghana	5,216	7,148	9,356	9,567 (4.61)	9,638 (4.32)	10,218 (4.32)	11,351 (4.88)	12,231 (5.08)
Nigeria	27,073	32,053	34,669	41,565 (20.05)	45,721 (20.51)	43,410 (20.51)	44,582 (19.18)	n.a.
Tanzania	7,281	5,666	4,651	5,539 (2.67)	6,158 (2.76)	6,600 (2.76)	6,600 (2.84)	n.a.
<i>Latin America and Caribbean</i>								
Brazil	23,420	20,686	22,973	25,872 (12.48)	26,639 (11.95)	26,541 (11.73)	26,703 (11.49)	26,031 (10.80)
<i>Asia</i>								
India	5,530	5,895	6,135	7,463 (3.60)	7,855 (3.52)	8,232 (3.64)	9,056 (3.90)	9,623 (3.99)
Indonesia	16,263	15,742	17,601	19,321 (9.32)	19,987 (8.97)	19,988 (8.83)	21,593 (9.29)	22,039 (9.15)
Thailand	20,011	16,757	19,097	16,938 (8.17)	22,584 (10.13)	26,916 (11.89)	25,156 (10.82)	30,088 (12.49)
Viet Nam	2,421	2,051	4,213	6,716 (3.24)	7,783 (3.49)	8,193 (3.62)	9,396 (4.04)	8,557 (3.55)
<i>Others</i>	51,038	53,709	61,609	64,809	66,705	65,534	66,969	119,593

¹ The numbers in parenthesis represent the percentage of total world production.
n.a. = not available

Source: Food and Agriculture Organization of the United Nations [FAO], 2011

Table 1. Annual production of cassava roots by major producers.

12.64 tons/hectare (Table 2). The world leading cassava producers, i.e. Nigeria and Brazil, however, do not have much improvement in root productivities in the past 10 years; only by 2.10 tons/hectare (from 9.70 to 11.80 tons/hectare since 2000 to 2008) and by 0.35 tons/hectare (from 13.55 to 13.90 tons/hectare since 2000 to 2009), respectively.

The production of cassava can be simply increased by expanding planting areas. Nevertheless, in most regions, no new marginal land is accessible as well as forestry areas are not allowed for area expansion. Moreover, in some countries, there is a competition for land uses among other economic crops such as sugar cane and maize in Thailand. The sustainable and effective means of increasing root production should be achieved by an increase in root productivity. Yields or root productivities of cassava roots vary significantly with varieties, growing conditions such as soil, climate, rainfall as well as agronomic practices. Better root yields can be obtained by well-managed farm practices including time of planting (early of a wet season), land preparation (plowing by hand or mechanically and ridging), preparation of planting materials (ages of mother plants, storage of stems, length & angle of cuttings, chemical treatment), planting method (position, depth of planting and spacing), fertilization (type of fertilizers – chemical vs. organic, dose, time and method of fertilizer application), erosion control, weed control, irrigation and intercropping (Howeler, 2001; 2007). The agronomic practices implemented by farmers vary markedly from regions to regions, depending greatly on farm size, availability of labor, soil and climatic conditions as well as socio-economic circumstances of each region (Table 3). It is very interesting to note that the highest root productivity was reported in India (i.e. 40 tons/hectare) which was irrigated cassava rather than rainfed one, with a highest amount of fertilizer application. In some planting areas such as in Thailand, irrigation is now introduced instead of relying only on rainfall. Yet, the investment cost is high and farmer's decision is upto market demand, price of cassava roots as well as other competitive crops. By effective farm management, it is expected that the root productivity can be increased twice, from 25 to 50 tons/hectare. By combining that with varietal improvement, the root productivity can be potentially improved upto 80 tons/hectare (Tanticharoen, 2009).

The production cost of cassava is classified into fixed costs and variable costs. The fixed costs include land rent, machinery, depreciation cost and taxes. The variable costs are consisted of labor costs (for land preparation, planting material preparation, planting, fertilizer & chemical application, weeding, harvesting and irrigation) and others including planting materials, chemicals (herbicides, sacks), fuels and tools. Except China, all countries demonstrate that the labor cost is greater than 40% of total production cost. In particular, the labor cost as well as the fixed costs of cassava plantation in India is quite high comparatively to other countries, making their production cost quite high. A semi-mechanized practice for cassava plantation is therefore developed in some countries such as Brazil and Thailand in order to minimize the labor cost, and hence total production cost.

1.4 Cassava attributes

Cassava plants photosynthesize and store solar energy in a form of carbohydrate, mainly as starch in edible, underground roots. The roots are very moist having the water content around 59-79% w/w (Table 4). On dry solid basis, starch is a major component of cassava roots, accounting upto 77-94% w/w, the rests are protein (1.7-3.8% w/w), lipid (0.2-1.4% w/w), fiber (1.5-3.7% w/w as crude fiber, i.e. cellulose and lignin) and ash (1.8-2.5% w/w) (Table 4). Some sugars, i.e. sucrose, glucose and fructose are also found in storage roots at 4-8% w/w (dry basis). In addition to cellulosic fiber, the roots also contain non-starch

Regions	Root productivity (tons/ hectare)									
	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
Nigeria	9.70	9.60	9.90	10.40	11.00	10.99	12.00	11.20	11.80	n.a.
Brazil	13.55	13.54	13.77	13.44	13.63	13.61	14.05	14.01	14.14	13.90
Thailand	16.86	17.54	17.07	19.30	20.28	17.18	21.09	22.92	21.25	22.68
Indonesia	12.53	12.94	13.25	14.88	15.47	15.92	16.28	16.64	18.09	18.75
Ghana	12.28	12.34	12.25	12.69	12.42	12.76	12.20	12.76	13.51	13.81
India	26.91	26.70	27.27	26.21	27.04	30.50	32.11	32.22	33.54	34.37
Viet Nam	8.36	12.01	13.17	14.28	14.98	15.78	16.38	16.53	16.91	16.82
World	10.38	10.68	10.71	10.93	11.29	11.33	12.12	12.11	12.45	12.64

n.a. = not available

Source: Food and Agriculture Organization of the United Nations [FAO], 2011

Table 2. World average root productivity (tons/ hectare) and those of major producers.

	Thailand	Indonesia ¹	India ²	Vietnam ³	China
Cassava area (hectare/ farmer)	2-3	0.3-1.0	0.5-1.0	0.2-0.9	0.2-0.4
Intercrops	None (95%), Maize (5%)	Maize+rice- soybean/ peanut	None/ vegetables	None/ maize	None/ peanut
Land preparation	Tractor (3 + 7 disc)	Manual/ animal/ tractor	Tractor	Animal/ tractor	Manual/ animal
Fertilizer use					
-Organic (ton/hectare)	Little	Low, 3-10	10-20	0-5	3-5
-Inorganic (kg N+P ₂ O+K ₂ O/hectare)	30-120	Medium, N-only	High	0-60	NPK
Planting time	March-May (70%)	Oct-Dec (90%)	Jan-Mar (90%)	Feb-May (80%)	Feb-Apr (90%)
Harvest time	Sept-Nov	Jul-Sept	Sept-Oct	Oct-Nov	
	Dec-May		Oct-Jan	Feb-Mar	Nov-Jan
	Aug-Dec			Sept-Oct	
Planting space (m)	0.8x1.2, 0.8x0.8	1.0x0.8, 2.0x0.5	1.0x1.0	1.2x0.8, 0.8x0.8	1.0x1.0, 0.8x0.8
Planting method	Vertical	Vertical	Vertical	Horizontal	Horizontal
Weed control	Hoe 2-3x small tractor/ Paraquat	Hoe 1-2x	Hoe 4-5x	Hoe 2-3x	Hoe 2-3x
Harvest method	Hand/ tractor	Hand	Hand	Hand	Hand
Main varieties	KU 50, Rayong 90, Rayong 60, Rayong 5	Adira 4, local varieties	H-226, H-165, local varieties	KM 94, KM 60, 34, HL 23	SC 205, SC 201, SC 124
Labor use (m-days/hectare)	50-60	150-300	200-350	100-200	90-180
Yield (tons/ hectare)	23.40	20	40 ⁴	25	20
Production cost					
-Variable costs (USD/hectare)	365.91	265.92	663.85	384.67	427.62
(Labor cost)	(167.18)	(185.37)	(421.70)	(213.60)	(167.40)
(Other costs: Fertilizers, chemicals, cuttings, transportation)	(198.73)	(80.55)	(242.15)	(171.07)	(260.22)
- Fixed costs (USD/hectare)	48.89	46.67	236.50	60.00	94.94
- Total production costs					
USD/ hectare	414.80	312.59	900.35	444.67	520.56
USD/ ton fresh roots	17.73 27.33 ⁵	15.63	22.51	17.79	26.03

¹ Information of Java and Sumatra ² Information of Tamil Nadu ³ Information of South Vietnam
⁴ Irrigated cassava ⁵ Source: Office of Agricultural Futures Trading Commission [AFTC], 2007
n.a. = not available Source: Howeler, 2001

Table 3. Agronomic practices and production cost of cassava plantation in some Asian countries.