



Artigo

Perspectives for Biomass Production and Use in Brazil Galembeck, F.;* Abreu Filho, P. P.*

Rev. Virtual Quim., 2017, 9 (1), 274-293. Data de publicação na Web: 16 de dezembro de 2016 http://rvq.sbq.org.br

Perspectivas para Produção e Uso de Biomassa no Brasil

Resumo: O uso de biomassa como uma fonte de energia e de matérias-primas industriais tem crescido, mas com oscilações associadas aos preços do petróleo. Uma frequente objeção ao uso da biomassa como fonte de energia e matérias-primas é a competição com a produção de alimentos, aumentando seus preços e reduzindo a segurança alimentar global. A experiência brasileira das últimas quatro décadas e a recente experiência da Etiópia mostram a possibilidade de se criar sinergias no uso de solo agrícola para múltiplas finalidades. No Brasil, os esforços de produção de combustíveis de biomassa, o álcool e o biodiesel, ocorreram em paralelo com um grande aumento na produção de alimentos e com um aumento relativamente menor na área cultivada. Isso só foi possível graças a um grande aporte de novas tecnologias. O aumento na produção de alimentos produz grandes quantidades de resíduos que são novas oportunidades para P&D. A produção sinérgica de alimentos, energia e matérias-primas é um fator decisivo na busca da sustentabilidade.

Palavras-chave: Combustível; alimentos; uso da terra; biomassa; energia renovável; Produtividade vegetal; cana-de-açúcar.

Abstract

The use of biomass as a source of energy and raw materials shows an overall growing trend with ups and downs related to oil prices that are in turn heavily affected by political and strategic factors. A frequent objection to the growing use of biomass as a source of energy and raw materials is its competition with food production, decreasing global food security. The Brazilian experience from the past four decades and the recent experience from Ethiopia show that synergies are created by the multipurpose use of agricultural land. In Brazil, the energy push took place in parallel with a large increase in food supply and a relatively small increase in the used land, thanks to technological inputs. A side product of increased food production is the growing amount of biomass residues that are by themselves new opportunities for R&D. Synergic production of food, energy and raw materials are presented as essential features of the roadmap to sustainability.

Keywords: Fuel; food; land use; biomass; renewable energy; crop productivity; sugarcane.

M fgalembeck@gmail.com; pompeu@sigmabbs.com.br

DOI: 10.21577/1984-6835.20170018

^{*} University of Campinas, Institute of Chemistry, Cidade Universitária Zeferino Vaz, P.O. Box 6154, CEP 13083-970, Campinas-SP, Brazil.



Perspectives for Biomass Production and Use in Brazil Fernando Galembeck,* Pompeu P. de Abreu Filho*

University of Campinas, Institute of Chemistry, Cidade Universitária Zeferino Vaz, P.O. Box 6154, CEP 13083-970, Campinas-SP, Brazil.

* fgalembeck@gmail.com; pompeu@sigmabbs.com.br

Recebido em 1 de novembro de 2016. Aceito para publicação em 16 de dezembro de 2016

1. Introduction

- 1.1. A little history: the first century
- **1.2.** Early use of biomass and its consequences
- 1.3. Enter the fossil fuels
- 1.4. Food vs. fuel
- 1.5. Oil fights back

2. From sugar to the sugarcane-based industries

- 2.1. Praise and criticism
- 3. Land use: competition and impacts
- 4. Prospects for biofuels
 - **4.1.** Emerging crop species
- 5. Outstanding properties of materials from biomass
 - 5.1. Natural rubber
 - 5.2. Cellulose
- 6. Conclusion

1. Introduction

1.1. A little history: the first century

Brazil was named after the "pau-brasil" or brazilwood (*Caesalpinia echinata*) that was wildly exploited by the colonizers soon after they first landed in this part of the world. Aged aqueous extracts of the wood sawdust produce a brilliant red dyestuff that was

highly valued to produce fashionable red clothing, in Europe.¹ Brazilwood trunks loaded a ship from the Cabral fleet that was immediately sent back to Portugal² Few decades later, Martim Afonso de Souza brought the first sugar cane plantlets to Brazil and initiated sugar production in 1533, in São Vicente. This spread to other parts of the country and became very important in Pernambuco. Sugar was then a highly valuable product that brought great wealth to the Portuguese crown. Sugar and



brazilwood dye were thus the two first industrial products from this country and both derived from biomass.

1.2. Early use of biomass and its consequences

More than 500 years later, this country looks again to biomass as a major source of wealth but in a completely different global context. Instead of navigators from different countries fighting for territorial domain that brought wealth, the whole mankind is or should be engaged in the transition to sustainable or at least durable economy. The concern for sustainability is not only environmentalists expressed by and unorthodox economists, but by industrialists, politicians and growing number of citizens, everywhere.

Biomass already provided all of the food and nearly all of the energy for mankind growth, for millenia. Together with minerals, it also provided the required raw materials for housing, clothing, transportation and other needs that appeared as civilization developed. This happened in a scenario of abundance but it implied in a profound modification of the environment, due to land use change. Maps presented by Sir Mark Walport³ show the deforestation of Europe from 1000 BC to 1500 AC. The extracted wood was used for building houses, ships and other human needs or burned, for heating and cooking. The deforested land was used for agriculture, husbandry of for building human dwellings and cities.

Extensive deforestation also took place in the US⁴ and throughout the world, with very few exceptions. Deforestation continues today and hotspots are in the Amazonian Brazil, Colombia, Venezuela and Peru, Central America and Mexico, in Africa, Asia and Australia but we can also identify net gains of planted forest in many places, including Europe, the US, Brazil and the Asian Pacific rim (Figure 1).⁵

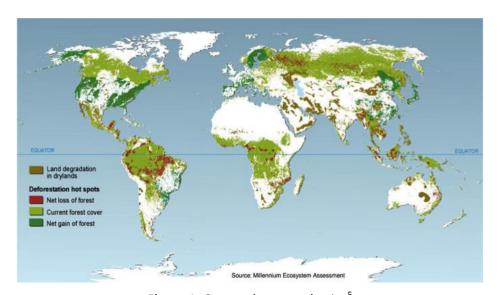


Figure 1. Current losses and gains⁵

1.3. Enter the fossil fuels

By 1800, coal started to be widely used, followed by oil and gas. At the same time, human population started to grow much

faster, paralleling the growth in the consumption of fossil fuel. Today, there is a strong correlation between energy consumption and economic indicators for the various countries.

At one point, oil was so abundant and



inexpensive that it was even considered as an attractive source of food protein. Oil was used as the carbon source for growing yeast and it was thus the source for single-cell protein (SCP). Development of industrial process was fast and nine plants operated in the Soviet Union, ranging from 50 to 240,000 tons/year.⁶ These are huge amounts: supplying 100 g protein to a human per day means that approximately 6 million persons could be supplied during one year, by such a large plant. Success in making SCP from oil was received enthusiastically and the Unesco Science Prize in 1976 was given to Alfred Champagnat, a researcher from the BP oil company working in the Lavera oil refinery, in France, for his achievements in this area.⁷

Coal, oil and gas formation in the nature requires very long times leading to concerns arose due to the depletion of reservoirs. The situation appears even more serious if other mineral resources needed to make metals, fertilizers, semiconductors and other large-scale industrial products are considered. These concerns were expressed for instance in the work of the Club of Rome and their World 3 model, predicting a collapse in food availability, industrial production and the production of services, from ca. 2030 onwards. This would finally trigger a decrease in the human population, with severe shortages of resources.

Many policies were put in place to prevent this collapse and an important one was to substitute renewable for nonrenewable sources of energy. This progressed but there is a long way to go: in 2014, the total share of renewable sources in global energy production was still less than 20% and biofuels accounted for 0.8% only. The total share of biomass, including wood burning, was between 11 and 12%, suggesting that it could not possibly make a significant contribution towards replacing fossil fuels.

1.4. Food vs. fuel

Moreover, a red light was turned on in 2007-8, during the food crisis and food riots that were soon followed by the financial crisis. At this time, FAO Food Price Index steeply rose to 220 in July 2008, then falling and rising again to 238 in 2011. Many persons assigned the rising food prices to the diversion of food crops to make fuel, but there were other important, if not dominating factors.

A major factor for increasing food prices was financial speculation: by early 2008, speculators started to migrate from the real-state American market to the international commodities markets. It is quite clear from Figure 2 that the FAO food price index and phosphate rock prices paralleled each other in this period, even though phosphate rock cannot be used to make fuel. Both rose manifold: the 9-fold increase in phosphate rock caused a 3-4 fold price increase for phosphoric acid used to make fertilizers that in turn put an additional pressure on food production costs.



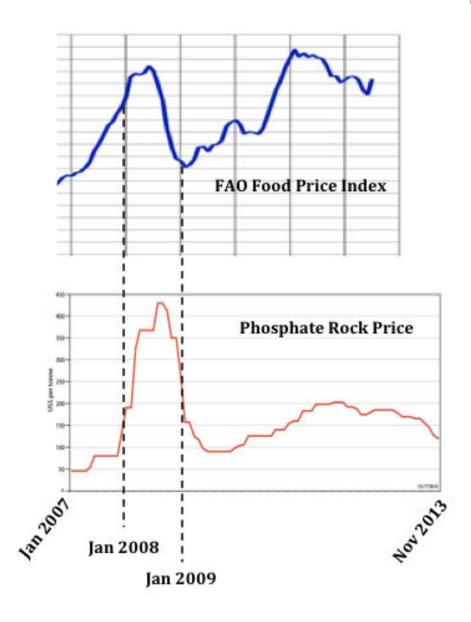


Figure 2. Food¹¹ and phosphate rock¹² prices

The real situation of food availability or not is revealed by the FAO Hunger Map from 2015. This shows which countries achieved the World Food Summit Target, from 1990 to 2014-16, which did not meet the target due to slow progress and which even showed a deterioration. No South American country showed deterioration and most met the target, while Cameroon, Ethiopia, the Gambia and Mauritania also met it by 2014, followed in 2015 by Angola, Gabon, Mali and

Mozambique. This showed that there was nothing like a growing scarcity of food throughout the world, due to the use of land and crops to produce fuels and raw materials. The really decisive factor is policy, as shown is Table 1: Brazil shows a steady improvement since the early 1990s while Vietnam progressed much faster than India and also showed greater improvement rates than China.



Table 1 . Global Hunger Index scores for some countries ¹⁴	
--	--

	1990	1995	2000	2005	2013
Brazil	8.7	7.6	6.4	<5	<5
Angola	39.5	38.5	31.6	22.7	19.1
India	32.6	27.1	24.8	24.0	21.3
China	13.0	10.4	8.4	6.7	5.5
Vietnam	30.9	25.1	18.1	13.7	7.7

Another relevant set of data is the share of agriculture in total national expenditure by different countries. ¹⁵ Table 2 presents data for a few countries, in 1995 and 2011, showing again large differences in policy. If we want more food, we should spend more funds in food production. However, some countries actually decreased the share of agriculture on their expenditure, between 1995 and 2011. Surprisingly, Brazil and South Africa did it while Argentina, Angola, Chile, India and China increased expenditure and it is not obvious why this happened.

1.5. Oil fights back

In the case of Brazil, this decrease is likely due to the important oil discoveries in Brazil, in 2007. Brazil had collected many successes in prospecting and exploiting offshore fields but in 2007 great findings were made beneath the salt rock layer deep down the sea floor. This created great optimism throughout the country, in view of the prospects for one of the six or seven greater oil producer in the world, with acceptable extraction costs at US\$ 8/bbl and a lowering trend. These prospects are now being confirmed and the "pre-salt" growing oil production reached 1 million bbl/d in June 2016. 16

Oil production grew fast and by then Brazil had the prospect to become the 5th or 6th oil producer in the world, at reasonably low extraction cost of 8 US\$/barrel. Other developments led to something previously inconceivable: Brazilian federal government actually subsidized fossil fuel consumption to help curb inflation and the same happened in two other countries.

Table 2. Share of agriculture in total expenditure in some countries

	1995	2011
Brazil	5.7	2.05
Argentina	0.58	1.65
Chile	1.18	1.26
Angola	1.75	2.27
South Africa	0.51	0.33
India	5.26	6.51
China	8.42	9.10
Switzerland	9.24	6.81
Republic of Korea	11.59	4.67



The artificial stimulus to oil consumption hit the production of fuel ethanol and sugarcane that was eventually buffered by high prices for sugar. Climate problems also affected the plantations so that cane production and sugar yield index actually decreased in 2010-11, for the first time in twenty years as shown in Figure 3.¹⁷ This caused an income loss for the sugarcane and ethanol producers that then faced a serious crisis that was partly countered by the electricity production.

This negative situation also had a beneficial effect: the ethanol-sugar plants became also significant producers of electrical energy, using surplus vapor in the cane processing plants. The result is

impressive: the amount of electricity supplied to the grid grew from mill in the early 2000 years to 11 Twh in 2012, generating as much as 15% of the ethanol/sugar producers income.

Two details are important, in this picture. The first is the coincidence between the peak cane cropping season with the dry weather season, in the Brazilian southeast were the larger hydroelectricity plants are situated. This means that electricity from sugar processing plants is available when it is most needed. Second, thermal generation can be turned on and off relatively easily so that electricity can be sent to the grid in peak consumption hours, when it gets premium prices.

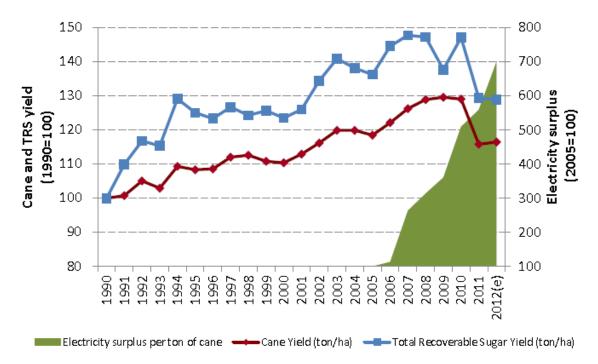


Figure 3. Cane production, total recoverable sugar (TRS) index and electricity surplus per ton of cane, from 1990 to 2012.¹⁷

2. From sugar to the sugarcanebased industries

At this point, I should recall that ethanol production in Brazil started as a byproduct from sugar. Sugar crystallization residues were used in various ways or just discarded in

the environment. It could be fermented to produce ethanol used to make lower grades of cachaça. In the 1920s, the Usga fuel factory operated in the state of Alagoas, making a mixture of ethanol, ethyl ether and castor oil that was used in cars.

Later in 1942, a large plantation of sugarcane was established in the Campinas region in São Paulo, by the Rhodia company.



It was needed because Rhodia used to import ethanol from Germany, for its processes in Brazil and this was not feasible, during war time. By then, ethanol was not seriously considered as an alternative fuel, in Brazil. Indeed, cars that could not be fueled with the hardly imported gasoline in Brazil used water gas (gasogênio) as fuel, a very ineffective solution.

In 1976, the second oil crisis led the government to create subsidies for fuel ethanol production. This was then critical because the country was not a significant oil producer, at this time and its dependence on fuel imports was unbearable. Indeed, the country was then buying foreign oil with borrowed money that led to financial default in the early 80s, creating one of the biggest crises in the country, ever.

Fuel ethanol production was initially strongly subsidized at an estimated overall cost of 10-12 US\$ Billions but this was worthwhile. In 1990, subsidies were eliminated in the Southeast that was the origin of 90% of the total Brazilian production.

Its production spread to other states adjacent to São Paulo: Mato Grosso, Goiás, Minas Gerais and Paraná, without subsidies. Sugarcane soon became the input for a highly diversified industrial production, including butanol, polyethylene, wax, green solvents and surfactants, nanosilica, cellulose, paper and pulp, microcrystalline cellulose, PHB-and other thermoplastics, lysine (>600,000 tons/year), electricity, as much as 15% of the overall electricity production, in the country.

New products derived from sugarcane and ethanol are appearing in different places. Two examples are the MyraleneTM solvent from the Amyris company, in the US. It is presented as a new high-performance, sustainably sourced and cost-competitive product based on β -farnesene. It is produced in Brazil on a commercial scale by fermentation of sugarcane juice using special strains of baker's yeast. The SIP Ltd (UK) company worked on a product containing

farnesene and farnesane, SIPDRILL RS, as the first renewable, hydrocarbon drilling base fluid for high performance drilling mud systems.

2.1. Praise and criticism

Sugarcane production growth drew much praise and criticism, within Brazil and abroad. Praise came from those who viewed the Brazilian sugarcane industry as a case of sustainable production based on renewable resources. Criticism can be read in many places, as for instance in earlier documents of the International Food Policy Research Institute (IFPRI). A frequent argument used by many critics is: "if you use land to produce fuel or industrial raw materials, you are diverting land from food production and thus you are contributing to global hunger."

However, the 2016 report from IFPRI states, "...biofuels may offer an opportunity to improve food security. Yet, for many poorer countries in Africa and elsewhere, biofuels may be better viewed as a potential export or as a means for reducing fossil fuel imports. ...producing conventional biofuels in low-income countries could raise rural incomes beyond what is required to offset rising food prices." Studies in Ethiopia revealed "... farmers' participation in biofuel programs encouraged greater use fertilizers and improved farming technologies, leading to higher food-crop productivity and better food security during the year. One precondition for success, however, was farmers' access to high-quality, productive biofuel crops".20 This report is because extremely important demonstrates the synergy between food and fuels production from biomass, away from the frequently touted food vs. arguments. To the present author, this carries an important learning: human as well as natural processes are non-linear and we cannot rely on simple-minded arithmetic arguments, even though these may look quantitative and thus "exact". This was found



during studies in Ethiopia and it confirms what has been abundantly verified in Brazil, for more than twenty years now.

3. Land use: competition and impacts

Key issues are the availability of land and the consequences of land-use change (LUC). How is the available land distributed and is there more land available for agriculture? Figure 4 shows that crops, fruits and the planted forests currently occupy 5.7% of the Brazilian territory while 18.8% are occupied by pastureland land, out of which 60 million hectares are suitable for agriculture. Shortly, the area used for agriculture in Brazil can be doubled, at least, without introducing any change in the forest and other native biomes.

This explains why the 92% expansion in the sugar cane planted area shown in Figure 5 did not constrain the expansion of the area for annual crops and commercial forests, in Brazil.

productivity is actually more important than the planted area and it has been growing fast (Figure 6). This is the reason why Brazil became a major food exporter during the same period when sugarcane area was on expansion, with a much more modest expansion on the overall planted area. This graph shows that 4-fold increase in food grain production was concurrent with only 20% increase in the area used for grains, largely soybeans and corn. So, there is no need in Brazil to harm the forest or other environments that provide important environmental services to the whole world.

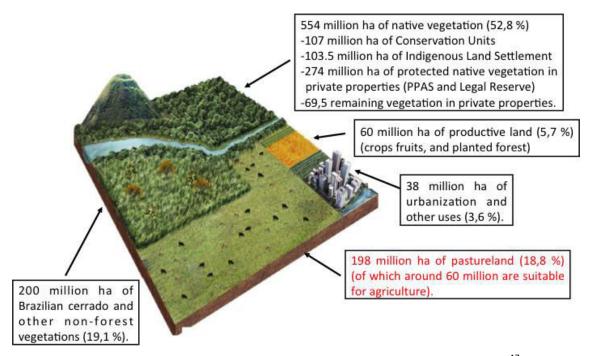
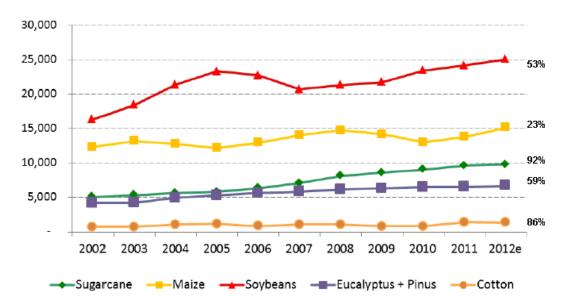


Figure 4. Different uses of land in Brazil (Measured from satellite in 2011)¹⁷

Indeed, Brazil has been among the world leaders in productivity growth, for some decades now (Figure 7). There is no indication that Brazilian productivity will not

continue to grow significantly, given some results that are currently available from some leading producers.





Sources: IBGE, ABRAF and UNICA.

Note: Numbers on the right indicate relative growth from 2002 to 2012.

Figure 5. Simultaneous expansion of sugarcane and major crops (1,000 hectares)¹⁷

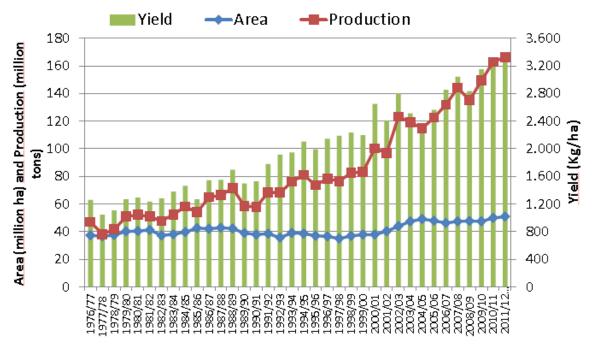
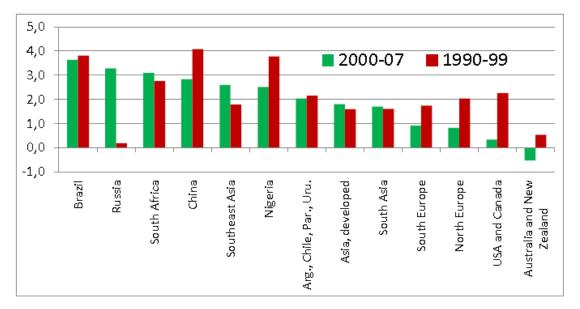


Figure 6. Grains: Strong yield and production increase¹⁷





Note: TFP (total factor productivity) represents resources efficiency (labor, capital and land), Higher TFP, higher production efficiency.

Figure 7. Productivity growth (Total Factor Productivity), % CAGR (Compound Annual Growth Rate)¹⁷

boom of Following the sugarcane expansion in the first decade of this century, in Brazilian southeast, 3 Mha of land were changed between 2000 and 2010, into sugarcane production. This land was originally used for annual crops (25.08%), pastureland (73.04%), and 0.52% cerrado (natural vegetation). Sixty-five sites were sampled in this land (down to 1-meter depth), for carbon determinations that allowed calculation of additional emission of greenhouse gases. The result was 0.7 - 1.0 Mg CO₂ ha⁻¹ y⁻¹. This is significant but small, as compared to biofuel offset from sugarcane ethanol: 9.8 Mg CO₂ ha⁻¹ y⁻¹. This means that LUC has not been, in practice, a significant source of increased emissions, as opposed to many estimations that have been published in the literature.21

Data in the previous paragraphs is a strong demonstration of the immense possibilities for increasing the global output from agriculture, as opposed to arguments that claim that since the amount of land in the world is fixed, food production is at its maximum.

There are many other factors to consider. For instance, in many parts of the world

water is a key limiting factor for agricultural production. This situation may change since desalination is becoming growingly feasible, especially under low energy prices. Experience in Kuwait shows the feasibility of water production at a cost that in 2011 already approached the prices for irrigation water in Jordan. Further progress in the availability of desalinated water may create new perspectives for agricultural production in the Middle East and in other dry areas in the world.

New ideas are arising, concerning the patterns of land use. In an important paper, Tomei and Helliwell state that "...reality is rarely so simple and this paper has drawn attention to interrelated issues...food versus fuel (debate) does not address the multiple uses of crops and their by-products...". "Land Moreover, is a highly multifunctional resource, providing not just food but...feed, fertilizers, fibre, flowers, drugs as well as biodiversity, livelihoods, cultural and existence value and other ecosystem services."22



4. Prospects for biofuels

To find about the future of bioenergy and biofuels we may ask how is investment in renewable energy distributed among the various possibilities, throughout the world? Figure 8 shows that the biggest share goes to solar and wind power, followed by biomass at a distance. Interestingly, developed countries make heavier investment in biomass energy and fuels than developing countries and the same has been observed since 2005.

Is biofuel production going up, in the world? Not much, as you can see in Table 3. It is led by the US followed by Brazil and ethanol (first-generation) and biodiesel are the leaders, but hydrogenated vegetable oil (HVO) is prominent in the Netherlands, Singapore and Colombia. This slide shows this information, more concisely.

In 2016 sugarcane some companies are producing second-generation ethanol from bagasse and other cellulosic materials Table 4 production, in Brazil.

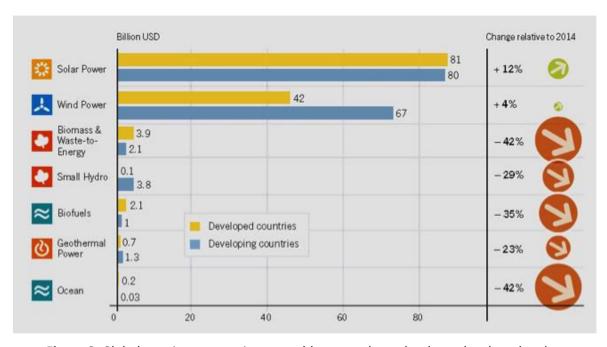


Figure 8. Global new investment in renewable energy by technology, developed and developing countries, 2015²³



Table 3. Biofuels global production, top 16 countries and EU-28, 2015²³

COUNTRY	ETHANOL	BIODIESEL	HVO¹	TOTAL	CHANGE RELATIVE TO 2014
			billion litres		
United States	56.1	4.8	1.2	62.1	+2.0
Brazil	30	3.9		32.3	+2.6
Germany	0.9	2.8		3.8	-0.6
Netherlands	0.4	1.5	1.7	3.5	+0.8
France	0.9	2.4	0.1	3.4	+0.3
China	2.8	0.4		3.1	-0.4
Argentina	8.0	2.1		2.9	-0.7
Thailand	1.2	1.2		2.4	+0.2
Singapore	~0	1.0	1.2	2.2	+0.3
Canada	1.7	0.3		2.0	no change
Indonesia	0.1	1.7		1.8	-1.2
Spain	0.5	0.6	0.2	1.3	no change
Colombia	0.5	0.6	1.0	1.0	no change
Belgium	0.6	0.4		1.0	no change
India	0.7	0.1		8.0	+0.3
Malaysia	~0	0.7		0.7	+0.2
EU-28	4.1	11.5	2.5	16.1	+0.6
World	98.3	30.1	4.9	130.7	4.5

Table 4. Companies with ethanol cellulosic plants in the world

Country	Company	Plant status	Capacity (Million Liters)
Drazil	GranBio ²⁴	Commercial	82
Brazil	Raízen ²⁵ Commercial		42
Australia	Ethanol Technologies Ltd. ²⁶	Pilot	-
Denmark	Inbicon ²⁷	Pilot	-
Italy	Mossi & Ghisolfi Group ²⁸	Commercial	49

4.1. Emerging crop species

There is active search for new uses for well-known agricultural species as well as for species that are currently non-used or underused. Many species are now considered in Brazil, both native and exotic but only one important case will be discussed here.

Macaúba or bocaiúva, Acrocomia aculeata (Aracaceae) is a palm tree native from the Brazilian cerrado in the south to northern Mexico. It is perennial, taking 3-6 y to start fruit production and lives up to 50 y.

Its water requirements are relatively low, 1 to 1.5 m rain/year and they are met in most parts of Brazil except in the Northeast. The fruit pulp contains 20-75% weight oil, 60 to 80% oleic. The pulp meal resulting from oil pressing is suitable used as human food (starch, 27.3%; fiber, 20%) and it has already been used to replace up to 54% wheat flour in cakes. The fruit seeds also contain large amounts of oil (3 Ton ha/y, 50-60% weight, 50% lauric) and the meal resulting from oil extraction contains 22-50% protein.

Macaúba has been considered for economic exploitation for decades but it is



still largely undomesticated. For this reason, the variability of any data relative to this species is very large and there is active search for outstanding specimens in natural environments. An accepted figure for the output of oil output from macaúba is 4 Ton

oil/ha.y, but recent findings revealed specimens with a potential to produce as much as 10 Ton oil/ha.y. This compares favorably to palm and is higher than any annual plants shown in Table 5.

Table 5. Productivity of oil based on biodiesel feedstocks²⁹

Species	Oil yield (L . 10 ³ /ha)
Palm (<i>Elaeis guineensis</i>)	5.5 – 8.0
Macaúba (<i>Acrocomia aculeata</i>)	3.5 – 4.0
Babassu (<i>Attalea speniosa</i>)	1.5 – 2.0
Sunflower (<i>Helianthus annus</i>)	0.8 – 1.5
Castor bean (Ricinus communis)	0.4 - 1.0
Peanut (Arachis hipogaea)	0.8 – 1.2
Soybean (Glycine max)	0.4 - 0.65

Last but not least, macaúba is easily associated to other plants or animals in the integrated crop-livestock-forest systems that are developing fast in Brazil and are proving highly productive and sustainable.³⁰

5. Outstanding properties of materials from biomass

Biomass provides important materials for human use. For some decades there was the feeling that these would be replaced by synthetic materials not only due to availability and cost but especially due to superior properties of the latter. It is now clear that some materials obtained from biomass actually display outstanding properties, unmatched by synthetics.

5.1. Natural rubber

An important case is natural rubber from *Hevea brasiliensis* that is usually referred to plainly as "cis-poly(isoprene)". However, this

designation cannot explain why has it not yet been fully replaced by the synthetic product and why is it still required to participate from compounds used to make tires and adhesives. Reasons from industry experts are found as in this statement, relative to choosing natural or synthetic rubber to make tires: "In general, as the tire size increases and the level of punishment the tire will take goes up, the amount of natural rubber increases due to natural rubber's good shear resistance, load bearing capability, and high level of resistance to cuts."³¹

Beyond cis-poly(isoprene), natural rubber contains many non-rubber constituents, notably inorganic compounds, proteins, phospholipids. Their distribution in the rubber is evidenced in Figure 9 that shows elemental maps obtained in the transmission microscope. The rubber is filled with small particles containing compounds of sulfur, aluminum, phosphorus, calcium and other elements, dispersed throughout the rubber. Most remarkable, these particles surprisingly adherent to the rubber, evidenced by the thickened areas seen in the C map.



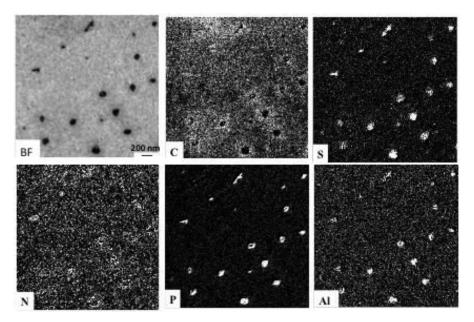


Figure 9. Bright-field and elemental images from dialyzed rubber latex film, average thickness 63 nm. The dark spots in the bright-field image are inorganic particles containing Al, P, S. C map shows that the polymer adheres strongly to these particles. Scale bar is 200 nm. Images acquired by electron spectroscopy imaging (ESI) based on energy-filtered transmission electron microscopy (EFTEM)³²

Natural rubber is thus natural nanocomposite, filled with reinforcing mineral nanoparticles and mobile calcium ions that also form crystallites.³³ Proteins and probably contribute to phospholipids particle-rubber adhesion thanks to their amphiphilic character and to electrostatic adhesion that will be presented ahead. This is

emulated in the laboratory or in the chemical plant by making nanocomposites, starting from synthetic and natural rubber latexes following the "latex route", this means: mixing aqueous Na-montmorillonite clay to rubber latex, blending and drying, ³⁴ as shown in Figure 10.

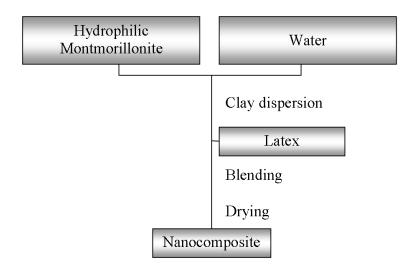


Figure 10. Preparation of clay-polymer nanocomposites in aqueous media using latex



Figure 11 shows that the mechanical properties of nanocomposites may be tuned by changing the clay content within a broad range. Transmission electron micrographs Figure 12 of thin slices of the rubber-clay nanocomposites show that the exfoliated clay platelets or tactoids adhere strongly to

the rubber matrix, even though clay is notoriously difficult to mix with rubber. Moreover, the nanocomposite films resist to swelling under xylene and they show anisotropic swelling: little expansion along the x-y plane but pronounced extension along the z axis.

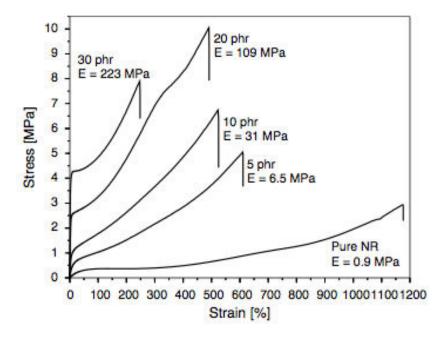


Figure 11. Stress vs. strain curves for natural rubber (NR) and Na⁺ -montmorillonite (NaMMT) filled composites³⁴

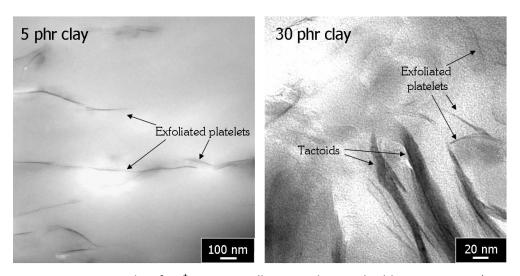


Figure 12. TEM micrographs of Na⁺-montmorillonite and natural rubber composite (NaMMT-NR). The thin cuts were made normal to the nanocomposite film plane³⁴



Most interesting, the mechanical properties of the clay-synthetic latex nanocomposites depend on the clay counterions as an evidence of electrostatic adhesion between clay lamellae and rubber. Detailed examination of polymer-clay nanocomposites prepared by the latex route allowed the mechanism development of а nanocomposite formation and stability that is depicted in Figure 13.35 This can now be seen

as a general approach for the development of functional complex materials based on biomass, since it overcomes well-known problems in miscibility and compatibility of the different constituent phases. We can thus say that water is a general-purpose cohesive agent. This was further explored to make blends of incompatible polymers, including synthetics, cellulose and starch, as shown in Figure 14.

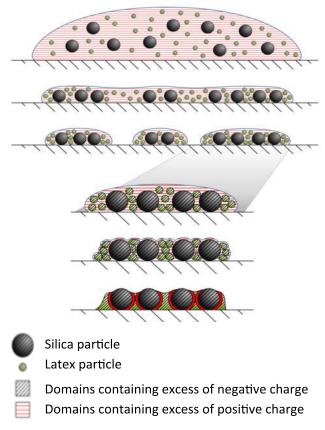


Figure 13. Schematic description of events involved in the adhesion of Stöber silica to styrene-acrylic latex³⁵

These ideas were extended to polymer blends and also blend nanocomposites, producing a host of interesting materials. ³⁶⁻³⁸ These included blends from well-known

incompatible polymer pairs, like natural rubber-starch (Figure 14), rubber – PVC. There seems to be no limit for the number of possible combinations that can be obtained.



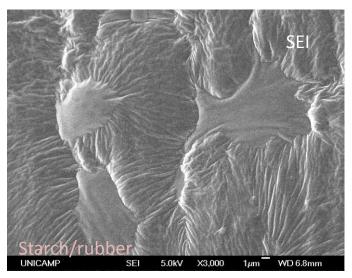


Figure 14. SEM micrograph from the cut surface of a rubber and starch³⁹

5.2. Cellulose

Cellulose is another very well-known material that has revealed important new aspects. Dissolving cellulose has been a great challenge that is now overcome using alkaline media that show unprecedented results. For instance, they are useful as repulpable cellulose adhesives that are effective even on moist paper, wood or cardboard.⁴⁰

6. Conclusion

Biomass production in Brazil may grow manifold yielding a great output of food, energy and raw materials. Opposed to simple-minded concepts often expressed in the literature, the production of food creates opportunities for concurrent production of energy raw materials and *vice-versa*, in growing amounts. Key to this development is the abandonment of simple arithmetic arguments on the extension of available land, replacing them by the detection of opportunities for simultaneous increase in the production of food, energy and raw materials. This is based on three main inputs: carbon dioxide, water and sunlight and it is

the essential part of the roadmap to sustainability.

References

- ¹ Ribeiro, R. C. L. F.; Barbedo, C. J.; Alves, E. S.; Domingos, M.; Braga, M. R.; *Pau-Brasil da semente à madeira*, Instituto de Botânica, São Paulo, SP, 2008.
- ² Allan, C.; Brazilwood: A Brief History. Available in: https://www.lib.umn.edu/bell/tradeproducts/brazilwood. Accessed on: 26 October 2016.
- ³ Walport, M.; Sharing the planet: Humanity's greatest challenge. Available in: http://www.slideshare.net/bis_foresight/natural-history-museum-annual-science-lecture-2013. Accessed on: 26 October 2016.
- ⁴ U. S. Forest Facts and Historical Trends 2000, p. 3; Available in: http://www.fia.fs.fed.us/library/brochures/d ocs/2000/ForestFactsMetric.pdf. Accessed on: 26 October 2016.
- ⁵ Site of Caithness.org. Available in: http://www.caithness.org/photos/nature/millenniumecosystem/14.jpg>. Accessed on: 26 October 2016.



- ⁶ Shabad, T. Soviet plant to convert oil to protein for feed. The New York Times Site. http://www.nytimes.com/1973/11/10/archives/soviet-plant-to-convert-oil-to-protein-for-feed-use-of-yeast.html. Accessed on: 26 October 2016.
- ⁷ United Nations Educational, Scientific and Cultural Organization; Summary list of UNESCO prizes, 1998, Paris, France, p 14. Available in: http://unesdoc.unesco.org/images/0011/001 111/111158E.pdf. Accessed on: 26 October 2016.
- ⁸ Hall, C. A. S.; Day Jr., J. W. Revisiting the Limits to Growth After Peak Oil. *American Scientist* **2009**, *97*, 230. [Link]
- ⁹ RENEWABLES 2016- Global Status Report. Renewable Energy Policy Network for 21st Century, p. 28. Available in: http://www.ren21.net/wp-content/uploads/2016/06/GSR 2016 Full Report.pdf. Accessed on: 26 October 2016.
- ¹⁰ Jashuah Own work by uploader, data from Food and Agriculture Organization, CC BY-SA 3.0. Available in: https://commons.wikimedia.org/w/index.ph p?curid=19394247. Accessed on: 26 October 2016.
- ¹¹ Food and Agriculture Organization of the United Nations (FAO) Available in: http://www.fao.org/worldfoodsituation/foodpricesindex/en/>. Accessed on: 26 October 2016.
- ¹² Australian Atlas of Minerals Resources, Mines & Processing Centres. Available in: http://www.australianminesatlas.gov.au/aimr/images/phosphate-figure3.jpg>. Accessed on: 26 October 2016.
- ¹³ Food and Agriculture Organization of the United Nations (FAO) Available in: http://www.fao.org/3/a-i4674e.pdf>. Accessed on: 26 October 2016.
- ¹⁴ International Food Policy Research Institute (IFPRI). 2013 Global Hunger Index Data. Available in: < https://dataverse.harvard.edu/dataset.xhtml?persistentId=doi:10.7910/DVN/22795>. Accessed on: 26 October 2016.

- ¹⁵ Food and Agriculture Organization of the United Nations (FAO) Available in: <http://faostat.fao.org/beta/en/#data/IG>. Accessed on: 26 October 2016.
- ¹⁶ Petrobras S. A. Site. Available in: em < http://www.petrobras.com.br/pt/nossasatividades/areas-de-atuacao/exploracao-eproducao-de-petroleo-e-gas/pre-sal/>. Accessed on: 26 October 2016.
- ¹⁷ Nassar, A. M.; Moreira, M. Evidences on sugarcane expansion and agricultural land use changes in Brazil. Institute for International Trade Negotiations. Available in: <<u>www.iconebrasil.org.br</u> >. Accessed on: 26 October 2016.
- 18 Benjamin, R. K.; Silva, I. R.; Cherubin, J. P.; McPhee, D.; Paddon, C. J. Developing Commercial Production of Semi-Synthetic Artemisinin, and of β-Farnesene, an Isoprenoid Produced by Fermentation of Brazilian Sugar. *Journal of the Brazilian Chemical Society* **2016**, 27, 1339. [CrossRef]
- ¹⁹ SIP Ltd Site, UK, London, <<u>htp://www.sip.com/products/sipdrill/</u>>.
 Accessed on: 26 October 2016.
- ²⁰ Arndt, C.; Msangi, S.; Thurlow, J. Fueling the path to food security. *Global Food Policy Report* 2016. International Food Policy Research Institute (IFPRI), chapter 7, p 63.
- ²¹ Mello, F. F. C.; Cerri, C. E. P.; Davies, C. A.; Holbrook, N. M.; Paustian, K.; Maia, S. M. F.; Galdos, M. V.; Bernoux, M.; Cerri, C. C. Payback time for soil carbon and sugar-cane etanol. *Nature Climate Change* **2014**, *4*, 605. [CrossRef]
- ²² Tomei, J.; Helliwell, R. Food versus fuel? Going beyond biofuels. *Land Use Policy* **2016** *56*, 320. [CrossRef]
- ²³ RENEWABLES 2016- Global Status Report. Available in: http://www.ren21.net/wp-content/uploads/2016/06/GSR 2016 Full Report.pdf. Accessed on: 26 October 2016.
- ²⁴ GranBio Site. Available in: http://www.granbio.com.br/conteudos/biocombustiveis/. Accessed on: 26 October 2016.
- ²⁵ Raízen Site. Available in: http://www.raizen.com.br/energia-do-



- <u>futuro-tecnologia-em-energia-renovavel/etanol-de-segunda-geracao</u>>. Accessed on: 26 October 2016.
- ²⁶ Ethanol Technologies Ltd Site. Available in: < http://www.ethtec.com.au/ >. Accessed on: 26 October 2016.
- ²⁷ Larsen, J.; Hensriksen N., Status for the Inbicon technology by end of 2014. DONG Energy, Denmark, Available in: https://assets.dongenergy.com/DONGEnergyDocuments/Inbic/Status%20for%20the%20Inbicon%20technology%20by%20end%20of%202014.pdf Accessed on: 26 October 2016.
- ²⁸ BETARENEWABLES Site. Available in: http://www.betarenewables.com/en/cresce ntino/the-project>. Accessed on: 26 October 2016.
- ²⁹ Melo, P. G.; *Dissertação de Mestrado*, Universidade Federal de Uberlândia, 2012. [Link]
- ³⁰ Kichel, A. N.; Costa, J. A. A.; Almeida, R. G.; Paulino, V. T. Sistemas de integração lavoura-pecuária-floresta (ILPF) Experiências no Brasil. 2014 *Boletim de Indústria Animal* 71(1), 95.
- ³¹ Velson, J. Available in: <https://www.quora.com/ls-natural-rubber-a-substitute-for-synthetic-rubber-in-tire-manufacturing>. Accessed on: 26 October 2016.
- ³² Rippel, M. M.; Leite, C. A. P.; Galembeck, F. Elemental mapping in natural rubber latex films by electron energy loss spectroscopy associated with transmission electron microscopy. *Analytical Chemistry* **2002**, *74*, 2541. [CrossRef] [PubMed]
- ³³ Rippel, M. M.; Leite, C. A. P.; Lee, L. T.; Galembeck, F. Formation of calcium crystallites in dry natural rubber particles. *Journal of Colloid and Interface Science* **2005**, *288*, 449. [CrossRef] [PubMed]

- ³⁴ Valadares, L. F.; Leite, C. A. P.; Galembeck, F. Preparation of natural rubbermontmorillonite nanocomposite in aqueous medium: evidence for polymer–platelet adhesion. *Polymer* **2006**, *47*, 672. [CrossRef]
- ³⁵ Valadares, L. P.; Linares, E. M.; Bragança, F. C.; Galembeck, F. Electrostatic Adhesion of Nanosized Particles: The Cohesive Role of Water. *Journal of Physical Chemistry C* **2008** *112*, 8534. [CrossRef]
- ³⁶ Linares, E. M.; Leite, C. A. P.; Valadares, L. F.; Silva, C. A.; Rezende, C. A.; Galembeck, F. Molecular Mapping by Low-Energy-Loss Energy-Filtered Transmission Electron Microscopy Imaging. *Analytical Chemistry* **2009** 81, 2317. [CrossRef] [PubMed]
- ³⁷ Linares, E. M.; Rippel, M. M.; Galembeck, F. Clay Platelet Partition within Polymer Blend Nanocomposite Films by EFTEM. *ACS Applied Materials & Interfaces* **2010**, *2*, 3648. [CrossRef] [PubMed]
- ³⁸ Linares, E, M.; Jannuzzi, S. A. V.; Galembeck, F. Electrostatic Contributions in the Increased Compatibility of Polymer Blends. *Langmuir* **2011**, *27*, 15199. [CrossRef] [PubMed]
- ³⁹ Rippel, M. M.; Linares, E. M.; Bragança, F. C.; Valadares, L. F.; Galembeck, F. Electrostatic Interactions: An Effective Mechanism for Rubber Adhesion and Blending. *Journal of Adhesion Science and Technology* **2012**, *26*, 767. [CrossRef]
- ⁴⁰ Ferreira, E. L.; Lanzoni, E. M.; Costa, C. A. R.; Deneke, C.; Bernardes, J. S.; Galembeck, F. Adhesive and Reinforcing Properties of Soluble Cellulose: A Repulpable Adhesive for Wet and Dry Cellulosic Substrates. *ACS Applied Materials & Interfaces* **2015**, *7*, 18750. [CrossRef] [PubMed]