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Biofuels: From Hopes to Reality

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1. Introdution

Recently, the United Nations System addressed to the world a report to create a green economy based in the following directions: *the potential to achieve sustainable development and to eradicate poverty on an unprecedented scale, with speed and effectiveness.* A green economy with low carbon potential to substitute fossil fuels, which addresses climate change, creates decent jobs, and reduces import dependencies. Much more than biofuels, green economies pay attention for market high values bioproducts. According to the United Nations Systems, this potential derives from two concurrent changes. First, there is a change indicating society risks and the necessity of rethinking the economy process considering the necessity of changing material availability; second, there is an increasing recognition that the natural environment forms the basis of our physical assets and must be managed as a source of growth, prosperity, and well-being [1]. Also this program addresses some questions related to important issues and directions concerning research like: *How to manage a smooth and fair transition from a brown economy to a green one at global level? How to ensure that green policies are not used as an excuse for trade protectionism? How to measure progress in the transition to a green economy?* As it can be seen, the United Nations Systems was precisely able to address specific directions related with a sustainable economy and the use of natural resource globally. Certainly the three global conferences on the environment and the UNEP's Green Economy Initiative, launched in late 2008 [2] were important steps to achieve such broad comprehension involving a large number of themes like: agriculture, renewable energy, cities, fisheries, water, forest, wastes, buildings, transports, tourism and manufacturing.

Certainly, these conclusions came out from the long time of understanding related with the indiscriminate use of natural resources and from the importance they have to achieve a sustainable world, as well as, contribute to diminish the environmental problem created by the use of fossil fuels for transport and electricity generation. To exemplify the importance of this report, since the 18th century, wood was the main source of material and energy for mankind. At that time, wood was primarily used for heating, house, ships, bridge constructions and metal processing. These historical uses caused a large deforestation in many areas of Europe. Unfortunately, this kind of process still continues devastating the Amazon forest, as well as other bioresources in Africa and Asia [3], [4]. At the end of the

19th century, the discovered of coal surpassed biomass use as a main source of energy and materials, mainly due to the beginning of the industrial era in England. Since then, the use of coal expanded in large proportion in Europe. As a consequence, it was observed the starting of an extensive use of non-renewable fossil sources of raw materials in the world, which was succeeded by the use of oil since the First World War. Below in Table 1 is shown data on the proportion of fossil fuels use, as well as renewable and nuclear according to the United Nations System report on green economy [5].

Global energy consumption sharing	%
I- Fossil fuels	78.0
II- Renewable	19.0
Wind/solar/biomass/geothermal power –generation	0.7
Biofuels	0.6
Biomass/solar/geothermal hot water/heating	1.4
Hydropower	3.2
Traditional biomass	13.0
III -Nuclear	2.8

Source: [5]

Table 1. Renewable energy share of global final energy consumption in 2008

Unfortunately, the contribution of fossil fuels is still very high, contributing to increase the greenhouse gas effect, and therefore the increasing of the CO_2concentration in the atmosphere. Another worse situation is related with the use of biomass in developing countries, mainly in Sub-Saharan Africa, Latin America and South Eastern Asia. Certainly, it is due to the lack of education and capital investment to access modern technological processes, like power generation using boilers and modern turbines, efficient heat transfer systems, as well as, biofuels production [6].

So, it is urgently necessary to increase the contribution of biofuels, still very low, to diminish environmental impacts. It is interesting to point out the message addressed to the world by Giácomo Ciamician in 1912 [7] known as the father of Photochemistry. At that time he expressed his environmental worries and concerns about the use of coal in Europe during the International Congress of Applied Chemistry in the USA, claiming that biomass should be used for chemical synthesis instead of energy. Fortunately the scientific development related with the agricultural resources, a green revolution is happening since 1970, promoting the intense use of advanced biotechnologies aiming at cell, protoplasts, tissue, and vegetable cultures by the use of genetic engineering to multiply plants and to create new productivity clones rapidly. These extraordinary advances and experiences together with the increase in the photosynthetic efficiency could be applied to increase agricultural productivity of some species to attend new society demands, such as biofuels production. Certainly, the choice of the right cultures in terms of its photosynthetic yields is of primary importance for the success of the biofuels production systems. The photosynthetic capacity of each vegetal depends on the quantity of CO_2 absorbed per unit of time on the foliar surface, and also, on the type of mechanisms (C3 or C4) involved in this process according to Melvin Calvin, the 1961 Chemistry Nobel Prize. Normally, it also depends on the radiation intensity, temperature, and CO_2 concentration and availability. Unfortunately, the maximum theoretical yield of the photosynthetic process is about 6.5%, but the practical yield is no more than 2.5% for some species like sugar cane and corn depending on the place where the plant is cultivated. Fortunately, there is a large amount of land and water resources available to grow C4 photosynthetic mechanism type of plants which is more appropriate to higher biomass production. The World Energy Outlook 2006 [8] is absolutely emphatic in recognizing that the world use of renewable resources is the only way to invert the actual CO_2 concentration in the atmosphere. As part of the photosynthesis process specific type of microalgae may produce vegetable oil or carbohydrates, as well as protein as its main constituents. It can generate much more oil per hectare than other plants used for biofuels production, such as traditional oil seed plants like soya, cotton and castor beans. Microalgae can grow in salt water, freshwater or even in domestic effluents, in ponds or photobioreactors using land not suitable for food production.

So, after the oil price crisis of 1967, which elevated the fossil fuels prices to a new platform much higher than the original one, as well as the environmental problems originated by the increasing of CO_2 concentration in the atmosphere, many countries created biofuel programs by themselves to replace fossil fuels. In conclusion, many of these biofuels programs are facing a lot of problems, such as; competition on land use for food and energy, fuels specifications, as well as environmental issues, like effluent disposal. In spite of biomass biodiversity and the renewable character of biofuels, they are still gaining space at regional level and impacting land use. As good examples, ethanol has gained space in Brazil and in the United States of America as well as in Asia. A second generation of technologies is in course to convert cellulose into ethanol through thermal conversion or bio conversion. Thermal processes present better results in terms of yields [9]. Biodiesel from vegetable oils are still receiving large subsidies in many countries where it is produced. Unfortunately it is based on traditional oil plants which have low productivity, and it is non economic under the actual oil prices scenario. Fortunately, a new technology based on yeast synthetic biology is able to produce a new molecule Biofene^R [10] which promises to be an adequate substitute for diesel soon in Brazil. But clearly, no one can predict what kind of biofuel will properly succeed fossil fuels derivates realistically at the international market. So, regulations, standards, and targets are important issues to provide a realistic direction to the biofuel in the market. It is possible to see now some conflicts between countries resources availability to produce certain types of biofuels and the international standard motor specifications, yields and construction materials. It is important to point out that the sugar cane agroindustry development in Brazil is presenting a new phase related with companies association to gain production scale. That is the case of Corsan agribusiness alcohol group and Shell [11] which will be soon the greatest company in the biofuels sector in Brazil. Other international groups as BASF [12] and DOW [13], and a national group BRASQUEM [14] are investing in green biopolymers production like polyethylene based into dehydrated ethanol. This is a new reality of the bioresources use in direction to add-value products. Naturally, it is the right way to achieve green economy goals which will contribute to create jobs in the field improving simultaneously the environmental problem.

2. Biofuels and renewable scenarios best option

The studies made by OECD-FAO Agricultural Outlook 2008-2017 [15], as well as the Energy Out look-2006 [8], related to trends, scenarios and policies for fuel production and supply, emphasize that there will be an instability if economies will continue as before. So, instead of using these studies, this work will use the United Nations Green Economy report which offers one of the best options to be taken into consideration in the future analysis of the role of world renewable energy and biofuels production and use, once it comprises several progressive studies made in several areas like; agriculture, renewable energy, cities, fisheries, water, forest, wastes, buildings, transports, tourism and manufacturing. The United Nations green economy report was compiled by UNEP´s Green Economy Initiative, launched in late 2008, in straight collaboration with economists and experts worldwide. It demonstrates that the greening of economies is not generally a drag on growth but rather a new engine of growth; that it is a net generator of decent jobs, and that it is also a vital strategy for the elimination of persistent poverty. The report also seeks to motivate policy makers to create the enabling conditions for increased investments in a transition to a green economy. For its purpose, UNEP has developed a working definition of a green economy as one that results in *improved human well-being and social equity, while significantly reducing environmental risks and ecological scarcities*. In its simplest expression, a green economy can be thought of as one which is low carbon, resource efficient and socially inclusive [2].

Greening the energy sector aims at a renewable and sustainable energy system. This process involves improvements in energy efficiency, a much greater supply of energy from renewable sources and reducing greenhouse gas emissions and pollution. The most direct approach is to reduce the use of fossil fuels – an energy source whose combustion accounts for two thirds of all GHG emissions [16], as mentioned by the chapter on renewable [5]. According to [5] an adequate definition to *renewable energy is that one derived from natural processes that are replenished constantly. In its various forms, it derives directly or indirectly from the sun, or from heat generated deep within the earth. Included in this definition is energy generated from solar, wind, biomass, geothermal, hydropower and ocean resources, and biofuels and hydrogen derived from renewable resource.*

Following the UNEP´s Green Economy Initiative, it will be now set up the basic assumptions related with renewable energy and biofuels:

1. According to Table 1, the share of renewable energy in global final energy consumption in 2008 was 19%, but it could increase to the order of 27% depending of the investments done;
2. World primary energy demand is expected to continue growing. The International Energy Agency's Current Policies Scenario, which assumes no change in policies as of mid-2010, projects a world growth rate of 1.4 per cent per year up to 2035 according to data shown in Table 2.
3. World primary energy mix in the IEA Current Policies Scenario is shown in Table 3. These data show the importance of biomass, traditional and modern, in relation to other sources.
4. per cent at the peak in 2007, and is projected to remain high in the period to 2030 [18];
5. Worldwide investment in renewable energy assets – without large hydropower – grew by a factor of seven from US$17 billion in 2004 to US$126 billion in 2008. For OECD countries the share of renewable has risen from 4.6 per cent in 1973 to 7.7 per cent in 2009 [17];
6. In April 2010, the UN Secretary-General's Advisory Group on Energy and Climate Change-AGECC [19] published a report, which calls on the UN and its Member States to commit themselves to two achievable goals: universal access to modern energy services and a global energy intensity reduction of 40 per cent by 2030;
7. Expenditure on oil alone increased from 1 per cent of global GDP in 1998 to around 4 IPCC (2007) and IEA (2008c) estimate that in order to limit the rise of average global

temperature to 2 degrees Celsius, the concentration of GHG should not exceed 450 parts per million (ppm) CO2-eq. This translates to a peak of global emissions in 2015 and at least a 50 per cent cut in global emissions in 2050, compared with 2005. In 2009, the G8 committed to an 80 per cent cut in their emissions by 2050 in order to contribute to a global 50 per cent cut by 2050, although a precise baseline was not specified. The 80 per cent reduction would yield some space for developing countries to have a less stark reduction trajectory while reaching the global 50 per cent target.

	Total energy demand [Mtoe]		Growth rate 2008-2035[a] [%]	Share in total energy demand [per cent]	
	2008	2035		2008	2035
OECD	5421	5877	0.3	44.2	32.6
Non-OECD	6516	11,696	2.2	53.1	64.8
Europe/Eurasia	1151	1470	0.9	9.4	8.1
Asia	3545	7240	2.7	28.9	40.1
China	2131	4215	2.6	17.4	23.4
India	620	1535	3.4	5.1	8.5
Middle East	596	1124	2.4	4.9	6.2
Africa	655	948	1.4	5.3	5.3
Latin America	569	914	1.8	4.6	5.1
World[b]	12,271	18,048	1.4	100.0	100.0

a. Compound average annual growth rate. b. World includes international marine and aviation bunkers (not included in regional totals), and some countries/regions excluded here.

Source: [17]

Table 2. Primary energy demand by region in the IEA Current Policies scenario

	Total energy demand [Mtoe]		Growth rate 2008-2035[a] [%]	Share in total energy demand [per cent]	
	2008	2035		2008	2035
Coal	3,315	5,281	1.7	27.0	29.3
Oil	4,059	5,026	0.8	33.1	27.8
Gas	2,596	4,039	1.7	21.2	22.4
Nuclear	712	1,081	1.6	5.8	6.0
Hydro	276	439	1.7	2.2	2.4
Biomass and waste[b]	1,225	1,715	1.3	10.0	9.5
Other renewables	89	468	6.3	0.7	2.6
Total	12,271	18,048	1.4	100.0	100.0

a. Compound average annual growth rate. b. Includes traditional and modern uses.

Source: [17]

Table 3. World primary energy mix in the IEA Current Policies scenario

8. So, biofuels importance to modernize energy sector and help economy to attend the Millennium Development Goals and its links to energy access as shown in Table 4 [21].

Millennium Development Goal		How modern energy will help attain the MDGs
1	Eradicate extreme poverty and hunger by reducing the proportion of people whose income is less than US$1 per day (in US$PPP)	Increases household incomes by improving productivity in terms of time saving, increasing output, and value addition, and diversifying economic activity. Energy for irrigation increases food production and access to nutrition.
2, 3	Achieve universal primary education and promote gender equality	Provides time for education, facilitating teaching and learning by empowering especially women and children to become educated on health and productive activities, instead of traditional energy related activities.
4, 5, 6	Reduce child and maternal mortality and reduce disease	Improved health through access to clean water, cleaner cooking fuels, heat for boiling water, and better agricultural yields. Health clinics with modern fuels and electricity can refrigerate vaccines, sterilise equipment, and provide lighting.
7	Ensure environmental sustainability	Cleaner fuels, renewable energy technologies, and energy efficiency can help mitigate environmental impacts at the local, regional and global levels.

Source: [21]

Table 4. Millennium development goals and links to energy access

3. Biofuels and the green mobility

Transport sector and the electric power generation are the two most important sectors responsible for the actual climate change due to their large contribution for the production of greenhouse gases emissions. At present, transportation sector consumes more than half of global liquid fossil fuels; emits nearly a quarter of the world's energy-related CO_2; generates more than 80 per cent of the air pollution in developed countries cities; results in more than 1.27 million fatal traffic accidents per year; and produces chronic traffic congestion in many of the world's urban areas. These costs to society, which can add up to more than 10 per cent of a country's GDP, are likely to grow, primarily because of the expected growth of the global vehicle fleet [22]. According to the green economy report chapter on ***green transport*** is hereby defined as one that supports environmental sustainability through e.g. the protection of the global climate, ecosystems, public health and natural resources. It also supports the other pillars of sustainable development, namely economic (affordable, fair and efficient transport that supports a sustainable competitive economy as well as balanced regional development and the creation of decent jobs) and social (e.g. allowing the basic access and development needs of individuals, companies and society to be met safely and in a manner consistent with human and ecosystem health, and promoting poverty reduction and equity within and between successive generations). This definition was developed through extensive discussions with transport experts including those at UN agencies, and was based on a review of existing and well-acknowledged definitions such as ECMT [23]. Commercial vehicles comprise over of land transportation energy consumption [24]. So the changing in the standard of use **of fossil fuels by biofuels should be the central question**

to improve efficiency and environmental pollution. In this sense, the introduction of mixtures of biofuels and traditional fuels is a relevant theme to improve environmental impacts and expand biofuels in the market. Improving vehicles efficiency and biofuels use is a priority to reduce urban air pollution and greenhouse gas emissions.

The executive summary on Transport Technologies and Policy Scenarios to 2050 made by the Energy Council [24] emphasizes important directions concerning biofuels and the importance to increase vehicle efficiency. According to this summary, the following points should be observed:

1. Fuel sustainability is measured in terms of three important points: accessibility, availability and acceptability. Quantitatively, the sustainability can be expressed by the consume reduction, it means, by the vehicle efficiency increase. So, sustainability of fuels is straight related to vehicle technologies;
2. Alternative fuels will also increase steadily in penetration with second generation of biofuels such as synthetic biomass-to-liquid **(BTL) growing significantly by 2035** and synthetic gas-to- liquid (GTL) already expected to grow strongly in the coming decade;
3. Aviation fuels present a particular opportunity for alternative fuels, since they can be produced through synthetic Fisher-Tropsch process, which can use gas, coal, or biomass as a feedstock. In aviation, efficiency could increase up to 30%, through engine and materials technologies and flight management;
4. Assuming economically, environmentally and socially sustainable production, the highest potential lies in biofuels to reduce fossil energy and therefore greenhouse gases. They have potential to **reduce fossil energy up to 90%;**
5. Conventional biofuels like ethanol and biodiesel or hydro-treated vegetable oils from plants can be expected to retain some market share even to 2050;
6. Hybrid vehicle may penetrate in certain applications. Electric power utilization in transport will also increase, in particular in OECD and richer countries;
7. **Hydrogen fuel and fuel cell vehicles are expected to gain a market firmly by 2035** and grow towards 2050. Until 2050, gasoline and diesel fuels will still play a major role, but their biofuel portion will be significant;
8. Hydrogen and fuel calls can contribute significantly in the passenger vehicle sector if the mayor challenge of fuel cells cost, hydrogen storage, hydrogen production and hydrogen delivery can be overcome. In order to make substantial improvements in sustainability of energy for transport sector over the next 43 years, breakthroughs in technology will be necessary.

Another important analysis and contribution for the energy sector was done by LBST in Germany [25]. They pointed out the unsolved dilemma of industrialized society: **economy grows versus the need to reduce emissions to mitigate climate change from the years beyond 2000**. According to them, the oil peak will be around 2005-2010; the gas peak around 2015 – 2025; coal peak around 2010-2040; and nuclear peak will be 2015-2020. So, to achieve a sustainable growth, several types of renewable energy should be introduced beyond the year 2004. This study shows a similar situation like IEA model presented. So, they came to the conclusions that **hydrogen is the adequate carrier for future transport sector due to its potential, yield, storability and efficiency.** Besides that, it has a broad feedstock flexibility to be produced from fossil or renewable. Once using hydrogen, it will facilitate the development of green transport.

3.1 Battery and the fuel cell driven cars

The energy conversion via electrochemical cells is not subject to the limitation of Carnot cycle [26] which presents a very low efficiency and dissipates a large amount of heat associated with CO_2 emissions. Fuel cell technology offers a better way to convert fuels energy, mainly hydrogen, into electric energy given as reaction product, water, a fact that mitigates CO_2 – emissions. This concept was first demonstrated by William Grove, in 1839 when he connected four cells containing platinum electrodes with sulfuric acid, in series at which hydrogen and oxygen were consumed to produce electricity, and the electricity in turn was used to decompose water [27]. However, electrode kinetic has a great influence in the whole electrochemical process efficiency. This pioneer discovery started the enormous research work which resulted in the improvements in fuel cell technology and certainly in the conception of different types of fuel cells like; alkaline, acid, proton exchange membrane, and solid polymer electrolyte, among others [27]. Certainly, the first field of application was associated with the use of fuel cell technology for space vehicles where safety, life of the components, and system launch weight were critical factors in the late fifties. The excellent results obtained in this application encouraged the research and development program for terrestrial uses in the sixties. The mobile application came as natural development in the beginning of seventies. As long as oil derived liquid fuels are available, there was a very little competition for the internal combustion engine or diesel powered vehicles. Several conventional and advanced batteries are being considered for vehicles, which will eventually replace the mechanically powered vehicles. According to the Ragone plot, a very useful illustration for predicting performance characteristics of electrical vehicles is shown in Figure 1. According to these data, the plots of the specific power (W/kg) versus specific energy relations (Wh/kg) are shown for several types of vehicles using batteries, fuel cells.

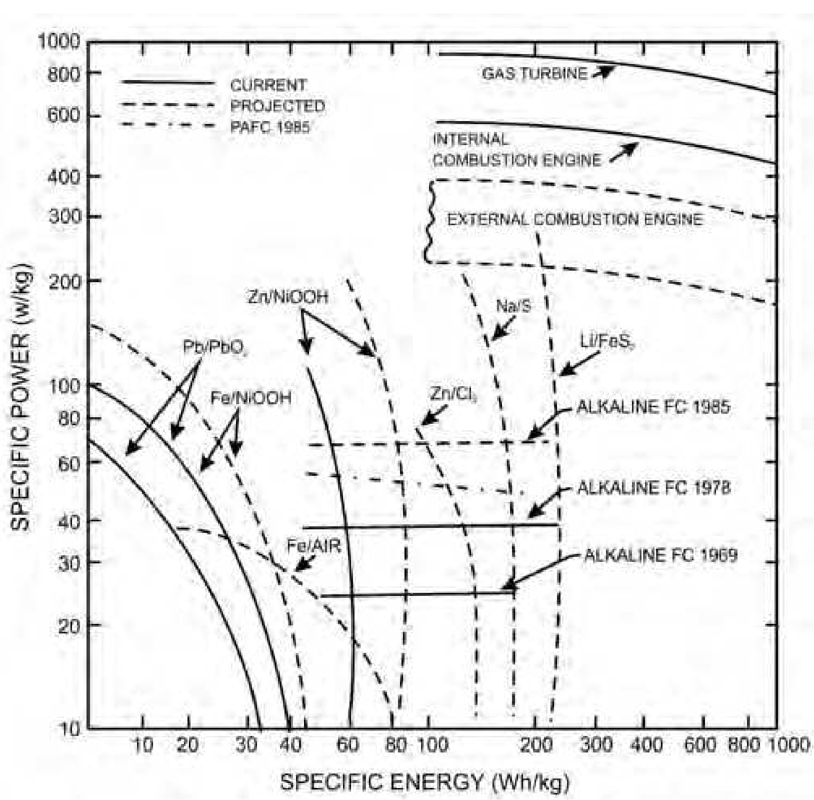

Fig. 1. Ragone Plots: Batteries, Fuel Cells and Heat Engines

They are compared with internal and external combustion engines and gas turbine. In conclusion, the plot demonstrates:

- The mechanical energy converters have the desirable characteristics of high power/weight required for start-up and acceleration, and energy/weight ratio required for range;
- Fuel cell systems have low power/weight ratios, but can attain high energy ratios;
- Batteries can attain high power/weight ratios but have relatively low energy/ weight ratios.

3.2 Future scenarios for new vehicles – Vector 21

At the Institute of Vehicle Concepts- which is part of the German Aerospace Centre in Stuttgart, the tool VECTOR 21 [28] has been developed that predicts the distribution of future vehicle fleets according to some boundary conditions, especially those related with potential “Climate Change Protection Scenarios”. For this purpose the software combines different customer groups with vehicles which, subject to rational decision, best fits the respective requirement profile. Influences of exogenic scenario boundary conditions such as CO_2 restrictions of new vehicle fleets, the price of oil, taxes, subsidies and charges are also taken into account. In the course of this the algorithm accesses an extensive database filled with different technologies. In addition to the type of technology this database contains projections on the influence on the energy consumption of the whole vehicle and the production costs of numerous energy-efficient technologies. All technologies permitted for the respective year are combined in a matrix and a specific CO_2 emission determined. Table 5 clarifies the boundary conditions stored in the model using the example of a "Climate Protection" scenario.

Scenario assumptions		2010	2020	2030	2040
Oil price	[€/bbl]	80	**100**	130	
CNG taxes	[%]	20	from 2018: 100		
Electricity price	[€ ct/kWh]	21,5	34,1	37,3	36,4
Hydrogen price	[€ ct/kWh]	22,3	39,0	37,6	36,5
Hydrogen share from electrolysis	[%]	100%			
CO_2 intensity of electricity	[g/kWh]	540	510	21 (from 2025)	
CO_2 intensity of hydrogen	[g/kWh]	648	612	25 (from 2025)	
CO_2 target (EU)	[g CO_2/km]	2015: 130	**95**	70	60
CO_2 penalty	[€/ g CO_2/km)]	95			
Willingness-to-pay	[%]	0-20			
Vehicle size categories (small /medium / large)	[S/M/L %]	(25/55/20)	(28/50/22)	(30/45/25)	

Source: [29]

Table 5. Boundary conditions of an exemplary "Climate Protection" scenario

The outcome for the composition of the new vehicle fleet as well as the overall vehicle fleet is shown in Figure 2. Due to severe penalties, alternative vehicle concepts will achieve a considerable market introduction. The ambitious CO_2 targets together with the high CO_2 reduction potential of hydrogen and electricity will encourage costomers to buy more innovative technologies. In 2040, only 10 % of conventional combustion engines would still be in the vehicle fleet under these conditions. The CO_2 emissions of new cars can be reduced by almost 70 % in 2040 compared to 2010. The results show that the number of different propulsion and vehicle concepts on the market will grow. For the introduction of electricity and hydrogen, progressive decisions regarding CO_2 targets and energy production have to be taken. Biomass based liquid fuels can contribute to this development as despite of the growing importance of alternative propulsion technologies, conventional vehicles will still play an important part in the mid-term future.

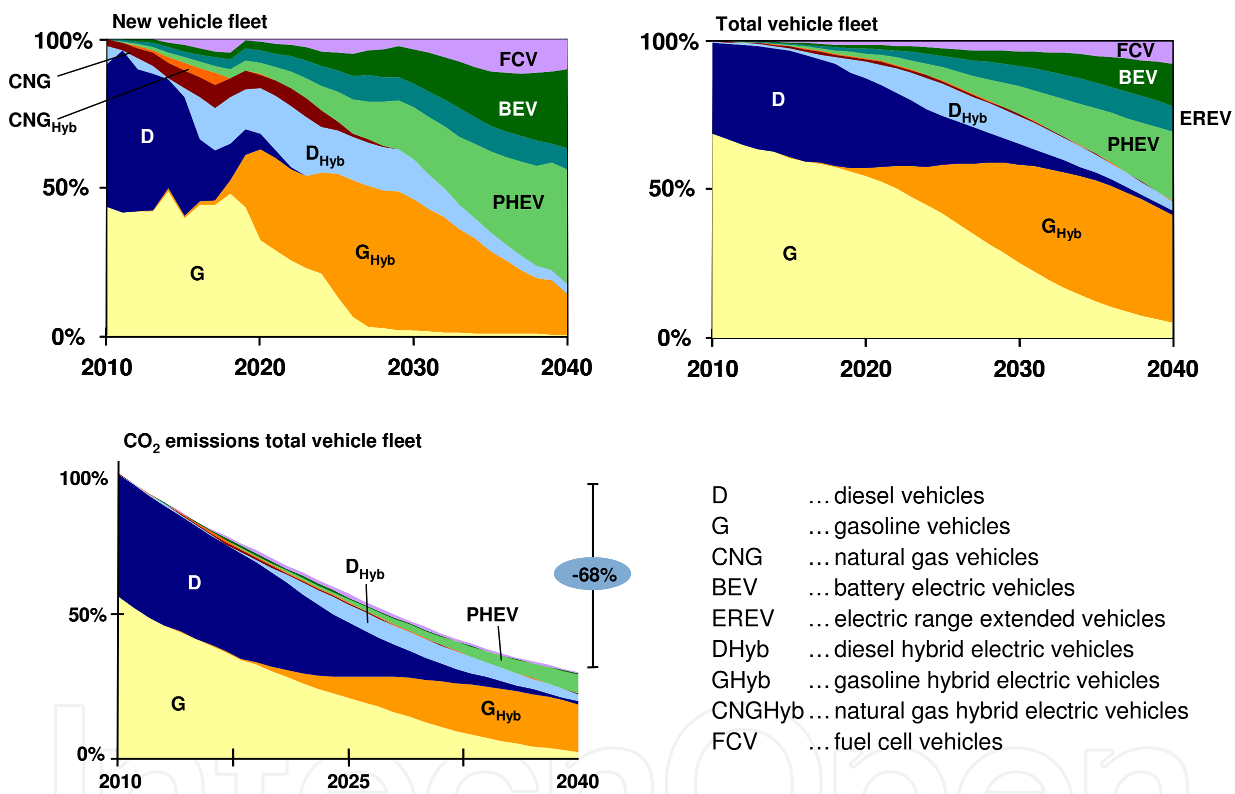

Fig. 2. Vehicle fleet development and CO_2 emission reduction for "Climate Protection" scenario

3.3 The Brazilian experience with the "flex car technology"

After the economic crisis of the seventies, Brazilian Government decided to implement the National Alcohol Program – *Pro-Álcool* in 1975. It was a program financed by the government to phase out automobile fuels derived from fossil fuels, such as gasoline, in favor of ethanol produced from sugar cane. To achieve this goal, they provided three important initial directions for the ethanol industry: to guarantee purchases by the state-owned oil company Petrobras; to apply low-interest loans for agro-industrial ethanol enterprises and fixed gasoline and ethanol price where hydrous ethanol sold for 95% of the government-set gasoline price at the pump. Concerning to the car industry, initially it was necessary to develop several important changes in the existing Otto cycle motors related to new materials to avoid corrosion, motor rate of compression, as well as, the injection systems [30]. All of these initial efforts came out with the development of the "flex car technology" which permitted the existing gasoline motor specification to be adapted for using a full range of ethanol–gasoline blends nationally.

Basically, "**flex car technology"** comprises a set of three important devices; a software, an injector and a level sensor, which works integrated with the existing gasoline motor, permitting the use of different mixtures of ethanol and gasoline fuels, including, pure ethanol and pure gasoline. It was the most important improvement done in the injection fuel system since ethanol was nationally launched late in the seventies as a biofuel. Its main purpose was to achieve an adequate fit between the existing gasoline motor specifications and the ethanol characteristics, mainly its specific heat (cal/g). In order to achieve a desirable motor performance, the motor compression rate was established in 11.5:1, an intermediate value between the gasoline motor compression rate 9.5:1 and the rate for alcohol fuel 12:1 [30]. The success of "flex technology" vehicles together with the mandatory mixture (E25) blend throughout the country, have allowed ethanol fuel consumption in the country to achieve a 50% market share of the gasoline-powered fleet by February 2008 [31].

The Brazilian car manufacturing industry introduced the flexible car technology in 2003, reaching 92.3% share of all new cars and light vehicle sales by 2009. In December 2009 they represented 39% of Brazil's registered Otto cycle engine vehicle fleet, and the cumulative production of flex-fuel cars and light commercial vehicles reached the milestone of 10 million vehicles in March 2010. There are around 70 flex models available in the market since 2010, from 11 major car makers [32]. This technology has been extended to bus and now for motorcycles [33].

The Brazilian Government has developed and establish of agreement which allows the technology transfer to some Latin American Countries, Caribbean, Andean Countries and also with the USA, which imposed a U$D 0.54 tariff on every gallon of imported ethanol from Brazil [31].

4. Biofuels processing technologies – scenarios of options

Chemical and biochemical industry all over the world is facing an unprecedented change with respect to its basic sources of material [34]. Oil that has supported the society needs in terms of its basic products for such a long time. Now industry is facing a real change towards the use of biomass facing the declining of oil production in the near future. As it was pointed out in the introduction, in the 18th century, wood was used mainly for heating and constructions purposes. At that time, animal oil was used mainly for illumination, as well as horse power was used basically for human transportation. With the advent of coal and oil processing industry in the 19^{th} and 20th centuries, the automobile came to substitute animal power, mainly with the arrival of the vapor machine in the end of the 19th century. Now, at the beginning of the 21st century the world is facing another change towards the use of renewable resources to produce biofuels to fit car specifications.

A broad analysis of the state of art of different biofuels technologies was presented by the author in the publications [3], [35], [36]. In this paper, the main focus will be dedicated to build a realistic vision related to the biofuels introduction in the international market. So, it will be presented possible options of scenarios for biofuels from 2010, from the current status, until the year 2040, when the green mobility should be in course. As it can be seen in

Figure 3 (annexed), the current status of ethanol, biodiesel and biogas production processes demonstrate that these technologies are already in the market in spite of some technical or environmental problems they present. Moreover, Figure 3 shows that some results of the second generation of technologies are coming out until 2015 -2020, and some new results concerning biohydrogen production will permit and contribute for the achievement of the green mobility, that will be available around 2025 which will permit the use of vehicles free of CO2-emissions. This constitutes one important vision of the present work. The data and analysis presented in several papers consolidate this vision. However, it is possible to conclude that it is not possible to foresee what type of biofuel will succeed properly the fossil fuels. Society is still facing several options, perhaps due to the large biodiversity of biomass present in nature at regional level [37]. In practical terms, effort has been done in terms of the scientific knowledge to use these materials to produce different types of biofuels in these regions. But unfortunately, motor technologies are very restrictive in terms of biofuels specifications. However, due to other society needs it is necessary to point out those two categories of plant materials that should be considered to attend sustainability: food and non-food plant materials, residues and wastes. Primarily, the technological efforts need to drive biomass to human food demands in terms of plants with components to supply food purposes using specific land resources. Wastes and non-food material like lignocellulosic (wood, straw, grass, wastes and residues) are present all over the world and technological efforts should be directed to convert them into sustainable energetic sources of biofuels. Acting this way, it is possible to avoid competitiveness with food sector, one of the great problems of the countries involved with biofuels production in our days. Associated with such types of plant materials, its photosynthetic process is straight related with their productivity and land use, as well as, the process requirements to the use of chemical or biochemical catalysts to achieve good processing yields and high productivity. Genetic tools today offer great chances to improve microorganisms and plant species yields and productivity, so, they must be considered essential knowledge to be applied [38]. Finally, process net energy ratio, life cycle analysis and the use of biorefinery concept are today important means to attain process sustainability and economic production scale in general terms [39],[3],[35]. Certainly, science, education and training are the basic requirements to reach technological development and to provide the countries with the support for the best use of their natural resources, which should be guided by sustainable and ethical policies.

4.1 Ethanol production from renewable resources

As mentioned in the Figure 3, ethanol production from sugar cane in Brazil is a **current mature technology** in use all over the country. An important and realistic analysis of the results of the sustainability of the sugar cane agroindustry in Brazil is presented in the publication edited by Carvalho [40], who pointed out some interesting themes, which are subdivided in other smaller themes during the discussions of the five main themes mentioned in sequence: impacts of the use of materials resources; environmental impacts; sustainable basis of the agricultural production; impacts of the commercial actions; socioeconomic impacts of the sector. In synthesis, nowadays Brazilian ethanol production is a commercial technology practiced with yields of about 6000 liters of ethanol per hectare, presenting a cost of approximately US$ 0.20 per liter. About 8 Million of hectares are being used for the production of about 22.5 Million of ethanol liters in 2008 [41]. The use of this technology has contributed for the reduction of CO_2-emissions in the country, as well as to create a large number of jobs in the field [40]. Ethanol from starch raw materials is a quite close technology which hydrolyzes amylose and amylopectin carbohydrates into sugars. Nowadays **hydrolysis has been used on industrial scale** to convert grains, potatoes and roots like cassava to produce ethanol in those countries where sugar cane is not available. Actually, the USA is using about 20% of their corn to ethanol, having a total production of about 33.8 million of liters [41]. Corn and cassava have been considered to the **current ethanol production in the USA**, in some Asian and Latin American. Maize (Zea mays L. ssp.), hybrid maize, due to its high grain yield is preferred by farmers over conventional varieties. Cassava or manioc (Manihot esculenta) is a woody shrub of the Euphorbiaceae (spurge family) native from South America extensively cultivated as an annual crop in tropical and subtropical regions for its edible starchy tuberous root. Cassava is the third largest source of carbohydrates for human food in the world, where Africa is the largest center of production. In spite of having a positive energy balance, starchy plants present a lower net energy ratio than sugar cane, a fact that is being considered very critical [42].

The development of integrated biorefineries is a new theme which is being considered relevant with high priority for this sector [3], [43]. The conversion of sugar cane residues, like bagasse, leaves and straw through an enzymatic hydrolysis unit coupled to the ethanol traditional plant is being considered as the second generation technology to increase ethanol production to about 13,000 liters per hectare [9]. Certainly, the development of an **effective pre-treatment process** and components separation is essential to achieve this goal [44]. Lignocellulosic are complex materials and its fractioning is considered a **hard task** [45]. In this paper, there is still a process under development which will possibly be ready for commercial use around the year 2015, as indicated in Figure 3.

4.2 Vegetable oils as diesel substitute

Biodiesel from vegetable oils is a **mature technology** which is in use in several countries, but it still has many problems [46]. One of the most important problems it is related to the low productivity of the traditional oleaginous species, like seeds soya, cotton, coconut, rapeseed and castor to support biodiesel production. These plants present C3 mechanism, which is responsible for its low productivity. This fact demands large areas of land, besides the competitiveness with the food products. Glycerin is a byproduct of the reaction between vegetable oils and alcohols (methyl or ethyl) which represent about 12% of the original oil used. Due to its large production, it does not have a definite market. Actually, this technology receives a lot of subsides, fact that is related with their non economic aspect. So, considering land use in medium and long terms, Biodiesel will not achieve the global market even in the actual context of oil price. In our view, this technology could be used in specific cases in order to attend social or energetic ends as it is shown in the scenarios detailed in Figure 3.

4.2.1 HBio – process: A mixture of diesel and vegetable green fuels

In Brazil, Petrobras developed an interesting process denominated Hbio, which is a patented technology [47]. This process is adequate to use vegetable oils in the existing catalytic oil refining process to produce green fuels, as shown below, in the Figure 4. The process improves the quality of fossil diesel due to the good qualities of the vegetable oils derivates obtained in this process mainly in those countries that does not have oil adequate to diesel production. Once there is vegetable oil available, it is possible to produce green

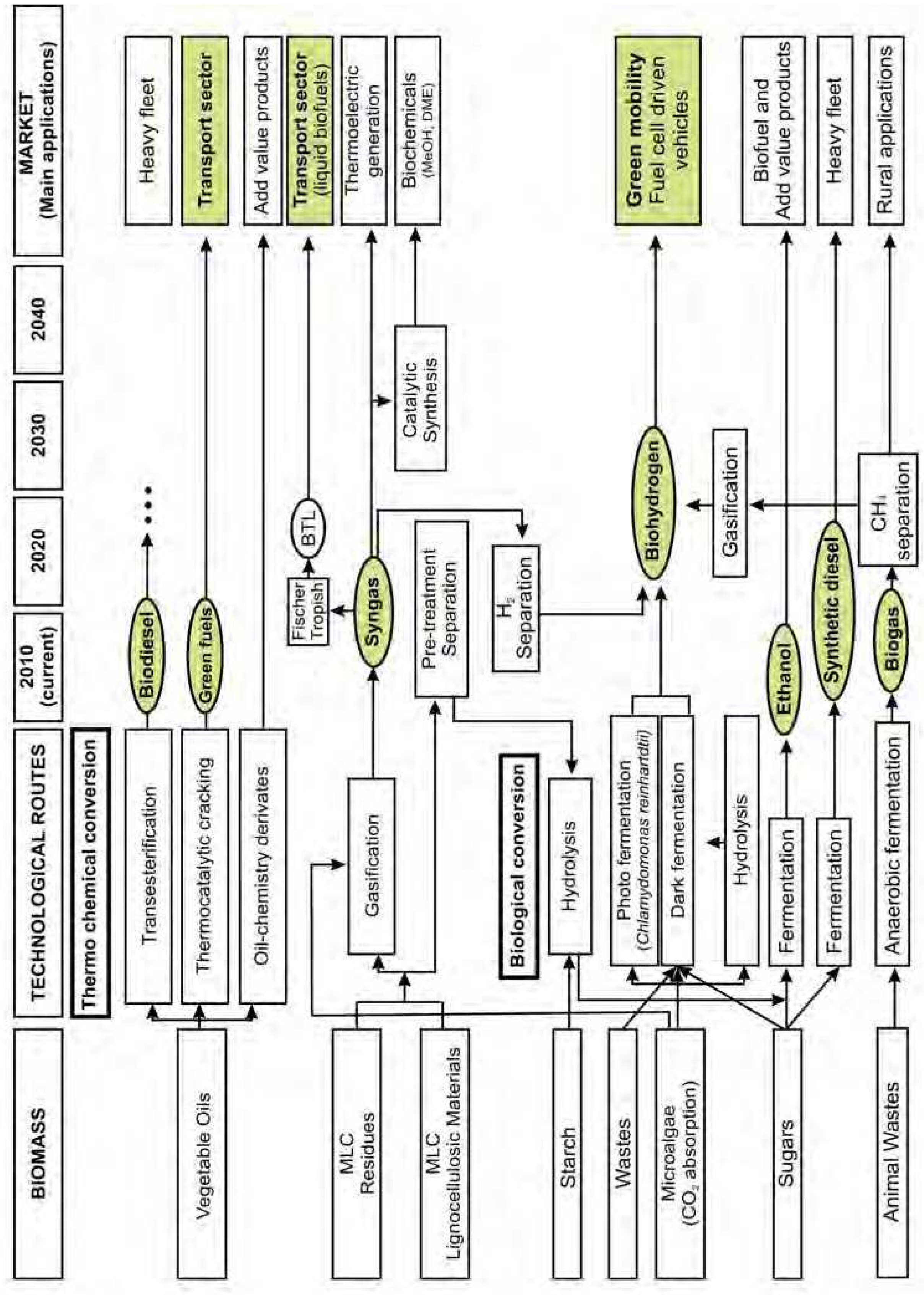

Fig. 3. Biofuels realistic options market scenarios

fuels or mixture of green fuels with diesel. Other oil companies developed equivalent process in the USA. It is important to observe that there is no glycerin production in this process. So, this process is considered an option for future specific applications. This technology is considered ready for implantation in refineries, depending on the availability of vegetable oils, as well as, from the Brazilian Government decision, since Petrobras is a State Company.

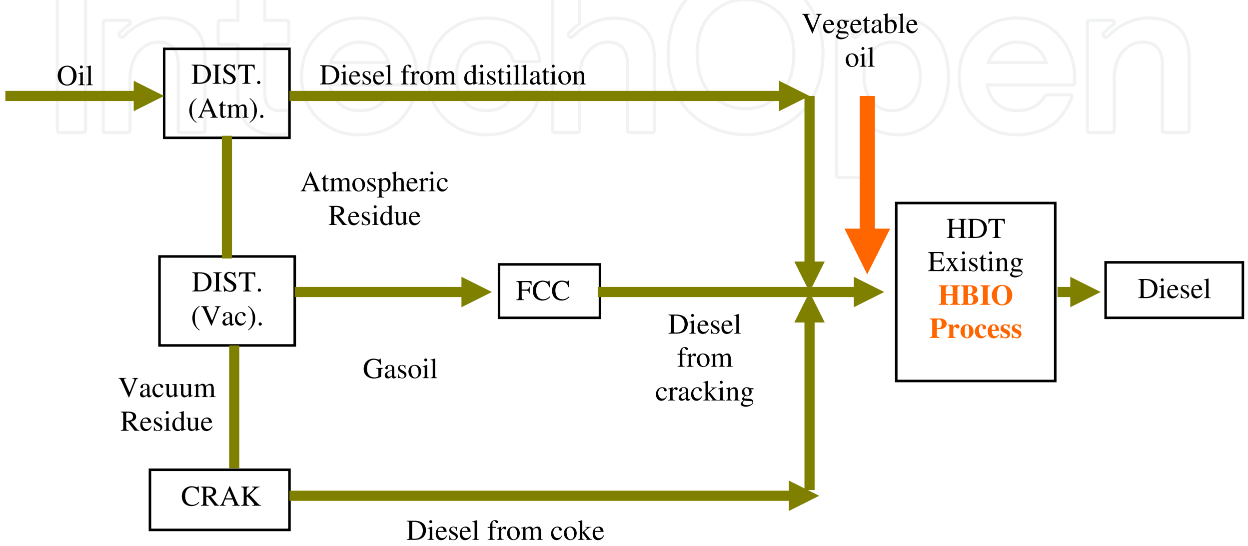

Fig. 4. Flow diagram of the HBio – Process

4.2.2 Synthetic diesel

Finally, Figure 3 mention the work been developed in pilot scale by the Amyris Company in Campinas São Paulo [10] on synthetic biology. This process use a specific engineered strain of *S. cerevisiae* yeast to convert sugar into a hydrocarbon molecule Biofene^R, from which it is produced Fersene, the synthetic diesel. It is a well-known fact that microorganisms can metabolize sugars to produce a large number of isoprenoid compounds [38]. Isoprenoid compounds are commonly known as terpenes and carotenoids. In fact, it is a sustainable product that could be used to substitute diesel oil with a positive impact on the transport sector. It is expected that this technology will enter in commercial scale, in the next decade in those countries that have sugar available in large scale.

4.3 Thermal conversion of lignocellulosic materials - LCM into syngas

Two technologies have been considered to produce biofuels from LCM: Biological conversion and thermal conversion as it is shown in Figure 3. Urban LCM fraction also is considered into this broad category of materials. Actually, many countries are engaged in the development of these technologies. Table 6 presents a comparison between three different processes for biomass conversion according to the second generation technologies mentioned. They are: Biomass Integrated Gasification with Gas Turbine–BIG/GT; thermochemical and bioconversion. According to the data presented in Table 6, thermo chemical conversion of biomass into biofuels is considered more attractive.

Products	BIG/GT	Thermochemical	Biochemical
Ethanol (liters /ton, DM)	--	333	246
Electricity(kWh/ton, DM)	1750	606	226
Total efficiency (%)	35	50	33

Source: [9]

Table 6. Products and processes efficiencies from second of generation of LCM conversion (It was considered one dry ton of dry biomass)

According to Huber [43] the production of biofuels from lignocellulosic biomass can significantly reduce the external countries dependence on foreign oil, create new jobs, improve rural economy, reduce greenhouse gas emissions, and improve national security. Wayne and collaborators [48] pointed out the importance of the future biomass gasification role concerning biofuels production and conversion through the use of fluidized bed biomass gasifier.

According to the most relevant publications discussed in this paper, thermal conversion of LCM into synthetic gas (Syngas) is a possible candidate technology to be used at international basis, not only because cellulose is present all over the world as urban and plant residues or as straight biomass, but also, due to its flexibility to produce biofuels and chemicals of great interest for the chemical industry like; ethanol, methanol, dimethyl ether (DME), higher alcohols, diesel, gasoline, wax and other chemicals, as shown in Figure 3. Basically, it uses the Fisher–Tropsch process that was developed in Germany in 1920 to produce liquid fuels from coal. Now it is being adapted to use biomass. The Biomass to Liquids (BTL) process produces hydrocarbons via synthetic Fischer–Tropsch technology through synthesis gas derived from biomass. Concerning the gasification process, the main constrain is related to the great variety of types of cellulose residues to be used and their low density, fact that requires large gasifier units. So, it is necessary that a biomass pre-treatment unity linked with an adequate gasifier to produce and adjust the H_2/CO ratio to feed the Fischer– Tropsch process through a shift reactor. A more specific problem to be solved is the cleaning of the synthesis gas to avoid contamination of the catalysts system used in the Fischer–Tropsch process. Basically, two types of liquid products can be manufactured, namely, hydrocarbons and oxygenates, such as methanol. Furthermore, dimethyl ether (DME), which is a high cetane number product, can also be obtained when methanol undergoes dehydration. Because of the hydrocarbons linearity in the product mixtures, synthetic diesel produced presents a high cetane number. In Brazil, the "Centro de Pesquisas da Petrobras-CENPES" [49] is deeply involved with this technological development.

Integrated biorefineries employ various combinations of feedstocks and conversion technologies to produce a variety of products, with the main focus on producing biofuels. Side products can include chemicals (or other materials), heat and power. The renewable feedstocks utilized in integrated biorefineries include, but are not limited to: grain such as corn, wheat sorghum, and barley; energy crops such as switch grass, miscanthus, willow and poplar; forest and industrial residues such as bagasse, stover, straws, sawdust and paper mill waste. Taking into consideration the original biomass, the yield on syngas varies between 75 e 88 % [50].

Another interesting option using microalgae to produce syngas is being developed by Ofelia and collaborators [51], according to Figure 5. In this study, microalgae are produced using a photobioreactor (PBR) using stack gas from capture of CO_2 emissions from an NGCC (Natural-Gas-fired Combined Cycle) power plant. The process was simulated in UNISIM Design (Honeywell). The results should be used to the synthesis of chemical products and fuels, in an industrial ecologic arrangement, where CO_2 is promoted from waste to feedstock, referred to as Carbon Capture and Industrial Sequestration – CCIS.

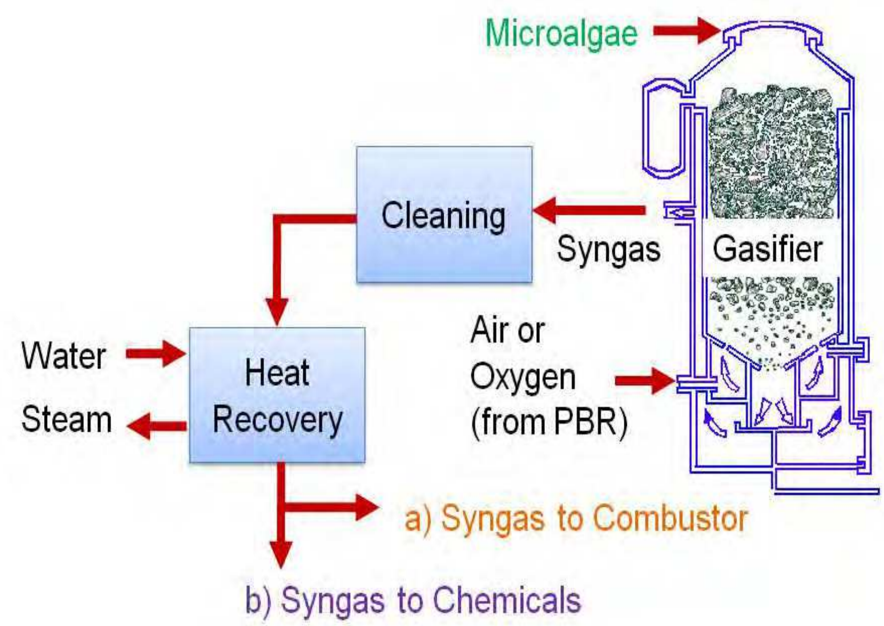

Fig. 5. Integrated microalgae production and gasification

According to these results, it is possible to foresee that thermochemical conversion of LCM present a great potential to produce biofuels and chemicals from non-food plant material, being a strong candidate to succeed fossil fuels. This technological route can produce liquid fuels with a life cycle of greenhouse gases practically zero. This possibility is indicated also in Figure 4 as possible commercial technology around the year 2020-2030. Main restriction is due to microalgae production in large scale.

Microalgae will become the most important biofuel source of biomass in the near future. Besides syngas, it also can be used to produce biogas, or biodiesel using CO_2 stack gas from thermoelectric plants, reducing CO_2 concentration in the atmosphere. Microalgae are unicellular photosynthetic microorganisms living in saline or freshwater environments that convert sunlight, water and carbon dioxide to algal biomass [52].

4.4 Biohydrogen production

4.4.1 Introduction

In this article, it will be covered only a discussion on the biohydrogen process, once they are straight connected with the main focus of this article. However, it is necessary to have a clear idea of the existing hydrogen technologies, mainly, its cost, in order to understand the potential for the biological hydrogen production technologies. Also it is important to recognize that hydrogen can be produced straight from biomass, without intensive technology use, including also, decentralized production.

Hydrogen is an energy carrier that could be produced actually by different processes like, natural gas reforming, coal gasification, nuclear, water electrolysis, thermal water splitting and biomass, photo-electrolysis and biological processes [53]. Hydrogen can be used for power generation or used as a transport fuel, mainly in association with fuel cells. Natural gas and coal are the two most current and cheapest sources of H_2 production. These processes release CO_2, and so, capture and storage are required to reduce the CO_2-emissions. Decentralized production of Hydrogen is the best choice for market uptake and for avoiding distribution costs due to the need of infrastructure.
According to IEA – Energy Technology Essentials [53] hydrogen could gain market share in the transport sector if costs of production, distribution and end-use technologies decrease in consonance with the expectations, as well as, if strong policies are placed in order to reduce CO_2 emissions. Under adequate circumstances, hydrogen could be entering the market around the year 2020. For that, it should be powering around 700 million fuel cell driven vehicles by 2050, which means, 30% of the projected global fleet [53]. According to IEA report, costs varies, depending of sources and raw materials costs. In summary, hydrogen from electrolysis costs above \$30/GJH_2, once considering electricity cost at \$35/MWh with 80% efficiency; hydrogen from steam methane reforming (SMR) costs ranges between \$10-\$15/GJH_2, considering natural gas price between \$6-\$9/GJ; coal gasification costs range between \$7-\$10/GJH_2, assuming \$1-\$1.5/GJ for coal price, and \$35-40/MWh for electricity with 45% electrical efficiency; hydrogen from nuclear using its high temperature heat costs about \$10-\$20/GJ, and from megawatt-scale concentrating solar power systems \$20-30/GJ .

4.4.2 Biological hydrogen processes

A number of photosynthetic processes for H_2 production from water have been proposed and studied for over three decades [54]. These include direct and indirect water-splitting ("bio-photolysis") processes using microalgae that contain the enzymes hydrogenase and nitrogenase. Alternative processes are briefly reviewed for potential practicality and a novel process for photo-biological water splitting is proposed [55].
In the late 1999, Melis [56] discovered that the green algae, *Chlamydomonas reinhartdtii* could be forced to produce straight hydrogen under sulphur-free anaerobic conditions, jointly with researchers of the National Renewable Energy Laboratory-NREL, Golden, Colorado, which developed a preliminary cost analysis of this process [56]. Subjected to this condition, this algae switches from oxygen production (normal photosynthesis), to the hydrogen production. Unfortunately this development still require advances in genetic engineering to improve the efficiency of the photosynthetic process, now understood as performed in two stages.
The biology provides a wide range of approaches to produce hydrogen, including direct and indirect bio-photolysis as well as photo-fermentation and dark-fermentation [57]. Currently these biological technologies are not suitable for solving every day energy problems, but they present high potential for that according to the research perspective. Dark-fermentation is a promising approach to produce hydrogen in a sustainable way and was already examined in lab-scale in many projects [58], [59]. Short hydraulic retention times and high metabolic rates are advantages of the process. The incomplete transformation of the large organic molecules into various organic acids is a disadvantage. So a second process step is required.

Within Europe union strong effort has been made to develop an integrated project denominated by Hyvolution using resources of the 6th Framework Programme on Sustainable Energy Systems aiming at the development a blue print for an industrial scale process for decentralized hydrogen production at small scale from locally produced biomass according to the Figure 6, below [60]. Another important work is being developed in Germany, at Duisburg- Essen University which has as main focus to demonstrate the feasibility of biological hydrogen production using sustainable waste and wastewater treatment concept. A pilot project is under the development and now it comprises and integrated process involving dark fermentation technology and anaerobic digestion of process effluents which presents higher yield of conversion [61] and [62].

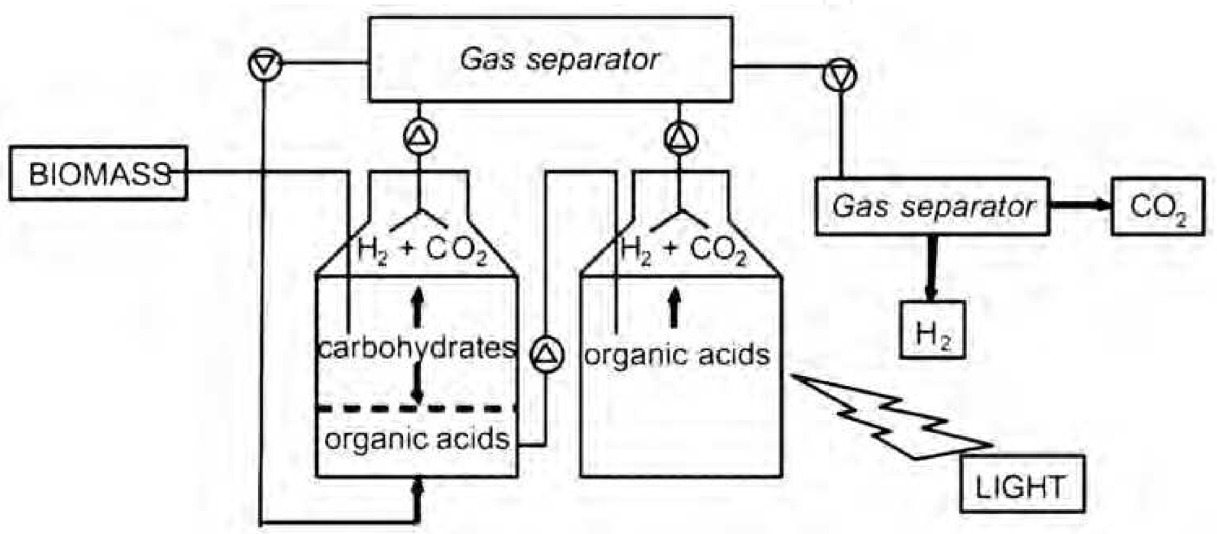

Fig. 6. Hyvolution biohydrogen integrated process

4.4.3 Comparison of biohydrogen production processes

Using sugar as the main carbon source, Manish and Bannerjee [63] made an interesting analysis of four processes (dark fermentation, photo-fermentation, two-stage process and the biocatalyzed electrolysis) and compared with the steam methane reforming (SMR), taking into consideration, energy ratio, energy efficiency and greenhouse gas (GHG) emissions. Processes for biohydrogen production operate at ambient temperature and pressure. So it is expected that they are less intensive in energy than thermochemical processes to produce hydrogen. In this study it was used three different feedstocks: sugar cane bagasse, sugar cane juice, and potato processing wastewater and four processes were analyzed: photo–fermentation; dark– fermentation, two-stage process (integration of dark with photo-fermentation) and biocatalyzed electrolysis, considering the two cases; with by-products and without byproducts. The following definitions were used: **Net Energy Ratio (NER)**, which is the ratio between the hydrogen outputs to the **Non-Renewable Energy (NRE)** input; **Energy Efficiency (EE)** which is calculated by the ratio between hydrogen energy output and energy input. Using emissions factors, corresponding to **Greenhouse Gas (GHG)** emissions were obtained. Inventory results for **Steam Methane Reforming (SMR)** process were taken from Spath and Man [64] and the mass and energy balance were provided as input for the life cycle analysis using the software SimaPro 6 [65].

In order to show the importance of the biohydrogen processes studied by Manish and Bannerjee [63], the authors of this paper organized their data according to Table 7 for the case without by-products. This Table was built to discuss and compare the results of the biohydrogen processes. The following conclusions were driven from these comparisons:

- Efficiency of biohydrogen process increase significantly when by-products are taking into consideration, and all processes present higher efficiencies than the SMR one, according to item 4;
- Biohydrogen process use biomass. All processes considered in this analysis reduce GHG emissions and non-renewable energy use by 57-73% and 65-79%, respectively, as compared to the SMR process, according to items 2 and 3.
- NER are higher for all biohydrogen processes studied. The SMR process presented a non favorable results according item 1.

Process	**SMR**	**Dark fermentation**	**Photo Fermentation**	**Two-stage Process**	**Biocatalyzed Electrolysis**
Analysis for the case without by-products					
1- **NER**	0.64	1.9	3.0	3.1	1.8
2- **GHG** (kg CO_2/kg H_2)	12.8	5.5	3.5	3.4	5.3
a) Reduction to SMR	-	7.3	9.3	9.4	7.5
b) % reduction	-	57	73	73	58
3- **NRE** (MJ)	188	61.7	40.1	39.3	64.8
a) Reduction to SMR	-	126.3	147.9	148.7	123.2
b) % reduction	-	67.2	78.7	79.1	65.5
4- **EE** (%)	-	-	-	-	-
a) With by-products	64	89.1	82.3	81.6	76.8
b) Without by-products	64	9.6	25.6	27.2	25.7

Table 7. Results of the NER, GHG and NRE analysis for hydrogen processes compared with SMR

5. Conclusions

From the analysis of the material presented in this work it is possible to conclude that, in spite of biomass biodiversity and the renewable character of biofuels they are still gaining space at regional level and impacting land use. However, thermochemical conversion process to syngas of lignocellulosic resource –LCM and microalgae are gaining international importance due to the potentiality of these bioresources to produce biofuels.

This process also presents higher yields which greatly contribute for its economic aspects. Moreover this is a flexible technology that can produce also add value products, favoring the greenish of the chemical industry. So, thermal conversion products seem to be the most adequate to substitute some fossil derivates at the international market. Besides gasoline, green diesel and hydrogen, this technology enables the production of other biofuels to attend aviation and ships motors, as well as power generation. From this platform of applications, biomass thermal conversion is considered the promising technology to succeed fossil fuels, diminishing the CO_2-emissions and attending the IPPC and Millennium goals.

In spite of the research level, biohydrogen technology is another process that has a great contribution to achieve future green mobility, it means, to turn the transport sector free of CO2-emisions through the use of batteries and fuel cell driven vehicles. With a very innovative approach, biohydrogen technology will be emerging around the year 2020 as a powerful candidate to be the greenish fuel in global terms, as well as, to definitively implement the concept of green mobility on the roads. However, it is necessary to intensify the research to increase biohydrogen productivity process continuously, as well as, to diminish the cost of the fuel cell for the transport sector. This is the only decentralized technology that is in full accordance with the Millennium goals. It is important to observe the straight relationship of this technology with the anaerobic fermentation process which is the current practice to convert waste into biogas worldwide.

The ethanol productions in the USA, Brazil and in other countries are good examples of regional importance that are entering in the international market, but they will certainly have transport costs restrictions, as well as, internal impacts on land use. The actual and realistic opportunity to apply it as a real candidate to replace polyethylene or other biopolymers to produce green plastic is one important point to be considered. It is important to consider also the development of alcohol chemistry as add value products. At the moment it is possible to emphasize that, ethanol, biodiesel, and biogas are the current biofuels technologies in the market, attending automotive motor specifications. In our vision, biodiesel could not compete at international level in the long range, once the traditional oil seeds present low yields, which creates instability and will strongly impact negatively land use. However, vegetable oils cracking process is a possible technology to be applied to improve diesel specifications in the countries which do not have good oil to produce diesel according to automotive standards. Also this technology could use existing oil refineries infrastructure. A new patented on synthetic biology is emerging in Brazil from Amyris Company using specific microorganism which metabolize sugars to produce Biofene$^{R.}$. From this molecule synthetic diesel and jet fuel can be produced. Actually, this technology is being tested in demonstration phase.

Finally, it is possible to conclude that the development of biofuels technologies will definitively contribute to the increase of the renewable participation in the global primary energy supply, but also it will contribute to the achievement of the green economy goals, mainly those related to the arising of bioproducts which are strongly increasing in the market. These facts will also contribute for the achievement of the Millennium goals, ensuring environmental sustainability and helping to eradicate extreme poverty.

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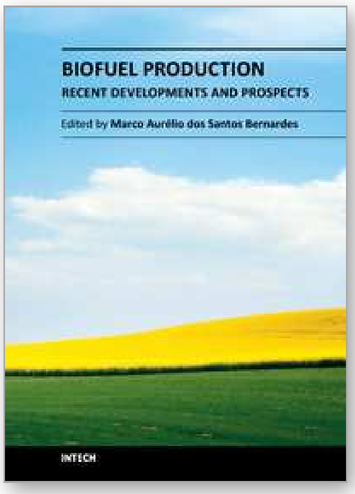

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This book aspires to be a comprehensive summary of current biofuels issues and thereby contribute to the understanding of this important topic. Readers will find themes including biofuels development efforts, their implications for the food industry, current and future biofuels crops, the successful Brazilian ethanol program, insights of the first, second, third and fourth biofuel generations, advanced biofuel production techniques, related waste treatment, emissions and environmental impacts, water consumption, produced allergens and toxins. Additionally, the biofuel policy discussion is expected to be continuing in the foreseeable future and the reading of the biofuels features dealt with in this book, are recommended for anyone interested in understanding this diverse and developing theme.

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