

Development of a methodology for net energy analysis in biorefineries, regarding microalgae cultivation to improve energy yields in industrial wastes

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Abstract

In general, biomass processing plants are considering the use of biorefinery concept to evaluate the net energy balance, as well as, the life cycle analysis of agroindustrial plants to meet sustainability requirements. Among the several types of biomass processing plants, biofuels production plants are becoming of great importance due to the increasing demand of biofuels to attend the desirable energetic sustainable global scenario. From the other side, energy recovering from wastes is an essential theme to achieve both, energy and environmental requirements. Inside this context, this paper considered the evaluation of energy recovering from vinasse of ethanol plants in Brazil to produce biogas or biodiesel through microalgae cultivation, once this kind of industrial plant produces a large amount of wastes. For such purpose, it was developed initially, a methodology to evaluate the net energy ratio in ethanol or biodiesel agroindustrial plants. Having this methodology in mind, it was considered the complementary energetic contribution of the biogas or biodiesel obtained from microalgae cultivation in vinasse and its processing. Based on this approach it was possible to evaluate the best options in terms of resources utilization, considering the analysis of the net energy ratio of ethanol agroindustrial plants. In conclusion, this type of analysis contributes to a better use of biomass resources, as well as, to the best design of the agroindustrial plant. Certainly, the energy recovered from the cultivation systems contributes to diminish the pressure on land use and consequently the competitiveness between food and energy.

Keywords: *Biofuels, biodiesel, ethanol, microalgae, net energy analysis.*

Resumen

En general, las plantas de procesamiento de la biomasa está considerando el uso del concepto de biorrefinería para evaluar el balance energético neto, así como, el análisis del ciclo de vida de las plantas agroindustriales para satisfacer los requisitos de sostenibilidad. Entre los varios tipos de plantas de procesamiento de biomasa, plantas de producción de biocombustibles se están convirtiendo en una gran importancia debido a la creciente demanda de biocombustibles para asistir al deseable escenario energético mundial sostenible. Desde el otro lado, la energía se recupera de residuos es un tema esencial para lograr tanto la energía como los requisitos

medioambientales. Dentro de este contexto, este trabajo considera la evaluación de la energía se recupera de la vinaza de plantas de etanol en Brasil para la producción de biogás o biodiesel a través del cultivo de microalgas, una vez que este tipo de planta industrial produce una gran cantidad de desechos. Para tal efecto, se desarrolló inicialmente, una metodología para evaluar la relación de energía neta de las plantas de etanol o biodiesel agroindustriales. Después de esta metodología en la mente, se consideró la contribución complementaria energética del biogás y el biodiesel obtenido a partir de cultivo de microalgas en la vinaza y su tratamiento. Sobre la base de este enfoque fue posible evaluar las mejores opciones en términos de utilización de los recursos, teniendo en cuenta el análisis de la relación de energía neta de las plantas de etanol agroindustriales. En conclusión, este tipo de análisis contribuye a un mejor aprovechamiento de los recursos de biomasa, así como, para el mejor diseño de la planta agroindustrial. Ciertamente, la energía recuperada de los sistemas de cultivo contribuye a disminuir la presión sobre el uso del suelo y por lo tanto la competitividad entre los alimentos y la energía.

Palabras clave: *biocombustibles, biodiesel, etanol, microalgas, análisis de energía neta.*

1. Introduction

Biorefinery concept has emerged in the seventies inside the wood American technological community (Sarkanen, 1976); (Hayes, 1977). Since that time, two big problems were raised related to the biomass conversion into chemicals: the economic competition of synthetically produced chemicals from oil, versus the necessity to depolymerize cellulose-lignin complex to provide society with the same products derived from oil. As the oil prices have increased continuously since the first oil shock in 1973, great efforts have been made to produce and efficiently convert biomass into chemicals and biofuels, which can be based on two different technological routes: bioconversion and thermal-conversion (Leal, 2008).

In Brazil, bioconversion process is being used economically to convert sugar cane into ethanol. Alternatively, vegetable oils have been extracted from oleaginous species, to the production of biodiesel, food, feed, and chemicals. For its time, the organic matter present in solid residues and/or in domestic or industrial effluents has been anaerobically fermented to obtain biogas (Leal, 2008). Emerging areas like alcohol-chemistry (Pereira, 2008); (Conde, 2008) and oil

chemistry (Cardoso, 2008) are now under consideration and development for the production of added value bioproducts, inside the Green Chemistry approach.

By its turn, biomass conversion through thermal processes is still on pilot scale, probably, achieving the stage of technological demonstration scale around 2015. Inside this context, Brazilian sugar cane straw and bagasse are designed to convert cellulose and hemi-cellulose components into ethanol via enzymatic and/or acid routes (Leal, 2008). Alternatively, the sugar cane residues are being gasified to produce synthetic gas, which can be converted by catalytic process into hydrocarbons via Fischer-Tropisch synthesis (Falabella, 2008).

Throughout this long developing period, microalgae cultivation and processing is achieving an advanced stage of utilization, and certainly can be used in Brazil or other tropical countries in a much more interesting way, due to its favorable net energy conversion factor (Carioca *et al*, 2007). This fact can place microalgae in a new frontier, as a new biomaterial for energetic and chemical purposes.

Several countries and multilateral institutions like UNIDO are proposing the development of a green economy to attend

future sustainable scenarios, in which, biofuels play an important role to diminish environmental global impacts. The construction of a sustainable society will require primordially two main urgent political actions: from one side, to reduce dependence on fossil fuels and from the other to eliminate the big amount of pollution generated by the industrial society, where wastes tend to become a valuable source of materials, for biofuels and/or biochemical's production, using a fundamental strategy, to recycle water. In this context, sustainable waste management is facing a fundamental role and challenge, related to the climatic change phenomena and the management of finite resources. So, one of the main directions will be the change of waste treatment processes, which consume a lot of energy, into a waste biorefining platform to give support to the development of a green economy.

In Brazil, the transportation sector accounts for approximately one third of the total energy consumption, in which the heavy transportation fleets, absorb the major parcel. The country has achieved self-sufficiency in oil around 2005, but it is still necessary to import diesel to meet oil domestic demand. Besides this, Brazilian oil production is considered heavy, requiring investments in the oil refining system to maximize diesel refining production. So considering these facts, as well as, the environmental restrictions, biodiesel was considered as a desirable option to reduce diesel imports.

In 1976, the country implemented a National Alcohol Program to replace gasoline as the initial stage of biofuels production (Governo Brasileiro, 2006). In 2005, the country set up the Biodiesel National Production Programme (PNPB) as an effort to replace diesel oil according to the Law N. 11,097 of January 13th, 2005. Among the main guidelines considered in this regulatory mark, the Biodiesel program intends to

promote the social inclusion, ensuring competitive pricing, quality and supply of products, as well as, the use of different sources of oleaginous plants, according to the regional availability (Miki, 2009). It was established that, from January 2008, it would be required the addition of a minimum percentage of 2% biodiesel to all diesel oil consumed in Brazil, a value that should gradually increase to achieve 5% around January, 2013 (Brieu, 2009). The use of traditional oilseeds such as soybeans, cotton, coconut, canola and castor for biodiesel production, demand the use of large tracts of land, due to low productivity and competitiveness of vegetable oil with food and export sector (Carioca *et al*, 2009). Therefore, it is important to investigate other raw materials that can really meet the demand for biodiesel in the country, and the possibility of their production in different regions of the country, without affecting the food market. Unfortunately Brazil still imports a large quantity of diesel oil to attend its intern demand (Governo Brasileiro, 2009).

The oil reserves located in the pre-salt layers will be sufficient to supply not only the domestic market, but to export oil derivatives. Unfortunately, this will take time, probably decades, to most of the oil fields become productive on a large scale. So, biofuels are one of the most viable alternatives for oil replacement because the country has a large tradition in Ethanol production from sugar cane, and now the production from biodiesel from oleaginous plants. In fact, Brazil has a quite successful experience in the use of ethanol from sugar cane as a substitute for gasoline.

1.1. Energy balance fundamentals

There are studies in the literature based on the computational analysis of production systems in order to evaluate mass and energy balances to generate data for economic studies and environmental impact, as well as,

to the development of biorefineries to biofuels production (Carioca *et al*, 2008). According to this methodology, it is possible to evaluate the energy consumption during the production of biofuel, including the indirect consumption of energy used in manufacturing and transportation of all inputs. It is also necessary to compute the energy extracted from biomass from the plant material in order to calculate the ratio between the energy produced and energy consumed during the whole process. Through this relationship, it is possible to have an assessment of energy efficiency of processes. In the Brazilian case, these studies are important to know a priori the possibility of regional production based on various raw materials. Literature data show that microalgae can be one of the alternative raw materials for production of biodiesel and biogas because its photosynthetic efficiency is greater than the traditional oilseeds. In addition, microalgae can grow in any type of water resources, including waste like the vinasse of the ethanol plants. So, the main objective of this paper is to develop a methodology to calculate the mass and energy balance involved in the production of biodiesel and biogas from microalgae, in order to establish process data base adequate to meet regional needs in Brazil. This kind of theoretical analysis indicates the real possibilities to use natural resources, including wastes to produce biofuels. This kind of study could be done a priori to the industrial plant installation. The results of these studies could save time and financial resources. Scenarios could be established in order to foresee the best conditions for specific regional circumstances. In the Brazilian case, the main regions greatly differ one from the others. Technical parameters as well as social inclusions, land availability, employments, biofuels transports costs and process economy could be considered in each regional scenario, depending of its main characteristics.

Concerning to the environmental point of view, the use of biodiesel significantly reduces emissions of pollutants as compared to diesel. Normally it can reduce 98% of sulfur, 30% of aromatics and 50% of particulate material, and at least 78% of Greenhouse Gas (Castellanelli, 2008). At regional basis, there is a wide variety of plants suitable for biodiesel production in the country. The most significant area to the production of vegetable oil is the central-southern region. In this region there are large tracts of land suitable for agriculture where mechanization is widely used (Carioca *et al*, 2009). According to (Gazzoni *et al*, 2006) soy is currently responsible for 88.9% of vegetable oil production in Brazil, which does not comply with the objectives of PNPB.

2. Oleaginous plant in Brazil

2.1 Oil seeds

Vegetable oils can be produced from crops such as soybeans, rapeseed, sunflower, palm, physic nut (*Jatropha curcas* L.), cotton, among others. Depending on the yield of the photosynthetic process, each oleaginous species has a certain content of oil in its seeds. In general, the maximum theoretical yield of the photosynthetic process is about 6.5% (Sasson, 1993) but the observed yield is no more than 2.5% for some species, like sugar cane and corn, depending on the place where the plant is cultivated. According to Melvin Calvin photosynthetic yields are classified according to their production cycles (Curtis, 1977). So, in C4 plants, like sugar cane and corn, the photosynthetic mechanism is very much favourable to higher biomass production, while in C3 plants, like oleaginous, the photosynthetic yield is less favourable (Carioca *et al*, 2009). In Table 1, it is shown the main characteristics of some sources of vegetable oils.

Table 1. Oil productivity from some vegetable oleaginous species

Species	Oil Content (%)	Cycle for Maximum Efficiency	Harvesting Period (Months)	Oil Productivity (T/Ha)
African oil palm (<i>Elaxis guineensis</i>)	20 (almond)	8 years	12	3.0–6.0
Physic Nut (<i>Jatropha curcas L.</i>)	36-45 (seeds)	Perennial specie	12	4.0-6.0
Coconut (<i>Cocus nucifera</i>)	55-60 (fruit)	7 years	12	1.3-1.9
Babassu palm (<i>Orbinya martiana</i>)	66 (almond)	7 years	12	0.1-0.3
Sunflower (<i>Helianthus annus</i>)	38-48 (grain)	Annual	3	0.5-1.9
Rapeseed (<i>Brassica campestris</i>)	40-48 (grain)	Annual	3	0.5-0.9
Castor beans (<i>Ricinus comunis</i>)	43-45 (grain)	Annual	3	0.5-0.9
Peanuts (<i>Orachis hypogeeae</i>)	40-43 (grain)	Annual	3	0.6-0.8
Soya (<i>Glyne max</i>)	17 (grain)	Annual	2	0.2-0.4
Cotton (<i>Gossypium hirsut</i>)	15 (grain)	Annual	3	0.1-0.2

2.2 Microalgae

Microalgae are currently used commercially for the production of high nutritional value products for human and animal use; wastewater treatment; the production of added value products like carotenes, as well as, aquiculture. However, the industrial production of microalgae is still relatively small, once the total world production is only a few thousand tons of algae biomass per year (Becker, 1994). Meanwhile, the technologies of microalgae cultivation have been under intensive research development over the last decades, both in the context of mitigation of greenhouse gases and the production of biofuels (Amotz, 2007). The production of biodiesel from microalgae is an alternative process to the current biofuels production from higher plants. The microalgae cultivation can use CO₂ as a carbon source for lipids biosynthesis which can be converted later into biodiesel. The microalgae may be an ideal solution, for two main aspects: they have a higher rate of CO₂

absorption when compared to traditional plants and they do not compete with arable land. In addition, microalgae have a higher oil yield compared to oil seeds traditionally used to produce biodiesel. Another advantage of microalgae cultivation is that; it can be done all year-round in tropical areas, continuously (Carvalho, 2010). The microalgae can grow in open ponds, raceways or photobioreactors. The cultivation method adopted affects the energy consumed and the estimated yield of the process and directly influences the energy balance. The culture medium must provide the inorganic elements that constitute the cell nutrients. Essential elements include nitrogen, phosphorus, iron and silicon in some cases. The minimum required nutrients can be estimated using the approximate molecular form of the biomass of microalgae, which is CO_{0,48} H_{1,83} N_{0,11} P_{0,01} (Chisti, 2007).

Unlike oil crops, microalgae grow very rapidly and can be extremely rich in oil. The

microalgae can usually double their biomass in 24hs. Oil content in microalgae can exceed 80% of dry biomass. Microalgae oil levels of 20-50% are quite common, so they appear to be a very competitive source of vegetable oil for biodiesel production with potential to replace fossil diesel. As it can be seen in Table 2, microalgae have an oil yield per hectare superior to other sources, according to Chisti (Chisti, 2007).

Table 2. Comparison of some sources of biodiesel production plants

Crop	Oil Yield (L/ha)
Corn	172
Soybean	446
Canola	1190
Coconut	2689
Oil palm	5950
Microalgae	136.900
Microalgae	58.700

In Brazil, nowadays several groups, including our group from Fortaleza, (Carioca *et al*, 2009) are involved in the research of microalgae development aiming at to turn microalgae into a profitable source of vegetal lipids.

2.3 Processes to produce alternative fuels to diesel

Actually, there are several technological processes to produce alternative fuels to biodiesel, among them the transesterification process, the thermocatalytic cracking of vegetable oils, water-diesel emulsions, ethanol diesel blends, co-solvency using vegetable oils, GTL (Gas To Liquids) mentioned in the publication (Carioca *et al*, 2011). In particular, it will be considered in this net energy analysis the transesterification processes of vegetable oils and microalgae, as well as the anaerobic fermentation of microalgae to produce biogas.

2.4 Transesterification process for biodiesel production

The transesterification reaction between triglycerides molecules found in vegetable or animal oils with an alcohol (methanol or ethanol) to produce methyl esters (biodiesel) may be catalyzed by acids, alkali or enzymes. In this study it will be considered the use of alkali catalysis reactions because they present the best yields. The transesterification reaction as described is characterized by the equilibrium between the reactants and products (Carioca, 2011), and its stoichiometry requires 1 mol of a triglyceride and 3 mol of the alcohol. However, in practice it has been utilized a larger proportion of the alcohol aiming at to displace the equilibrium reaction to form products. In Brazil, it has been utilized ethanol as alcohol due to its availability and less toxic character. Among the alkalis it is possible to include NaOH, KOH, carbonates and corresponding sodium and potassium alkoxides such as sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide. Sulfuric acid, sulfonic acids and hydrochloric acid are usually used as acid catalysts. Alkali-catalyzed transesterification is much faster than acid-catalyzed transesterification, with yields about 99% and it is often used commercially (www.transesterification.net).

After the transesterification reaction the products consist of a mixture of esters, glycerol, alcohol, catalyst, mono, di and triglycerides. According to the specifications of “Agência Nacional do Petróleo, Gas Natural e Biocombustíveis-ANP” (www.anp.gov.br), biodiesel purity should be higher than 96.5%. In Figure 1, it is shown the process flowchart to produce biodiesel from vegetable oils or recycled greases according to the source.

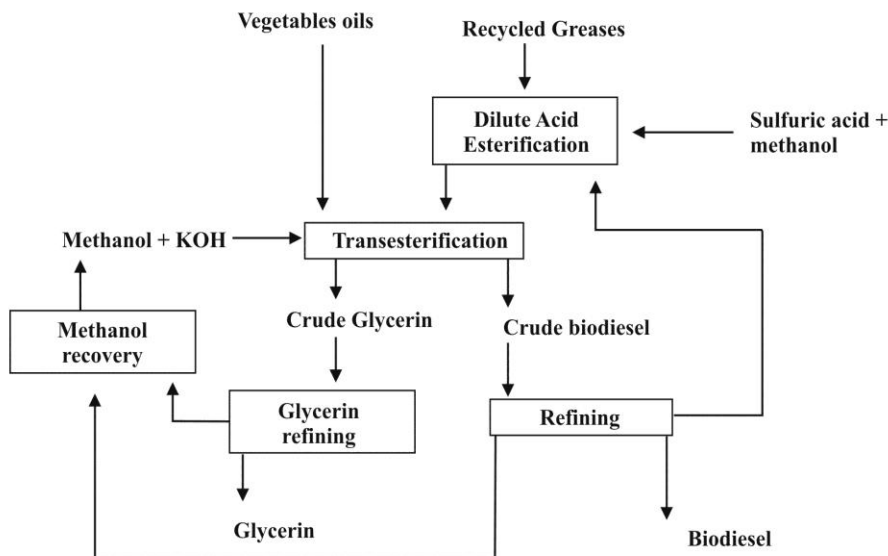


Figure 1. Process flowchart transesterification of vegetable oils.

A stream of biodiesel produced in the transesterification plant is neutralized at a convenient pH, and the soap formed is converted in free fatty acids, reducing the tendency of forming emulsions. A centrifuge is then used to separate the biodiesel aqueous phase, which is then taken to the glycerin recovery section aiming at to achieve the required market specifications. The glycerin-rich aqueous stream which is discharged from the reactors of transesterification and from the washing process is treated with hydrochloric acid in a reactor of continuous washing. The aim of this operation is to convert the soaps contaminants in the mixture in the free fatty acids, allowing their subsequent removal by centrifugation. The glycerin-rich aqueous stream is then neutralized with sodium hydroxide in a continuous neutralization reactor. The alcohol is then recovered from this stream by distillation and it is recycled to the operation of transesterification. Finally, the stream resulting from the operation of glycerin neutralization is subjected to distillation process to reduce its water content by a percentage equal to or greater than 80% (w/w) which has a considerable commercial value.

Glycerin is currently one of the ingredients used in the pharmaceutical composition of capsules, suppositories, anaesthetics, syrups and emollient for creams and ointments, antibiotics and antiseptics. In the food industry it is used in the preparation of sauces and frozen desserts and as humectants for food (Barbosa, 2009). The production of glycerin is already far than what the traditional market can absorb (Henn, 2009). Then, alternative studies are required to achieve the maximum yield of glycerin produced.

2.5. Biogas from the anaerobic fermentation

Anaerobic fermentation is the decomposition of organic matter such as dung, wastes, crop residues or microalgae, using anaerobic mixed bacteria population, which could be mesophilic or thermophilic. Normally, they work at ambient temperature with the pH varying between 6.8 and 7.2. Traditional biodigesters have a large retention time, but it can be less, once a pre-treatment step is employed, as well as the establishment of adequate parameters like the rate of organic load and the C/N and C/P ratios. During this decomposition, methane, carbon dioxide and

ammonia are produced, and normally this reaction takes place around 37°C, but it could be performed at thermophilic conditions (55°C). The carbon dioxide produced can be reused for the own cultivation of microalgae, as shown in Figure 2. This figure summarizes the process inputs required to biogas production, as well as, the energy consumption during the process. The methane can be either burned in a turbine to produce electricity or used through a catalytic process to be converted

into hydrocarbon fuels (Golueke, 1959). This process can solve the waste problem through the microalgae biodiesel production, as well as the economic-energy equilibrium (Chisti, 2008). As soon as methane, carbon dioxide, and other minority gases are produced, they are removed from the digester through a disposal unit where the carbon dioxide and ammonia are again available for photosynthesis, the supernatant and the retained solids recycled as nutrients to the culture of bacteria (Golueke, 1959).

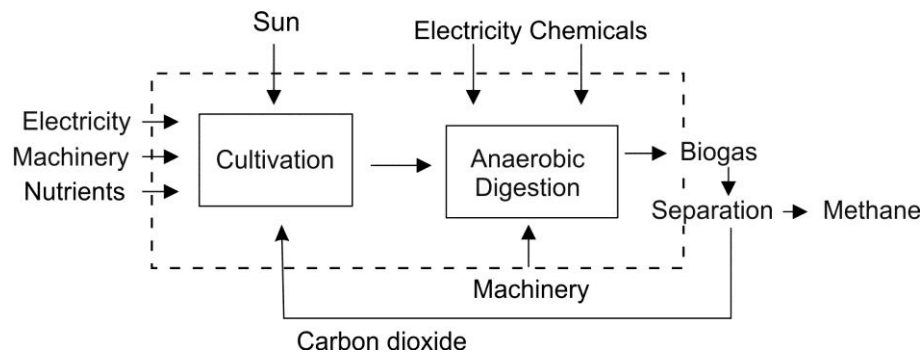


Figure 2. Process flowchart of biogas production.

3. Energy balance analysis methodology

The methodology developed in this paper is based on several publications related to the energy balance for biodiesel, biogas and ethanol processes found in the literature, which utilized the concept of Net Energy Ratio - NER, defined as the ratio between the total energy produced from the biomass and the total energy consumed in the process according to (Pradhan, 2008), described in equation (1). As it was stressed, soybean was chosen as oilseed because it is the culture

responsible for most of the biodiesel produced in Brazil. In this work it was observed from the literature that exist some differences in the NER values obtained by different authors, as well as some opportunities to improve energy efficiency. In principle, the evaluation of the biofuels energy balance in industrial production requires that the energy extracted from raw materials must be greater than the energy obtained from the production system. According to Figure 3, the methodology used to evaluate the energy balance should consider the integration of two sub-systems: the cultivation and biofuels production.

$$NER = E_{\text{prod.}} / E_{\text{cons.}} \quad (\text{Eq. 1})$$

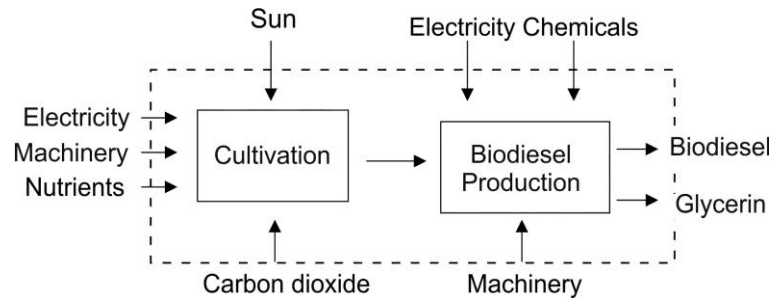


Figure 3. Structure of the system used to evaluate energy balance.

To evaluate the energy balance of the integrated system, it is necessary to analyze the energy input throughout the process, considering both for the cultivation and industrial phases. To calculate the power consumption of each variable, it is necessary to have the mass balance to know the quantities used in the process as well as, their energy coefficients. Each energy

coefficient is defined as the amount of energy per mass unit, or volume or even other adequate measure unit. In general, they have the units expressed in J/kg, or J/m³. Once known the energy coefficient (*u*) of each item (variable) and the amount of items used (*q*), it is possible to know the amount of energy, expressed for each item (variable) according to the equation (2):

$$E_1 = u_1 \times q_1 \quad (\text{Eq.2})$$

*E*₁ = energy consumed by the item (variable) 1
*u*₁ = energy coefficient of the item (variable) 1
*q*₁ = amount of item (variable) 1

To calculate the total energy consumed in the system, simply add the energy consumed by all variables of the process.

$$E_{\text{cons.}} = \sum (E_1 + E_2 + E_3 + \dots + E_N) \quad (\text{Eq. 3})$$

During the cultivation, the major energy consuming items are from the nutrients, fertilizers, electricity or fuel (diesel) and machinery. For each of these items, it is necessary to evaluate the energy coefficient and the amount of the item used. During the cultivation phase it is necessary to know the needs of CO₂ and solar energy, but as they are considered free, it makes no sense to consider it in the energy balance. During the biodiesel production, the main energy items consumed are: electric energy, chemicals and machinery. According to this methodology, it is necessary to consider also

the total energy consumed in the productive process, including the indirect energy, which is the energy used in the production, transport system of each product or equipment. To calculate the total energy produced from the system, it is necessary to know the volume of biofuel produced, in m³, and multiply by its coefficient energy in J/m³. Therefore it is necessary to calculate the energy produced in Joules available in the biofuel. Some authors also consider byproducts like glycerin and the cake in the calculation of extracted energy.

$$E_{\text{prod.}} = U \times V \quad (\text{Eq. 4})$$

$E_{\text{prod.}}$ = produced energy from the system

U = biofuel energy coefficient

V = biofuel produced volume

Taking these data into consideration, it is possible to calculate the value for the parameter NER, according to equation (1). This coefficient is an important coefficient to know the energetic yield and the environmental impact, as well as the process feasibility. According to (Braga *et al.*, 2008), studies on energy balance show that specific emissions of CO₂ (gCO₂/MJ) are inversely proportional to the value obtained from the balance (energy output / input) for biofuels. Moreover, the energy balance has a close relationship with the economic balance (Braga *et al.*, 2008).

It is possible to observe different approaches for energy balance calculating in the literature (Chisti, 2008); (Gazzoni *et al.*, 2009). Some authors consider only the energy from fossil fuels, while others consider the total energy consumed in the process. Concerning the produced energy, some authors consider important to involve the energy of byproducts like glycerin. These considerations may result in different data for the final energy balance and therefore for one specific methodology. For example, according to (Gazzoni *et al.*, 2009), for every unit of energy entering the system for production of canola, the energy produced is 2.9 units, and considering only the production of oil, this ratio falls to 1:1.4. Following, it will be presented first the energy balance for the biodiesel production from soya, since this seed is very important to biodiesel production in Brazil. This value could be used as a reference for comparison with that one obtained from the microalgae energy balance. The results presented in the literature show some differences according to the value of the energy coefficients utilized.

3.1 Biodiesel energy balance from soybean

Several authors performed the energy balance for the production of biodiesel from soybean as it will be detailed in sequence. As a first example, in Table 3 are listed the main energy consumptions coefficients per hectare used in the agricultural production of soybean in Brazil, according to (Soares *et al.*, 2008). It may vary from place to place.

The values of Net Energy Ratio – NER for the biodiesel production process presented in Table 4, were calculated using the data shown in Table 3, and evaluated according to data presented by Soares from Embrapa (Soares *et al.*, 2008). These authors found a value of 1.12 for the NER to biodiesel production process. Once considering the energy of the soymeal (cake) the NER increased to 1.87.

In another study made by (Pimentel, 2005), the energy coefficients for the soybean production were evaluated, according to the data indicated in Table 5. Based on these data, it was constructed the Table 6. Pimentel found a NER of about 0.79, demonstrating that the biodiesel production process from soybeans is unfeasible energetically. It means that for each unit of energy used in the process, it is produced only 0.79 units of energy in the form of biodiesel.

The largest discrepancy presented in the Pimentel and Patzek's results (Pimentel, 2005) comes from the fact that, such study assigned only 19.3% of the total energy input to the soymeal. In reality, 82% of the soybean mass goes into the soymeal. For its time, it pointed out an arithmetic error in this report and an error in the proper accounting of lime application, which contributed to a discrepancy in the results (Pradhan, 2008).

Table 3. Data on energy consumption coefficients for soybean production.

Item	Unit	Quantity	Energy (GJ)
Limestone	kg/ha	1000	1.18
Herbicide	L/ha	3.8	1.80
Fertilizer (0-20-20)	Kg/ha	400	0.62
Seed	Kg/ha	50	1.02
Fungicide	L/ha	1.8	0.57
Insecticide	L/ha	1.65	0.6
Bait	Kg/ha	1	0.36
Manual operation	h/ha	8	1.34
Equipments	Kg/ha	14.8	1.12
Fuel	L/ha	58	2.76
Transport	Ton	1.3	0.20
Total			11.57

Table 4. NER for biodiesel production from soybean according to Soares.

Item	Unit	Quantity	Energy (GJ)
Agricultural production	Kg/ha	1300	33.74
Energy in agricultural production			12.08
Industrial process			5.39
Total energy invested			17.47
Produced oil	Kg/ha	520	19.60
Soybean cake	Kg/ha	780	13.07
Energy balance	Biofuel	NER = 1.12	
	Total	NER = 1.87	

Table 5. Biodiesel energy balance from soybean per hectare.

Item	Unit	Quality	Energy Coefficient	Unit	Energy (Mcal)
Labor	h	7.1	40.0	Mcal/h	284
Machinery	Kg	20	18.0	Mcal/Kg	360
Fuel	L	77.8	9.5	Mcal/L	737
Nitrogen	Kg	3.7	15.9	Mcal/Kg	59
Phosphorus	Kg	37.8	4.1	Mcal/Kg	156
Potassium	Kg	14.8	3.2	Mcal/Kg	48
Limestone	Kg	4,800	0.3	Mcal/Kg	1,349
Seed	Kg	69.3	8.0	Mcal/Kg	554
Herbicide	Kg	1.3	100.0	Mcal/Kg	130
Electricity	Kw.h	10			29
Transport	Km	174	0.3	Mcal/Km	44
Total (input)					3,700
Soybean(output)	Kg	2,668	3.6	Mcal/Kg	9,605

Table 6. NER for biodiesel production from soybean according to Pimentel.

Item	Unit	Quality	Energy Coefficient	Unit	Energy (Mcal)
Soybean production	Kg	5,556			7,809
Electricity	Kw.h	270			697
Steam					1,350
Water					160
Heat					592
Losses					300
Stainless steel	Kg	11	14.4	Mcal/Kg	158
Steel	Kg	21	11.7	Mcal/Kg	246
Cement	Kg	56	1.9	Mcal/Kg	106
Total (input)					11,418
Biodiesel(output)	Kg	1,000	9.0	Mcal/Kg	9,000
NER	0.79				

Table 7. NER for biodiesel production from soybean according to Gazzoni.

Item	Unit	Quant	Energy Coefficient	Unit	Energy (Mcal)
Cultivation					
Labor	h	6.3	40	Mcal/h	252
Machinery	Kg	20	18	Mcal/Kg	360
Fuel	L	66	10	Mcal/L	660
Phosphorus	Kg	20	4.2	Mcal/Kg	83
Potassium	Kg	20	3.2	Mcal/Kg	63
Limestone	Kg	2,000	0.3	Mcal/Kg	562
Boron	Kg	1	4	Mcal/Kg	4
Seed	Kg	50	8	Mcal/Kg	400
Herbicide	L	0.47	100	Mcal/L	47
Insecticide	L	2.03	100	Mcal/L	203
Transport	Km	174	0.3	Mcal/Km	44
Biodiesel Production					
Production of 720 Kg of biodiesel					1,149
Total (input)					4,127
Biodiesel (output)	Kg	720	9.0	Mcal/Kg	6,480
NER	1.57				

Studies performed by Gazzoni (Gazzoni *et al*, 2006) adopted the value of Pimentel and Patzek (Pimentel, 2005) to evaluate the energy needed to manufacture machinery and implements, fertilizers and pesticides, as well as, the energy value of diesel oil and energy contained in the seeds. For the diesel oil consumption, it was used data from spreadsheets (Roessing *et al*, 1981). For limestone consumption, it was adopted 2 t / ha. The evaluation of the amount of seeds for soybeans was based on the formula $Q = (1000 \times P \times D) \times 1.1 (G \times E) - 1$; where, P = 10.4 g (means the weight of a hundred seeds); D = 14 (number of plants per meter); G = 80% (% field emergence); and E = 0.4 m (space used). So, based in these values Gazzoni evaluated the NER for the biodiesel

production process, which is summarized in the Table 7. It was found a value of 1.57 for the NER.

In Table 8, it is summarized the energy balance carried out by Ahmed (Ahmed *et al*, 1994), which adopted the industry's average energy consumption of soybeans in the United States. These authors obtained a value of 2.51 for NER for the overall biodiesel process.

According to Hill (Hill *et al*, 1994), the process of biodiesel production from soybean has a NER of 1.93, as indicated in Table 9. The author used data from the Department of Agriculture of the United States to estimate the energy consumed during the soybean cultivation.

Table 8. Biodiesel energy balance from soybean according to Ahmed.

Item	Quantity	Unit	Energy Coefficient	Unit	Energy (Btu)
Cultivation					
Diesel	0.11	gal	138,000	Btu/gal	14,552
Pesticide	0.02	lb	179,000	Btu/lb	3,739
Potassium	0.35	lb	4,280	Btu/lb	1,482
Phosphorus	0.19	lb	5,560	Btu/lb	1,079
Nitrogen	0.06	lb	31,100	Btu/lb	1,893
Others					6,691
Solvent Extraction					
Electricity			Electricity		6,858
Steam			Steam		23,620
Solvent (n-hexane)	0.015	gal	106,522		1,575
Refine					
Electricity					450
Steam					642
Estherification					
Electricity					2,666
Steam					18,225
Methanol	0.11	gal	66,542	Btu/gal	7,320
Catalyst (NaOH)	0.08	gal	11,275	Btu/gal	902
Transport					228
Total					91,922
Biodiesel	1	gal	132,902	Btu/gal	132,902
Glycerin					17,010
Soy (food)					81,229
Total (output)					231,141
NER	2.51				

Table 9. Biodiesel energy balance from soybean according to Hill.

Cultivation	
Item	Energy (MJ)
Fossil fuel	0.19
Fertilizers and pesticides	0.09
Electricity	0.21
Seed	0.03
Machinery	0.04
Biodiesel Production	
Transport	0.025
Construction	0.01
Labor	0.02
Electricity	0.25
Total (input)	0.865
Biodiesel	1
Soy (food)	0.56
Glycerin	0.11
Total (output)	1.67
NER	1.93

4. Integrated biofuels plants using microalgae cultivation from wastes

Several types of plants design could be performed aiming at biofuels production integrated with microalgae cultivation. This study considered two processes: one for biodiesel and another for ethanol. It is important to observe that, the effluents or

residues from these plants were utilized aiming at to generate additional energy which improves the NER of agroindustrial biorefineries.

4.1 Results of NER for biodiesel and biogas production plants using microalgae

Large scale microalgae cultivation plant is a growing subject all over the world, and so, there is an increasing consensus about the importance of having precise data concerning mass and energy balance for different processes. Many studies on pilot plants are still in development. It has been observed some difficulties in obtaining the value of the energy coefficients used in the microalgae cultivation system, as well as, the environmental impacts considered in certain types of processes. In this section it was evaluated the NER for biodiesel and biogas production plants using microalgae cultivation, to provide basic information concerning biofuels production related to the energetic yields of agroindustrial plants. In the first case (Hill *et al*, 1994), it was considered a biorefinery related to a biodiesel production plant based in algal oil, according to the design presented in Figure 4.

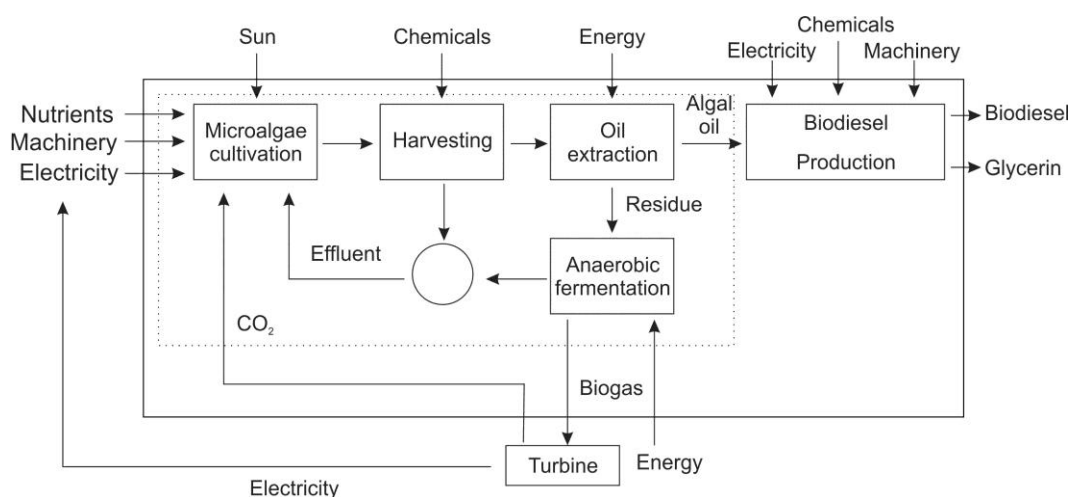


Figure 4. Biodiesel biorefinery integrated with microalgae cultivation.

For this process, there were considered the following energy coefficients shown in Table 10. Aiming at the evaluation of the NER for this plant, Chisti (Chisti, 2008) suggested initially the evaluation of an **energy rate coefficient**, which means the relation among the sum of the total renewable energy components produced (output) per unit of fossil energy used as energy (input), which was calculated according to the data presented in Table 10. The **energy rate coefficient** obtained was 2.8, which demonstrates that this plant is energetically feasible. According to Chisti (Chisti, 2008), depending on the microalgae productivity and their oil content, the NER could exceed 7, once microalgae separation uses especial flocculants agents before the vacuum filtration to obtain the final microalgae paste (Becker, 1994). This value could still be improved if the final effluent from the anaerobic fermentation could be recycled, as nutrients. Chisti analysis was based on the use of raceway ponds to microalgae cultivation having 20.5% (w/w) oil yield, and assuming the biomass productivity of about 15 ton per ha per year. However, it was considered for the microalgae cultivation calculus, the biomass productivity of 25g per m² day, and the final concentration in the broth was assumed as been 0.5 kg per m³. These data are considered normal for tropic conditions according to Chisti. To obtain the NER for a biodiesel and biogas production plant it is necessary to convert the algal oil into biodiesel and the biogas into electricity. For that, it will be considered one NER coefficient for the biodiesel unit as being 2.51, according to Ahmed, for an analogous biodiesel unit (biodiesel and glycerin); and a NER coefficient of 1.56 for the conversion of biogas into electricity, as suggested by Chisti. Taking these new outputs coefficients into consideration the value for the NER was calculated as been 5.563, as it is shown in Table 11.

Table 10. Energy rate coefficient for biodiesel and biogas production plant integrated with microalgae cultivation according to Chisti.

Energy Coefficients	Energy (MJ Kg ⁻¹ Oil)
Inputs	31.24
Energy in nutrients	14.12
Electric energy for cultivation	8.77
Energy for harvesting (chemicals)	0.30
Energy for oil recovery	3.17
Energy for biogas production	0.88
Energy for construction (entire facility including maintenance)	4.00
Energy embodied in equipment (including maintenance)	62.8 x 10 ⁻⁶
Outputs	87.90
Energy in the algal oil	37.90
Energy in biogas from residues	50.00
Energy Rate Coefficient (algal oil + biogas)	2.8

Table 11. Energy rate for the algal oil and biogas production plant.

Energy Coefficients	Energy (MJ Kg ⁻¹ Oil)
Inputs	31.24
Energy in nutrients	14.12
Electric energy for cultivation	8.77
Energy for harvesting (chemicals)	0.30
Energy for oil recovery	3.17
Energy for biogas production	0.88
Energy for construction (entire facility including maintenance)	4.00
Energy embodied in equipment (including maintenance)	62.8 x 10 ⁻⁶
Outputs	173.150
Energy in the Biodiesel	95.281
Electric energy from biogas	78.150
Net Energy Rate	5.563

4.2 Other NER data for a methane plant, algal oil and biodiesel from microalgae

In this section it will be regarded initially the work developed by Wagener (Wagener, 1978), in which it is presented a classical study related with the NER evaluation for a methane producing plant. They used one conversion coefficient in which, 1kg of dry algae mass can produce 427 L of CH₄, with an energy content of 3656 kcal, not taking into account the new bacteria formed after the biodigester discharge. Considering that the formation of new bacteria is repressed, it could produce 476 L of CH₄ with an energy value of 4078 kcal. According to these data, it was achieved a NER of 2.66. If the energy required to pump the tanks' culture is generated by waves, then it reaches a value of 12.9. Once the plant is heated with biogas and not with the heat lost from the gas engine, the new NER evaluation is about 8.5 according to (Wagener, 1978).

Ehimen (2010) found in his analysis a value of 0.31 for the NER for a biodiesel and biogas production plant integrated with microalgae cultivation, according to data indicated in Table 12, which characterizes the process energetically as non-feasible. In Ehimen's analysis, it was considered the use of a centrifugation process to separate microalgae, which spends a considerable amount of energy. Practically 85% of the total energy inputs shown in Table 13 are due to the electrical energy consumption.

4.3 Results related to NER for an ethanol biorefinery integrated with algal cultivation in vinasse

It is well known that agribusiness produce a large quantity of wastes, mainly those generated in the food sector, where there is plenty of sugar available in wastes and effluents, adequate to produce biofuels or biochemical. Among these, effluents from ethanol are worldwide produced generating huge environmental impacts. After the

seventies, world agricultural land use is suffering a challenging pressure to produce biofuels to replace fossil fuels, besides increasing food production to support the development of a green economy. The use of wastes to produce chemicals and/or biofuels has gained a considerable attention in the last decades, due to its sustainable conditions. In this context, sustainable waste management is a fundamental role to face the challenges related to climatic change phenomena and the management of finite resources. So, one of the main directions is to change from waste treatment processes, which consume a lot of energy, into a waste biorefining platform to support the development of a green economy (Carioca et al,2012). Ethanol plants produce a large quantity of wastes, which contain valuable nutrients that could be used to cultivate microalgae, improving energy balances and diminishing environmental impacts. It is estimated that in the next fifth years more than 40% of the world population will live in countries facing water stress or water scarcity according to the data presented by the United Nations Population Division, published in 2002, prepared by (Hinrichsen, 1998). If well managed, wastewater could help to recycle water and nutrients, like Nitrogen, Phosphorous, and other important minerals besides diminishing the cost of fertilizers with no environmental impacts.

In general, the expected algal yield, depend on several factors. Taking into consideration the solar radiation in the tropics, the expected value is around 25g/m²/day as it was utilized in the evaluation presented in this paper. However, data presented by Ben-Amotz *et al* (2007) indicate that the value of 20g/m²/day was achieved for normal *Dunaliella* cultivation in the Middle East conditions.

Table 12. Biodiesel NER from microalgae according to Ehimen.

Energy Consumption Per Hectare					
Item	Quantity	Unit	Energy Coefficient	Unit	Energy (MJ)
Ammonia (NH ₃)	5.76	t	37.8	GJ/t	217.73
Triple super-Phosphate	1.44	t	4.1	GJ/t	5.90
Electricity					6.05
Biodiesel Production					
Extraction					15.36
Transesterification and purification					8.64
Total energy (input)					1,693.7
Biodiesel (output)					531.4
Energetic yield	0.31				

Table 13. Results from biodiesel NER from microalgae, considering the use of free renewable energy.

Item	Quantity	Unit	Energy Coefficient	Unit	Energy (MJ)
Ammonia (NH ₃)	5.76	t	37.8	GJ/t	217.73
Triple super-phosphate	1.44	t	4.1	GJ/t	5.90
Machinery and infrastructure					6.05
Electricity					0.00
Biodiesel Production					
Extraction					15.36
Transesterification and purification					8.64
Total (input)					253.7
Biodiesel (output)					531.4
Energetic yield	2.09				

Data on *Chlorella vulgaris* cultivation presented by Bonini (Bonini, 2012), pointed out the need to hydrolyze these components in order to improve the microalgae yields. This information stresses the importance of the kinetic evaluation data prior to the cultivation under open system, in raceway ponds or photobioreactors in order to obtain high specific rates. Bonini (2012) has mentioned the optimum value for the glucose concentration of 5.6 g/L. Glucose concentrations higher than this value clearly inhibit the growing. Finally, in our studies, the water evaporation losses seems to be another important factor to be considered in the microalgae cultivation in vinasse under tropical conditions, due to the high value of

insulation rates (around 250 W/m²) (Carioca *et al*, 2010).

Inside the biorefinery concept, the plant presented in Figure 5 considered the microalgae cultivation in vinasse, integrated to an ethanol producing plant, in order to improve the energetic yields of current ethanol industrial plants, in Brazil.

Vinasse is a type of effluent from alcohol distilleries which has a desirable mineral composition as shown in the Table 14 (Elia Neto, 1995); (Leal, 2008). In spite of that, vinasse also contains a little amount of glycerin, ethanol, lactic and acetic acids. This is a rich effluent, which has been used to grow microalgae, utilizing CO₂ from the anaerobic fermentation unit, using residues

from the oil extraction unit, as proposed by Chisti (2008). It is important to know that in Brazilian ethanol plants there is a ratio of 12 liters of vinasse per liter of ethanol produced. Some species of microalgae could be utilized for this purpose, such as;

Chorella and *Nannochloropsis* (Carioca *et al*, 2009). It has been observed excellent results from growing *Scenedesmus* sp e *Chlorella* sp in the vinasse, utilizing CO₂ from the ethanol fermentation process Bonini (Bonini, 2012).

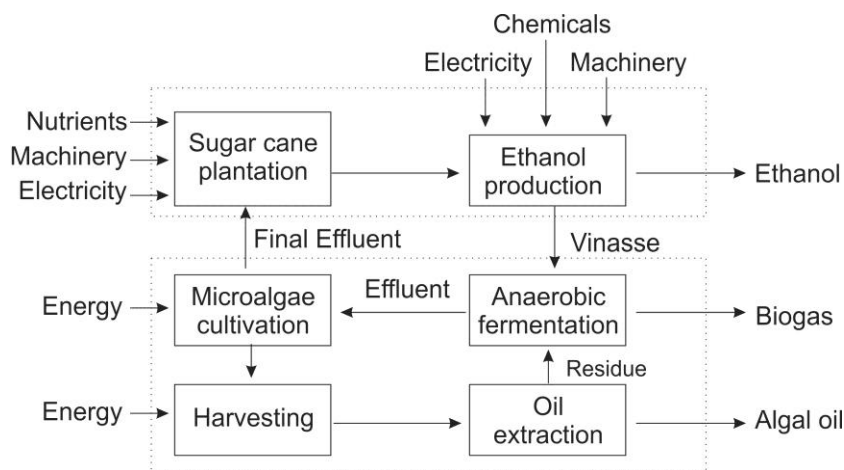


Figure 5. Ethanol biorefinery integrated to microalgae cultivation in vinasse.

Vinasse has a high content of nitrogen and phosphorous, which are basic nutrients for microalgae cultivation (Amotz, 2007). After the cultivation, microalgae are separated from the broth using sedimentation and a vacuum filter as proposed by (Chisti, 2008). The final effluent is directed to the sugar cane plantation, for irrigation purposes.

Using this approach, water and the residual nutrients are recycled. So, as it can be seen from the data presented in Table 15, it is possible to increase the NER for about 11.1. It means to increase the actual distilleries energetic yield for about 33.7% through the use of microalgae cultivation system in the vinasse from an ethanol plant.

Table 14. Typical composition of sugar cane vinasse in Brazil.

Components / units (Vinasse)	Types of substrates used		
	Molasses	Mixed	Juice
N (kg/m ³)	0.75 – 0.79	0.33 – 0.48	0.26 – 0.35
P ₂ O ₅ (kg/m ³)	0.10 – 0.35	0.09 – 0.61	0.09 – 0.50
K ₂ O (kg/m ³)	3.50 – 7.60	2.10 – 3.40	1.01 – 2.00
CaO (kg/m ³)	1.80 – 2.40	0.57 – 1.46	0.13 – 0.76
MgO (kg/m ³)	0.84 – 1.40	0.33 – 0.58	0.21 – 0.41
SO ₄ (kg/m ³)	1.50	1.60	2.03
Organic Matter (kg/m ³)	37 – 57	19 – 45	15 – 35
Mn (mg/dm ³)	6 – 11	5 – 6	5 – 10
Fe (mg/dm ³)	52 – 120	47- 130	45- 110
Cu (mg/dm ³)	3 – 9	2 – 57	1 – 18
Zn (mg/dm ³)	3 – 4	3 – 50	2- 3
pH	4.0 – 4.5	3.5 - 4.5	3.5 - 4.0

Table 15. Summary of NER in biofuels production plants.

Energy	Algal Oil + Biogas (MJ kg ⁻¹ oil)	Ethanol (kcal/Ton)
Agricultural Phase	31.24	48.208
Processing		11.800
Sub -Total	31.24	60.008
Energy from Products	87.9	499.400
Net Balance	56.6	439.392
Energetic Yield	2.8	8.3

5. Conclusions

This study demonstrates the importance of the applicability of net energy ratio analysis methodology to biofuels production aiming at to supply the entrepreneurs with realistic data and design for different processes. The methodology developed in this study employed energy coefficients available in the literature in order to evaluate net energy balance for agroindustrial plants, representing a valuable tool for entrepreneurship decision related with the best design for industrial plants. This kind of data are moving researchers and companies from all over the world to study and evaluate the best way of producing efficiently agricultural resources to guarantee the production of biofuels in a sustainable and economic way. In general, biomass processing plants consider the use of biorefinery concepts to evaluate the net energy balance, as well as, the life cycle analysis of agroindustrial plants to meet sustainability requirements, as shown in this paper. The basic idea is to find the highest net energy ratio (NER) for biofuels production processes according to a specific plant conception. So, the recovery of energy from agroindustrial plant wastes could be obtained through the use of microalgae cultivation to produce biodiesel, algal oil and/or biogas. This kind of approach results in a considerable increasing of the net energy balance of the agroindustrial plants. So, it can be concluded that it is possible to

increase the energetic yield of biodiesel plants through the use of microalgae cultivation based on its residues, as well as, the net energy ratio (NER) for the ethanol plants using its vinasse to grow microalgae.

6. References

- Ahmed I *et al.* 1994. How much energy does it take to make a gallon of soydiesel? The Institute for Local Self-Reliance. Report from ILSR, 2425. 18th Street NW-Washington D.C., 20.009-2096, USA.
- Amotz A.B; Jinjiikhashvily G. 2007. Production of marine unicellular algae on power plant wastes: from the black coal to green bio-fuel. In: CARIOCA J.O.B (editor). Anais, 1st Brazilian Workshop on Green Chemistry: Awareness, Responsibility and Action. Editora UFC. Fortaleza, Brasil. pp. 325-345.
- Barbosa C.R. 2009. Avaliação do glicerol proveniente da fabricação do biodiesel como substrato para produção de endotoxinas por *Bacillus thuringiensis* var. israelensis. Dissertação, Pós-Graduação em Biotecnologia Industrial, Universidade de São Paulo, Lorena, Brasil. 133 p.
- Becker, E.W. 1994. Microalgae – Biotechnology and Microbiology. Cambridge Studies in Biotechnology 10. Cambridge. 293p.
- Bonini, M.A. 2012. Cultivo heterotrófico de *Aphanothece microscopica Nägeli* e *Chlorella vulgaris* em diferentes fontes de carbono e em vinhaça. Dissertação, Universidade de São Carlos, Pós-Graduação em Agricultura e Ambiente. 96p.
- Braga F.L.P. *et al.* 2008. Balanço econômico da produção de mamona e balanço energético da obtenção de biodiesel no Estado do Ceará. In: Congresso da Sociedade Brasileira de Economia, Administração e Sociologia Rural, XLVI, Rio Branco, Brasil.
- Brieu T.P. 2009. Programa Nacional de Produção e Uso de Biodiesel: um Balanço

- da Primeira Fase até 2008. Dissertação, Pós-Graduação em Energia, Universidade de São Paulo, São Paulo, Brasil. 163 p.
- Cardoso, R. 2008. Óleo Chemistry. In: CARIOCA J.O.B (editor). Anais, 1st Brazilian Workshop on Green Chemistry: Awareness, Responsibility and Action. Editora UFC. Fortaleza, Brasil. pp.553-564.
- Carioca, J.O.B. *et al.* Mariculture as a New Challenging Resource. Trabalho apresentado no International Marine Biotechnology Conference. 11-16 March, 2007, Eilat, Israel.
- Carioca J.O.B. *et al.* 2009. The Hard Choice for Alternative Biofuels to Diesel in Brazil. *Biotechnol Adv* 27(6):1043-1050.
- Carioca, J.O.B.; Moraes, C. 2008. In: CARIOCA J.O.B (editor). Anais, 1st Brazilian Workshop on Green Chemistry: Awareness, Responsibility and Action. Editora UFC. Fortaleza, Brasil. pp. 35-73.
- Carioca, J.O.B. *et al.* 2011. Biofuels: from Hopes to Reality. Biofuel Production-Recent Developments and Prospects. InTech Book, Ed. Bernardes MAS. pp. 521-546.
- Carioca, J.O.B. 2011. Biofuels: Problems, Challenges and Perspectives. *Biotechnol J* 5(30): 260-273.
- Carvalho R.M. 2010. Desenvolvimento e análise energética do processo de obtenção do biodiesel de microalga por metanólise *in situ*. Dissertação, Engenharia, Universidade Federal do Paraná, Curitiba, Brasil. 85 p.
- Castellanelli C.A. 2008. Estudo da Viabilidade de Produção do Biodiesel, Obtido Através do Óleo de Fritura Usado, na Cidade de Santa Maria-RS. Dissertação, Pós-Graduação em Engenharia de Produção, Universidade Federal de Santa Maria, Santa Maria, Brasil. 111 p.
- Chisti Y. 2007. Biodiesel from microalgae. *Biotechnol Adv* 25(3):294-306.
- Chisti Y. 2008. Biodiesel from microalgae beats bioethanol. *Trends Biotechnol* 26(3): 126-131.
- Chisti Y. 2008. Response to Reijnders: Do biofuels from microalgae beat biofuels from terrestrial plants? *Trends Biotechnol* 26(7):351-352.
- Curtis, H. 1977. Invitation to Biology, Second Edition, Worth Publishers, Inc., New York. 624p.
- Conde, A. 2008. A gestão da inovação – Como manter um fluxo contínuo de inovação. Palestra apresentada no Seminário ABIQUIM de Tecnologia realizada nos dias 17 e 18 de junho de 2008. São Paulo/SP.
- Ehimen E. A. 2010. Energy Balance of Microalgal-derived Biodiesel. *Energy Source* 32(12):1111-1120.
- Elia Neto. A.; Nakhodo, T. 1995. Caracterização físico-química da vinhaça – Projeto nº 9500278. Relatório técnico da seção de tecnologia de tratamento de águas do Centro de Tecnologia Canavieira. Piracicaba-SP.
- Falabella, S.A.E. 2008. BTL: A solution to Brazilian sugar cane and other biomass residues. In: CARIOCA J.O.B (editor). Anais, 1st Brazilian Workshop on Green Chemistry: Awareness, Responsibility and Action. Editora UFC. Fortaleza, Brasil. pp.439-448.
- Gazzoni D.L. *et al.* 2006. Balanço energético das culturas de soja e girassol para a produção de biodiesel, <<http://www.biodiesel.gov.br/docs/congresso2006/agricultura/BalancoEnergético.pdf>>, acesso em 2010.
- Gazzoni D.L. *et al.* 2009. Balanço energético da cultura da canola para a produção de biodiesel. *Espaço Energia* 11:24-28.
- Governo Brasileiro - Ministério das Minas e Energias. 2006. Balanço Energético Nacional. Empresa de Pesquisa Energética, Brasília-DF.

- Governo Brasileiro - Ministério das Minas e Energias. 2009. Balanço Energético Nacional. Empresa de Pesquisa Energética, Brasília-DF.
- Golueke C.G; Oswald W.J. 1959. Biological conversion of light energy to the chemical energy of methane. *Appl Microbiol* 7(4):219-227.
- Hayes, D. 1977. Biological sources of commercial energy. *BioScience* 27 (8):540-546.
- Henn J. D; Zanin A. 2009. O agronegócio do biodiesel: potencialidades e limitações da utilização da glicerina (co-produto) na alimentação de suínos e aves. In: Congresso da Sociedade Brasileira de Economia, Administração e Sociologia Rural, 47º, Porto Alegre-RS.
- Hinrichsen, D.; Robey, B. and Upadhyay, U.D. 1998. Solutions for a water-short world. Baltimore, M.D. Johns Hopkins University, School of Public Health. *Population Reports, Series M*, 14.
- Hill J. *et al.* 2006. Environmental, economic, and energetic costs and benefits of biodiesel and ethanol biofuels. *Proceedings of National Academy of Science* 103 (30):11.206-11.210.
- Leal, M.R.L.V.; Leite, A.L. 2008. Biomass Future Based Supply. In: CARIOCA J.O.B (editor). Anais, 1st Brazilian Workshop on Green Chemistry: Awareness, Responsibility and Action. Editora UFC. Fortaleza, Brasil. pp. 217-234
- Pereira, B.R. Polietileno de Cana. 2008. Trabalho apresentado no 12º Congresso de Atuação Responsável. Parte 3: Ações da indústria – A produção de polímeros a partir de matérias-primas renováveis. 17-18/06/08. São Paulo-SP.
- Pimentel D; Patzek T.W. 2005. Ethanol Production Using Corn, Switchgrass, and Wood; Biodiesel Production Using Soybean and Sunflower. *Nat Resour Res* 14(1):65-76.
- Pradhan A. *et al.* 2008. The energy balance of soybean oil biodiesel production: a review of past studies. *Transactions of the ASABE* 51(1):185-194
- Roessing, A.C. *et al.* 1981. Consumo de energia na produção de soja. In: Congresso Brasileiro de Energia, 2º, Rio de Janeiro. coppe/ufrij,. V.b p.561-572.
- Sarkanen, K.V. 1976. Renewable resources for the production of fuels and chemicals. *Science* 191(20):773-776.
- Sasson, A. 1993. La alimentación del hombre del mañana. 1ª Ed., Editorial Reverté S.A., Barcelona, 807p.
- Soares L.H.B *et al.* 2008. Eficiência energética comparada das culturas do girassol e soja, com aptidão para a produção de biodiesel no Brasil. Circular Técnica da Embrapa, Rio de Janeiro-RJ.
- Wagener, K., Inden, P. 1978. Mariculture on Land: Production of biofuels from marine phytoplankton. Seminário sobre Energias de Biomassas no Nordeste.