Exergy Evaluation of the Production Process of Babassu Biodiesel Synthesized via Methanolic and Ethanolic Route

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Abstract

The State of Maranhão has an area of 33.2 million of hectares. It is the state with the highest occurrence of babassu in Brazil, reaches around 27% of its territory. The exploitation of babassu extraction activity was, for decades, very significant in the economy of Maranhão. Today this activity is based on lauric oil market. Given the various fossil fuel crises and emerging environmental issues, babassu is an alternative of the renewable energy sector (biodiesel). It is important to face into the feasibility of producing biodiesel from babassu oil obtained by ethanolic and methanolic route. Exergy assessment evaluates the functioning of the thermodynamic process from the location and quantification of the inefficiencies of the organization as well as being a utilitarian instrument for the effective utilization of innate resources.

Keywords: babassu, exergy, biodiesel, transesterification

1. Introduction

Ignacy Sachs wrote in the preface of the book *Sustainable Development: The Challenge of the Twenty First Century* that “the sustainability of the human civilization in time will depend on their ability to submit themselves to the principles of ecological prudence and to make beneficial use of nature.” Thus, he emphasizes that sustainable growth should be based on three grounds: socially inclusive, environmentally friendly and economically viable in time.

The babassu economics welcome such precepts since around three thousand families in the state of Maranhão are supported by the sale and home consumption of its various products. The oil market proceeding from almonds, the primary product of babassu, contributes significantly to the economy of Maranhão. The babassu oil can be applied as an alternative source of fuel (biodiesel) replacing fossil fuel and reducing up to by 78% carbon dioxide emission in the air according Lima (2004).

Aiming to leverage the economy of babassu, several efforts have been attempted. Such attempts have always been in order to implement the broad use of babassu, but the success has not been achieved primarily due to inadequate supply chain management, the difficulty of supply of raw materials, the lack of an effective and appropriate technology to crack the coconut and to extract the almond, and finally, due the withdrawal of government subsidies. The babassu economy suffers from these obstacles until today.

Currently the babassu industry does not have the same economic relevance of the 1970s, when there was a significant investment from domestic and abroad stakeholders in the energy potential of this fruit, motivated by the global fossil fuel crisis.

Concern about environmental issues and the use of non-renewable resources brought it back to the regional scenario as a potential alternative biodiesel production in order to efficiently replace fossil fuel and leverage the babassu market.

Thus, it is necessary to check the efficiency of processing babassu oil into biodiesel, since previous studies found that the physicochemical properties of the extracted oil from babassu are suitable for fuel production.

The aim of this work was to perform an exergy analysis of the biodiesel production process using babassu oil in order to localize the inefficiency and quantify the process losses. The exergy analysis of biodiesel production was made by the transesterification reaction using two routes of production: methyl and ethyl.

The analysis was performed using 630kg of refined babassu oil, and sodium hydroxide, commonly known as caustic soda, as a catalyst. The quantities referred to the transesterification process as well the determination of the physicochemical properties of the oil and the babassu biodiesel were based by the research of Lima et al (2007).

2. Theoretic Referential

2.1 Biodiesel: Definition and General Considerations

Biofuel is a fuel produced from biomass. Biogas, biodiesel and ethanol from sugarcane are classified as biofuel.

Biodiesel, as a fuel derived from renewable sources, has become an alternative to fossil fuel dependency and a new market for oilseeds. There are several species in Brazil that can produce biodiesel, among them are the palm oil palm, sunflower, soybean, babassu and castor bean.

Biodiesel can be used as fuel, replacing partially or totally diesel derived from petroleum in automotive oil cycle engines as trucks, tractors, vans, cars, among others, without modifications or adaptations. It can be used pure or mixed with diesel in different proportions. A mixture of 2% biodiesel to petroleum oil is called B2, 5% B5, 20% B20 until pure biodiesel called B100.

Biodiesel is clean burning, thus the emission of CO_2, the main greenhouse gas, compared to petroleum oil is reduced by 7% in the use of B5 when the mixing ratio is 5% of biodiesel and 95% of fossil fuel), 9% when using the B20 and 46% in B100 use. According to the report of PETROBIO, the emissions of particulate matter and soot are reduced up by to 68% with the use of biodiesel and 36% reduction of unburned hydrocarbons. The decrease of sulfur gases, those responsible for the acid rain, is also significant. Using the mixing B5, the reduction of the sulfur is about 17% to B20, 25% to B20 and 100% to of pure biodiesel. Unlike petroleum oil, biodiesel contains no sulfur.

In addition to the economic benefits arising from the implementation of biodiesel-petroleum oil blend in reducing the use of fossil oil, there is also the economic advantage linked to environmental issues, to be in compliance with the Kyoto Protocol, which calls for reducing the emission of greenhouse gases.

The implementation of B5 will increase the domestic demand for vegetable oils at 50% in addition to promoting employment in agriculture. Nowadays Brazil consumes about 36 billion liters/year of diesel. To 5% biodiesel blend will be required approximately 3.5 billion liters/year of vegetable oil (LIMA, 2007).

According to Lima et al, 2007, Brazil has approximately a 150 million hectare area that could be integrated with agricultural production. 90 million of this area refers to new borders and 60 million relating to soil and grasses. This area is distributed throughout the home territory and oilseed production depends on edaphic climatic factors, and Brazil is really diverse in this aspect. Thus, crops such as soybean, maize, peanut, sunflower, castor, babassu palm among others, may be exploited in the production of this biofuel. Brazilian Northeast has about 12 million hectare area of babassu, which 9 million hectares in the state of Maranhão.

2.2 Description of the Production Process of Biodiesel

Biodiesel is made by chemically combining a vegetable oil or animal fat with an alcohol (such as methyl alcohol or ethanol) and a catalyst (usually sodium hydroxide or potassium hydroxide) via a process known as transesterification. This takes on an alkyl ester of fatty acid, making up an alcohol group attached to a single hydrocarbon chain comparable in duration to that of diesel.

Glycerin, also called glycerol, is the primary co-product of biodiesel production. It can be used as soap, as well as in the cosmetic industry and its sale can offset the cost of biodiesel production.

To use biodiesel, it must be of high purity, containing no traces of glycerin, water, residual catalyst or surplus alcohol and it must go through purification steps.

The transesterification process is a reversible reaction. To increase the production of alkyl esters (biodiesel) and to permit the formation of a separate phase of glycerol it is necessary an alcohol excess in the reaction.

The main factors that influence the transesterification reaction are the type of oil, the type of alcohol, the molar ratio of oil/alcohol, the amount and type of catalyst and the reaction time (SANTOS, 2008).The presence, in the oil, of non transesterificants substances at higher levels than 2% affects the quality of biodiesel contributing to the deposit of materials in nozzles, increased viscosity, and consequently increases the capacity of crystallization of biodiesel at low temperatures (SANTOS, 2008).

The most commonly used alcohol to obtain biodiesel is methanol, which promotes better yields. However, considering that Brazil is the largest producer of ethyl alcohol (ethanol) in the world and that ethanol is an alcohol 100% green, there is an incentive for the replacement of fossil methanol by ethanol, generating a fully independent agricultural fuel oil and environmentally sustainable.

The use of anhydrous alcohol is a way to decrease the formation of soap since water is a causative agent of parallel reactions of saponification and it consumes the catalyst and reduces the efficiency of the transesterification reaction.

According to Santos (2008), homogeneous catalysis in alkaline medium is the predominant technological route in industry for the production of biodiesel due to its speed and ease, which make this option viable. It is suitable to use about 0.5% based on the weight of the oil. Basic catalysts such as those mentioned above, accelerate the reaction in about 4 billion times more than acid catalysts such as hydrochloric acid (HCl).

However, the use of basic catalysts promotes a higher level of the saponification process, since the catalyst reacts with the free fatty acids in the oil, making soap. For each 1% of caustic soda used as a catalyst, about 7% by weight of soap are derived.

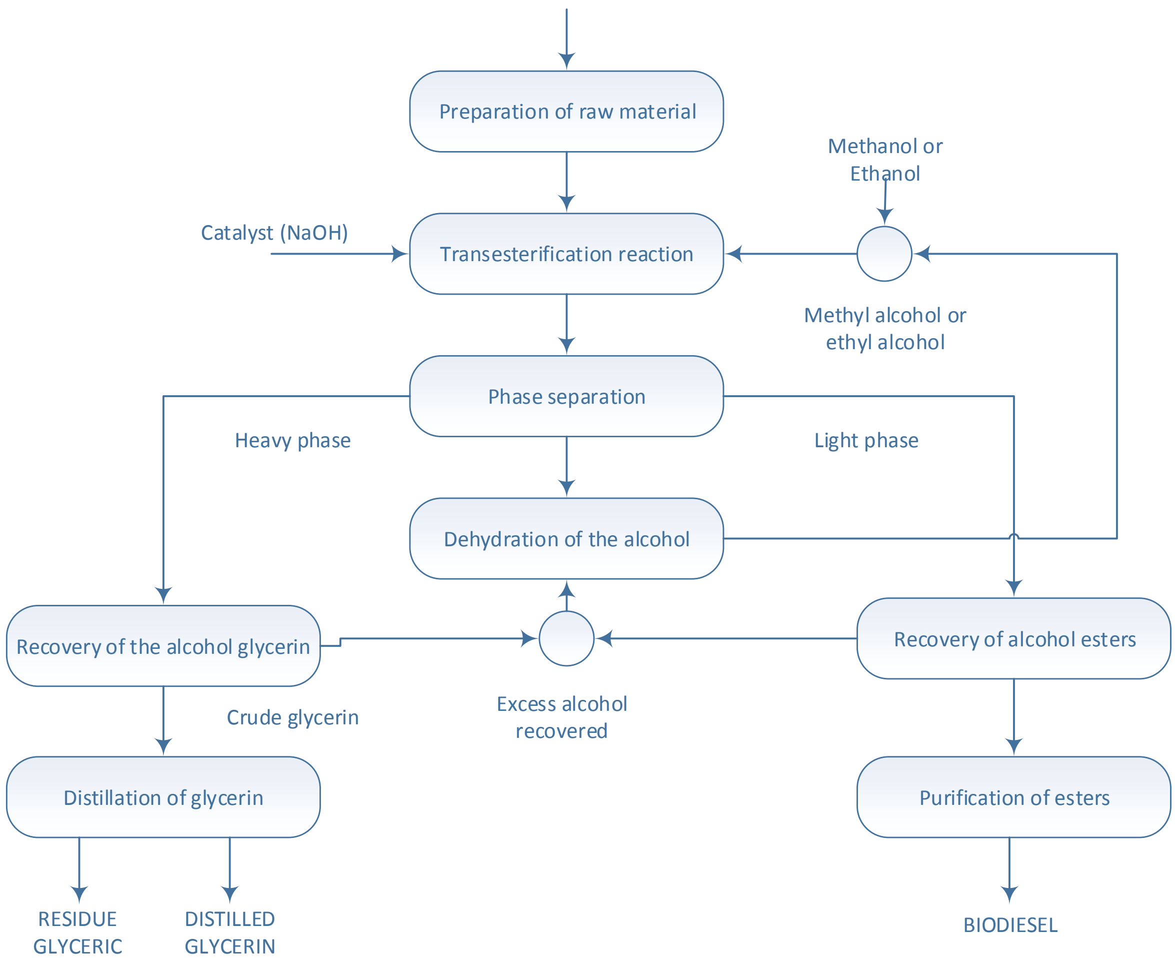
The transesterification reaction must be conducted in a reactor with stirring. A very vigorous shaking can cause soap formation, resulting in an emulsion of difficult separation. The process temperature can be ambient or even to 70°C, so there is no release of alcohol by evaporation. The higher the temperature implies lower reaction time. Temperatures set at 45 ° show good yields for the procedure.

A mixture of alcohol and catalyst should be prepared and added to the preheated oil (for systems that employ heat). The reaction time varies depending on the raw material, the catalyst and the alcohol used, but the reaction is considered complete when there is a return to the original color after the darkening of the mixture.

Settling of the mixture must be made for the separation of the obtained products. The upper phase corresponds to the primary product, biodiesel. Since the lower stage are glycerin (a byproduct of the reaction), catalyst residue, excessive unreacted alcohol, water, soap formed during the reaction and some traces of glycerides and esters.

The biodiesel must be purified to remove catalyst residue. An alternative is washing with hot water to remove impurities. When the basic catalyst is used, the washing with acidified water (0.5% HCl) neutralizes the catalyst. The aqueous phase can be separated from the esters by decantation and then heating and drying to remove humidity. The following illustration outlines the production process through the transesterification reaction.

Figure 1: Stages of the Production of Biodiesel by Transesterification



Source:http://www.agencia.cnptia.embrapa.br/.Visited 10/09/2013

2.3 Features of Babassu Oil

The babassu oil is one of the most suitable oils for biodiesel production. Vegetable oils are composed of fatty acids with short chains, such as lauric acid, present in large quantities in babassu oil, ensuring better performance of the process. The interaction of babassu oil with the transesterificant agent and catalyst is more effective so that it gets a product with excellent physicochemical especially when the catalyst used in the transesterification process babassu oil is heterogeneous.

The babassu oil consists of saturated and unsaturated fatty acids, but by presenting a percentage from 84.4 to 96.6% saturated fatty acids in its composition, babassu oil is classified as saturated oil. It presents in its composition eight types of fatty acids according to the table below.

Table 1: Composition of Babassu Oil

Fatty Acids	Composition	Nomenclature
C 8:0	2,6 – 7,3	Capric
C 10:0	1,2 – 7,6	Caprylic
C 12:0	40 – 55	Lauric
C 14:0	11 – 27	Myristic
C 16:0	5,2 – 11	Palmitic
C 18:0	1,8 – 7,4	Stearic
C 18:1	2,0 – 9,0	Oleic
C 18:2	1,4 – 6,6	Linoleic

Source: ANVISA (1999), http://portal.anvisa.gov.br/wps/wcm/connect/a2190900474588939242d63fbc4c6735/RDC_482_1999.pdf?MOD=AJPERES. Visited by: 10/09/2013.

This composition is defined by ANVISA through Resolution No. 482 of September 23th, 1999, regulating the identity and quality of vegetable oils for human consumption. Not yet exist in Brazil, an official institution that regulates the quality of oils and fats for biodiesel production. To attest to the quality of the final product, tests are performed based on standards of the Brazilian Association of Technical Standards-ABNT and international standards such as ASTM D6751 (2006) from American Society for Testing and Materials - ASTM which regulates the production of biodiesel in the United States and European standard UNE-EN 14214 (2003).

3. Material and Methods

3.1 Steps of Productive Chain of Babassu

Until its transformation into biodiesel, babassu oil goes through the following activities that make up its supply chain: (i) gathering babassu coconut in the forest, (ii) fruit storage, (iii) transportation coconut, (iv) dried coconut, (v) almond extract, (vi) almond transport, (vii) almond processing, (viii) production of crude oil and (ix) babassu processing into biodiesel.

The stage of planting palm does not apply to babassu because it is a species that is not cultivated. Babassu is not a domesticated species, sprouts and regrowth naturally and very quickly without need the help of man to reproduce itself in nature. (CARVALHO, 2007).

The activities of the productive chain of babassu oil are classified in four stages: the first one is collect, storage, transport, dry the coconut and almond extract that occur consecutively in the same place. The second step is the almond transport, the next step consists in processing the almond and product babassu oil. Finally, the fourth stage is the conversion of oil into biodiesel.

Although the four stages were described, the exergy analysis was performed only in the last step: the production of biodiesel from babassu obtained through transesterification process. This step is considered the control volume - CV to be studied.

The data for the biodiesel production from babassu such as its production plant and physicochemical data of oil and babassu biodiesel process were taken from the literature.

First step: collecting, storing, transporting and drying the coconut and almond extract.

The collection of babassu coconut is done manually. It is recommended to collect the ripe coconuts when they begin to fall to the ground. These coconuts produce an oil of better quality. The babassu coconut breakers women, by their knowledge, know the localization of the palm trees that produce more coconuts. They prevent the exploitation of all the palm trees in the same area and collect the fruits from the palm trees that accumulate the highest number of coconuts around and leave the palm trees that produce less fruit to provide food for the animals and for the perpetuation of the species.

Helping loosen the mature coconut that has not fallen its possible use a stick to "poke" the bunch, but it is not a recommended practice because it can tear the whole bunch which besides wasting green coconuts can also compromise coconut production the following year.

The fruit collection requires some basic care. To produce the best quality oil, coconuts breakers women select the healthy fruits and seeds, without signs of deterioration, holes or germination. Then, they sanitize the almonds with water before transporting to a storage site in order to eliminate microorganisms on fruit and seeds that may contribute to their degradation process

The collected coconut is selected for different purposes. The clearest coconuts are those newly fallen. From them are extracted the mesocarp that is used to manufacture a nutritious flour widely used as a food supplement for children. The dark coconuts, that have fallen some time ago, are used for oil production. The bored or gnawed coconuts can be used to make charcoal.

After collection, the coconuts are transported in baskets made of dried leaves taken from “pindovas” (palm tree in the initial stage). Coconuts are accumulated underneath the palm trees or other shaded area and there they are broken and almonds are extracted. This work of gathering and extracting almonds is done by women, "the breakers women", and children. The extraction of almonds is still done in a rudimentary way and despite the primitiveness requires great skill and patience. Breakers, sitting on the floor, holding the ax under one of the legs and break the coconut beating with a stick.

According Wilhelms (1964), one “breaker” has an average yield for 8 hours of work, of 5 to 10kg of almonds.

Although 300,000 families approximately meet their needs with the extractive culture of babassu, this activity has always been considered complementary to agriculture and an alternative resource to the households to generate income once the harvest season of babassu occurs between the months of September to March during the off-season of corn and soybeans.

According Porto (2004), various efforts have been made to build a device to mechanically break the babassu in order to achieve the full use of coconut as well as increase the production of almonds. Until now, none of them was satisfactory for technical, administrative or financial reasons.

Almonds are placed temporarily in raffia bags for transport to the place where they will be processed for the production of oil or pie. Care must be taken in order to not let the almonds for so long in the bags. They can get rancid and so lose commercial value.

Second step: almond transportation

Almonds are brought to the small regional merchants who buy or exchange the almonds for groceries and then sell them to industry. (Barbieri, 2004).

Transport to the small merchant is done in baskets using small animals or the breakers lead the basket on their own head.

The productivity of coconut breakers is generally low because the whole process is still very rudimentary, with barriers from access to the collection and transportation, commercialization and transportation. (ROSE, 2011).

Third step: almond processing and production of crude oil from babassu

Primarily, an almond selection is made. Broken almonds, scratched or those that got so long stored, got rancid, and become unfit for the oil production for food and for cosmetic use, thereby losing economic value.

The babassu oil can be obtained manually or industrially by mechanical or by solvent extraction. Manually, the “breakers” use boiling process to extract the oil. Almonds are pounded in a mortar and cooked to facilitate the release of the oil.

The process of extracting vegetable oil into micro power plant makes it possible to work with various oilseeds (especially those with high levels of oil).

The technical dossier prepared by the Centre for Technological Development at the University of Brasilia gave a detailed description of the characteristics of each stage and will be presented below:

1. Cleaning seed: seed to be processed must be free of dross that can damage equipment and reduce the yield of oil. Sieves are used.
2. Seed peeling: equipment for the removal of the husks as breakers and sieves for separation are used.
3. Weighing: it is performed to control the income earned. It can be performed before peeling, but the volume will be higher.

4. Grind: used to facilitate cooking and pressing. The breaking of stripping may be sufficient in some cases. The grind is dispensable when the seed is high in oil.
5. Decoction: it is carried out in kilns, where the control of temperature, humidity and time that the seed remains in the equipment is intended to release the oil particles contained in the cell casing. Controlled cooking allows also eliminate toxins. The cooker is constructed with saturated steam chambers, however, for small productions it may be performed in direct fire, without boiler for steam generation.
6. Pressing: pressure to expel the oil. It may be continuous or discontinuous. In continuous pressing, the mass is pressed by an auger which rotates within a vented container where the oil comes out. In discontinuous press, the mass is pressed by a hydraulic cylinder within the container. This latter is widely used in the extraction of castor oil "cold" because its operation allows operation at low temperatures.
7. Oil filtering: mass particles present in the oil must be separated before storage. Filter press is used, the vertical filter plates and eventually vibrating screens.
8. Grinding Pie: After oil extraction, the residual mass (pie) can be milled to homogenize its particle size. The grinding is done in hammer mill type with adjustable screens.

The oil obtained through solvent is a more efficient extraction process although more expensive because residual oil content in the cake is lower. In this process, plants are dipped in the appropriate solvent (acetone or any other petroleum-derived), and the separation is carried out chemically, by distillation in particular temperatures which cause only oil condensation and no condensation of the solvents. In this case, the oils obtained are generally not used in aromatherapy because they generally contain traces of solvent (CARVALHO, 2007).

The fourth step is control volume, which the exergy analysis was made and it is detailed below.

4. Exergy: Concept and General Considerations on the Exergy Analysis

The concept of exergy began to be worked in the mid nineteenth century by Frenchman Nicolas L. Sadi Carnot and the American Josiah Willard Gibbs. In 1824, Carnot studied the possibility of quantifying the maximum work in order to get the most efficient steam machinery while Gibbs in 1873 called "available energy of the body" the maximum amount of mechanical work that can be achieved by a body with no heat transfer or exchange volume (Rojas, 2007).

The combination of the First Law of Thermodynamics, commonly called the "law of conservation of energy" that shows how energy transforms into another shape and allows us to assess how much energy can be used from a source with the Second Law of Thermodynamic limits for establishing a transformation that results in a thermodynamic quantity called exergy. The exergy is the amount of energy that is available for use.

Szargut et al (1988) cited Arredondo (2009) define exergy as "the maximum amount of work obtained when a mass is brought to a state of thermodynamic equilibrium with the common components to the environment through reversible processes involving interactions only with components of the environment. "

The entropy, other thermodynamic quantity, is essential to measure the exergy of a system. The entropy indicates the degree of disorder of the system and measures the energy which cannot be converted into work and then it is dissipated as heat. It is inferred that the larger the entropy generation of the system less energy will be available and the greater the exergy destroyed.

Thus, Gibbs shows in his work that the concept of entropy is as essential to the study of a thermodynamic system as the concept of energy, temperature, pressure and volume.

Rojas (2007) believes that exergy is a useful tool used by scientists and engineers to record locate and identify the causes of inefficiencies and losses of the system and to identify improvements that can be performed on the system. The exergy is a measure of both quantity and quality.

When a system is not in equilibrium with the environment, the amount of energy required to bring the system into a state of thermodynamic equilibrium (mechanical, chemical and thermal) is called exergy. This unbalanced system own positive exergy, if the system is in equilibrium its exergy is zero. According Szargut (2005) *apud* Arredondo (2009), this property allows exergy be a tool for environmental studies.

The exergy analysis measures how much exergy is being destroyed. Considering a closed room being heated using an electrical resistance in all the heat released from the conversion of electrical energy into heat in the room is a process featuring 100% energy efficient, however there is high exergy destruction. The process can be optimized by reducing the exergy destruction, just by changing the resistance by a heat pump that consumes less energy.

4.1 Calculation of Exergies and Exergy Balance of Biodiesel Production Plant

Considering the exergy as all streams entering and leaving the plant can make the balance of exergy according to the equation below.

$$E_O + E_{In} + E_V + E_{H2O} + E_W = E_P + E_{Sp} + E_R + E_C + E_D \quad \text{Eq. (1)}$$

Entrance exergies are: E_O–oil exergy, E_{In} – inputs exergy (methanol, water and H_2SO_4), E_V – steam exergy, E_{H2O} - exergy of the water used in washing the biodiesel and E_W – exergy of mechanical working. Output exergies are: E_P - exergy of the product (biodiesel), E_{SP} - exergy of byproducts (glycerol, FFA, recovered methanol and Na_2SO_4), E_R - waste, E_C - condensed and finally E_D - destroyed.

To calculate the exergy of compounds of biomassic origin follows the procedure proposed by Arredondo, 2009.

-Calculation of the chemical exergy

The chemical exergy of biomassics compounds is calculated by the following equation:

$$E^{CH} = \beta LCV \quad \text{Eq. (2)}$$

Where:

β – Coefficient;
LCV– Lower Calorific Value

The coefficient β has different expressions depending on the phase and chemical composition of substances. For liquid biomassic substances, such as biodiesel, glycerin, FFA and TG is used the equation:

$$\beta = 1{,}0374 + 0{,}0159\frac{H}{C} + 0{,}0567\frac{O}{C} \quad \text{Eq. (3)}$$

Where:

H, C e O – mass percentage of hydrogen, carbon and oxygen present in the oil or biodiesel.

The calorific power is one of the most important characteristics of a fuel and indicates the amount of heat that is released during the complete combustion of the fuel. It can be obtained experimentally or analytically whenever the chemical composition of the substance is known.

The LCV-Lower Calorific Value and Higher Calorific Value-HCV of liquid fuels can be found as:

1. Arredondo (2009), which calculates the LCV assuming that the water formed from the hydrogen that is forming part of the composition of the fuel is in the vapor phase and using the following correlation:

$$LCV = HCV - 0{,}0894.2442{,}3H \quad \text{Eq. (4)}$$

The value of 2442.3 kJ/kg corresponds to the enthalpy of vaporization of water at a pressure of 1 bar and calculating the higher calorific value - HCV is made according to the following equation:

$$HCV = 349{,}1C + 1178{,}3H + 100{,}5S - 103{,}4O - 15{,}1N - 21{,}1A \quad \text{Eq. (5)}$$

2. As the empirical formula of Mendeleyev:

$$LCV = 339C + 1030H - 109(O - S) - 24W \quad \text{Eq. (6)}$$
$$LCV = PCS - 225H - 25W \quad \text{Eq. (7)}$$

Where C, H, S, O, N, A and W are respectively the mass percentages of carbon, hydrogen, sulfur, oxygen, nitrogen, ash and moisture in the fuel. Where C, H, S, O, N, A and W are respectively the mass percentages of carbon, hydrogen, sulfur, oxygen, nitrogen, ash and moisture in the fuel.

The HCV and LCV have units kJ / kg and the values for C, H, S, O, N, A and W must be written in percentage.

Table 2: Values Found for the LCV and HCV According Arredondo (2009)

	Oil	Biodiesel	Glycerin	FFA
HCV (kJ/kg)	38.357,73	39.098,49	18.503,54	39.686,74
LCV (kJ/kg)	35.846,80	36.434,72	16.603,97	37.022,97

Table 3 – Values Found for the LCV and HCV According Mendeleev

	Oil	Biodiesel	Glycerin	FFA
HCV (kJ/kg)	38.407,80	39.206,40	18.483,60	39.788,80
LCV (kJ/kg)	35.820,30	36.461,40	16.526,10	37.043,80

According Texeira (2002) there are few studies mentioning the calorific value of the components of babassu coconut and these values vary from region to region, according to soil, climate, species, etc.

The different values of HCV and LCV founded through the two procedures have a small variation of only 0.13%. The method used by Arredondo, (2009) was chosen.

4.2 Calculation of Mass Percentage of Babassu Oil, Biodiesel, Glycerine and FFA

The calculation of the mass percentage of carbon, hydrogen and oxygen present in babassu oil and babassu biodiesel was made based on the molar composition, which is the same both for oil and for biodiesel, in the constituent groups and the number atoms of each compound as shown in the tables below.

Table 4: Composition Molar, Constituent Groups, Mass Percentage and Number of Atoms of the Constituent TGS from Babassu Oil

Triglyceride	%	CH_3	CH_2	CH	CH=	COO	N_C (12)	N_H(1)	N_O (16)
Caprylic	5%	3	14	1	0	3	21	38	6
Capric	6%	3	26	1	0	3	33	62	6
Lauric	44%	3	32	1	0	3	39	74	6
Myristic	17%	3	38	1	0	3	45	86	6
Palmitic	8%	3	44	1	0	3	51	98	6
Stearic	4%	3	50	1	0	3	57	110	6
Oleic	14%	3	44	1	6	3	57	104	6
Linoleic	2%	3	38	1	12	3	57	98	6
					Mass%		75,0%	11,7%	13,3%

Table 5: Composition Molar, Constituent Groups and Number of Atoms of Esters and Mass Percentage of Biodiesel from Babassu

Triglyceride	%	CH_3	CH_2	CH	COO	N_C (12)	N_H(1)	N_O (16)
Caprylic	5%	2	6	0	1	9	18	2
Capric	6%	2	8	0	1	11	22	2
Lauric	44%	2	10	0	1	13	26	2
Myristic	17%	2	12	0	1	15	30	2
Palmitic	8%	2	14	0	1	17	34	2
Stearic	4%	2	16	0	1	19	38	2
Oleic	14%	2	14	2	1	19	36	2
Linoleic	2%	2	12	4	1	19	34	2
				Mass %		74,7%	12,2%	13,1%

The mass percentage of carbon, hydrogen and oxygen from glycerol and FFA were calculated from the molecular weight and chemical formula of each one. These data are already known in the literature as detailed below.

Table 6: Chemical Formula, Number of Atoms and Mass Percentage of Glycerin and FFA

Substance	Glycerin			AGL		
Formula	$C_3H_8O_3$			$C_{17}H_{33}O_2$		
MP(kg/mol)	92			270,8		
	N_C	N_H	N_O	N_C	N_H	N_O
	36	8	48	204	33	32
Mass %	39,1%	8,7%	52,2%	76,0%	12,2%	11,8%

To determine the exergy of methanol, 2,214.104 kJ/kg, and ethanol, 4,329.104, it was used data-standard exergy in the literature. (OLIVEIRA, 2010?)

Specific exergies of inputs: NaOH, H_2SO_4, H_2O and Na_2SO_4 were obtained from the literature as well as the exergies concerning electricity; steam and mechanical work were based on work Arredondo (2009).

4.3 Exergy Evaluation of Biodiesel Production Process Using Oil from Babassu Almond

Transesterification is the process used for the transformation of babassu oil into biodiesel. The biodiesel was obtained via ethanolic and methanolic route using ethanol and methanol, respectively, as transesterificant agent, babassu oil refined as a raw material and NaOH as catalyst.

After the mixture of alcohol (methanol or ethanol) and the catalyst in a first reactor occurs, follows this reaction to transesterificant reactor where it is already refined babassu oil. Both reactors require a permanent agitation of 45rpm. The mixture to produce biodiesel needs a heating to 60 ° C during one hour and requires steam supplied at 2.6 bar.

After the transesterification reaction occurs, the products are separated by decantation. The glycerol or glycerin, denser, lies at the bottom of the reactor. The biodiesel stays at the top which is then washed with water to separate the alcohol excess. After process finished, biodiesel gets with an approximate moisture of 2% therefore it is necessary its drying by evaporation using steam and moderate agitation at 15rpm. The alcohol (methanol or ethanol) is recovered by distillation consuming steam from the process.

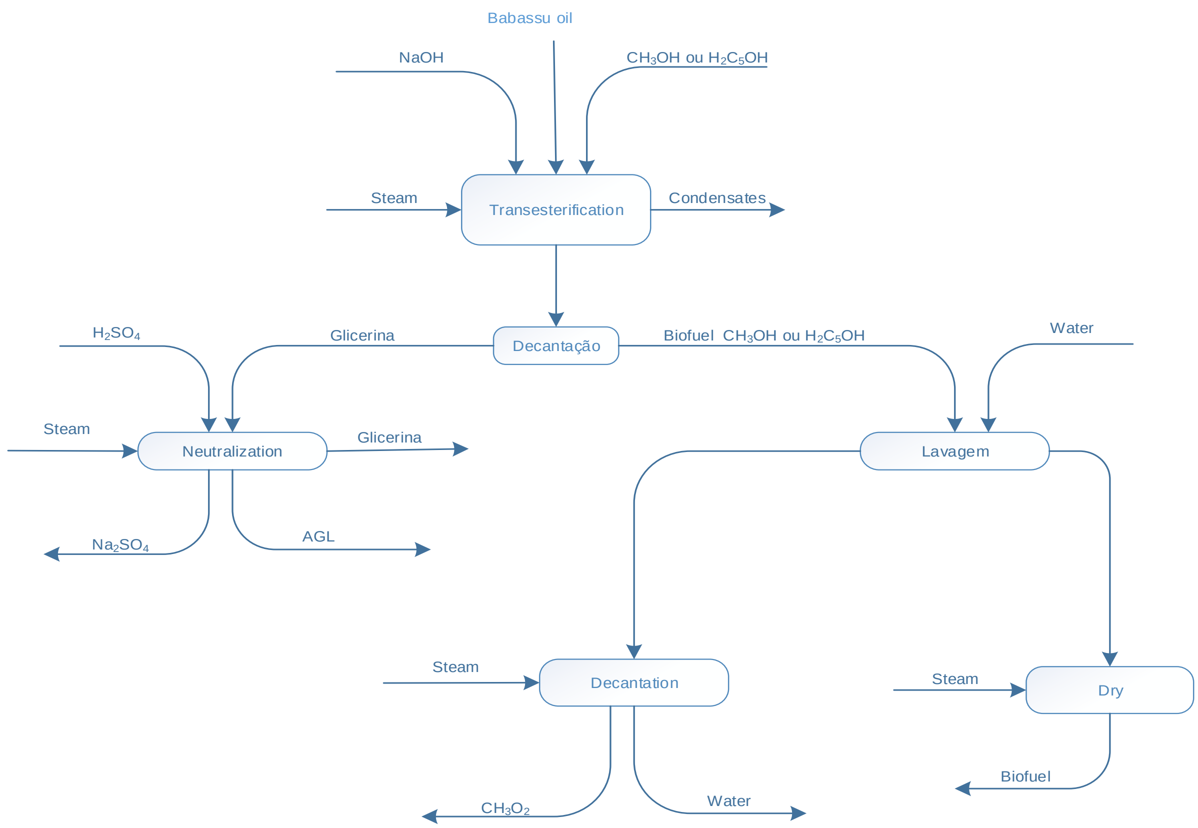
Neutralization of glycerol containing most of the catalyst is made. This step needs heating to 50 ° C for 30 minutes with moderate agitation of 20rpm. $H_2SO_4$is used to neutralize the saponification that happens between AGL and the catalyst during the transesterification. FFA are released and the formation of Na_2SO_4 (salt) occurs.

After the neutralization process, the fatty acids are removed from the top of the reactor and the salt precipitated at the bottom of the reactor, from where it is removed, is filtered and used in the composting plant.

Finally glycerol is purified to recover part of the excess alcohol.

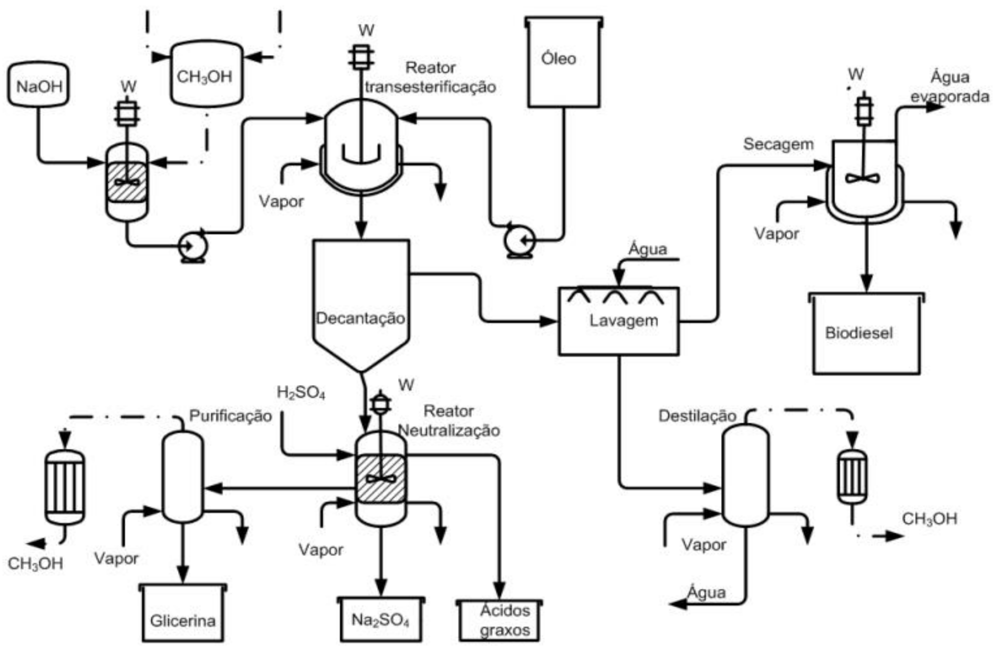
The figures 2 and 3 below show the description and the plant of babassu biodiesel production process that will be analyzed in this chapter.

Figure 2: Description of Biodiesel Production Process



Source: Arredondo (2009) Modified By Author

Figure 3: Biodiesel Production Plant



Source: Arredondo (2009)

All input values in the plant as babassu oil, methanol (CH_3OH), ethanol (H_2C_5OH), NaOH, H_2SO_4, water, electricity and steam, and the output as: biodiesel, glycerin, methanol (CH_3OH), ethanol (H_2C_5OH), Na_2SO_4, free fatty acids, necessary to perform the mass balance of the plant to produce biodiesel from babassu by methyl and ethyl route are shown in the tables below.

Table 7: Mass Balance of Babassu Biodiesel Production Plant Using Methanol (Kg / T-Almond)

Entrance		Outputs	
Oil	630	Biodiesel	550
CH_3OH (methanol)	126	Glycerin	63
NaOH	3,15	CH_3OH	125
H_2SO_4	6,3	AGL	7,1
		Na_2SO_4	7,7
H_2O	252	H_2O	226
Eletricity (kJ)	3.771	Discard	12,6
Steam	167	Condensades (Kg)	193

Table 8: Mass Balance of Babassu Biodiesel Production Plant Using Ethanol (Kg/T-Almond)

Entradas		Outputs	
Oil	630	Biodiesel	556
C_2H_5OH (ethanol)	252	Glycerin	63
NaOH	3,15	C_2H_5OH	250
H_2SO_4	6,3	AGL	14,2
		Na_2SO_4	7,7
H_2O	252	H_2O	226
Eletricity (kJ)	7.600	Discard	0,55
Steam	835	Condensades (kg)	861

Source: Arredondo (2009) Modified By Author

According to the specifications required by the ANP for pure biodiesel according to EN 14110, the maximum methanol or ethanol present in biodiesel is 0.5%.

For the production of biodiesel was used 630kg of refined babassu oil corresponding to one ton of almond as percentages of the products obtained from babassu coconuts known in the literature.

The entrance percentages of methanol, ethanol, catalyst and the yield of the transesterification process of babassu oil were based on experiment conducted by Lima et al (2007).

The amount of methanol or ethanol used was 20% and 40% respectively of the oil and it was added 0.5% of catalyst (NaOH) of the amount of oil

The amount of input was 6.3 kg H2SO4, value compatible with that found in the literature.

The yield of the reaction, observed in Lima et al (2007), was 71.8 wt% when methanol was used and 62.2% when used ethanol.

One of the byproducts of the process for obtaining biodiesel is glycerol. About 10% of the total weight of oil used is converted into glycerin (PETROBIO).

The steam used in all processes is recovered and led to the plant utilities. The recovered condensate corresponds with the steam used. Part of biodiesel wash water, about 10% is evaporated and goes to the condensate.

The steam consumption in methyl route is about 20% of consumption in ethyl route for the same biodiesel production and the electricity consumption to methyl route is less than half than the ethylic route (Costa, 2006).

The mass consumption of NaOH and H_2SO_4 is relatively low, and all outputs have some utility. The presence of 0.01% of free glycerol in biodiesel from babassu proved the efficiency of purification and meets legislation establishing a tolerance of 0.02% glycerin in biodiesel.

The acid number founded for methanol is 0.224 mgKOH/g and for ethanol 0.448 mgKOH/g. To determine the percentage of free fatty acids, FFA is assumed that the average molecular weight of the constituent fatty oils of babassu are equivalent of oleic acid (282g/mol), then calculating the acid according to following equation as recommended Lopes,(2006). % AGL = 0,503 x index of acidity Eq. (8)

In the table below are the physicochemical characteristics of babassu biodiesel obtained by methyl and ethyl route.

Table 9: Physical and Chemical Characteristics of Babassu Biodiesel Obtained by Methyl and Ethyl and Saw Some Cool Specs of the National Agency of Petroleum, Natural Gas and Biodiesels (ANP)

Physico-chemical characteristics	*methyl biodiesel*	*ethyl biodiesel*	*ANP Resolution 42/04*
Oil Acidity in nature (mg KOH / g)	0,505 ± 0,004	0,505±0,004	NA
Saponification of oil (mg KOH / g)	233,767 ± 1,270	233,767±1,270	NA
Free alkalinity (meq / g)	0,000	0,000	NA
Combined Alkalinity (meq / g)	0,004±0,000	0,006±0,001	NA
Total alkalinity (meq / g)	0,004±0,000	0,006±0,001	NA
Biodiesel acidity (mg KOH / g)	0,224±0,001	0,448±0,003	0,8
Free glycerin (%)	0,01±0,00	0,02±0,00	0,02
Density at 20 ° C (g/cm3)	0,88±0,00	0,87±0,00	(1)
Flash Point (° C)	112±0,6	122±0,6	Min*. 100
Sulfur content (%)	0,003±0,001	0,003±0,001	NA
Viscosity 40.0 ± 0.1 ° C (mm2)	4,0±0,02	3,8±0,02	Max**.6,0

NA = Not available.(1) = Limits for diesel type B:0,82 a 0,88 g/cm^3.* = Min. ** = Max.
Source: LIMA et al, 2007.

5. Results and Discussion

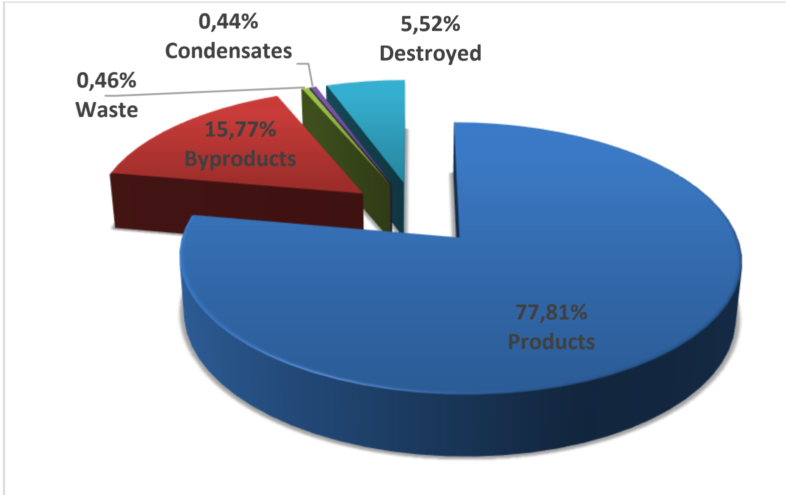
The tables below show the exergy balance of plant to produce biodiesel from babassu obtained via methanol and ethanol.

Table 10: Exergetic Balance of Plant to Produce Biodiesel from Babassu Using Methanol (Kg/T-Oil)

Entrance		**Outputs**	
E_O (oil exergy)	23.6x10^6	E_P (biodiesel exergy)	20,9x10^6
E_{In} (inputs exergies)		E_{Sp}(byproducts exergies)	
CH_3OH	2.79x10^6	Glycerin	1,160,654
NaOH	5.935	CH_3OH	2.81x10^6
H_2SO_4	163.025	AGL	274,337
		Na_2SO_4	2,222
E_{H2O}	137,970	H_2O	123,735
E_W	11,340	E_C	119,065
E_V	199,715	**E_D(E_e=E_S+E_D)**	1.49x10^6

The distribution of the exergy output of the production of babassu biodiesel obtained by the methanol route plan can be better visualized when represented as a percentage pie chart below.

Graph 1: Percentual Distribution of Exergy at the Exit of the Production Plant of Babassu Biodiesel by Methyl Via



Analyzing the graph it can be seen that the useful exergy was 77.81% however, considering that the byproducts can be used as products, the useful exergy of the system passes to 93.58%.

The destroyed exergy (5.52%) has three components: physical exergy of steam, mechanical work and destruction by converting TG into FFA.

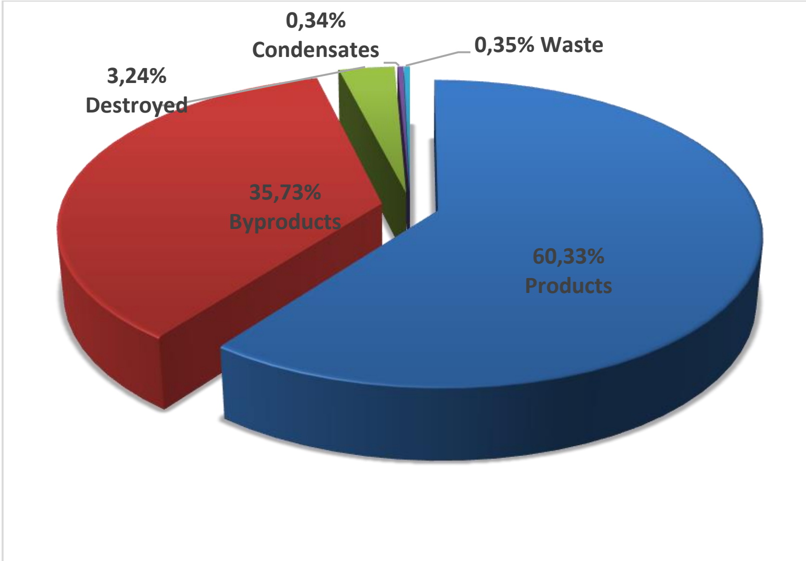
The chemical reaction of transesterification, according Arredondo (2009), may be considered reversible, so it was found a low exergy destroyed in the conversion of TG in FFA, around 1%. The remainder of the destroyed exergy occurs by steam and mechanical work.

Table 11: Exergetic Balance of Babassu Biodiesel Production Plant Using Ethanol (Kg / T-Almond)

Entrance		**Outputs**	
E_O (oil exergy)	$23{,}6.10^6$	E_P (biodiesel exergy)	$21{,}2.10^6$
E_{In} (inputs exergies)		E_{Sp}(byproducts exergies)	
C_2H_5OH (ethanol)	$11{,}.10^6$	Glycerin	1.160.654
NaOH	5.935	C_2H_5OH (ethanol)	$10{,}8.10^6$
H_2SO_4	163.025	AGL	548.675
		Na_2SO_4	2.222
E_{H2O}	137.970	E_R (H_2O)	123.735
E_W	22.854	E_C	531.165
E_V	998.660	**E_D(E_e=E_S+E_D)**	$1{,}53.10^6$

The percentage distribution of the exergy output of biodiesel production plant obtained by ethanol via is shown in the graph below.

Graph 2: Distribution of Exergy at the Exit of the Production of Biodiesel from Babassu Plant Obtained Via Ethanol



The useful exergy of the babassu biodiesel production system by ethylic route was 60.33% but considering the byproducts as products of the system, the useful exergy goes to 90.06%. The destroyed exergy of 3.24% was considered a low exergy. The transformation of TG in FFA was 1.56%.

Exergetic Efficiency of the Babassu Biodiesel Production Plant

The equation below shows the definition of efficiency, according Arredondo (2009), used to evaluate the biodiesel plant ($\eta_{E,\,B}$):

$$\eta_{E,B}= \frac{E_P}{E_O+E_{In}+\Delta E_V+\Delta E_{álcool}+E_W+\Delta E_{H2O}} \qquad \text{Eq. (9)}$$

Where, $\Delta E_{alcohol}$exergy corresponds to the alcohol, ethanol or methanol consumed in the transesterification reaction and ΔE_{H2O}corresponds to the exergy of evaporated water during the washing of biodiesel.

The result of the efficiency of the exergetic balance using methanol was 88% and 86% using ethanol.

If we consider the glycerin as product the exergetic efficiency balance using methanol goes into 92% and goes into 91% when ethanol is used.

Conclusion

It's possible to verify that the exergetic balance of biodiesel obtained either via methanol as ethanol pathway by which the value of physical exergy of steam and mechanical working of pumps and agitators is small compared to the chemical exergy that occurs in the process of transesterification oil.

Methanol and ethanol are alcohols commonly used in the transesterification process. The use of methanol is the most widely used because it is cheaper than ethanol, to be free of water, which favors the saponification, and has a higher polarity, which property facilitates the separation between the esters and glycerol. The advantage of ethanol is alcohol being a renewable source and does not possess the methanol toxicity. (ARAUJO, 2008).

The production of biodiesel obtained by ethanol via has a lower exergy useful than methanol by means, this can be attributed to the fact that the ethanol used in the transesterification process is not dry and water is one of the causative agents of side reactions saponification with this soap consumes catalyst and reduces the efficiency of the transesterification reaction.

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