EXERGETIC ANALYSIS OF THE BIODIESEL PRODUCTION PROCESS IN A BIOFUEL PLANT

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Abstract. *This paper deals with the exergy analysis of the biodiesel production process from the binary mixture of soybean oil and beef tallow. The biodiesel is produced by transesterification of the methyl group and through basic catalysis. Thus, it was investigated the biofuel production process of a specific plant in the State of Minas Gerais, Brazil, characterizing the parameters of the main equipment and analyzing the raw material and by-products of the process and quantify the mass and energy. The exergy analysis methodology followed the mass balance of each step, calculating irreversibility and exergetic balance and exergy efficiency of the plant. The calculation of chemical exergy of the compounds of biomass from soybean oil and beef tallow, biodiesel, glycerol and free fatty acids was accomplished by raising the calorific value of the compounds by their chemical composition, and mass percentage. Were also calculated the specific irreversibility of methanol and process inputs, the irreversibility concerning electricity, mechanical work and steam were. It can be seen that the useful exergy was 63,4 %, however, considering that the glycerim can be sold as a final product and that some raw materials can be reused, the useful exergy of the system passes to 94,2 %. The exergy efficiency of the plant is 71,7%, due to the irreversibility of the system. The exergy destroyed was 5,8 % and can be minimized by changing variables such as temperature, reaction time and type of catalyst.*

Keywords*: Exergy, Biofuel, Biodiesel, Transesterification.*

1. NOMENCLATURE

E_O - oil exergy
E_{In} - exergy inputs
E_V - exergy of steam
E_{H2O} – exergy of water used in the washing of biodiesel
E_W - exergy of mechanical work
E_P – exergy of product (biodiesel)
E_{Sp} – exergy of by-products
E_R – residues
E_C – condensed
E_D – exergy destroyed or irreversibility
Ex^{PH} – physical exergy
Ex^{EN} – potential exergy
Ex^{KN} – exergy kinect
Ex^{CH} – chemical exergy
β – chemical exergy correction factor
FFA – Free fatty Acids
LHV – lower calorific value

2. INTRODUCTION

With the advent of globalization and the increased use of energy, plus the population increase, emerges the concern with the use of fossil fuels in the face of the need to preserve the environment for future generations. Given this, it is remarkable the search for new technologies for the development of biofuels such as ethanol and biodiesel being the last object of this study.

Biodiesel, a product for which historically the first patent is Brazilian, presents itself as the most promising and with great possibility of optimization in their production, whether by methyl or ethyl route. Biodiesel is a biofuel used as a replacement to the conventional diesel, with the purpose of reduction of greenhouse gas emissions from diesel combustion and as a strategic reserve of energy before a future shortage, exhaustion and/or dispute of the main international oil reserves.

On this basis, the present study aims to analyze the production process of a biodiesel plant installed in the State of Minas Gerais, whose installed capacity is of 152 million liters/year of biodiesel. The analysis will be based on the second law of thermodynamics or exergy.

Moran and Shapiro (2009) state that a goal of exergy analysis is to identify where the exergy loss occur and ranks them in order of importance.

According to Ferreira (2014), exergetic analysis measures how much of exergy is being destroyed and verifies which system components are responsible for the losses in order to minimize them.

To Rojas (2007) the exergy is a useful tool used by scientists and engineers to account for, find and know the causes of inefficiencies and losses in a system and to identify improvements that can be made. Exergy is a measure both of quantity and quality.

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

Based on this, the identification of energy loss during the process of biodiesel production of a biofuel plant is a way of identifying the production bottlenecks, since that throughout the exergetic analysis it is possible to locate and quantify the destruction of exergy in various processes.

2.1 Plant description

The studied plant has an installed capacity of 152 million liters per year.

In Fig. 1, it can be observed the flowchart of the process of production of biodiesel in the studied plant.

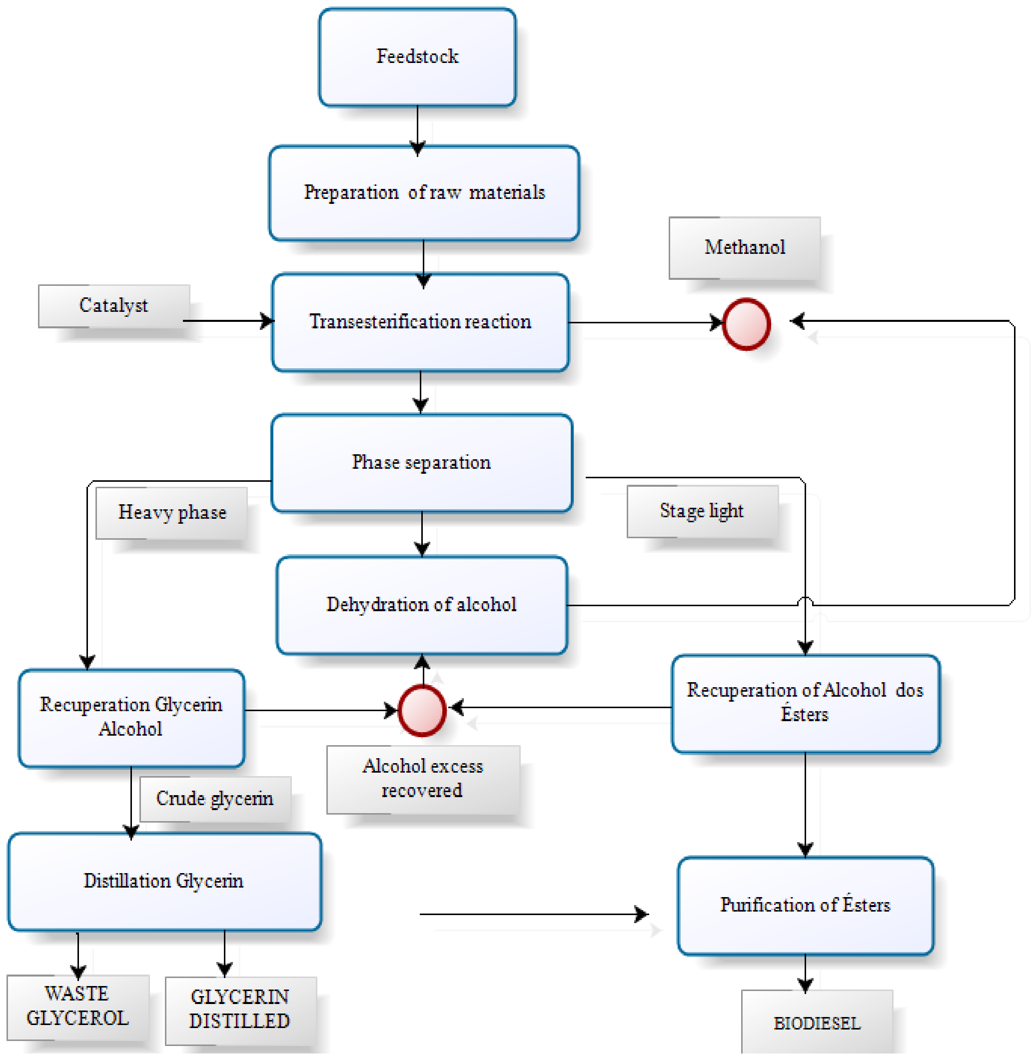

Figure 1. Flowchart of the biodiesel production process

Biodiesel is produced in continuous flow, the following steps describe the production. Initially the oil (soybean oil and beef tallow), methanol and catalyst are mixed in a reactor, this mixture then proceeds to the transesterifying reactor. Both reactors require a permanent agitation.

After the Transesterification reaction, the products are separated by decanting. The glycerin, which is denser, sinks to the bottom of the reactor. The biodiesel at the top part of the reactor is then washed with water to separate the excess of alcohol in. On the other hand, the methanol is recovered through a distillation process, consuming process steam through a heat exchanger.

The neutralization of the glycerin is achieved with the addition of HCL or NaOH. Most of the catalyst in this step is used to thwart the saponification that happens between the excess of Free Fatty Acids (FFA) and the methanol not utilized during the transesterification. This is results in the release of Na_2SO_4 (salt) and FFA.

After the process of neutralization, the salt is precipitated at the bottom of the reactor, where it is removed.

Finally, the glycerol is purified to retrieve part of the excess of alcohol. The recovered alcohol and the water previously utilized during the biodiesel washing are both used in the process again. The glycerin and the FFA can be sold to a chemical or food industry, respectively.

The process of production of biodiesel from transesterification process using refined soybean oil and beef tallow , was defined as the control surface to be analyzed in accordance with the second law of thermodynamics.

2.2 Exergy

Exergy can be defined as the maximum theoretical work that can be obtained from a global system, composed of a system and environment as its reaches the dead state, that is, comes into equilibrium with the environment.

As Jimenez *et al.*, (2015) exergy is based on the second law of thermodynamic in function of enthalpy and entropy. The total of exergy of a system consists of four types of exergy: physical (Ex^{PH}), potential (Ex^{EN}), Kinetic (Ex^{KN}) and Chemical exergy (Ex^{CH}) determined by the equation

$$Ex_{Flow} = Ex^{PH} + Ex^{PT} + Ex^{KN} + Ex^{CH} \tag{1}$$

$$Ex_{flow}^{PH} = (h - h_0) - T_0(s - s_0) \tag{2}$$

The exergy of a stream can be calculated in two different ways as equations:

$$Ex_{flow}^{CH} = \sum_i (\mu_{io} - \mu_{oo})N_i \tag{3}$$

$$Ex_{Flow}^{CH} = \Delta G_f + \sum_i x_i\, N_i \tag{4}$$

Sotomonte (2009) states that the kinetic exergy concerns the system speed in relation to the environment, and the exergy potential concerns the height difference of the system in relation to the environment.

Second Çengel (2013), chemical exergy is obtained when the system passes the restricted state until the dead state and the system comes to mechanical, thermal and chemical equilibrium with the environment.

According to Çengel (2013) destroyed exergy, E_D, represents the potential work lost, also called the irreversibility or lost work. It is the energy which could have been converted into work, but it wasn't. Second to Ferreira (2014), exergetic analysis measures how much of exergy is being destroyed and verifies which system components are responsible for losses in order to minimize them.

3. METHODOLOGY

For the calculation of the exergy originating from the biomass, it was followed the procedure proposed by Arredondo (2009) and Ferreira (2014).

3.1 Chemical exergy

The Chemical Exergy of the biomass compound is calculated by the following equation:

$$Ex^{CH} = \beta . LHV \quad (5)$$

Where:
β = coefficient
LHV= Lower Calorific Value

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

$$\beta = 0{,}1374 + 0{,}0159\frac{H}{C} + 0{,}0567\frac{O}{C} \quad (6)$$

Where C, H and O are respectively the mass percentages of carbon, hydrogen and oxygen in the fuel. To calculate the calorific value of binary mixture (soybean oil and beef tallow), biodiesel, glycerin and FFA, it was considered the empirical formula of Mendeleev:

$$LHV = 339{,}13C + 1029{,}25H - 108{,}85(0 - S) - 25{,}12W \quad (7)$$

Where C, H, S, O, N, and W are, respectively, the mass percentages of carbon, hydrogen, sulfur, oxygen, nitrogen, ash and moisture in the fuel. The PCS and LHV have units in kJ/kg and the values for C, H, S, O, N and W must be written in percentage.

3.2 Phisical exergy

The specific exergies of sodium methoxide inputs, NaOH, the H_2O and Na_2SO_4 were obtained in the literature, as well as the exergies for electricity, mechanical work and steam were based on work by Arredondo (2009).

3.3 Exergy analysis to biodiesel production

Whereas the exergy of all streams entering and leaving the plant, it is possible do the exergy balance according to the Eq. (8):

$$E_o + E_{in} + E_v + E_{H_2O} + E_w = E_p + E_{sp} + E_R + E_c + E_d \quad (8)$$

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

$$\eta_{E,B} = \frac{E_p}{E_o + E_{In} + \Delta E_v + \Delta E_{methanol} + E_w + \Delta E_{H_2O}} \quad (9)$$

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

4. RESULTS

To analyze the system of biodiesel production via transesterification of methyl exergetic point of view, it was considered the productive structure presented in Fig. 2

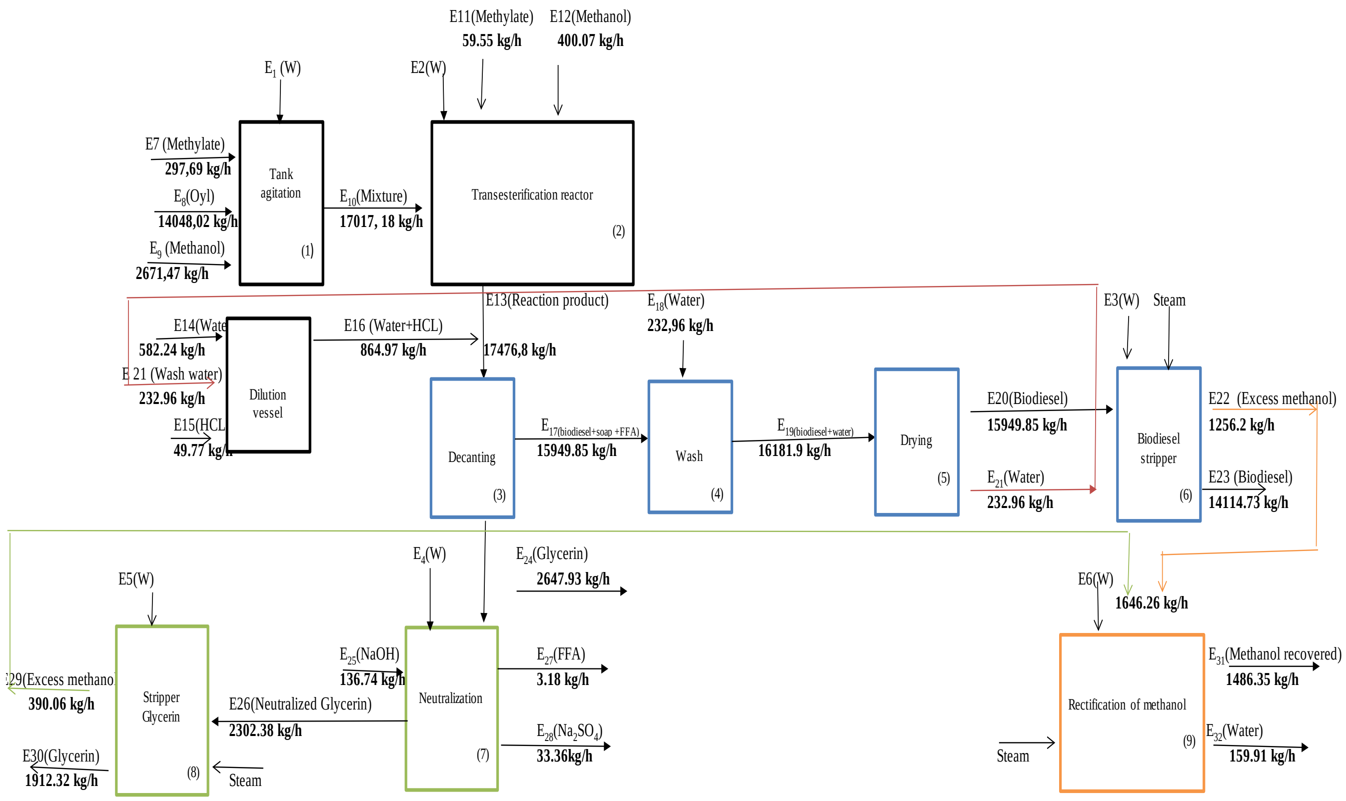

Figure 2. Scheme flow of biodiesel plant.

In this flowchart, were considered the following aspects: exergy flows of electricity (E1, E2, E3. E4.E5 and E6). The productive structure of this plant has 9 subsystems and 32 exergetic flows.

The parameters of the main flows of the plant are presented in Tab. 1

Table 1. Parameters of the main flows of the plant

Flows	Substance	Mass flow (kg/h)	Temperature (K)	Pressure (Kpa)	Enthalpy (kJ/kg)	Entropy (KJ/kg.k)
E7	Methylate	297.69	293	100	178.77	0.57
E8	Oil	14048.02	322	100	29.55	0.09
E9	Methanol	2671.47	285	100	130.31	0.42
E10	Mixture	17017.18	337	100	147.10	0.15
E11	Excess methylate	59.55	293	100	178.77	0.57
E12	Excess methanol	400.07	285	107.87	130.31	0.42
E13	Reaction product	17476.8	337	107.87	146.83	0.16
E14	Water	232.96	337	107.87	163.18	0.51
E15	HCL	49.77	337	107.87	116.61	0.37
E16	Water+HCL	864.97	337	107.87	154.98	0.16
E17	Biodiesel+soap+FFA	15949.85	337	107.87	69.67	0.22
E18	Water wash	232.96	337	107.87	163.18	0.51
E19	Biodiesel+water	16181.9	337	107.87	47.79	0.22
E20	Biodiesel	15949.85	359.5	100	46.10	0.22
E21	Water	232.96	337	100	163.18	0.51
E22	Excess methanol	1256.2	423.69	100	347.56	0.99

E23	Biodiesel	14114.73	423.69	15.89	177.63	0.47
E24	Glycerin	2647.93	337	100	100.00	0.32
E25	NaOH	136.74	337	100	158.46	0.50
E26	Neutralized Glycerin	2302.38	351.16	100	37.10	2.51
E27	FFA	3.18	351.16	100	36.31	0.11
E28	Na2SO4	33.36	351.16	100	36.25	2.67
E29	Excess methanol	390.06	356.3	100	178.68	0.56
E30	Glycerin	1912.32	356.3	941.43	50.57	0.15
E31	Methanol recovered	1486.35	384.85	100	250.22	0.75
E32	Water	159.91	306	98.06	33.47	-0.40

In the Tab. 2 are presented the percentage mass of hydrogen, carbon and oxygen present in soybean oil, beef tallow, biodiesel, glycerin and FFA.

Table 2. Composition.

	C%	**H%**	**O%**
Soy oil	39,27	5,76	52,95
Beef tallow	76,98	0,34	10,44
Biodiesel	74,7	12,2	13,1
Glycerin	39,1	8,7	52,2
FFA	76	12,2	11,8

For the calculation of the exergies of oil, biodiesel, glycerin and FFA, it was necessary to find the lower calorific value of these substances as presented in Tab. 3

Table 3. Values found for LHV and chemical exergy.

Discrimination	**Oil**	**Biodiesel**	**Glycerin**	**FFA**
LHV (kJ/kg)	18.217,42	36.462,93	16.432,89	37.046,3
Ex^{ch}	18.286,68	38541,16	18.714,25	18.714,25

After performing the calculation of input and output exergies, the exergetic balance of the plant was calculated as shown in Tab. 4

Table 4. Exergy of the main streams of the process.

Streams		**Physical Exergy**	**Chemical exergy**	**Total Exergy**
Inlet	Outlet	(kJ/kg)	(kJ/kg)	(kJ/kg)
Oil		1,81	18.286,68	18.288,49
Methanol		8,41	22.140,00	22.148,41
Methylate		1,28	21.604,00	21.605,28
NaOH		18,61	2.112,25	2.130,86
Water		12,38	173,33	185,71
EW		11.340	0	11.340,00
	Biodiesel	19,55	38.541,16	38.560,71
	Glycerin	1,39	18.714,25	18.715,64
	Methanol	35,7	21.770,00	21.771,39
	FFA	0,74	18.714,25	18.714,99
	Na2SO4	0,74	30,13	31,04
	Water	0	173,33	173,33

It can check in the exergetic balance of biodiesel production to the value of the exergy of the steam and the work value is small compared with the exergy chemistry that occurs in the process of transesterification of the oil.

The distribution of exergy on the output of biodiesel production plant of soybean oil and beef tallow obtained by methyl route can be best viewed when represented as a percentage, as shown in the graphic of the Fig. 3.

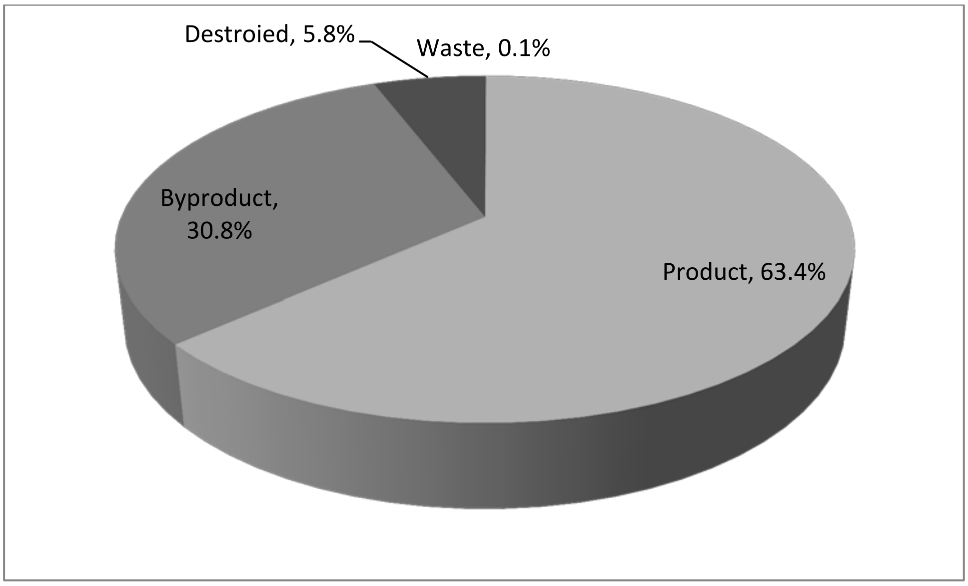

Figure 3. Percentage distribution of plant exergy.

Analyzing the Fig. 3, it can be verified that the exergy useful was 63.4% however, whereas the by-products can be used as products, the exergy of the system passes to 94,2%. The residues exergies correspond to 0.1%

The destroyed exergy (5,8%) has three components: the exergy of the mechanical work and destruction by the conversion of triglycerides (TG) in FFA.

The overall exergetic efficiency of the plant was 71.7%.

5. CONCLUSIONS

Following the definition of exergetic efficiency, it was sought to analyze the process of the biodiesel production considering it as a control volume in permanent regime. The result obtained when biodiesel is considered only as a product was 63,4% and the overall efficiency of the process is 71.7%, a result that can be considered in accordance with the expected. In addition, the value of the exergy of the steam and mechanical pumps and agitators is small, when compared with the chemiscal exergy of biodiesel.

If the by-products are considered as products (because they are also useful in the plant), the exergetic efficiency would be 94,2%, a fact which can be explained by the low exergy destruction in the chemical reactions that occur in the process. Some observations can be made in order to increase the efficiency as well as to decrease the temperature and time of agitation, to reduce the steam consumption and mechanical work and decrease the content of FFA in oil. This has as a consequence the growth of biodiesel produced and reduced use of methanol excess, catalyst and agent consumption neutralizer.

In addition, to minimize the exergy destroyed and improve the efficiency of the plant some process variables can be changed, such as: temperature, time and type of catalyst.

6. ACKNOWLEDGEMENTS

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