Exergetic Analysis of the Biodiesel Production Process in a Biofuel Plant

Marina M. Silva, Antonella L. Costa* and Emílio G. D. Neto

Universidade Federal de Minas Gerais, Departamento de Engenharia Nuclear, Av. Antônio Carlos Nº 6627, Campus Pampulha, CEP 31270-901, Belo Horizonte, MG, Brasil

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 quantifying the mass and energy. The exergy analysis methodology followed the mass balance of each step, calculating irreversibility and exergetic balance and 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. Moreover, they were also calculated the specific irreversibility of methanol and process inputs, the irreversibility concerning electricity, mechanical work and steam. It was found that the useful exergy was 63.4%, however, considering that the glycerin can be sold as a final product and that some raw materials can be reused, the useful exergy of the system could be equal 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 could be minimized by changing variables such as temperature, reaction time and type of catalyst.

Keywords: Exergy, biofuel, biodiesel, transesterification.

1. INTRODUCTION

With the population growth and the consequent energy consumption, emerges the concern with the use of fossil fuels in the face of the need to preserve the environment for future generations. An option to substitute part of diesel from fossil fuel is the biodiesel generated from vegetal oils and animal fats. This type of biofuel has received considerable attention because it is biodegradable, renewable, non-toxic, and low polluting in relation to atmosphere gases emission. Therefore, 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. Biofuels will be fundamental in the process of combating climate change, as alternative to higher energy consumption and complementarity to the energy supply of several countries. With the significant increase in biodiesel production process in recent years, innovations have been introduced to improve efficiency and productivity, as for example, the use of ultrasonic-assisted technology (Badday *et al.*, 2012).

Biodiesel is a product for which historically the first patent is Brazilian; it presents to be a very promising renewable energy source. It has a great possibility of optimization in the production process, whether by methyl or ethyl route. According to ANP (2016), in Brazil, soybean oil remains the main raw material for the production of biodiesel B100 equivalent to 77.71% of the total, with 16.6% of increase compared to 2014. The second is bovine fat (18.09% of the total), after an increase of 9.3% in relation to 2014, followed by cotton oil (2% of the total) and other types of fat with 1.01% of participation according to Figure **1**.

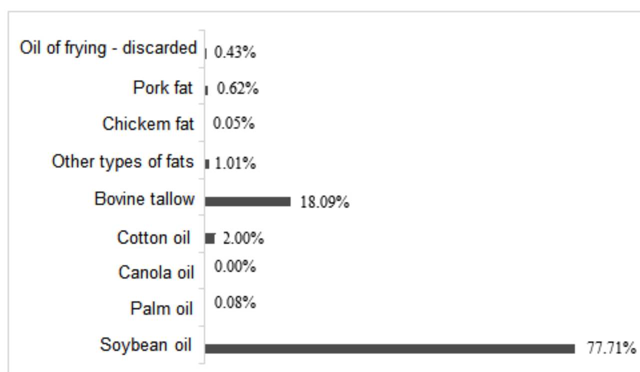

Figure 1: Main raw materials used in the biodiesel production in Brazil. Adapted from ANP (2016).

In this way, the present study analyzes the production process of a biodiesel plant installed in the State of Minas Gerais, in Brazil, whose installed capacity is of 152 million liters/year of biodiesel. The analyses were based on the second law of thermodynamics or exergy.

Moran *et al.*, (2011), state that a goal of exergy analysis is to identify where the exergy loss occur and to classify them in order of importance. Unlike

*Address correspondence to this author at the Universidade Federal de Minas Gerais, Departamento de Engenharia Nuclear, Av. Antônio Carlos Nº 6627, Campus Pampulha, CEP 31270-901, Belo Horizonte, MG, Brasil;
E-mail: antonella@nuclear.ufmg.br

E-ISSN: 2409-5818/18

thermodynamic properties such as enthalpy and entropy, which are defined from the system conditions, exergy is a property that depends on the system-environment combination. In the particular case of setting environmental conditions, exergy can be analyzed as a property of the system (Moran *et al.*, 2011). As a consequence of the definition of exergy, this can alternatively be seen as the minimum theoretical value of labor supply needed to bring the dead state system to a given state.

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. The exergy content of a substance may also be an indicator of how it reacts with the environment, possibly causing harm to humans or other organisms. For example, the production of biodiesel from used frying oil allows recycling an industrial and domestic waste with high exergetic content. Large amounts of waste lipids are generated around the world from restaurants, mainly fast food, food processing industries and households, and their disposal becomes a serious environmental problem in many countries. This environmental problem could be solved by proper utilization and management of waste cooking oil as a diesel fuel, as it has been related by several authors, as for example in (Borugadda and Goud, 2012). Even though the final biodiesel from frying oil has a high exergy compared to the virgin oil, the reuse of this oil minimizes the waste stream and reduces the environmental impact on the water and soil routes (Talens *et al.*, 2007).

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.

In this paper, the exergy analysis of the biodiesel production process from the binary mixture of soybean oil and beef tallow was valuated considering a real befouls plant. The biodiesel is produced by transesterification of the methyl group and through basic catalysis.

2. DESCRIPTION

2.1. Plant Description

The studied plant is located in the State of Minas Gerais, in Brazil. It has an installed capacity of 152 million liters per year. In Figure **2**, it can be observed

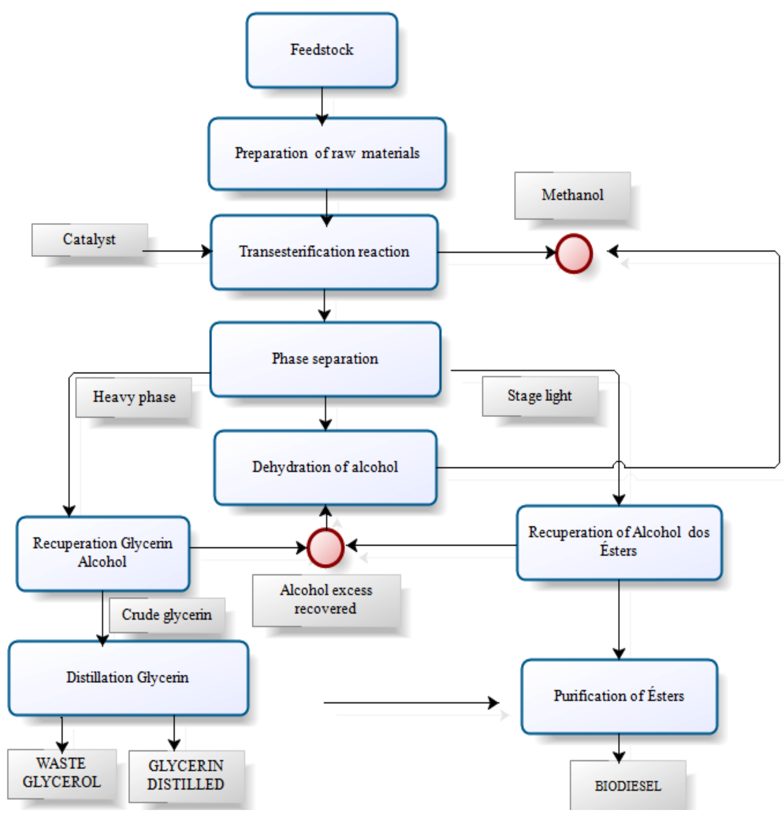

Figure 2: Flowchart of the biodiesel production process in the considered plant.

the flowchart of the process of production of biodiesel in the studied plant.

Biodiesel is produced in continuous flow; 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 the saponification that happens between the excess of Free Fatty Acids (FFA) and the methanol not utilized during the transesterification. This results in the releasing 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

The exergy analysis has been used to investigate the energy utilization in chemical processes, as in the biofuel production process, in several works (Madheshiya and Vedrtnam, 2018, Figueroa-Jimenez *et al.*, 2015, Arredondo *et al.*, 2012, Talens *et al.*, 2007). Exergy can be defined as the maximum theoretical work that can be obtained from a global system, composed of a system and environment as it reaches the dead state, that is, comes into equilibrium with the environment. 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^{PT}), kinetic (Ex^{KN}) and chemical exergy (Ex^{CH}) determined by the equation;

$$Ex - KN + Ex - CH \quad (1)$$

In the calculation of the total exergy of biofuel production, the potential and kinetic exergies are negligible.

3. METHODOLOGY

For the calculation of the exergy originated from the biomass, it was followed the procedure as detailed in the work of Silva, (2017).

3.1. Chemical Exergy

The chemical exergy of the biomass compound is calculated by the equation (2):

$$Ex - CH = \beta \quad (2)$$

where:

β = coefficient.

LCV = Lower Calorific Value.

The coefficient β has different expressions depending on the phase and chemical composition of substances. For liquid biomass substances, such as biodiesel, glycerin, FFA and TG, it is used the equation (3):

$$\beta = 0.1374 + 0.0159, H - C + 0.0567, O - C \quad (3)$$

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 (1949):

$$LCV = 339.13C + 1029.25 \quad (4)$$

where C, H, S, O and W are, respectively, the mass percentages of carbon, hydrogen, sulfur, oxygen and ash and moisture in the fuel. The LCV has unit of kJ/kg.

3.2. Phisical Exergy

The specific exergies of sodium methoxide inputs, NaOH, the H_2O and Na_2SO_4 were obtained in the

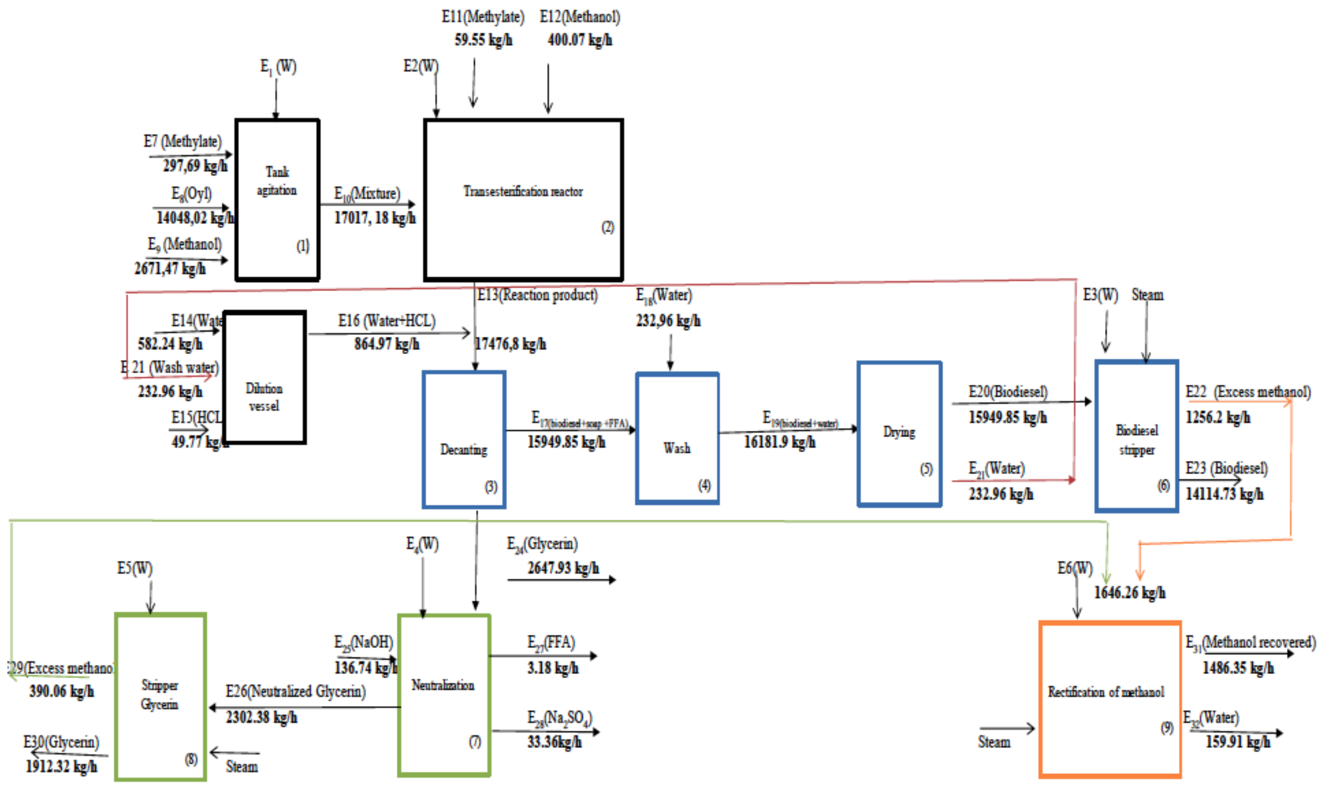

Figure 3: Scheme flow of biodiesel plant.

literature, as well as the exergies for electricity, mechanical work and steam were based as purposed by Arredondo (2009).

3.3. Exergy Analysis to Biodiesel Production

Considering the exergy values of all streams entering and leaving the plant, it is possible do the exergy balance according to the Eq. (5):

$$bp + E - R + E - c + E - d \qquad (5)$$

E_o = Oil exergy.

E_{in} = Inputs exergy (metanol, water and H_3PO_4).

E_s = Steam exergy.

E_{H2O} = Water exergy (used to biodiesel washing).

E_w = mechanical work exergy.

E_p = Product exergy (biodiesel).

E_{bp} = Byproducts exergy (glycerin, AGL, recovered methanol and Na_2SO_4).

E_R = Residues exergy.

E_c = Exergy of the condensed.

E_d = Destroyed exergy or irreversibility.

The equation (6) is the definition of efficiency used to evaluate the biodiesel plant ($\eta_{E, B}$):

$$hanol + E_w + \Delta E - H_2O \qquad (6)$$

where $\Delta E_{methanol}$ corresponds to the consumed methanol exergy in the transesterification reaction and ΔE_{H_2O} is the exergy of the evaporated water in the washing process 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 Figure **3**.

In the flowchart presented in Figure **3** was considered the exergy flows of electricity (E1, E2, E3, E4, E5 and E6) and the productive structure of this plant with 9 subsystems and 32 exergetic flows (E7 – E32). The parameters of the main exergetic flows of the plant are presented in Table **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	Na_2SO_4	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

Table 2: Composition of the Substances

	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	76.0	12.2	11.8

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

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

After performing the calculation of input and output exergies, the exergetic balance of the plant was calculated and the results are presented in Table **4**.

Table 3: Values Found for LCV and Chemical Exergy

Discrimination	Oil	Biodiesel	Glycerin	FFA
LCV (kJ/kg)	18,217.42	36,462.93	16,432.89	37,046.30
Ex^{ch} (kJ/kg)	18,286.68	38,541.16	18,714.25	18,714.25

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
	Na_2SO_4	0.74	30.13	31.04
	Water	0	173.33	173.33

Considering 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 is represented as percentage in the graphic of the Figure **4**.

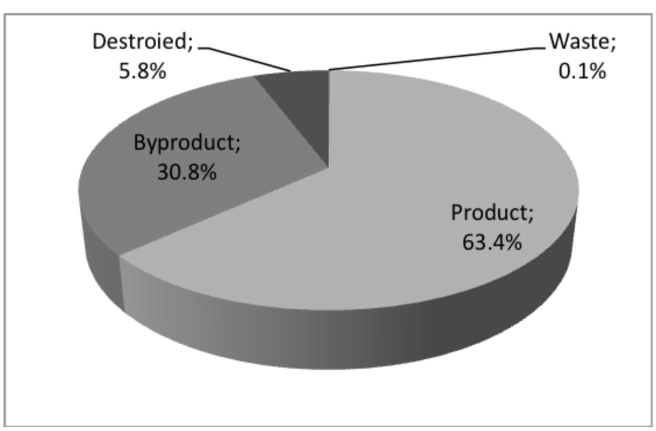

Figure 4: Percentage distribution of plant exergy.

Analyzing the Figure **4**, it can be verified that the exergy useful was 63.4% however, but considering that the byproducts could be used as products, the exergy of the system passes to 94.2%. The exergy from the wastes correspond to 0.1%.

The destroyed exergy (5.8%) has as 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%.

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, mechanical pumps and agitators is small, when compared with the chemical exergy of biodiesel.

If the byproducts 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.

ACKNOWLEDGEMENTS

The authors are grateful to CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior) and FAPEMIG (Fundação de Amparo à Pesquisa do Estado de Minas Gerais) for the support.

NOMENCLATURE

E_o Oil exergy.

E_{in} Inputs exergy.

E_s Exergy of steam.

E_{H_2O} Exergy of water used in the washing of biodiesel.

E_W Exergy of mechanical work.

E_P Exergy of product (biodiesel).

E_{bp} Exergy of byproducts.

E_R Exergy of residues.

E_C Exergy of the condensed.

E_d Destroyed exergy or irreversibility.

Ex^{PH} Physical exergy.

Ex^{PT} Potential exergy.

Ex^{KN} Kinect exergy.

Ex^{CH} Chemical exergy.

β Chemical exergy correction factor.

FFA Free fatty acids.

LCV Lower calorific value.

TG Triglycerides.

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Received on 11-05-2018 Accepted on 21-06-2018 Published on 10-09-2018

DOI: http://dx.doi.org/10.15377/2409-5818.2018.05.4