25th ABCM International Congress of Mechanical Engineering
October 20-25, 2019, Uberlândia, MG, Brazil

# COB-2019-1241

# EXERGETIC AND THERMOECONOMIC ANALYSIS OF BIODIESEL PRODUCTION PROCESS FROM WASTE COOKING OIL

**Daniela Yumi Sugai**
**Priscila Paola Dario**
Universidade Federal do Paraná - Francisco H dos Santos, S/N Centro Politécnico, Setor de Tecnologia - Jardim das Américas, Curitiba - PR, 81531-990
daniela.sugai@gmail.com
priscila.dario@ufpr.br

**Wellington Balmant**
wbalmant@gmail.com

**Diego de Lima Sousa**
diego.ls@ufopa.edu.br

**Leonardo Cavalheiro Martinez**
leonardo.cmartinez@live.com

**Lorena Castanho Chagas Duarte**
lorenaccastanho@gmail.com

**José Viriato Coelho Vargas**
vargasjvcv2@gmail.com

***Abstract.*** *In the search for new energetic alternatives biodiesel appears however its main source of raw material, vegetable oils, has a high cost when compared to fossil fuels. The use of waste cooking oils becomes attractive due to its low cost and, the optimization of biodiesel production processes makes this biofuel more economically competitive. Therefore, the main objective of this study is to carry out an exergetic and thermoeconomical analysis of the biodiesel production process from waste cooking oil, to locate the largest losses in the system and minimize them. Thus the mass, energy and exergy balance of the system were performed, obtaining the destroyed exergy of the system. Then, two objective functions were established in order to optimize the process. The results showed that the biodiesel production process studied was able to be optimized, generating a profit of $ 137.04 per second for a mass flow rate for waste cooking oil of 206* $kg.s^{-1}$ *and an oil/methanol ratio of 5 /1.*

***Keywords:*** *Biodiesel, exergetic analysis, thermoeconomical analysis, waste cooking oil.*

## 1. INTRODUCTION

The increase in demand for energy, there was a need to search for alternative fuels and, thus, biodiesel appears. Its main source of raw material are vegetable oils and animal fats and the most common process to obtaining this biofuel is through the transesterification reaction, Eq. (1).

$$1\ \text{TAG} + 3\ \text{ALCOHOL} \underset{k2}{\overset{k1}{\rightleftharpoons}} 3\ \text{ESTER} + 1\ \text{GLYCEROL} \tag{1}$$

However, the high cost of vegetable oils in comparison to petroleum diesel makes this biofuel not economically competitive. Thus, an alternative is use waste cooking oils as they do not compete with the food sector, confer destination to an unwanted by-product and reduce the production costs of biodiesel due to its low cost of obtaining (KOLHE et al, 2017; ARAUJO et al, 2010).

Another alternative is through optimization of existing processes through exergetic and thermoeconomic analyzes. From the analysis of exergy it is possible to account for, locate and know the causes of losses and inefficiencies of the process and allied to thermoconomy, it is possible to attribute costs to these causes in order to minimize them (ROJAS, 2007).

Thus, the present work aims to perform the exergetic and themoeconomic analysis of biodiesel production process from waste oils and methanol and perform an optimization of the process based on these analyzes.

## 2. METHODOLOGY

The simulations were performed using the Engineering Equation Solver (EES) software for the process presented in Figure 1.

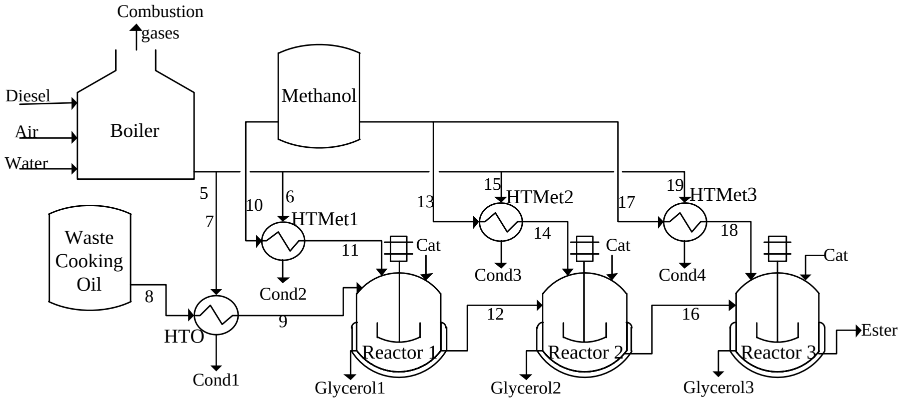


Figure 1. Process flowchart of biodiesel production.

Figure 1 presents the biodiesel process production. The waste cooking oil (WCO), from the oil tank (WCOT), passes through a heat exchanger (HTO) to achieve a temperature of 80 °C and goes to Reactor 1 (Reat1). Methanol (Met), from the Methanol Tank (MetT), passes through a heat exchanger (HTMet1), reaching a temperature of 65 °C and goes to Reactor 1. In Reactor 1, after the transesterification reaction, two streams come out: one with the blend of glycerol and methanol and, the second with the blend of unreacted oil and produced ester. The blend of glycerol and methanol goes to the glycerol storage tank (GST) and the blend of oil and ester goes to Reactor 2 (Reat2). In the reactor 2 (Reat2), a methanol stream heated by a heat exchanger (HTMet2) is added and, from this reactor, two streams also come out, one with the blend of methanol and glycerol, which flows into the storage tank (GST) and the second, with a blend of unreacted oil and produced ester, which flows into the Reactor 3 (Reat3). In the reactor 3 (Reat3), a methanol stream heated by a heat exchanger (HTMet3) is also added and, from this reactor, two streams come out, one the blend of methanol and glycerol, which goes to the storage tank (GST) and the second, with the produced ester, flows into the ester tank (ET). The currents that pass through the heat exchangers (HTO, HTMet1, HTMet2, HTMet3) are heated by saturated steam generated in the Boiler at a temperature of 165 °C.

For the development of the mathematical model, 8 control volumes were considered: Boiler, Heat exchanger for oil, Heat exchanger for reactor 1, Reactor 1, Heat exchanger for reactor 2, Reactor 2, Heat exchanger for reactor 3, Reactor 3.

Mass, energy and exergy balances were performed for each control volume. The enthalpy and entropy values of each line were obtained by ESS using temperature and pressure values established by the authors, the potential and kinetic energies were disregarded and for the transesterification reaction, waste cooking oil and methanol were used. The parameters of the process are shown in Table 1.

For the development of the model, it considered that the system operates in a steady state and the mass balance is presented in Eq. (2).

$$\sum \dot{m}_{in} = \Sigma \dot{m}_{out} \tag{2}$$

where $\dot{m}$ are the mass flow rates (kg.s$^{-1}$).

For the energy balance, Eq. (3) was used.

$$\dot{Q} + \sum \dot{m}_{in} h_{in} = \dot{W} + \sum \dot{m}_{out} h_{out} \tag{3}$$

where h are the enthalpies (kJ.kg$^{-1}$) and $\dot{Q}$ is the rate of heat transfer (kJ.s$^{-1}$).

The exergy balance is presented by Eq. (4).

$$\Sigma \dot{E}_q + \Sigma \dot{E}_{in} = \dot{W} + \Sigma \dot{E}_{out} - \dot{E}_D \tag{4}$$

Table 1. Parameters of the process.

| Parameter | Value | Parameter | Value | Parameter | Value | Parameter | Value |
|---|---|---|---|---|---|---|---|
| $T_{ag}$ (°C) | 25.0 | $T_{19}$ (°C) | 165.0 | $P_{13}$ (kPa) | 102 | $\eta_{Cald}$ (%) | 85 |
| $T_{ar}$ (°C) | 25.0 | $T_{cond1}$ (°C) | 80.0 | $P_{14}$ (kPa) | 102 | rac | 10 |
| $T_{die}$ (°C) | 25.0 | $T_{cond2}$ (°C) | 80.0 | $P_{15}$ (kPa) | 700 | $\rho_{oil}$ (kg.L$^{-1}$) | 0.92 |
| $T_5$ (°C) | 165.0 | $T_{cond3}$ (°C) | 80.0 | $P_{16}$ (kPa) | 102 | $\rho_{Met}$ (kg.L$^{-1}$) | 0.792 |
| $T_6$ (°C) | 165.0 | $T_{cond4}$ (°C) | 80.0 | $P_{17}$ (kPa) | 102 | $\rho_{Est}$ (kg.L$^{-1}$) | 0.86 |
| $T_7$ (°C) | 165.0 | $T_0$ (°C) | 25.0 | $P_{18}$ (kPa) | 102 | $c_{p,die}$ (kJ.kg$^{-1}$.°C$^{-1}$) | 1.75 |
| $T_8$ (°C) | 25.0 | $P_{ag}$ (kPa) | 102 | $P_{19}$ (kPa) | 700 | $c_{p,oil}$ (kJ.kg$^{-1}$.°C$^{-1}$) | 1.96 |
| $T_9$ (°C) | 65.0 | $P_{ar}$ (kPa) | 102 | $P_{cond1}$ (kPa) | 700 | $c_{p,est}$ (kJ.kg$^{-1}$.°C$^{-1}$) | 2.1 |
| $T_{10}$ (°C) | 25.0 | $P_{die}$ (kPa) | 102 | $P_{cond2}$ (kPa) | 700 | $c_{p,gly}$ (kJ.kg$^{-1}$.°C$^{-1}$) | 2.4 |
| $T_{11}$ (°C) | 65.0 | $P_5$ (kPa) | 700 | $P_{cond3}$ (kPa) | 700 | $M_{oil}$ (kg.mol$^{-1}$) | 0.854 |
| $T_{12}$ (°C) | 65.0 | $P_6$ (kPa) | 700 | $P_{cond4}$ (kPa) | 700 | $M_{Met}$ (kg.mol$^{-1}$) | 0.032 |
| $T_{13}$ (°C) | 25.0 | $P_7$ (kPa) | 700 | $P_0$ (kPa) | 102 | $M_{gly}$ (kg.mol$^{-1}$) | 0.092 |
| $T_{14}$ (°C) | 65.0 | $P_8$ (kPa) | 102 | $V_{Rt1}$ (L) | 15000 | $M_{est}$ (kg.mol$^{-1}$) | 0.301 |
| $T_{15}$ (°C) | 165.0 | $P_9$ (kPa) | 102 | $V_{Rt2}$ (L) | 12000 | $M_{die}$ (kg.mol$^{-1}$) | 0.185 |
| $T_{16}$ (°C) | 65.0 | $P_{10}$ (kPa) | 102 | $V_{Rt3}$ (L) | 10000 | $M_{air}$ (kg.mol$^{-1}$) | 0.028 |
| $T_{17}$ (°C) | 25.0 | $P_{11}$ (kPa) | 102 | k1 (s$^{-1}$) | 0.008 | $LHV_{die}$ (kJ.kg$^{-1}$) | 43100 |
| $T_{18}$ (°C) | 65.0 | $P_{12}$ (kPa) | 102 | k2 (s$^{-1}$) | 0.0001 | $e_{x,die}$ (kJ.kg$^{-1}$) | 44730 |

where $\dot{E}$ is the exergy rate (kJ.s$^{-1}$), $\dot{E}_D$ is the destroyed Exergy (kJ.s$^{-1}$), and $\dot{W}$ is the Power (kJ.s$^{-1}$).

The exergy rate and the specific exergy relation are presented by Eq. (5) and Eq. (6), respectively.

$$E_i = \dot{m}_i e_{x,i} \tag{5}$$

$$e_{x,i} = \left(h_i - \mathrm{h}_0\right) - \mathrm{T}_0\left(s_i - \mathrm{s}_0\right) \tag{6}$$

where, $e_x$ is the specific exergy of the component (kJ.kg$^{-1}$), $h_0$ is the enthalpy at the reference temperature (kJ.kg$^{-1}$), $T_0$ is the reference temperature (°C), s is the entropy of the component (kJ.kg$^{-1}$) and $s_0$ is the entropy at the temperature of reference (kJ.kg$^{-1}$).

### 2.1 Heat exchanger for oil

From Eq. (3), was carried out the energy balance for the oil heater, as presented by Eq. (7).

$$\dot{m}_9.c_{p,oil}.\left(T_8 - \mathrm{T}_9\right) + \dot{m}_{vap,7}.\left(h_7 - h_{cond,1}\right) = 0 \tag{7}$$

where $\dot{m}_9$ is the mass flow of oil (kg.s$^{-1}$), $\dot{m}_{vap,7}$ is the mass flow of steam in heat exchanger of oil (kg.s$^{-1}$), $c_p$ is the specific heat of oil (kJ.kg$^{-1}$.°C$^{-1}$), $T_8$ is the temperature of inlet oil (°C), $T_9$ is the temperature of outlet oil (°C), $h_7$ is the enthalpy of inlet steam (kJ.kg$^{-1}$) and $h_{cond,1}$ is the enthalpy of outlet steam (kJ.kg$^{-1}$).

As simplification, the value of the specific heat of the oil was considered constant and enthalpies of the inlet and outlet lines of steam were obtained from the values of temperature and pressure data. The exergetic analysis was performed and the destroyed exergy rate of the equipment was obtained, Eq. (8).

$$\dot{m}_9.\left(e_{x,8} - \mathrm{e}_{x,9}\right) + \dot{m}_{vap,7}.\left(e_{x,7} - \mathrm{e}_{x,cond,1}\right) - E_{D,HTO} = 0 \tag{8}$$

where, $e_{x,8}$ is the specific exergy of inlet oil (kJ.kg$^{-1}$), $e_{x,9}$ is the specific exergy of outlet oil (kJ.kg$^{-1}$), $e_{x,7}$ is the specific exergy of inlet steam (kJ.kg$^{-1}$), $e_{x,8}$ is the specific exergy of outlet steam (kJ.kg$^{-1}$) and $\dot{E}_{D,HTO}$ is the destroyed Exergy of heater exchanger for oil (kJ.s$^{-1}$).

Specific exergy values were obtained from the entropy data of each analyzed line.

### 2.2 Heat exchanger methanol for reactor 1

The energy balance is given by Eq. (9).

$$\dot{m}_{met,1}.\left(h_{10} - \mathrm{h}_{11}\right) + \dot{m}_{vap,6}.\left(h_6 - h_{cond,2}\right) = 0 \tag{9}$$

where, $\dot{m}_{met,1}$ is the mass flow of methanol in reactor 1 (kg.s$^{-1}$), $\dot{m}_{vap,6}$ is the mass flow of steam in heat exchanger methanol for reactor 1 (kg.s$^{-1}$), $h_{10}$ is the enthalpy of inlet methanol (kJ.kg$^{-1}$), $h_{11}$ is the enthalpy of outlet methanol (kJ.kg$^{-1}$), $h_6$ is the enthalpy of inlet steam (kJ.kg$^{-1}$) and $h_{cond,2}$ is the enthalpy of outlet steam (kJ.kg$^{-1}$).

The enthalpies were obtained by the temperature and pressure data of each line. With this data, the steam flow rate was obtained to heat the exchanger. Then, the exergetic balance was performed and the destroyed exergy of the equipment was obtained, Eq. (10).

$$\dot{m}_{met,1}.\left(e_{x,10} - \mathrm{e}_{x,11}\right) + \dot{m}_{vap,6}.\left(e_{x,6} - \mathrm{e}_{x,cond,2}\right) - E_{D,HTMet1} = 0 \tag{10}$$

where, $e_{x,10}$ is the specific exergy of inlet methanol (kJ.kg$^{-1}$), $e_{x,11}$ is the specific exergy of outlet methanol (kJ.kg$^{-1}$), $e_{x,6}$ is the specific exergy of inlet steam (kJ.kg$^{-1}$), $e_{x,cond,2}$ is the specific exergy of outlet steam (kJ.kg$^{-1}$) and $\dot{E}_{D,HTMet1}$ is the destroyed Exergy of heat exchanger methanol for reactor 1 (kJ.s$^{-1}$)

The entropy values, to calculate the specific exergy, were obtained by the temperature and pressure of each line.

### 2.3 Reactor 1

It was considered that the reactions are reversible, homogeneous and the enthalpy is. The reactor is isothermal and ideal mixing and sodium methoxide, the reaction catalyst, was disregarded in the calculations because of its low concentration compared to the rest of the components.

The direct reaction kinetics is represented in the Eq. (11) and the inverse reaction kinetics in the Eq. (12), both are specified in equations below.

$$R_1 = \frac{k_1.C_{oil1}.C_{met1}.V_{Rt1}}{M_{oil}.M_{met}} \tag{11}$$

$$R_2 = \frac{k_2.C_{est1}.C_{gly1}.V_{Rt1}}{M_{est}.M_{gly}} \tag{12}$$

where, k1 is the direct reaction kinetic constant (s$^{-1}$), k2 is the inverse reaction kinetic constant (s$^{-1}$), $C_{oil1}$ is the oil concentration in reactor 1 (kg.L$^{-1}$), $C_{met1}$ is the methanol concentration in reactor 1 (kg.L$^{-1}$), $C_{est1}$ is the ester concentration in reactor 1 (kg.L$^{-1}$), $C_{gly1}$ is the glycerol concentration in reactor 1 (kg.L$^{-1}$), $M_{oil}$ is the molar mass of oil (kg.mol$^{-1}$), $M_{met}$ is the molar mass of methanol (kg.mol$^{-1}$), $M_{est}$ is the molar mass of ester (kg.mol$^{-1}$), $M_{gly}$ is the molar mass of glycerol (kg.mol$^{-1}$).

The mass balance for the reactor was performed for each component of the transesterification reaction, being those oil (Eq. (13)), methanol (Eq. (14)), ester (Eq. (15)) and glycerol (Eq. (16)).

$$\dot{m}_9 - \dot{\mathrm{V}}_1.\mathrm{C}_{oil1} - \mathrm{M}_{oil}.R_1 + \mathrm{M}_{oil}.R_2 = 0 \tag{13}$$

$$\dot{m}_{met1} - \dot{\mathrm{V}}_1.\mathrm{C}_{met1} - 3.\mathrm{M}_{met}.R_1 + 3.\mathrm{M}_{met}.R_2 = 0 \tag{14}$$

$$-\dot{\mathrm{V}}_1.\mathrm{C}_{est1} + 3.\mathrm{M}_{est}.R_1 - 3.\mathrm{M}_{est}.R_2 = 0 \tag{15}$$

$$-\dot{\mathrm{V}}_1.\mathrm{C}_{gly1} + \mathrm{M}_{gly}.R_1 - \mathrm{M}_{gly}.R_2 = 0 \tag{16}$$

where, $\dot{V}_1$ is the volumetric flow in reactor 1 (L.s$^{-1}$).

For the exergetic analysis, as the temperature of the components remains constant, the specific exergy will be the same at the inlet and the outlet of the reactor. In relation to the mass flow, as there is a reaction, this will not be constant, having the consumption of oil and methanol and formation of ester and glycerin. In this way, for the calculation of the exergy rate of the oil and methanol, the mass flow of each component will be considered, presented in Eq. (17) and Eq. (18), respectively:

$$\dot{m}_{oil,Rt1} = \dot{m}_9 - \dot{m}_{oil,12} \tag{17}$$

$$\dot{m}_{met,Rt1} = \dot{m}_{met1} - \dot{m}_{met,out} \tag{18}$$

where $\dot{m}_{oil,Rt1}$ is the mass flow of unreacted oil in reactor 1 (kg.s$^{-1}$), $\dot{m}_9$ is the mass flow of inlet oil in reactor 1 (kg.s$^{-1}$), $\dot{m}_{oil,12}$ is the mass flow of outlet oil in reactor reactor 1 (kg.s$^{-1}$), $\dot{m}_{met,Rt1}$ is the mass flow of unreacted methanol in reactor 1 (kg.s$^{-1}$), $\dot{m}_{met1}$ is the mass flow of inlet methanol in reactor 1 (kg.s$^{-1}$), $\dot{m}_{met,out}$ is the mass flow of outlet methanol in reactor 1 (kg.s$^{-1}$).

The mass flow rates of ester and glycerol are presented in Eq. (19) and Eq. (20), respectively:

$$\dot{m}_{est,Rt1} = \dot{V}_1.C_{est1} \tag{19}$$

$$\dot{m}_{gly,Rt1} = \dot{V}_1.C_{gly1} \tag{20}$$

where $\dot{m}_{est,Rt1}$ is the mass flow of produced ester in reactor 1 (kg.s$^{-1}$) and $\dot{m}_{gly,Rt1}$ is the mass flow of produced glycerol in reactor 1 (kg.s$^{-1}$).

For the enthalpy of ester and glycerin, the specific heat values were considered constant. Below, Eq. (21) shows the destroyed exergy of the reactor 1:

$$\dot{m}_{oil,Rt1}.e_{x,9} - \dot{m}_{met,Rt1}.e_{x,11} - \dot{m}_{est,Rt1}.e_{x,est} - \dot{m}_{gly,Rt1}.e_{x,gly} - E_{D,Rt1} = 0 \tag{21}$$

where, $e_{x,est}$ is the specific exergy of ester (kJ.kg$^{-1}$), $e_{x,gly}$ is the specific exergy of glycerol (kJ.kg$^{-1}$) and $\dot{E}_{D,Rt1}$ is the destroyed Exergy of reactor 1 (kJ.s$^{-1}$)

### 2.4 Heat exchanger methanol for reactor 2

The energy balance is given by Eq. (22).

$$\dot{m}_{met,2}.(h_{13} - h_{14}) + \dot{m}_{vap,15}.(h_{15} - h_{cond,3}) = 0 \tag{22}$$

where, $\dot{m}_{met,2}$ is the mass flow of methanol in reactor 2 (kg.s$^{-1}$), $\dot{m}_{vap,15}$ is the mass flow of steam in heat exchanger methanol for reactor 2 (kg.s$^{-1}$), $h_{13}$ is the enthalpy of inlet methanol (kJ.kg$^{-1}$), $h_{14}$ is the enthalpy of outlet methanol (kJ.kg$^{-1}$), $h_{15}$ is the enthalpy of inlet steam (kJ.kg$^{-1}$) and $h_{cond,3}$ is the enthalpy of outlet steam (kJ.kg$^{-1}$).

From the results, the destroyed exergy of the equipment was obtained, Eq. (23).

$$\dot{m}_{met,2}.(e_{x,13} - e_{x,14}) + \dot{m}_{vap,15}.(e_{x,15} - e_{x,cond,3}) - E_{D,HTMet2} = 0 \tag{23}$$

where, $e_{x,13}$ is the specific exergy of inlet methanol (kJ.kg$^{-1}$), $e_{x,14}$ is the specific exergy of outlet methanol (kJ.kg$^{-1}$), $e_{x,15}$ is the specific exergy of inlet steam (kJ.kg$^{-1}$), $e_{x,cond,3}$ is the specific exergy of outlet steam (kJ.kg$^{-1}$) and $\dot{E}_{D,HTMet2}$ is the destroyed exergy of heat exchanger methanol for reactor 2 (kJ.s$^{-1}$)

The entropy values, to calculate the specific exergy, were obtained by the temperature and pressure of each line.

### 2.5 Reactor 2

The direct reaction kinetics is presented in the Eq. (24) and the inverse reaction kinetics in the Eq. (25), both are specified in equations below.

$$R_3 = \frac{k_1.C_{oil2}.C_{met2}.V_{Rt2}}{M_{oil}.M_{met}} \tag{24}$$

$$R_4 = \frac{k_2.C_{est2}.C_{gly2}.V_{Rt2}}{M_{est}.M_{gly}} \tag{25}$$

where, k1 is the direct reaction kinetic constant ($s^{-1}$), k2 is the inverse reaction kinetic constant ($s^{-1}$), $C_{oil2}$ is the oil concentration in reactor 2 ($kg.L^{-1}$), $C_{met2}$ is the methanol concentration in reactor 2 ($kg.L^{-1}$), $C_{est2}$ is the ester concentration in reactor 2 ($kg.L^{-1}$), $C_{gly2}$ is the glycerol concentration in reactor 2 ($kg.L^{-1}$), $M_{oil}$ is the molar mass of oil ($kg.mol^{-1}$), $M_{met}$ is the molar mass of methanol ($kg.mol^{-1}$), $M_{est}$ is the molar mass of ester ($kg.mol^{-1}$), $M_{gly}$ is the molar mass of glycerol ($kg.mol^{-1}$).

The mass balance for the reactor was performed for each component of the transesterification reaction, being those oil (Eq. (26)), methanol (Eq. (27)), ester (Eq. (28)) and glycerol (Eq. (29)).

$$\dot{m}_{oil,12} - \dot{V}_2.C_{oil2} - M_{oil}.R_3 + M_{oil}.R_4 = 0 \tag{26}$$

$$\dot{m}_{met2} - \dot{V}_2.C_{met2} - 3.M_{met}.R_2 + 3.M_{met}.R_4 = 0 \tag{27}$$

$$- \dot{V}_2.C_{est2} + 3.M_{est}.R_3 - 3.M_{est}.R_4 = 0 \tag{28}$$

$$- \dot{V}_2.C_{gly2} + M_{gly}.R_3 - M_{gly}.R_4 = 0 \tag{29}$$

where, $\dot{V}_2$ is the volumetric flow in reactor 2 ($L.s^{-1}$).

The oil and methanol consumed mass flow rates are shown in Eq. (30) and Eq. (31), respectively. And the ester and glycerol mass flow rates produced are shown in Eq. (32) and Eq. (33), respectively.

$$\dot{m}_{oil,Rt2} = \dot{m}_{oil,12} - \dot{m}_{oil,16} \tag{30}$$

$$\dot{m}_{met,Rt2} = \dot{m}_{met2} - \dot{m}_{met,out2} \tag{31}$$

$$\dot{m}_{est,Rt2} = \dot{V}_2.C_{est2} \tag{32}$$

$$\dot{m}_{gly,Rt2} = \dot{V}_2.C_{gly2} \tag{33}$$

where, $\dot{m}_{oil,Rt2}$ is the mass flow of unreacted oil in reactor 2 ($kg.s^{-1}$), $\dot{m}_{oil,12}$ is the mass flow of inlet oil in reactor 2 ($kg.s^{-1}$), $\dot{m}_{oil,16}$ is the mass flow of outlet oil in reactor reactor 2 ($kg.s^{-1}$), $\dot{m}_{met,Rt2}$ is the mass flow of unreacted methanol in reactor 2 ($kg.s^{-1}$), $\dot{m}_{met2}$ is the mass flow of inlet methanol in reactor 2 ($kg.s^{-1}$), $\dot{m}_{met,out}$ is the mass flow of outlet methanol in reactor 2 ($kg.s^{-1}$), $\dot{m}_{est,Rt2}$ is the mass flow of produced ester in reactor 2 ($kg.s^{-1}$) and $\dot{m}_{gly,Rt2}$ is the mass flow of produced glycerol in reactor 2 ($kg.s^{-1}$).

The destroyed exergy of the reactor 2 is presented in Eq. (34):

$$\dot{m}_{oil,Rt2}.e_{x,12} - \dot{m}_{met,Rt2}.e_{x,14} - \dot{m}_{est,Rt2}.e_{x,est} - \dot{m}_{gly,Rt2}.e_{x,gly} - E_{D,Rt2} = 0 \tag{34}$$

where, $\dot{E}_{D,Rt2}$ is the destroyed Exergy of reactor 2 ($kJ.s^{-1}$)

## 2.6 Heat exchanger methanol for reactor 3

The energy balance is given by Eq. (35).

$$\dot{m}_{met,3}.(h_{17} - h_{18}) + \dot{m}_{vap,19}.(h_{19} - h_{cond,4}) = 0 \tag{35}$$

where, $\dot{m}_{met,3}$ is the mass flow of methanol in reactor 3 (kg.s$^{-1}$), $\dot{m}_{vap,19}$ is the mass flow of steam in heat exchanger methanol for reactor 3 (kg.s$^{-1}$), $h_{17}$ is the enthalpy of inlet methanol (kJ.kg$^{-1}$), $h_{18}$ is the enthalpy of outlet methanol (kJ.kg$^{-1}$), $h_{19}$ is the enthalpy of inlet steam (kJ.kg$^{-1}$) and $h_{cond,4}$ is the enthalpy of outlet steam (kJ.kg$^{-1}$).

The enthalpies were obtained by the temperature and pressure data of each line. With this data, the steam flow rate was obtained to heat the exchanger. Then, the exergetic balance was performed and the destroyed exergy of the equipment, Eq. (36).

$$\dot{m}_{met,3}.(e_{x,17} - \mathrm{e}_{\mathrm{x},18}) + \dot{m}_{vap,19}.(e_{x,19} - \mathrm{e}_{x,cond,4}) - E_{D,HTMet3} = 0 \tag{36}$$

where, $e_{x,17}$ is the specific exergy of inlet methanol (kJ.kg$^{-1}$), $e_{x,18}$ is the specific exergy of outlet methanol (kJ.kg$^{-1}$), $e_{x,19}$ is the specific exergy of inlet steam (kJ.kg$^{-1}$), $e_{x,cond,4}$ is the specific exergy of outlet steam (kJ.kg$^{-1}$) and $\dot{E}_{D,HTMet3}$ is the destroyed Exergy of heat exchanger methanol for reactor 3 (kJ.s$^{-1}$)

## 2.7 Reactor 3

The direct reaction kinetics is represented in the Eq. (37) and the inverse reaction kinetics in the Eq. (38), both are specified in equations below.

$$R_5 = \frac{k_1.C_{oil3}.C_{met3}.V_{Rt3}}{M_{oil}.M_{met}} \tag{37}$$

$$R_6 = \frac{k_2.C_{est3}.C_{gly3}.V_{Rt3}}{M_{est}.M_{gly}} \tag{38}$$

where, k1 is the direct reaction kinetic constant (s$^{-1}$), k2 is the inverse reaction kinetic constant (s$^{-1}$), $C_{oil3}$ is the oil concentration in reactor 3 (kg.L$^{-1}$), $C_{met3}$ is the methanol concentration in reactor 3 (kg.L$^{-1}$), $C_{est3}$ is the ester concentration in reactor 3 (kg.L$^{-1}$), $C_{gly3}$ is the glycerol concentration in reactor 3 (kg.L$^{-1}$), $M_{oil}$ is the molar mass of oil (kg.mol$^{-1}$), $M_{met}$ is the molar mass of methanol (kg.mol$^{-1}$), $M_{est}$ is the molar mass of ester (kg.mol$^{-1}$), $M_{gly}$ is the molar mass of glycerol (kg.mol$^{-1}$).

The mass balance for the reactor was performed for each component of the transesterification reaction, being those oil (Eq. (39)), methanol (Eq. (40)), ester (Eq. (41)) and glycerol (Eq. (42)).

$$\dot{m}_{oil,16} - \dot{\mathrm{V}}_3.\mathrm{C}_{\mathrm{oil3}} - \mathrm{M}_{\mathrm{oil}}.R_5 + \mathrm{M}_{\mathrm{oil}}.R_6 = 0 \tag{39}$$

$$\dot{m}_{met3} - \dot{\mathrm{V}}_3.\mathrm{C}_{\mathrm{met3}} - 3.\mathrm{M}_{\mathrm{met}}.R_5 + 3.\mathrm{M}_{\mathrm{met}}.R_6 = 0 \tag{40}$$

$$-\dot{\mathrm{V}}_3.\mathrm{C}_{\mathrm{est3}} + 3.\mathrm{M}_{\mathrm{est}}.R_5 - 3.\mathrm{M}_{\mathrm{est}}.R_6 = 0 \tag{41}$$

$$-\dot{\mathrm{V}}_3.\mathrm{C}_{\mathrm{gly3}} + \mathrm{M}_{\mathrm{gly}}.R_5 - \mathrm{M}_{\mathrm{gly}}.R_6 = 0 \tag{42}$$

where, $\dot{\mathrm{V}}_3$ is the volumetric flow in reactor 3 (L.s$^{-1}$).

The oil and methanol consumed mass flow rates are shown in Eq. (43) and Eq. (44), respectively. The ester and glycerol mass flow rates produced are shown in Eq. (45) and Eq. (46), respectively.

$$\dot{m}_{oil,Rt3} = \dot{m}_{oil,16} - \dot{m}_{oil,out3} \tag{43}$$

$$\dot{m}_{met,Rt3} = \dot{m}_{met3} - \dot{m}_{met,out3} \tag{44}$$

$$\dot{m}_{est,Rt3} = \dot{V}_3.C_{est3} \tag{45}$$

$$\dot{m}_{gly,Rt3} = \dot{V}_3.C_{gly3} \tag{46}$$

where $\dot{m}_{oil,Rt3}$ is the mass flow of unreacted oil in reactor 3 (kg.s$^{-1}$), $\dot{m}_{oil,16}$ is the mass flow of inlet oil in reactor 3 (kg.s$^{-1}$), $\dot{m}_{oil,out3}$ is the mass flow of outlet oil in reactor reactor 3 (kg.s$^{-1}$), $\dot{m}_{met,Rt3}$ is the mass flow of unreacted methanol in reactor 1 (kg.s$^{-1}$), $\dot{m}_{met1}$ is the mass flow of inlet methanol in reactor 1 (kg.s$^{-1}$), $\dot{m}_{met,out}$ is the mass flow of outlet methanol in reactor 3 (kg.s$^{-1}$), $\dot{m}_{est,Rt3}$ is the mass flow of produced ester in reactor 3 (kg.s$^{-1}$) and $\dot{m}_{gly,Rt3}$ is the mass flow of produced glycerol in reactor 3 (kg.s$^{-1}$).

The destroyed exergy of the reactor 3 is presented in Eq. (47).

$$\dot{m}_{oil,Rt3}.e_{x,16} - \dot{m}_{met,Rt3}.e_{x,18} - \dot{m}_{est,Rt3}.e_{x,est} - \dot{m}_{gly,Rt3}.e_{x,gly} - E_{D,Rt3} = 0 \quad (47)$$

where, $\dot{E}_{D,Rt3}$ is the destroyed Exergy of reactor 3 (kJ.s$^{-1}$)

From the energetic analysis of the heaters, the mass flow rate of total steam required to be produced in the boiler was determined, Eq. (48):

$$\dot{m}_{vap,5} = \dot{m}_{vap,6} + \dot{m}_{vap,7} + \dot{m}_{vap,15} + \dot{m}_{vap,19} \quad (48)$$

where, $\dot{m}_{vap,5}$ is the total mass flow of steam (kg.s$^{-1}$),

## 2.8 Boiler

The energy balance was divided into two control volumes: for water/steam and for diesel/air.

For the first control volume, water/steam, the relation is given by Eq. (49).

$$\dot{m}_{vap,5}\left(h_w - \mathrm{h}_5\right) + \dot{Q}_{abs} = 0 \quad (49)$$

where, $h_w$ is the enthalpy of inlet water (kJ.kg$^{-1}$), $h_5$ is the enthalpy of outlet steam (kJ.kg$^{-1}$) and $\dot{Q}_{abs}$ is the rate of heat transfer (kJ.s$^{-1}$).

For the energy balance of the second control volume, the mass flow rate of diesel and air required to burn the fuel, Eq. (50) and Eq. (51), respectively, was calculated. For these calculations, an efficiency of 85% of the boiler and an air/fuel ratio (rac) of 30 were considered, ensuring the all the fuel will burning.

$$\dot{Q}_{abs} = \dot{m}_{die} LHV_{die} 0.85 \quad (50)$$

$$\dot{m}_{air} = 30.\dot{m}_{die} \quad (51)$$

where, $\dot{m}_{die}$ is the diesel mass flow (kg.s$^{-1}$), $\dot{m}_{air}$ is the air mass flow (kg.s$^{-1}$) and $LHV_{die}$ is the lower calorific value of diesel (kJ.kg$^{-1}$).

From the mass flow values obtained and considering the specific heat of diesel constant, the energy balance was performed for the second control volume presented by Eq. (52):

$$\dot{m}_{die}.\left(LHV_{die}.0.15 + c_{p,die}T_{die}\right) + \dot{m}_{air}h_{air} - \left(\dot{m}_{die} + \dot{m}_{air}\right).h_{cg} = 0 \quad (52)$$

where, $h_{air}$ is the enthalpy of inlet air (kJ.kg$^{-1}$), $h_{cg}$ is the enthalpy combustion gases (kJ.kg$^{-1}$), $c_{p,die}$ specific heat of diesel (kJ.kg$^{-1}$.°C$^{-1}$) and $T_{die}$ is temperature of inlet diesel (°C).

Specific exergy of diesel was obtained from the literature and to obtain the specific exergy values of steam and the air, the entropy of the lines was calculated from the temperature and pressure data. Then, the exergetic analysis, Eq. (53), was performed to obtain the destroyed exergy of the boiler.

$$\dot{m}_{die}e_{x,die} - \dot{m}_{vap,5}e_{x,5} - \left(\dot{m}_{air} + \dot{m}_{die}\right).e_{x,cg} - E_{D,B} = 0 \quad (53)$$

where, $e_{x,die}$ is the specific exergy of diesel (kJ.kg$^{-1}$), $e_{x,5}$ is the specific exergy of outlet steam (kJ.kg$^{-1}$), $e_{x,cg}$ is the specific exergy of combustion gases (kJ.kg$^{-1}$) and $\dot{E}_{D,B}$ is the destroyed exergy of boiler (kJ.s$^{-1}$).

The destroyed exergy in the system is calculated by Eq. (54).

$$E_{D,sist} = E_{D,HTO} + E_{D,HTMet1} + E_{D,Rt1} + E_{D,HTMet2} + E_{D,Rt2} + E_{D,HTMet3} + E_{D,Rt3} + E_{D,B} \quad (54)$$

where $\dot{E}_{D,Sist}$ is the total destroyed exergy of system (kJ.s$^{-1}$).

### 2.9 Optimization Procedure

From the energy and exergy analysis, a process optimization was performed and two objective functions were created. The first objective function relates the destroyed exergy in the system by the amount of ester produced, Eq. (55).

$$r_{opt} = \frac{E_{D,sist}}{\dot{m}_{est,Rt3}} \tag{55}$$

where, $r_{opt}$ is the ratio of destroyed exergy of system by the amount of ester produced and $\dot{m}_{est,Rt3}$ is the mass flow of produced ester in reactor 3 (kg.s$^{-1}$).

For the second objective function, the profit of the system was analyzed in relation to the First Thermodynamics Law. The costs were attributed to the ester mass flow produced and the oil mass flow, methanol and diesel consumed. This relation is presented by Eq. (56).

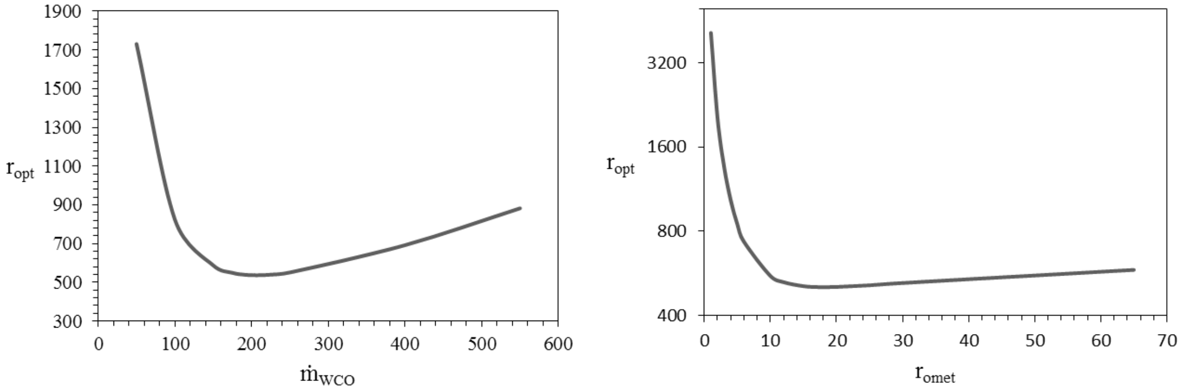
$$L = \dot{m}_{est,Rt3}.ct_{est} - \dot{m}_{oil}.ct_{oil} - \left(\dot{m}_{met1} + \dot{m}_{met2} + \dot{m}_{met3}\right).ct_{met} - \dot{m}_{die}.ct_{die} \tag{56}$$

where, $ct_{est}$ is the cost of ester (\$.kg$^{-1}$), $ct_{oil}$ is the cost of waste cooking oil (\$.kg$^{-1}$), $ct_{met}$ is the cost of methanol (\$.kg$^{-1}$) and $ct_{die}$ is the cost of diesel (\$.kg$^{-1}$), .

## 3. RESULTS AND DISCUSSION

### 3.1 Fist Objective Function

For the first stage of the first objective function, the methanol flow rate was set at 18.7 kg.s$^{-1}$ and the waste cooking oil flows were varied. The optimum waste cooking oil flow was determined by the ratio of destroyed exergy by the amount of ester produced ($r_{opt}$). Then, this optimum flow rate was set and the proportion of methanol in relation of the oil was varied. it was obtained the best mass ratio of oil/methanol to the ratio of destroyed exergy by the amount of ester produced ($r_{opt}$). The results are shown in Fig. 2.



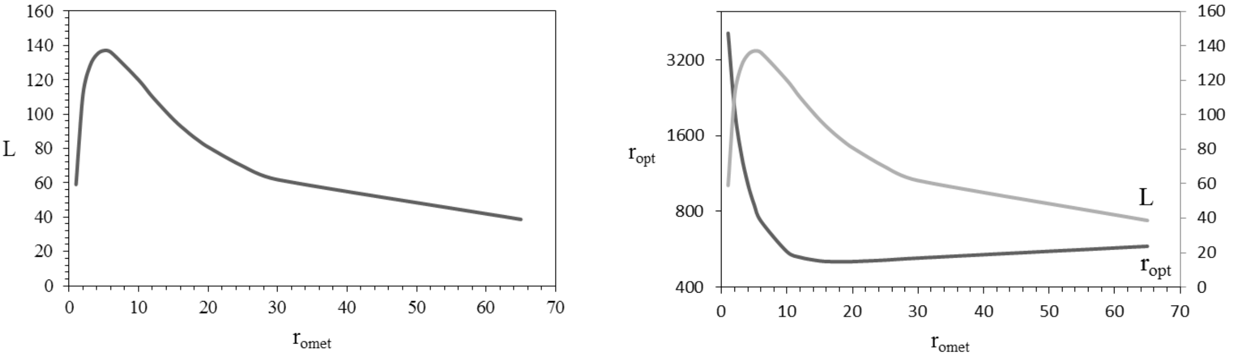
(a) (b)

Figure 2. (a) Effect of the mass flow of oil ($\dot{m}_{oil}$) on the ratio of destroyed exergy by the amount of ester produced ($r_{opt}$) and (b) effect of the ratio of oil/methanol ($r_{omet}$) to the ratio of destroyed exergy by the amount of ester produced ($r_{opt}$).

Figure 2 (a) shows the relationship between the exergy ratio destroyed by the amount of ester produced ($r_{opt}$) and the optimum mass flow rate of the oil. It was observed that this ratio has a local minimum value of 206 kg.s$^{-1}$ of oil. From Fig. 2 (b), it was found that for the mass ratio of 1/1 to 7/1 oil/methanol the $r_{opt}$ ratio is high. For reasons above 8/1 oil/methanol, $r_{opt}$ values decrease and remain centered over a range of values, reaching a local minimum in the 18/1 mass ratio. In this way, both relations can be optimized.

### 3.2 Second Objective Function

For the second objective function, the optimum mass flow of oil obtained previously was fixed and the ratio of oil/methanol was varied, obtaining the mass flows of consumed diesel and ester produced. Then, their respective costs were attributed and the system profit was obtained for each ratio of oil/methanol by the destroyed exergy ratio by the amount of ester produced ($r_{opt}$), Fig. 3.



(a) (b)

Figure 3. (a) Effect of the ratio of oil/methanol ($r_{omet}$) on profit of the system (L) and (b) curves of the profit of the system (L) and the destroyed exergy ratio by the amount of ester produced ($r_{opt}$) in relation to the ratio of oil/methanol ($r_{omet}$).

Figure 3 (a) shows that a maximum system profit of $ 137.04 per second is obtained with the ratio of oil/methanol of 5/1 for an oil flow rate of 206 $kg.s^{-1}$. From Fig. 3 (b) it can be seen that the objective functions have a positive relation, but their optimal ratio of oil/methanol differ by being a ratio of 18/1 for the first objective function and 5/1 for the second objective function.

## 4. CONCLUSION

Through the objective functions developed, it was possible to optimize the biodiesel production process. However the optimum ratio of oil/methanol is different for each function. Therefore, the conversion of the reaction was also analyzed for both cases and for the ratio 18/1 a reaction conversion of 62.1% was obtained and for the ratio 5/1 a conversion of 95.6% was thus obtained. Thus, despite a larger $r_{opt}$, the system is better optimized in relation to the second objective function, for a 5/1 ratio of oil/methanol.

## 5. REFERENCES

Araujo, V.K.W.S., Hamacher, S. and Scavarda, L.F., 2010. “Economic assessment of biodiesel production from waste frying oils”. *Bioresource Technology*, Vol. 101, pp. 4415–4422.

Kolhe, N.S., Gupta, A.R., Rathod, V.K., 2017.” Production and purification of biodiesel produced from used frying oil using hydrodynamic cavitation”. *Resource-Efficient Technologies,* Vol. 3, pp. 198–203.

ROJAS, S.P., 2007. *Análise Exergética, Termoeconômica e Ambiental de um Sistema de Geração de Energia. Estudo de Caso: Usina Termoelétrica UTE – Rio Madeira.* M.Sc. dissertation. Universidade Federal de Brasília, Brasília, Brasil.

## 6. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.