BURNING OF THE GLYCEROL AS ALTERNATIVE FUEL IN BIODIESEL PRODUCTION PLANTS. A CASE STUDY

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Abstract. *One of the challenges of the XXI century, in energy terms, is the reduction of the emission of pollutants gases and the search for alternatives relative to the oil's products dependence. The Brazilian government has encouraged the replacement of the common petroleum diesel by the biodiesel. This decision was started in 2005 with the law 11097/2005 and since that the ratio of biodiesel mixed with the common diesel has been increased gradually. With the increase of the biodiesel, the glycerol, the main sub product in the biodiesel production has also increased and unlike the biodiesel, the glycerol has his demand stable. The glycerol overproduction has generated an offer increase, with glycerol market stable, the glycerol has been stored with no apparent usefulness. Nowadays, the fuel used in boilers to produce the thermal energy in biodiesel production plant is the own biodiesel, decreasing the fuel net production.,In this work was studied the use of the glycerol like alternative fuel to boilers replacing the biodiesel or decreasing the consumption of this biofuel.Was studied a biodiesel production plant, taking into account technical aspects such ass energy balance and the gas emission generated by the combustion of the new fuel (glycerol). All the calculation was developed for the biodiesel produce from 1000 kg/h of raw material (soybean oil) and ethanol as alcohol reagent because of the ethanol availability in Brazil. It was used glycerol from tallow, soybean oil and chicken fat and it was compared with other standard fuels. It was presented to an economical and energy parallel using glycerol. It was concluded that the energy supply for this plant is not supplied only with glycerol combustion, being necessary the additional combustion with biodiesel. By using all glycerol produced, the consumption of biodiesel decreased from 310.441 kg/h to 256.896 kg/h. Before it was used 30.99% of the biodiesel produced to feed the boiler. By burning all the methylated glycerol (crude glicerol) produced the percentage of biodiesel used in boiler decreased to 25.65%. With the price of biodiesel set at about 30 cents/kg, the savings is about 15000 dollars/mouth.*

Keywords: Exergy, biodiesel, glycerin, irreversibility, thermo economy.

1. INTRODUCTION

With the growing concern to reduce emissions of polluting gases allied with the possible energy crisis that can be installed in the world has been studied possibilities to replace conventional fuels with biofuels which are fuels produced from organic products.

Nowadays for production of biodiesel, the fuel used to supply the boilers is own biodiesel. The main sub-product of the biodiesel production is glycerin which is used pharmaceutical and chemical industries, among others. The increase in biodiesel production increases the amount of glycerin available without apparent usefulness once the glycerin market demand is stable.

The purpose of this work is to promote the viability of supply the boilers of biodiesel production with glycerin, reducing the consumption of biodiesel as fuel, using the glycerin that before had no apparent usefulness, certifying that gas emission will be at acceptable levels.

2. BIODIESEL

Currently the most viable process for biodiesel production occurs by transesterification reaction, which basically consists in vegetable oil or animal fat chemical reaction (triglyceride) with alcohol reagent (for example, methanol or ethanol) in presence of an alkaline catalyst (sodium hydroxide or potassium hydroxide) producing biodiesel (mixture of esters) and glycerol. For every three moles of biodiesel one mole of glycerol is produced. Volumetrically between 10% and 20% of the initial reactants are transformed in glycerol, figure 1. From the several kinds of vegetable oils produced in Brazil, due to its large scale production, the soy is the most widely used. But there is another vegetal that may be important in the near future with its increased production like sunflower, cotton, castor beans, peanut, coconut, palm oil and castor oil mainly. Methanol is the most widely used alcohol in biodiesel production, despite having a large ethanol production in Brazil because ethanol is less reactive and there are some technical problems in using it in industry (phase separation).

Figure 1. Biodiesel and Glycerin

2.1 TRANSESTERIFICATION REACTIONS

In more details, we can say that transesterification reaction is divided in three parts, figure 2. First, triglyceride molecules are broken in diglycerides. Then, diglycerides molecules are broken in monoglycerides and after monoglycerides molecules are converted in glycerol producing in each reaction one mole of ester (biodiesel) (COSTA, 2009).

Figure 2. Transesterification reaction

The alcohol used to the process must have short chain, for this reason, the methanol and the ethanol are the main alcohol reagent used in the process. The most used alcohol in reaction is methanol due your low cost, by develop the reaction in a simple way, and provide a good yield and easiness to separate phases. Recently it have been increased the use of ethanol due your low toxicity, higher availability in Brazil, by be obtained from renewable resources, the extra atom increases the calorific value and cetane number at biodiesel, on the other hand, ethyl ester is more biodegradable that methyl ester (ENCIMAR et al., 2007). However, one of the disadvantages of ethanol is that is requires a high purity level (anhydrous ethanol) (CORONADO, 2010). Another disadvantage is the separation between organic phase (ethyl ester) and inorganic phase (glycerin). The ethanol must be used with potassium hydroxide catalyst (KOH) instead of sodium hydroxide catalyst (NaOH) because the NaOH dissolution in ethanol is too slow (CARRETO et al., 2004).

For this reaction, it may be employed different kinds of catalyst like inorganic bases (sodium hydroxide or potassium hydroxide), mineral acids (sulfuric acid or phosphoric acid), activated clay minerals, lipolytic enzymes, among others (VARGAS et al. 1998; RAMOS et al., 2003). Currently are used hydroxides of sodium and potassium

due to their simplicity, quickness and being economically viable (MA et al, 1999; Zagonel and RAMOS, 2001). Potassium hydroxide is more expensive than sodium hydroxide but the potassium hydroxide has the advantage of being used as a fertilizer at the end of the process when used as a catalyst in the production of biodiesel (CORONADO, 2010).

3. GLYCERIN

Glycerol is the name of pure substance. Glycerin is applied to glycerol with different percentages of other substances associated with glycerol or with different degrees of purity in relation to glycerol. The crude glycerol has about 40% - 90% glycerol, 8% - 50% water, less than 2% of methanol and 0% - 10% of salts and other materials, while pure glycerol (glycerin) has contents above 99.5% glycerol in its composition. This glycerin is known as U.S. Phamacopeia glycerin (°USP) (QUINTELLA, 2010).

The glycerol in pure form is a polyalcohol, viscous, odorless, colorless, and hygroscopic, with sweet taste, polar, highly reagent, soluble in water and alcohol, insoluble in hydrocarbons, ether and chloroform (MORRISON, 1994), and is used in various applications, figure 3.

The kind of oil or animal fat used in biodiesel production, as well the process, will influence the physical-chemistry properties of the biodiesel and glycerol (BUENO, 2007). The main difference between vegetable oils and animal fat is in the amount of fatty acids in its molecular chain. These fatty acids are linked with triglycerides and some dross affecting the color, smell and change of physical state, or producing soap changing the quality of the biodiesel and glycerin.

The crude glycerol produced from bovine fat is the glycerol with worst quality (OLEOLINE, 2010). Because of high amount of saturated fatty acids thus glycerol has a high melting point as well as high viscosity having even solid parts (MA; HANNA.; 1999).
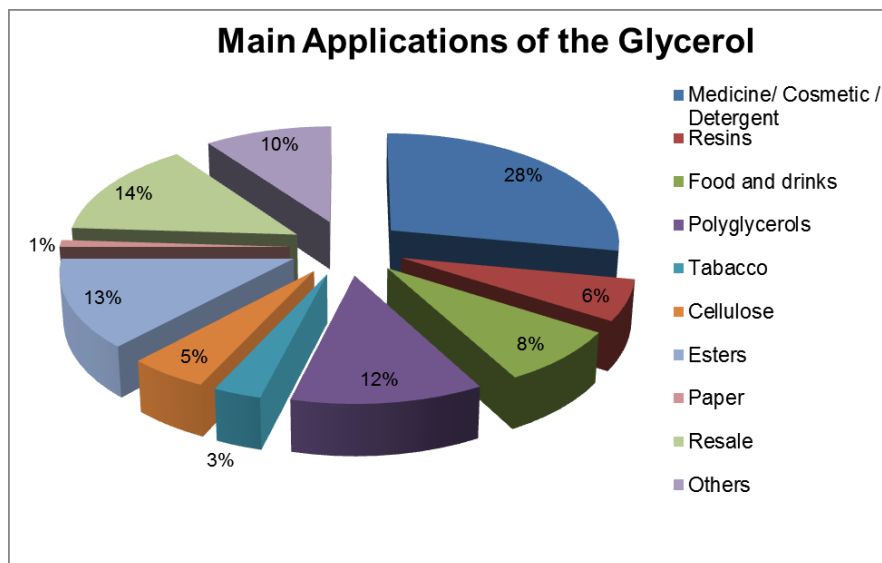

Figure 3. Main Applications of the Glycerol

3.1 Treatment of glycerol

The crude glycerol from transesterification process has about 40% to 90% of glycerol in your composition (QUINTELLA, 2010). To produce demethylated glycerol, its necessary make the treatment of the crude glycerin to remove the most of the salt, alcohol, water and dross contained in the crude glycerol.

It's possible to submit the crude glycerol in the flash evaporation process, then the filtration and addition of chemical products, figure 4. The flash evaporation process removes the most of alcohol because the alcohol is more volatile, while the filtration and addition of chemical products reacts with the dross. The glycerol obtained is always liquid and with glycerol content about 80% to 90% (HESS, 2007; THOMPSON; HE, 2006).

It's possible too for the treatment of crude glycerol the acidification with hydrochloric acid (HCL) or sulfuric acid (H_2SO_4). This acids neutralize the traces of catalyst and cause the hydrolysis of the soap present in the crude glycerin, forming insoluble salts, separating the mixture in two or more phases that can be removed by decantation or filtration (VAN GERPEN, 2004; SWEARINGEN, 2006).

The further treatment given to the demethylated glycerol seeks to produce the refined glycerin with glycerol content above of 99,5% used by the pharmaceutical, food, cosmetics, among others industries. The glycerin is also called of °USP glycerin when present glycerol content above 99,7%. The treatments to obtain this high content of purity is complex and of high cost involving the removal of salt, fatty acid and dross remaining by membrane filtration, reverse osmosis, distillation and drying (MATURANA, 2011).
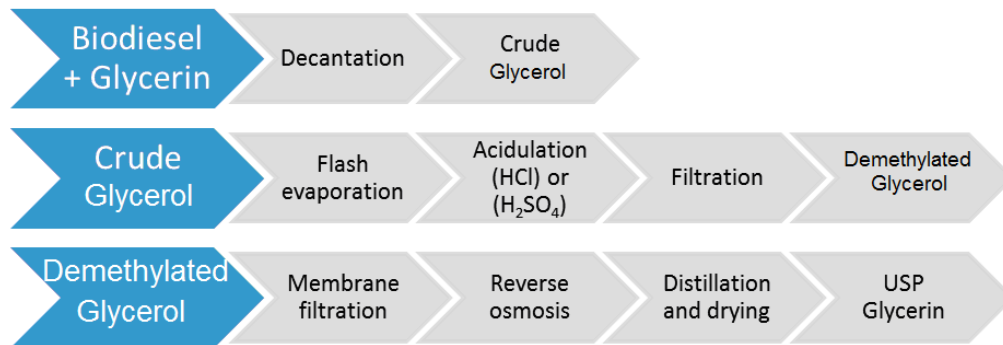
Figure 4. Treatment of glycerin

3.1. Glycerin market

The commercial use of glycerin is linked to your pureness content, above 95% (HÁJEK, 2010; MANOSAK, 2011). The crude glycerol, which have high dross content, was sold in 2008 about R$ 105,00 each ton, the demethylated glycerol, which have pureness content about 96%, was sold about R$ 2100,00 each ton, and the °USP glycerin, which have dross content above 99.7%, was sold about R$2500,00 each ton at the Brazilian market (BEATRIZ et at., 2011).

The world price of the crude glycerol and distilled glycerin has been decreasing year after year in consequence of the increasing production of biodiesel that generate a exceeding of the product at the market, figure 5.
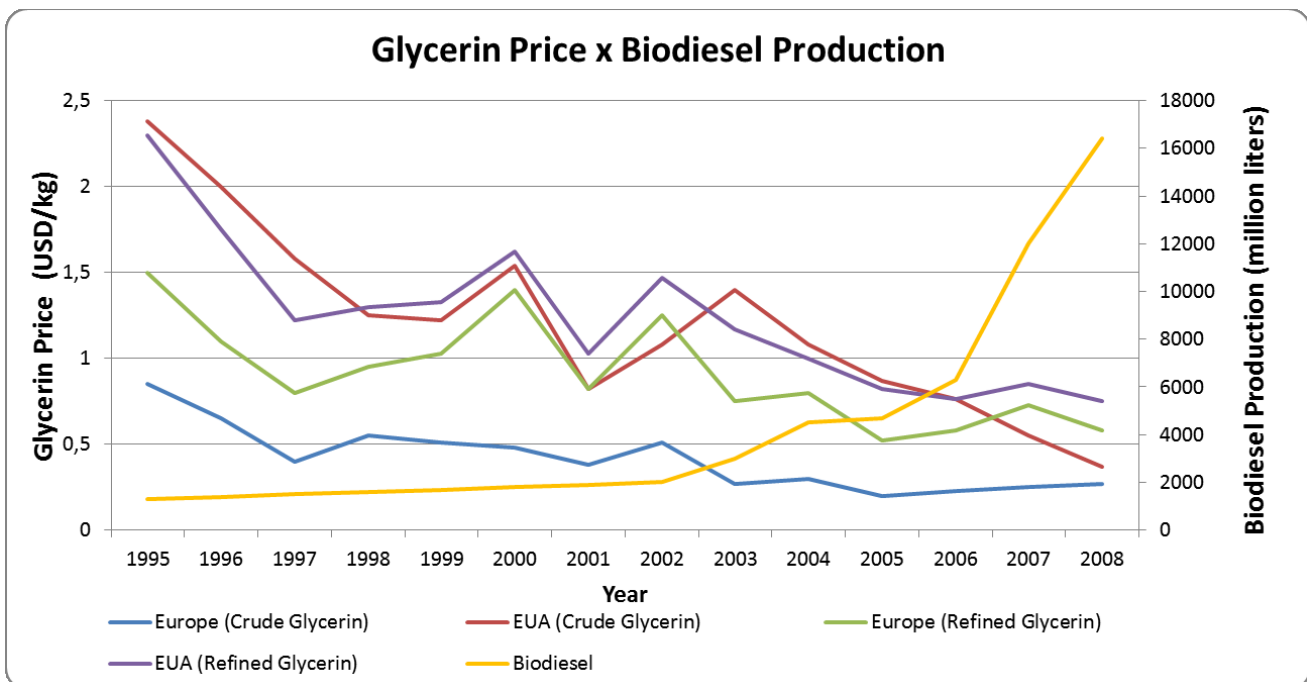
Figure 5. Glycerin Price x Biodiesel Production

4. PROCESS DESCRIPTION

For the plant in study was considered a feed with Soy Refined vegetable oil with flow rates of 1000 kg/h, the alcohol used was ethanol, due to its availability in Brazil with 8:1 molar ratio, the catalyst used was ethoxide potassium and transesterification process was performed in two steps, figure 6.

The process starts from the oil inlet (line 18) in the first reactor (J), maintained at 60 °C and atmospheric pressure. In this same reactor excess alcohol is added (line 19 and 20) with catalyst (line 19). It starts the process of transesterification between the triglyceride (oil) and ethanol in the presence of a catalyst to produce ethyl ester

(biodiesel) and glycerol. The reaction's products (line 21) are separated in the first decanter (K), the inorganic phase (glycerol, ethanol and sodium ethoxide) and the organic phase (ethyl ester oil, and alcohol). The glycerol phase (line 22) is collected in a tank (T). The ester phase (line 23) flows into a second reactor (L) maintained at the same pressure and temperature reactor (J). It is made a process similar to the above, excess alcohol is added (lanes 24 and 25) in the presence of catalyst (line 24), and after the transesterification process, the reaction products go into the second settling tank (M). The glycerol phase (line 27) is collected in the tank (T), while the ester phase (line 28) is heated to 70 ° C in heater (N) and passes to the washing step of the ester.

This washing step is made to separate impurities in the ester phase (line 29), as ethanol and glycerol free, of the ethyl ester which is the desired end product. This washing process is carried out with water (line 31) at 70 ° C. The aqueous phase (line 32) is collected in the tank (T), and washed ester (line 33) is passed to the settling tank (Q). The aqueous phase (line 34) that still exists in ethyl ester is separated in decanter (Q). The ethyl ester (line 35) is heated at 95 °C in a heater (R), and led into a vacuum dryer (S), with absolute pressure in the range of 4.7 kPa (35 mmHg) in order to remove traces moisture still remaining. So biodiesel is obtained (line 38).

The lines 22, 27, 32 and 34, collected in tank (T), are taken (line 39) to the heater (U) and heated to the boiling point of the alcohol (78.3 °C). Following to the stripper (V), the alcohol is extracted using superheated steam (line 41). The flow of saturated methanol vapor (line 42) feeds a distillation column to obtain pure ethanol steam (line 43). This pure ethanol is condensed in the condenser (X), where a portion is withdrawn (line 45) and the other part is recycled (line 52). The line 53 passes through a boiler (W), where a part is recycled (line 54) and contains part of the condensed steam and the remaining ethanol (line 44).

The glycerol solution (line 46) exits the bottom of the stripper (V) and is taken into the tank (Y). This glycerol is mixed with a solution of HCl (line 48) the acidification reactor (Z). In this reactor, the catalyst present in the line 47 reacts with HCl to form ethanol and NaCl. If there is soap at line 47, this reacts with HCl to form fatty acids and NaCl. In the decanter (AA), glycerol (line 51) is separated from impurities such as free fatty acids.
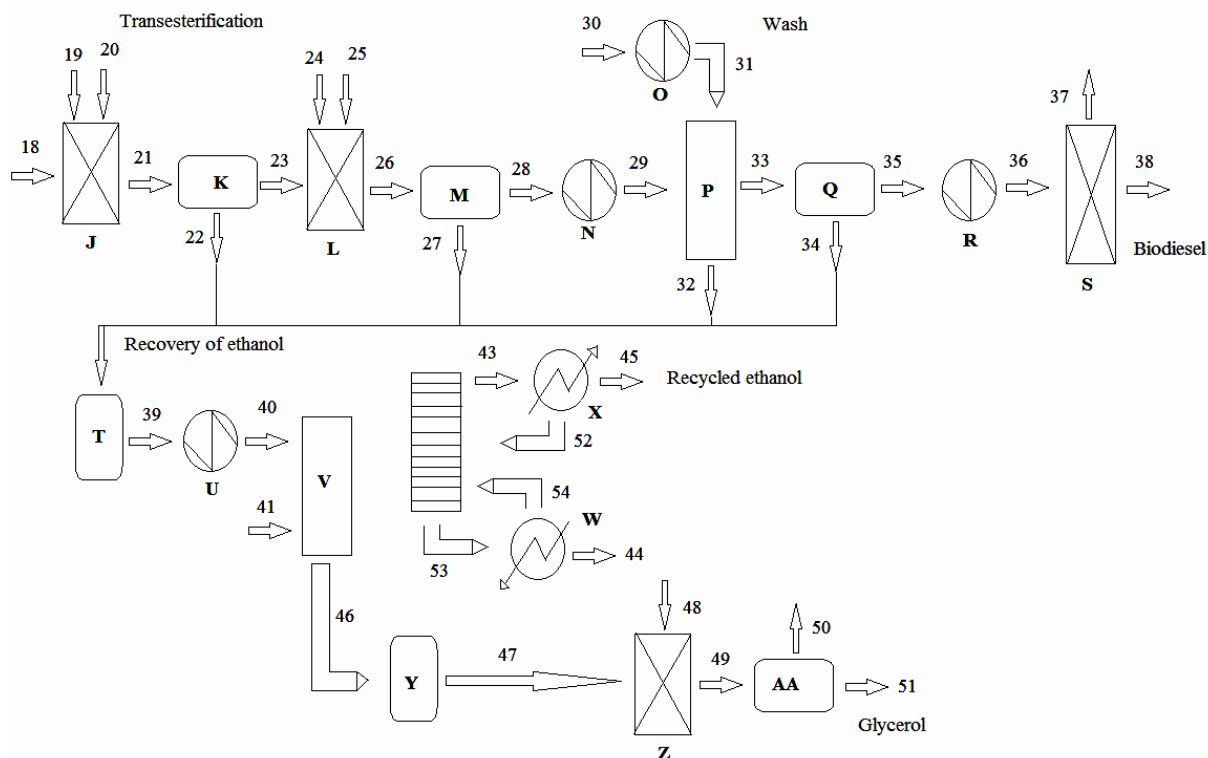

Figure 6. Biodiesel Plant (Adapted from Tapasvi, 2005)

5. METHODOLOGY
5.1. Mass balance

Considering a steady-state, the mass balance from a control volume can be given from Eq.(1).

$$\sum \dot{m}_e - \sum \dot{m}_s = 0 \qquad (1)$$

Where:

$\dot{m}_e$ is the mass flow in entrance of control volume, in kg/s;

$\dot{m}_s$ is the mass flow in exit of control volume, in kg/s.

5.2. Energy balance

The energy balance is obtained from first law of thermodynamics. If steady-state is considerate, the hypothesis of kinetic and potential energy values is adopted smaller than others, the equation can be written like Eq. (2).

$$Q_{vc} - W_{vc} + \sum m_e * h_e - \sum m_s * h_s = 0$$

(2)

Where:

Q_{vc} is the heat tax exchanged by environment with control volume, in (kW);
W_{vc} is the work transferring between environment and control volume, in (kW);
h_e is the specific enthalpy of entrance line in control volume, in (kJ/kg);
hs is the specific enthalpy of exit line in control volume, in (kJ/kg);

5.3. Enthalpy

Enthalpy is the amount of chemical and thermal energies of an element. When the energy of a volume control is realized, the enthalpy is present for searching wanted values. The enthalpy of an element can be given from Eq. (3).

$$H = \Delta H_f^0 + \int c_p dT$$

(3)

Where:

ΔH_f^0 is the formation enthalpy of species in consideration (kJ/mol ; kJ/kg);

c_p is the specific heat of species in consideration (kJ/°C.mol ; kJ/°C.kg);

dT is the difference of temperature of current (°C).

5.4. Calculation of mass balance and energy balance

An exemple will be presented for all processes steps, mass and energy balance of reactor J. Reactor J is a misture reactor (CSTR), quen reaction occours at 60°C, figure 7. Mass flows were found from mass balance and thermal load of reactor, found from energy balance.
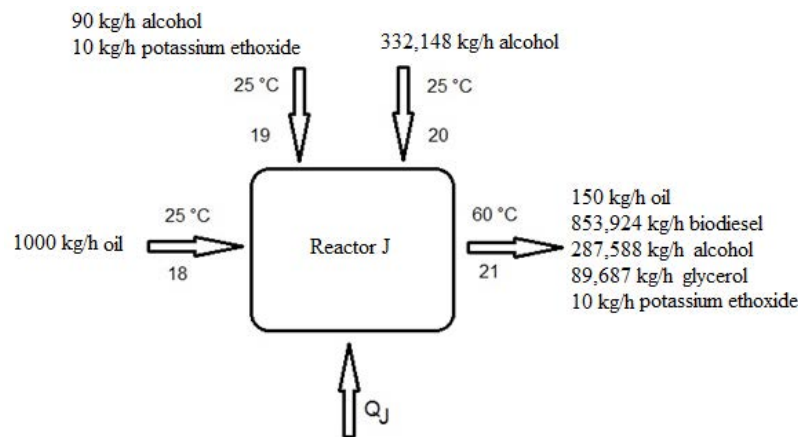

Figure 7. Reactor J

The energy balance can be found from Eq. (2), adapted for reactor J. Thus, Eq. (4) is presented. Using informations of formation enthalpy of oil and biodiesel from (DEMIRBAS, 2008), $\dot{Q}_J$ is found.

$$\dot{m}_{18} . h_{18} + \dot{m}_{19} . h_{19} + \dot{m}_{20} . h_{20} + \dot{Q}_J = \dot{m}_{21} . h_{21}$$ (4)

Replacing:

$\dot{m}_{18\,oil} . \{[c_{p\,oil} . (T_{18\,oil} - T_{ref})] + \Delta h_{f\,oil}^{\circ}\} + \dot{m}_{19\,alcohol} . \{[c_{p\,alcohol} . (T_{19} - T_{ref})]$

$+ \Delta h_{f\,alcohol}^{\circ}\} + \dot{m}_{20\,alcohol} . \{[c_{p\,alcohol} . (T_{20} - T_{ref})] + \Delta h_{f\,alcohol}^{\circ}\} + \dot{Q}_J = \dot{m}_{21oil} . \{[c_{p\,oil} . (T_{21} - T_{ref})] + \Delta h_{f\,oil}^{\circ}\} +$

$$\dot{m}_{21\ alcohol} \cdot \{[c_{p\ alcohol} \cdot (T_{21} - T_{ref})] + \Delta h_f^{\circ}{}_{alcohol}\} + \dot{m}_{21\ G} \cdot \{[c_{p\ G} \cdot (T_{21} - T_{ref})] + \Delta h_f^{\circ}{}_{G}\} + \dot{m}_{21\ biodiesel} \cdot \{[c_{p\ biodiesel} \cdot$$

$$(T_{21} - T_{ref})] + \Delta h_f^{\circ}{}_{biodiesel}\} \tag{5}$$

$\dot{Q}_J = 1399396.245\ kJ/h$

5.4. Thermal demand and steam consumption

Values of steam enthalpies were found in (SMITH, 2007). In operations over 100ºC, 10 kgf/cm² (980,7 kPa) is used, and in operations under 100ºC, 4 kgf/cm² (392.3 kPa) is used.

For this case study, were adopted that steam generator uses alimentation water in 20ºC temperature and 1 bar of pressure, and on the other side, the steam generated exit like saturated steam in 10 bar.

Considering that the steam generator with 80% thermal efficient, approximated value of flame tubular generators, the quantity of fuel can be estimated in Eq. (6).

$$\eta_{gv} = \dot{m}_{total\ steam} \cdot \lambda_{water} / \dot{m}_{fuel} \cdot LHV_{fuel} \tag{6}$$

Where:
η_{gv} efficiency of steam generator;
Λ_{water} vaporization enthalpy of water (MJ/kg);
LHV Low heat value of fuel (MJ/kg).

So, calculated values of thermal demand for each process steps are in Figure 7 and Table 1.

Table 1. Thermal Demand

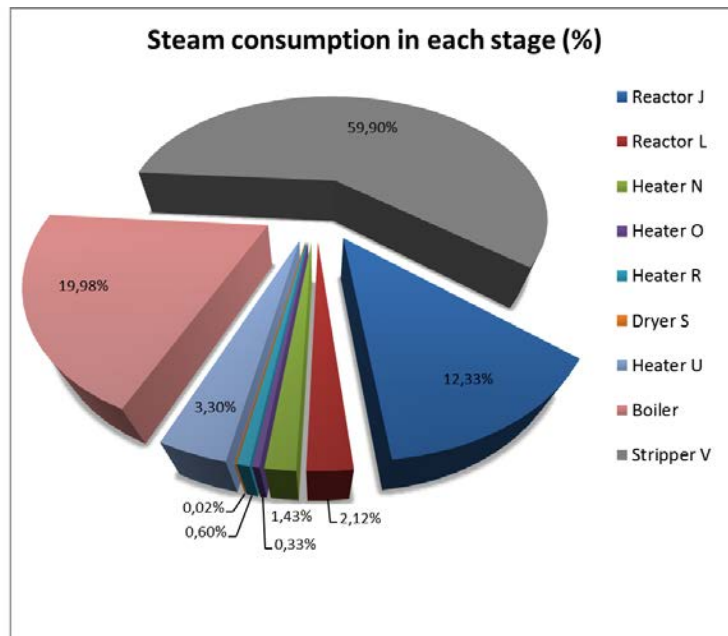| Thermal Demand (kJ/s)	
Reactor J	388.721
Reactor L	66.836
Heater N	44.950
Heater O	10.482
Heater R	18.764
Dryer S	0.635
Dryer U	103.994
Boiler	474.955
Stripper V	1753.267
Total	**2862.604**

Figure 7. Steam consuption in cach ctage

5.5. Glycerol Combustion and characterization of emissions

In order to point the possible environmental damage that glycerol combustion may cause in comparison with others fossil fuels, the stoichiometric balance were realized for glycerol used in this process to check this information.

For the realization of this study, methylated glycerol were used (BOHON et. al., 2011), by contain traces of methanol, that contributes with combustion and also values presented by author were more complete than others literatures. Thus, composition of methylated glycerol is presented in table (2).
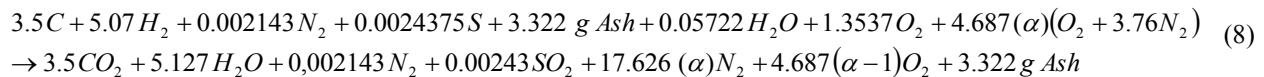
Table 2. Methylated Glycerol composition

(% mass)	Methylated Glycerol
Carbon	42.05
Hydrogen	10.14
Nitrogen	0.06
Oxygen	43.32
Sulfur	0.078
Water	1.03
Ash	3.322

Stoichiometric balance for methylated glycerin can be given for Eq. (7).

$$\frac{42,05}{12}C + \frac{10,14}{2}H_2 + \frac{43,32}{32}O_2 + \frac{0,06}{28}N_2 + \frac{0,078}{32}S + \frac{1,03}{18}H_2O + 3,322\ Ash \tag{7}$$

The combustion reaction for Eq. (5) is:

$$3.5\,C + 5.07\,H_2 + 0.002143\,N_2 + 0.0024375\,S + 3.322\ g\ Ash + 0.05722\,H_2O + 1.3537\,O_2 + 4.687(\alpha)(O_2 + 3.76N_2)$$
$$\rightarrow 3.5\,CO_2 + 5.127\,H_2O + 0,002143\,N_2 + 0.00243\,SO_2 + 17.626\,(\alpha)N_2 + 4.687(\alpha - 1)O_2 + 3.322\ g\ Ash \tag{8}$$

Emissions of gases products of methylated glycerol combustion can be checked in Figure 8 and Table 3. Values found are for reactions without excess of air.

Table 3 – Gas combustion products

Gases	(g/mol)
CO_2	154.1833
H_2O	92.29
N_2	493.5973
SO^2	0.156
O^2	0
Ash	2.331
Total	742.5574

Percentage of gaseous products of combustion reaction of methylated glycerol

- CO2
- H2O
- N2
- SO2
- O2
- Ashes

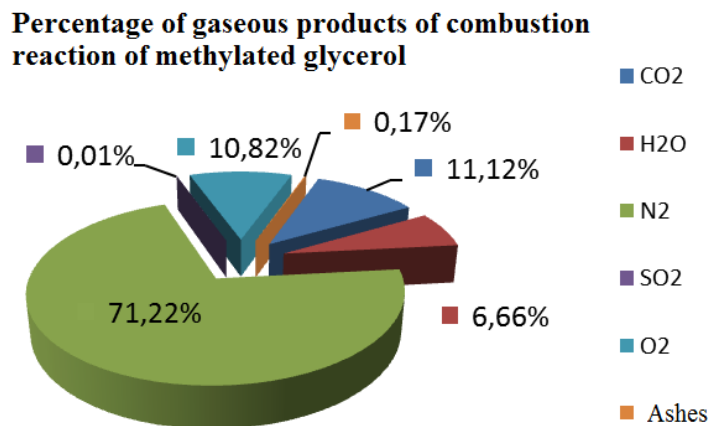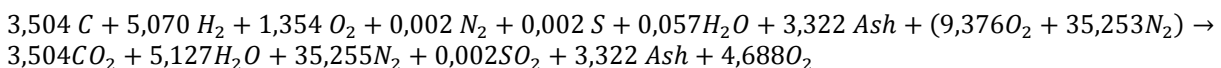0,01% 10,82% 0,17% 11,12% 71,22% 6,66%

Figure 8. Exhaust gas products

5.6. Reactions with excess of air

For gaseous fuels, an excess of air is provided about 1% and 2%, while for liquid fuels, about 5% and 10% (CARVALHO and MCQUAY, 2007). For solid fuels, like powdered coal, excess of air can reach 25% (GILL *et al.*, 1987). In incineration processes, is common to work with excess of air over 100% (DEMPSEY e OPPELT, 1993).

Acrolein is the product of glycerol combustion reaction, and even being in small proportions, the presence is unwanted, because is a carcinogenic chemical compound. To evite acrolein as product of reaction and considering, for this study, that glycerol is burnt in a small industrial burner, the reaction is used with excess of air, to ensure complete reaction of glycerol and acrolein will not be formed (MATURANA, 2011).

So, realizing combustion reaction with 100% of air excess:

$$3,504\,C + 5,070\,H_2 + 1,354\,O_2 + 0,002\,N_2 + 0,002\,S + 0,057\,H_2O + 3,322\ Ash + (9,376\,O_2 + 35,253\,N_2) \rightarrow$$
$$3,504\,CO_2 + 5,127\,H_2O + 35,255\,N_2 + 0,002\,SO_2 + 3,322\ Ash + 4,688\,O_2$$

Emissions of exhaust gases resultants of demethylated glycerol combustion of bovine fat with 100% air excess can be given in figure 9 and Table 4.

Tabela 4 - Gas combustion products

Gases	Amount (g/mol)
CO_2	154.1833
H_2O	92.29
N_2	987.1346
SO_2	0.156
O_2	150.0113
Ash	2.331
Total	1386.106
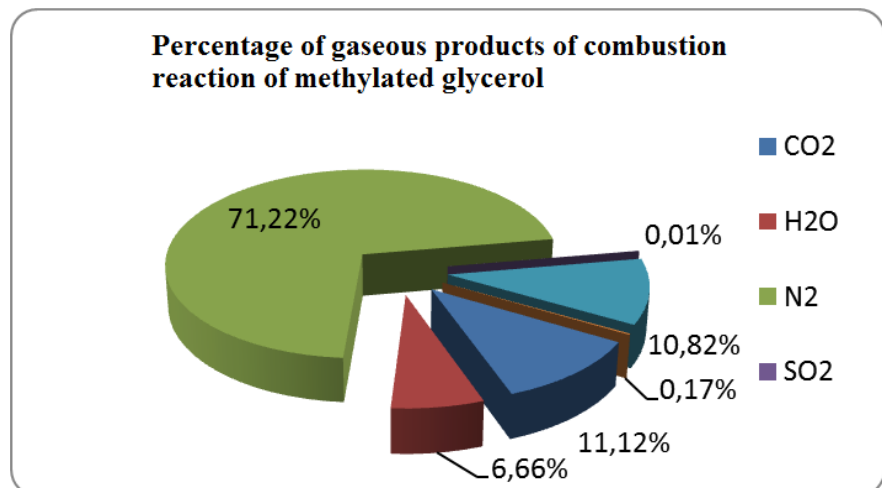
Figure 9. Exhaust gas products

6. CONCLUSION

Using ethanol to produce biodiesel, with 1000 kg/h mass flow of soybean oil, according this study, was produced 1001.603 kg/h of biodiesel and 105.197 kg/h of crude glycerol, corresponding to 10.50% of biodiesel, the same value found in another scientific literature.

The mass flow of crude glycerol necessary to supply the boiler was 609.907 kg/h, or 579% higher than produced flow. Thus, necessary biodiesel flow was calculated to use in supplementary burn in boiler. Necessary biodiesel flow is 256.896 kg/h, with all glycerol burned in boiler, Figure 10.
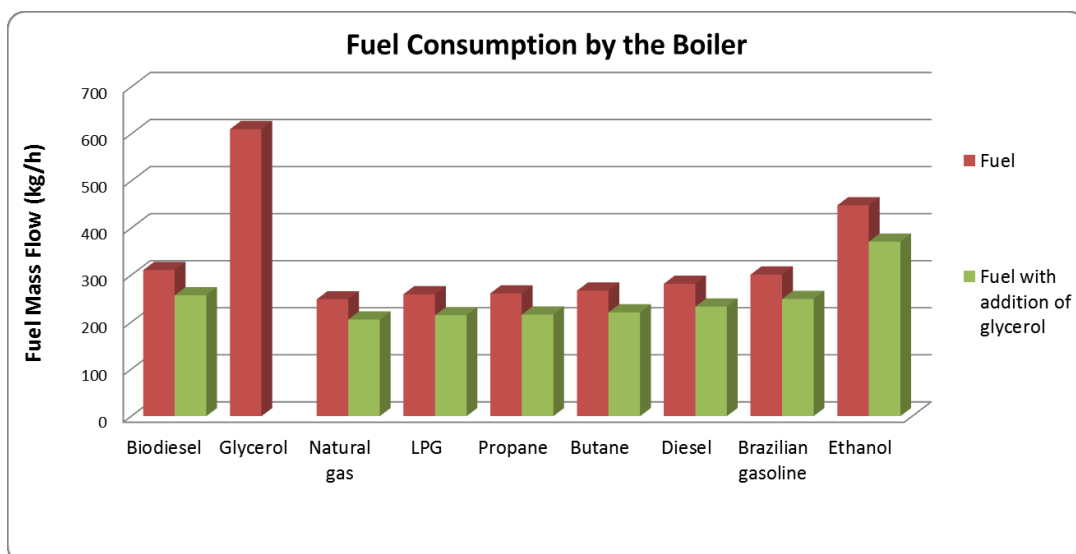

Figure 10. Fuel Consumption by the boiler

Considering that this biodiesel production plant could use own biodiesel as fuel in boiler. This plant need 310.441 kg/h, or 30,99% of biodiesel produced. On the other hand, adopting all crude glycerol burned in this plant, the value was reduced to 256.896 kg/h, or 25.65% of biodiesel produced. With the price of biodiesel set at about 30 cents USD/kg, the savings is about 15000 USD/mouth, Figure 11.
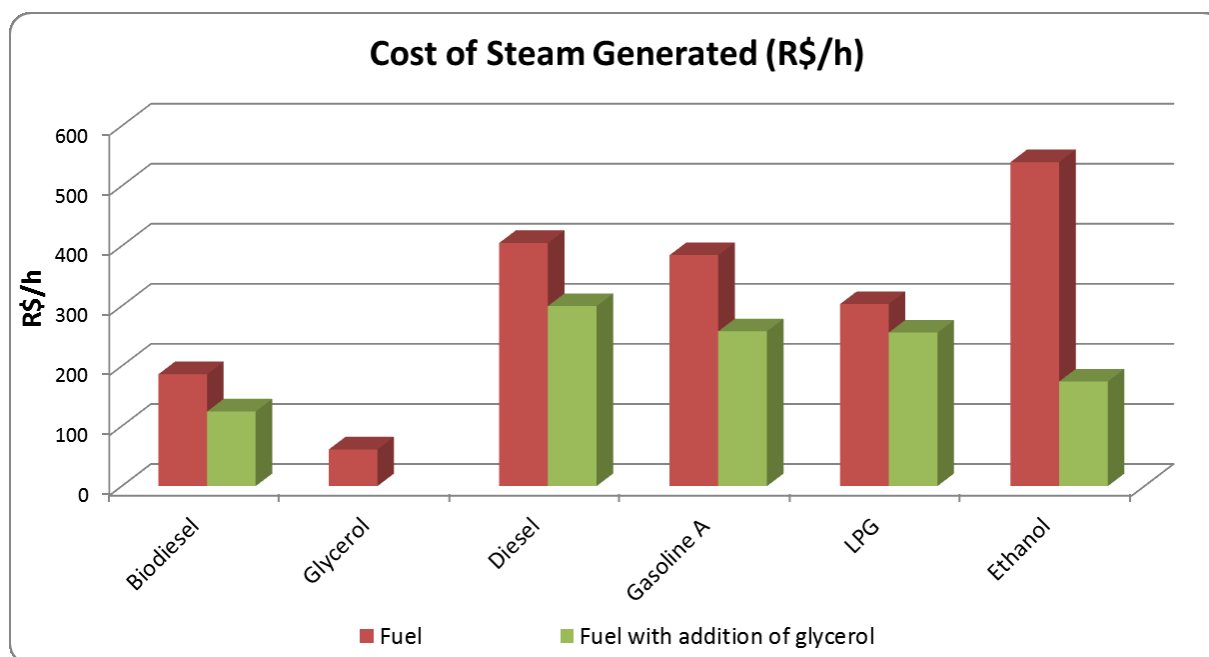

Figure 11. Cost of Steam Generated

In this study was proposed the burn of crude glycerol due to the higher calorific value compared with the demethylated glycerol, and also for his low cost. Crude glycerol has high calorific value because has higher concentration of dross in composition, including alcohol reagent used in process, increasing the HHV.

Between exhaust gases products in burn of methylated glycerol, N_2 is the most issued, follow by CO_2 and water. Ashes and SO_2, undesirable gases, are issued in smaller proportions, which is interesting for process, even the best was these gases weren't appear. SO_2 is only issued in methylated glycerin combustion of (BOHON, 2011), due presence of sulfur in composition.

The combustion reaction with excess of air, which was used in this study, it had the same position of gases, with addiction of oxygen. Oxygen is issued due air excess on reaction, with intention to evite the presence of acrolein as combustion product. Is important to highlight that one problem with combustion glycerol is about salts issued. These salts contribute with corrosion of boilers and heat exchanger. Recently various studies have been directed to resolve or decrease this problem. The content of salts is evidenced by the ash content in the crude glycerol has in its chemical composition.

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