Ecological efficiency in glycerol combustion

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HIGHLIGHTS

- Calculate the quantitative environmental factor by use glycerol as boiler fuel in biodiesel plants.
- Ecological efficiency mainly evaluates the Carbon Dioxide Equivalent.
- NO_x, SO_x and MP emissions from the combustion of glycerol.

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ABSTRACT

Growth in biodiesel production has led to a large surplus of glycerol. So the fundamental question arises: What can be done with glycerol? This is one of the main reasons current research is aimed at developing technologies for the conversion and/or use of glycerol in order to enhance the biodiesel industry and dramatically improve its profitability. This study evaluates and quantifies the environmental impact of glycerol combustion in biodiesel production plants that utilize boilers to produce thermal energy for the process. The concept of ecological efficiency mainly evaluates the environmental impact caused by CO_2, SO_2, NO_x and particulate matter (PM) emissions. It is possible to calculate the quantitative environmental factor and the ecological effect of a biodiesel plant utilizing glycerol as boiler fuel. °USP glycerin has the best ecological efficiency among the evaluated fuels while demethylated and methylated glycerols have the worst performance from the ecological point of view.

1. Introduction

For the last three decades, the world has been dealing with an energy crises caused by the depletion of fossil resources, increase in environmental problems, and the cost of derivates. This situation has resulted in a search for an alternative renewable fuel, which must not only be sustainable, but also environmentally friendly and technologically and economically competitive. Global production of biofuels has increased rapidly over the last decade; the production of biodiesel in the European Union has grown exponentially [1–3]. Among the key factors leading to increased production and demand for biofuels are rising oil prices, growing worldwide concern about global climate change, and improving energy stability. The benefits to agriculture and rural areas lead to increased economic development in many developing countries [4,5].

Biodiesel plants which utilize natural gas or fuel oil as fuels cause problems to the environment; their byproducts cause damage to human beings, animals, and plants. The main byproducts generated from combustion are carbon oxides (CO and CO_2), sulfur oxides (SO_2 and SO_3), and nitrous oxides (NO and NO_2, denoted by NO_x). There are other components that cause equal damage during combustion: particulate matter puts the environment at greater risk, as do other pollutants, for they change soil temperature and influence plant growth. CO_2 emission is directly linked to the greenhouse effect. One of the negative consequences of SO_2 is acid rain (to which NO_x contributes). Combustion of material such as heavy metals and dioxins produces other hazardous components which are harmful to the environment in even small concentrations [6].

This study consists of a comparative analysis of pollution from glycerol combustion in a biodiesel plant, utilizing boilers to produce thermal energy for the process and an examination of individual CO_2, SO_2, NO_x and PM emissions. The method analyzes boiler efficiency from an ecological standpoint.

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The main objective of this work is to briefly show the scope of glycerol, especially state of the art glycerol combustion and combustion reactions, and calculate the ecological efficiency of boilers that use glycerol as fuel to provide heat in the biodiesel production process. In spite of the authors having published previous work [7,8] related to the theme of ecological efficiency, in this manuscript the authors propose and argue that the ecological efficiency formula originally proposed by Cardu and Baica [6], and worked by Lora and Salomon [9] and Villela e Silveira [10], cannot be applied for any fuel and energy conversion process. In the special case of glycerol whose firing is carried out in small boilers, the formula proposed in this work is completely different from the original.

Finally, this manuscript does not address the technical issues concerning the combustion of glycerol. However, it mentions some of the difficulties to burn glycerol. The ecological efficiency values will be obtained for a thermodynamic efficiency of the steam generator between 50% and 90%.

2. Glycerol

Glycerol is the main component of triglycerides. It is found in animal fat, vegetable oil, or crude oil. Glycerol is derived in soap and biodiesel production [11,12]. Glycerol was isolated by heating fat mixed with ashes to produce soap in 2800 BCE [13]. However, it is considered to have been discovered in 1779 by Swiss pharmacist K.W. Scheele, who was the first to isolate this compound when he heated a mixture of litharge (PbO) with olive oil. In 1811, French chemist M.E. Chevrel stated that glycerol was a liquid, defining the chemical formulas of fatty acids and the formulas of glycerin in vegetable oil and animal fat. His work was patented. It was the first industrial method used to obtain glycerol soap by reacting fatty material with lime and alkaline material [14]. This manuscript does not discuss extensively a review of glycerol. For more details, it is recommended to see the studies published by Quispe et al. [15] and Rahmat et al. [3].

Biodiesel production results in a relatively large amount of byproducts and residue, such as gluten flour, gluten, pulp, waste water and crude glycerol [15]. Natural glycerol is initially produced in a raw form that contains water and other residues as impurities depending on the production process. Generally, glycerol is obtained as a byproduct when biodiesel is produced by transesterification using a basic catalyst (NaOH or KOH) and one short chain alcohol, preferably methanol (The reaction temperature and time is 55 °C and 60 min, respectively, with a molar ratio, alcohol:oil, 6:1). Crude glycerol is obtained as a result of this process. It is the form of glycerol that is most sold by biodiesel producers [11,15].

2.1. Properties and characterization

The term "glycerol" is only applicable to pure 1,2,3 propanotrial, while the term "glycerin" normally applies to purified commercial products with contents of more than 95% glycerol.

Many researchers report different values for glycerol's low heating value, or LHV. Soares et al. [16] report a LHV of 16.07 MJ/kg; Silva and Müller [17] report 16.18 MJ/kg; Vaz et al. [18] report LHV of approximately 19.0 MJ/kg; while Thamsiriroj and Murphy [19] report LHV 19.2 MJ/kg for glycerol obtained as a byproduct of biodiesel production using seeds and 14.82 MJ/kg for glycerol obtained from fat residue. Combustion heat of first use oil has an average LHV of 19.56 MJ/kg, around 10% higher than that of pure glycerol, which is 17.96 MJ/kg [20]. Table 1 lists the most important physical and chemical properties of glycerol.

Table 2 shows an analysis of three types of glycerol and 04 different authors [24–27]. Thompson and He [28] characterized glycerol obtained in biodiesel production utilizing various raw

Table 1
Chemical properties of glycerol.

Properties	Unit	Morrison [21]	Pagliaro and Rossi [22]	OECD-Sids [23]
Molecular formula			$C_3H_5(OH)_3$	$C_3H_8O_3$
Molar mass	g/mol	92.09	92.09382	92
Relative density	kg/m³	1260	1261	1260
Viscosity	Pa s	1.41	1.5	1.41
Melting point	°C	18	18.2	18
Boiling point (101.3 kPa)	°C	290	290	290
Flash point	°C	177	160(closed cup)	160
Specific heat	kJ/kg	2435 (25 °C)	–	–
Heat of vaporization	kJ/k mol	82.12	–	–
Thermal conductivity	W/(m K)	0.28	–	–
Heat of formation	kJ/mol	667.8	–	–
Surface tension	mN/m	63.4	64.0	63.4
pH (solution)		7	–	–
Self-ignition	°C	–	–	393

materials. Table 3 shows the analytical results of crude glycerol characterization.

Commercially, according to the degree of purity, glycerol receives the following names: raw or crude glycerol (methylated glycerol); blonde glycerol, commercial or semi-processed (demethylated glycerol); and refined glycerin (°USP glycerin). The crude glycerol generated from tallow or animal fats which are regarded in general is the lowest quality among glycerols. The crude glycerol typically contains between 40% and 80% glycerol. Blonde glycerol is produced from crude glycerol generally subjected to a process of flash evaporation, filtration, and addition of certain chemicals. Blonde glycerol contains 80%–90% of glycerol. The refined glycerin is a set of glycerin with industrial application. The names most known and used internationally, based on USP (U.S. Pharmacopeia) and FCC (Food Chemicals Code) standards are shown in Table 4. °USP Glycerin is one that meets the requirements for use in food and drugs and the FCC for food. The Kosher vegetable glycerin is one that meets the requirements for use in food in the Jewish community [1,26,29]. Finally, °USP grade glycerin is far from cost effective as a fuel; it will be used in the calculations only as a comparison. This explanation is reinforced in the final conclusions.

About Table 2, it can be observed that the water content reported by Bohon et al. [24] for both methylated and demethylated glycerol, are very low. On the other hand, the calorific value of demethylated glycerol reported by Steinmetz et al. [25] is very high, considering that demethylated glycerol should have a calorific value lower than methylated glycerol because it has less content of methanol in its chemical composition. The crude glycerol (methylated glycerol) and blonde glycerol reported by Maturana [26] present more reliable values according to the commercial market of glycerol.

2.2. State of the art of glycerol combustion

Glycerol is biologically produced, renewable, and biodegradable. The production process is part of the green refining industry, which gives it great environmental value and encourages independence from fossil fuel [3]. Using glycerol doesn't increase atmospheric pollution globally, even when it is burnt as fuel. Usage of glycerol as a fuel in industrial processes has advantages. It is advantageous because it doesn't require any purification. Combining this use of glycerol with biodiesel production would have additional advantages in energy integration, eliminating the cost of transportation and use of fossil fuels [30]. Though it is known that glycerol has a moderate calorific level ($\sim$16 MJ/kg), it hasn't yet been used as a fuel on an industrial scale [3,24,30–35].

Table 2
Analysis of three types of glycerol fuel derived from soybean oil.

Substance	Bohon [24]			Steinmetz [25]		Maturana [26]		Striugas [27]
	A	B	C	B	C	B	C	C
C (%)	39.1	42.05	67.27	45.21	49.46	50.29	30.48	
H (%)	8.7	10.14	11.43	10.40	9.57	9.66	7.64	
N (%)	0	<0.05	<0.05	<0.31	<0.27	2.60	1.96	
O (%)	52.2	43.32	17.06	41.79	37.72	37.21	49,91	
S (%)	0	0.078	<0.05	<0.28	<0.20	0.24	–	
H_2O (%)	0	1.03	1.47	3.48	2.48			
Ash (%)	0	3.06	2.23	2.28	3.12			
Glycerol (%)		50–70	70–88			48.5	80	80
MONG		1–5	1–5			46	3	
H_2O		3–10	5–15			1.5	7	9
Ash						4	10	0.085
Density (20 °C)	1280					1061	1290	1260[a]
HHV (MJ/kg)	16.0	21.8	20.6	22.7	26	25.23	14.75	12.2[b]

A = °USP glycerin.
B = Methylated glycerol (Crude glycerol).
C = Demethylated glycerol (Blond glycerol).
C = Demethylated glycerol (Blond glycerol).
MONG = material organics no glycerol.
  [a] (15 °C).
  [b] (LHV).

However, burning glycerol isn't easy from the technological point of view. Some of the difficulties cited by researchers are: a) it has a low calorific value, which makes it incapable of maintaining a stable flame in a conventional burner, which is made more difficult by water in the mixture; b) it has a high self-ignition temperature, approximately 370 °C. Gasoline self-ignites at 280 °C and kerosene at 210 °C; c) burning glycerol can form acrolein; d) it is highly viscous at room temperature (kinematic viscosity approximately 450 cSt), making it hard to atomize with conventional atomizers; e) its salt content causes corrosion problems in burner injectors and in post-combustion systems, and it is also a flame inhibitor, which makes it difficult to burn [24,29].

Glycerol hasn't yet been co-burned with other liquid or solid fuel on a large scale [36]. Based on its ignition point, direct thermal use of crude glycerol is an obvious choice. Studies have reported favorable results when co-burning crude glycerol with other biomass [1]. An attractive and relatively simple option for glycerol it to use it as furnace fuel to produce heat and electricity [37]. According to DAF [38] and Bombos et al. [39], modern boilers are designed to withstand high thermal loads in the furnaces, so using glycerol directly in existing boilers is unacceptable because of the high ignition point and low adiabatic flame temperature. For six years, one of the most common uses of crude glycerol was incineration [38,40].

The burning of a mix of crude glycerol with yellow grease has been investigated in an industrial tube boiler [41]; in order to maintain a flame in the industrial fire tube boiler, a small amount of glycerol (10% V/V) was co-fired with the grease (90% V/V). Waste glycerol was mixed with waste biomass to produce combustible pellets as an alternative to coal [42]. Patzer [41] reported that crude glycerol used in small amounts as a mixture could be a viable fuel, taking into consideration the price on the international market, but not when analyzed only as a fuel. He reported that glycerol couldn't maintain a stable flame and had a lot of mineral salt emissions that corrode equipment and reduce its life span.

Stiurgas [27] studied the possibility of commercial usage of stable emulsions of glycerol and heavy oil. According to this author, the final stable emulsion was made up of 1.3% sodium oleate or soap, 3% monoglyceride fatty acid, 8% methanol, 26.5% methyl ester (biodiesel), 27.2% glycerol, and 34% heavy fuel oil. The combustion system used was modified: the adiabatic combustion chamber was pre-heated to 1000.00 °C using natural gas, a modifier burner, and a 40 bar fuel pump. The fuel was electrically heated to between 60 and 85 °C and a cyclone was used to collect and analyze particulate matter. Table 5 shows a summary of combustion results obtained by Striugas [27].

Metzger [29] also utilized modified equipment to directly burn glycerol using a 7 kW vortex-type burner and an adiabatic combustion chamber to improve burn and flame stability. This author used laboratory grade glycerol (°USP glycerin), methylated glycerol, and demethylated glycerol as fuel.

Bohon et al. [24] continued Metzger's work and improved the burner he'd used before. Through elaborate computer simulations, Bohon et al. [24] improved insulation, operation, and experimental usefulness of the burner by diminishing loss and improving stability of the glycerol flame. He also used Metzger's 7 kW burner [29] and an 82 kW vortex-type burner linked to a small refractory furnace. The tests were carried out using °USP glycerin, methylated glycerol, and demethylated glycerol as fuel.

Table 3
Analysis results of measurement of macro elements carbon and nitrogen in crude glycerol [1].

Feedstock	IdaGolg	PacGold	Rapeseed	Canola	Soybean	Crambe
Calcium (ppm)	11.7	23	24	19.7	11.0	163.3
Potassium (ppm)	BDL	BDL	BDL	BDL	BDL	216.7
Magnesium (ppm)	3.9	6.6	4.0	5.4	6.8	126.7
Phosphorus (ppm)	25.3	48.0	65.0	58.7	53.0	136.7
Sulfur (ppm)	21.0	16.0	21.0	14.0	BDL	128.0
Sodium (%wt)	1.17	1.23	1.06	1.07	1.20	1.10
Carbon (%wt)	24.0	24.3	25.3	26.3	26.0	24.0
Nitrogen (%wt)	0.04	0.04	0.05	0.05	0.04	0.06

BDL indicates values that are below the detection limit for the corresponding analytical method. The detection limits in ppm were: calcium: 2, potassium: 40; magnesium: 0.20; sodium: 80; phosphorus: 5; sulfur: 15; carbon: 200; and nitrogen: 100.

Table 4
°USP glycerin Ref. [26].

Name	% Purity
Technical Grade	99.5
Bidistilled	99.5
USP, vegetable base	96
USP, based tallow or animal fat	99.5
USP/FCC – Kosher	99.5
USP/FCC – Kosher	99.7

Table 5
Summary of emissions tests results, combustion of demethylated glycerol (80% glycerol) [27].

Pollutant	Unit	Results	Process parameters	
			Glycerin consumption	13 kg/h
Particulate matter	g/m^3	11.9	Load	45 kW
Nitrogen oxides	ppm	88	O$_2$	2.4% v/v
Carbon monoxide	ppm	73	Coefficient of excess air	1.13
Sulfur dioxide	ppm	10	Pressure before atomizer	28 bar
Combustion of stable glycerol emulsion			Emulsion consumed	6 kg/h
Particulate matter	g/m^3	0.5	Load	37 kW
Nitrogen oxides	ppm	277	O$_2$	3.6% v/v
Carbon monoxide	ppm	100	Coefficient of excess air	1.18
Sulfur dioxide	ppm	993	Pressure before atomizer	10 bar

Acrolein is a product of thermal decomposition of glycerol when it is heated between 280 and 300 °C, which are well below glycerol's self-ignition temperature [38]. Acrolein is toxic in very small quantities, around 2 ppm. Some studies suggest human health risk with concentrations as low as 0.09 ppm. Acrolein is increasingly unstable at high temperatures and highly flammable, totally consumed between 930 and 1000.00 °C [43]. It's conceivable that an efficient glycerol flame could consume any acrolein produced before combustion gases are used up in the environment [29,44].

The remaining alcohol, along with sodium and potassium salt and other impurities, must be analyzed because they are known to inhibit various processes [45,46]. Mineral compounds sometimes found in glycerol are sodium or potassium chlorates, potassium sulfate, or potassium phosphate. Compounds based on alkaline metals Na and K have high fusion and softening temperatures. As a result, the conditions in which glycerol burns have a great potential to generate slag and pollution is greater than with liquid fossil fuels [37]. The salt that enters the boilers can become encrusted on the walls and shorten the equipment's life span [47]. If the salt isn't removed, it creates significant amounts of ash [48]. Amberlite 252 macroporous resin could be a good choice to remove sodium ions from glycerol/water solutions with high salt concentration [49,50].

3. Ecological efficiency

3.1. Pollutant emissions

Environmental impact studies of a boiler that burn glycerol must be made. They must take the following pollutants into consideration: nitrogen oxides (NO$_x$), carbon monoxide (CO$_2$), sulfur dioxide (SO$_2$), particulate matter (PM), volatile organic compounds (VOC), and total organic compounds (TOC-hydrocarbons).

3.2. Equivalent carbon dioxide

The coefficient for equivalent carbon dioxide (CO$_2$)$_e$, (a hypothetical pollutant concentrations factor) was introduced by Cardu and Baica [6] in a study entitled "Regarding a global methodology to estimate the energy-ecologic efficiency of thermopower plants". In that paper, the notions of "Carbon Dioxide Equivalent" and "Pollution Indicator" were introduced as two characteristics of the fuel used in thermopower plants [6,51]. To calculate this coefficient, the value of the CO$_2$ was divided by the maximum permissible concentration (10,000 mg/m^3, approximately 5160 ppm) and by the maximum admissible concentration for some harmful gases (SO$_2$ and NO$_x$) in the atmosphere of the work place (Table 6). The maximum admissible concentration for particulate matter (PM), according to CONAMA (Brazil's National Environmental Council)

Table 6
CO$_2$ multiplication factor of SO$_x$ gases, PM, and NO$_x$.

Maximum acceptable limit (mg/m^3)				Multiplication factor		
CO$_2$	SO$_x$	NO$_x$	PM	SO$_x$[a]	NO$_x$[b]	PM[c]
10,000	15	10	45	666	1000	222

[a] CO$_2$/SO$_x$ [6].
[b] CO$_2$/NO$_x$ [6].
[c] CO$_2$/PM [6].

Resolution n°382, 26 December 2006, for a maximum oxygen content of 5% is 50 mg/Nm^3.

Thus, the expression for (CO$_2$)$_e$ is:

$$(CO_2)_e = (CO_2) + 666\ (SO_2) + 1000\ (NO_x) + 222\ (PM) \qquad (1)$$

In Eq. (1), (SO$_2$)$_e$ = 666(SO$_2$) is the sulfur dioxide equivalent in (CO$_2$), (NO$_x$)$_e$ = 1000(NO$_x$) is the nitrogen dioxide equivalent in (CO$_2$), and the particulate matter equivalent in (CO$_2$) is (PM)e = 222(PM). The best fuel from an ecological standpoint is that which has a minimum amount of (CO$_2$)$_e$ released when burned. In order to quantify environmental impact, the Pollution Indicator ($\prod_g$) is defined by Eq. (2):

$$\prod_g = \frac{(CO_2)_e}{Q_i} \qquad (2)$$

in which (CO$_2$)$_e$ is expressed in kg/kg (kg per kg of fuel), Q_i is the low heating value of the fuel expressed in MJ/kg, and $\prod g$ is expressed in kg/MJ.

3.3. Ecological efficiency

Ecological efficiency "ε" is an indicator which allows the performance of a thermoelectric power plant to be evaluated in respect to pollutant emissions by comparing hypothetically integrated pollutant emissions (CO$_2$ equivalent emissions) to existing air quality standards. Conversion efficiency is also considered a determining factor for specific emissions; it is expressed by a fraction. As mentioned above, the methodology for environmental analysis using ecological efficiency was proposed initially by Cardu and Baica [51] for thermal power plants with steam cycles using coal as fuel. Eq. (3) is the ecological efficiency equation proposed by Cardu and Baica for thermoelectric power plants [6,51].

$$\varepsilon = \left[\frac{0.204\,\eta}{\eta + \prod_g} \ln\left(135 - \prod_g\right) \right]^{0.5} \qquad (3)$$

The aspects that define the environment impact intensity unit are fuel composition, combustion technology, pollution indicator, and thermodynamic efficiency. "ε" is directly proportional to thermodynamic efficiency (η), inversely proportional to $\prod_g$, and alternates between 0 and 1 as does thermoelectric efficiency. The situation is considered to be ecologically unsatisfactory when $\varepsilon = 0$ ($\prod_g = 134$) for any value of η; On the other hand, $\varepsilon = 1$ ($\prod_g = 0$) for any value of η indicates an ideal situation for standards of energy efficiency. To better explain this parameter, the fuel classification of two virtual fuels would be that pure hydrogen would have 0% of impact on the environment (if one considers that all the hydrogen reacts like water, ignoring the possible formation of NO$_x$ due to high temperatures in combustion equipment), while sulfur would cause a 100% impact.

3.4. Methodology

Ecological efficiency values of boilers in a biodiesel plant for °USP glycerin, demethylated glycerol, methylated glycerol, diesel,

fuel oil, natural gas, and LPG, and the characteristics of these fuels are examined next.

Table 2 shows the composition by weight of glycerol types evaluated. For the calculations, the methylated and demethylated glycerol reported by Maturana [26] and °USP glycerin reported by Bohon et al. [24] were chosen. For °USP glycerin used in this evaluation, density is 1280 kg/m^3, molecular weight is 92 g/gmol, and LHV is 12.8 MJ/kg. For methylated glycerol, density is 1061 kg/m^3 and LHV is 20.5 MJ/kg; for demethylated glycerol, density is 1290 kg/m^3 and LHV is 12 MJ/kg. The combustion reactions were carried out considering a air excess of 40%.

The traditional chemical formula for diesel is $C_{12}H_{26}$. Its density is approximately 860 kg/m^3, molecular weight is approximately 170 g/gmol, and LHV is 42 MJ/kg [52].

The chemical composition of liquefied petroleum gas (LPG) is 30% Butane and 70% Propane. Its density is approximately 2.152 kg/Nm^3, molecular weight is approximately 48.2 g/gmol, and LHV is 48 MJ/kg [52].

According to COMGAS (the Gas Supply Company for the State of São Paulo), the volumetric composition of natural gas may be the following: CH_4 (methane): 89.3%; C_2H_6 (ethane): 8%; C_3H_8 (propane): 0.8%; C_4H_{10} and C_5H_{12} (butane and pentane): 0.05%; CO_2 (carbon dioxide): 0.5%; and N_2 (nitrogen): 1.3%. Natural gas at normal temperature and pressure conditions (0 °C, 101.3 kPa) has a mass of approximately 790 g/Nm^3. The maximum total sulfur is Nm^3 of natural gas will be 20 mg, which is 0.0028% of fuel mass [10,53]. Molecular weight is approximately 17.7 g/gmol and LHV is 54 MJ/kg [52].

Finally, the fuel oil has a density of approximately 1036 kg/m^3 and LHV is 38.9 MJ/kg [52].

3.5. The case of carbon in glycerol

Biomass-derived fuels decrease net atmospheric carbon in two ways: first, they participate in the relatively rapid biological cycling of carbon to the atmosphere and from the atmosphere (via photosynthesis); second, they replace fossil fuels. Fossil fuel combustion releases carbon that took millions of years to be removed from the atmosphere. Combustion of biomass fuels participates in a process that allows CO_2 to be rapidly recycled to fuel [54]. The main goal of the use of bio-fuels such as glycerol and biodiesel is to reach the targets of the Kyoto Protocol by decreasing emissions of gaseous pollutants into the atmosphere, especially CO_2 emissions.

A 1998 biodiesel life cycle study [54] jointly sponsored by the US Department of Energy and the US Department of Agriculture concluded that biodiesel reduces by 78% the net CO_2 emissions compared to diesel derived from petroleum. This is because biodiesel has a closed carbon cycle. Taking this into consideration, the result for B100 (pure biodiesel) is: 0.578 ton CO_2 per m^3 of biodiesel [55]. Glycerol is a biofuel from the same vegetable oil that served as raw material for producing biodiesel. Therefore burning of glycerol will result in the same reduction of CO_2 (78%). There is 0.39 ton CO_2 per m^3 of glycerol.

3.6. Ecological efficiency calculation

A new equation is being proposed for this study following the methodology proposed by Cardu and Baica [6,51] for calculating ecological efficiency using as base different glycerol combustion and thermal efficiency scenarios for an industrial boiler. These results will be compared with traditional fuel. Cardu and Baica [6,51] introduced an equation that follows the proportionality of cycle efficiency and the inverse proportionality of the Pollution Indicator ($\prod_g$) in relation to ecological efficiency. The expression for the new ecological efficiency calculation can be given by Eq. (4):

Table 7
Carbon dioxide equivalent and pollutant indicator.

	CO_{2e} (kg/kg fuel)	LHV (MJ/kg)	Pollution indicator (kg/MJ)
Hydrogen[a]	0	120.1	0
Demethylated glycerol	23.242	12.00	1.936
Methylated glycerol	10.033	20.48	0.489
°USP glycerin	0.335	12.80	0.026
Diesel	12.512	42.71	0.293
Fuel oil	14.294	38.90	0.367
Natural gas	5.600	54.27	0.103
LPG	3.101	47.45	0.065
Sulfur[b]	1332	9.21	144.6

[a] $\varepsilon = 1$.
[b] $\varepsilon = 0$.

$$\varepsilon = \left[c \cdot \frac{\eta}{\eta + \prod_g} \cdot \ln\left(K - \prod_g\right) \right]^z \tag{4}$$

The following conditions apply to constants c, K and z:

1. K must be set at 145.6, which is the combustion point of sulfur. For this fuel, the lowest ecological efficiency ($\varepsilon = 0$) must be reached for any value of η (Table 7).
2. When the value of K had been determined, constant c is calculated using the combustion of hydrogen (an ideal fuel). For this fuel, the highest ecological efficiency ($\varepsilon = 1$) must be reached for any value of η (Table 7).
3. Among the fuels shown in Table 7, the Diesel has an intermediate value of Pollution Indicator ($\prod_g = 0.29$). To assess the value of constant z, the ecological efficiency value for diesel is set at 50% ($\varepsilon = 0.5$) for boiler efficiency values between 70 and 80%. Results obtained for z range from 2.2 (for 70% boiler efficiency) to 1.6 (for 80% boiler efficiency). The mean value is $z = 1.9$.

A new formula can be presented for calculating the ecological efficiency of different types of glycerol and traditional fuels using these conditions and values, Eq. (5):

$$\varepsilon = \left[0.2 \cdot \frac{\eta}{\eta + \prod_g} \cdot \ln\left(145.6 - \prod_g\right) \right]^{1.9} \tag{5}$$

The emission factors used for this study are shown on Table 7. Table 8 shows a comparison between the fuels (°USP glycerin,

Table 8
Emission factor used as reference to calculate ecological efficiency.

Item	Combustion process	Emission factors	Reference
NO$_x$	°USP Glycein burned in a furnace	9 at 0% O_2 (ppm)	[24]
	Crude glycerol in a furnace	14×10^{-5} kg/kg fuel	[26]
	Blonde glycerol in a furnace	58×10^{-5} kg/kg fuel	[26]
	Diesel burned in boilers	2.4 kg m^{-3}	[56]
	Fuel oil burned in boilers	5.04 kg m^{-3}	[56]
	Natural gas burned in boilers	0.00227 kg m^{-3}	[56]
	Liquid Petroleum Gas burned in a burner	22.94 mg/Nm^3	[57]
PM	Glycerol burned in a furnace	>3000 mg/m^3	[24]
	Diesel burned in boilers	0.24 kg m^{-3}	[56]
	Fuel oil burned in boilers	1.25 kg m^{-3}	[56]
	Natural gas burned in boilers[a]	8×10^{-5} kg m^{-3}	[56]
	Crude glycerol in a furnace	48×10^{-5} kg/kg fuel	[26]
	Blonde glycerol in a furnace	12×10^{-5} kg/kg fuel	[26]
SO$_2$	Diesel burned in boilers	17.04 kg m^{-3}	[56]
	Fuel oil burned in boilers	18.84 kg m^{-3}	[56]
	Natural gas burned in boilers	0.0028% of the fuel mass	[10,53]
	Liquid Petroleum Gas burned in burner	225.45 mg/Nm^3	[57]

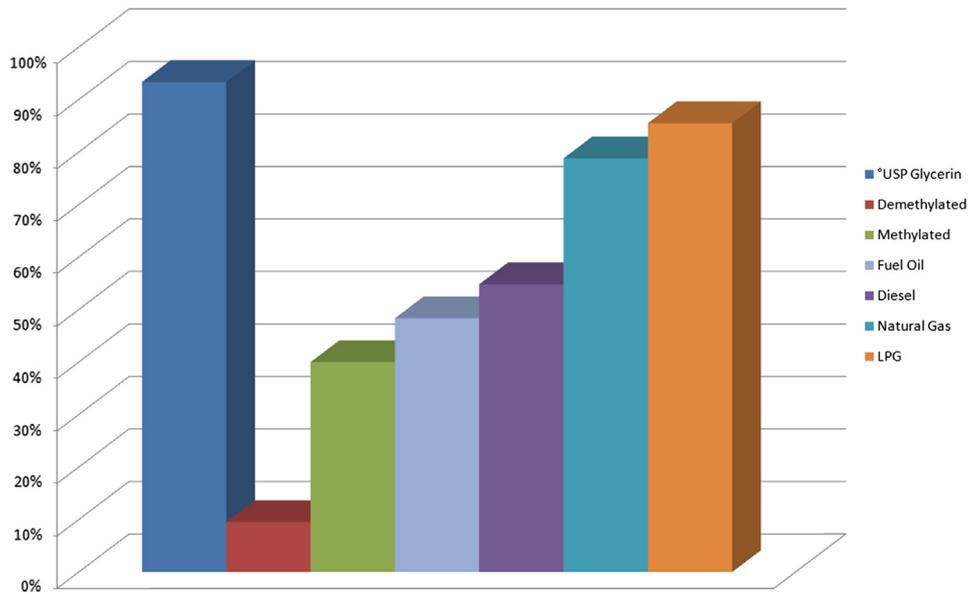[a] The same value will be used for LPG.

Fig. 1. °USP Glycerin, Demethylated glycerol, Methylated glycerol, Diesel, Fuel oil, Natural gas and LPG ecological efficiency. (Boiler efficiency = 80%).

demethylated glycerol, methylated glycerol, diesel, natural gas, fuel oil and LPG) in an industrial boiler. Note that all reactions were performed with an air excess of 40%. Fig. 1 and Table 9 show the ecological efficiency values for the fuels analyzed. Finally, Fig. 2 shows ecological efficiency values in function of boiler efficiency, due to a possible reduction in boiler efficiency when burning glycerol.

3.7. Results

The use of °USP glycerin in an industrial boiler is an excellent option from the global warming point of view. Glycerin fuel had the lowest atmospheric CO_2 emissions; the fuels that released the most CO_2 are diesel fuel and fuel oil.

The carbon released by petroleum diesel was captured from the atmosphere during the formative years of the earth, whereas the carbon released by glycerol and biodiesel gets continuously captured by plants and can be recycled by the next generation of crops. Emissions levels using this kind of biofuel are 78.45% of those of diesel fuel. Emissions calculated are 0.39 tons CO_2/m^3 of glycerol and 0.578 tons of CO_2/m^3 of biodiesel (B100).

Diesel has nine times the total emissions of °USP glycerin based on kg/kg of fuel ratio. Considering a boiler thermal efficiency of 80%, °USP glycerin had an ecological efficiency of 93.4%; demethylated glycerol had 9.5%; methylated glycerol had 40%; diesel had 54.8%; fuel oil had 48.4%; natural gas had 78.8%; and LPG had 85.5%.

In respect to the demethylated glycerol, this fuel, according to Maturana [26], presents 10% wt% of ash, so the content of PM is very high, thus decreasing its ecological efficiency presented (9.5%). As an example, if an ash content of 2.23% is considered, as reported by Bohon et al. [24], the ecological efficiency would be 38.7%; if an ash
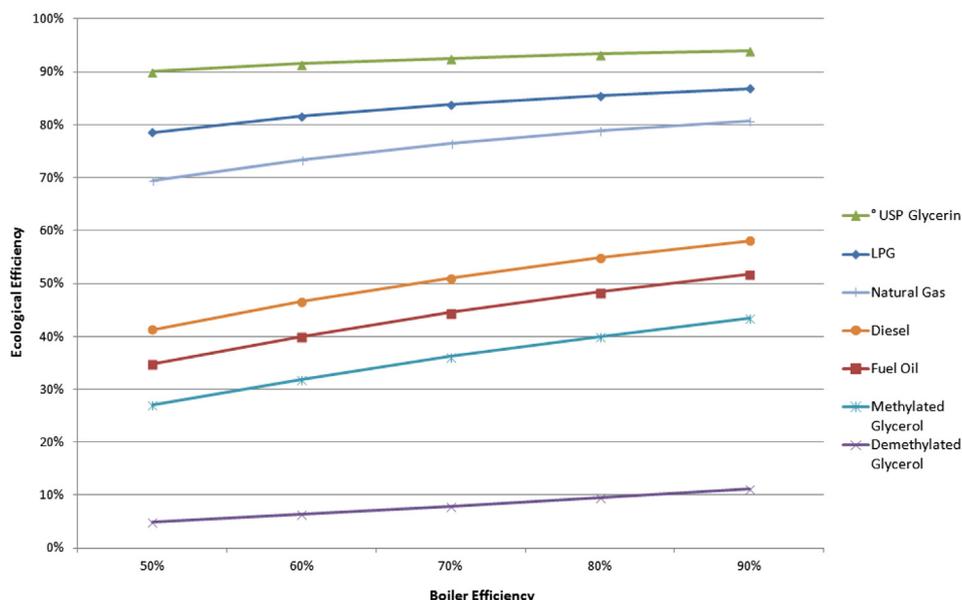

Fig. 2. Variation of ecological efficiency as a function of boiler efficiency.

Table 9
Comparison of pollutant emissions of fuels analyzed in an industrial boiler.

Pollutant emission kg/kg fuel	USP glycerin	Demethylated glycerol	Methylated glycerol	Diesel	Fuel oil	Natural gas	LPG
CO_{2e}	0.335	23.242	10.033	12.512	14.294	5.600	3.101
PM	–	0.1	0.04	2.78×10^{-4}	12.07×10^{-4}	1.013×10^{-4}	0.37×10^{-4}
NO_x	3.42×10^{-9}	58×10^{-5}	14×10^{-5}	2.777×10^{-3}	4.864×10^{-3}	2.874×10^{-3}	1.066×10^{-5}
SO_2	–	12×10^{-5}	48×10^{-5}	9.861×10^{-3}	9.09×10^{-3}	–	1.047×10^{-4}
CO_2	0.335^a	0.3826^a	0.6939^a	3.1058	3.1058	2.7038	2.3642
Total (kg/kg fuel)	0.33553	0.5159	0.7345	3.1188	3.1119	2.7068	3.0126
Ecological Efficiency (%) (Boiler Ef. = 80%)	93.4	9.5	40.0	54.8	48.4	78.8	85.5

[a] Considering the carbon cycle.

content of 2.48% is considered, as reported by Steinmetz et al. [25], the ecological efficiency would be 36.9%. Anyway the ecological efficiency of demethylated glycerol is the lowest of all analyzed fuels.

The use of demethylated and methylated glycerol (real waste from biodiesel production) appears to be a disadvantage from the ecological point of view. This is mainly due to sulfur dioxide and particulate matter emissions. However, application of a simple PM control technology or use of one of the new fixed-bed catalyst systems would solve this problem.

4. Conclusions

A brief review was conducted of the state of the art in glycerol combustion. It was also shown that it is possible to evaluate the environmental impact of burning glycerol in industrial boilers using ecological efficiency parameters.

This study shows that the use of °USP glycerin as is a better fuel alternative than diesel fuel, fuel oil, natural gas, and LPG from an ecological point of view because it has higher ecological efficiency values. However, the best ecological efficiency found (using °USP glycerin) isn't very attractive. Many refinement processes are needed to achieve the 99.5% purity of °USP glycerin, which increases the impact of the product. It is far more valuable as a chemical industry product, pharmaceutical product, or cosmetic feedstock.

Crude glycerol (methylated) is obtained at the end of the process after the acidulation stage. Blonde glycerol (demethylated) is already semi-refined. Crude glycerol should be the suitable glycerol suitable to be used in burning processes. Using these products could improve emissions of pollutants in a biodiesel production plant provided that they are co-firing with some kind fossil fuel (for example, liquefied petroleum gas, natural gas or ethanol). Burning unblended methylated glycerol has the lowest ecological efficiency, even less than diesel fuel.

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