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Ecological efficiency in glycerol combustion

Christian R. Coronado [a,*], João A. Carvalho Jr. [b], César A. Quispe [a,c], Cesar R. Sotomonte [a]

[a] Federal University of Itajubá, Institute of Mechanical Engineering, Av. BPS 1303, CEP 37500903 Itajubá, MG, Brazil
[b] São Paulo State University, Guaratinguetá Campus, Department of Energy, Av. Ariberto Pereira da Cunha, 333, CEP 12516-410 Guaratinguetá, SP, Brazil
[c] San Marcos National University, College of Mechanical and Fluids Engineering, Av. Universitaria/Av. Germán Amézaga s/n. University City, Lima 1, Lima, Peru

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.

* Corresponding author. Tel.: +55 35 3629 1544; fax: +55 35 3629 1238.
E-mail addresses: christian@unifei.edu.br, christian.coronado@pq.cnpq.br (C.R. Coronado).
URL: http://www.getec-unifei.com.br

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

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/m^3	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

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 (~16 MJ/kg), it hasn’t yet been used as a fuel on an industrial scale [3,24,30–35].