

METHODOLOGY FOR FULL COMPARATIVE ASSESSMENT OF DIRECT GROSS GLYCERIN COMBUSTION IN A FLAME TUBE FURNACE

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Abstract. *This study is to develop a methodology to identify and evaluate the emissions and heat transfer associated to combustion of gross glycerin a by-product of the Brazilian biodiesel manufacture process as alternative energy source. It aims to increase the present knowledge on the matter and to contribute to the improvement of the economic and environmental perspective of biodiesel industry. This methodology was considered to be used for assessment of gross glycerin combustion from three different types of biodiesel (bovine tallow, palm and soy). The procedures for evaluation and quantification of emissions of sulphur and nitrogen oxides, total hydrocarbons, carbon monoxide, carbon dioxide, and acrolein were analyzed, described and standardized. Experimental techniques for mutagenic and toxic effects assessment of gases similarly were analyzed and standardized, as well as the calorific power, the associate heat transfer and fundamentals operational parameters. The methodology was developed, using a full-instrumented flame tube furnace, continuous gas analyzers, a chromatograph, automatic data acquisition systems and other auxiliary equipments. The mutagenic and toxic effects of the study was based on Tradescantia clone KU-20, using chambers of intoxication and biological analytical techniques previously developed and others were specially adapted. The benchmark for the initial set up was based on the performance evaluation of the previous equipment tested with diesel considering its behavior during direct combustion. Finally, the following factors were defined for the combustion of crude glycerin, configurations of equipments types, operational parameters such as air fuel ratio adiabatic temperature and other necessary aspect for successful application of the methodology. The developed and integrated methodology was made available to the concern industry, environmental authorities and researchers as procedures to access the viability of gross glycerin or similar fuels as an alternative energy source.*

Keywords: Glycerol, emissions, acrolein, biofuels, biodiesel

1. INTRODUCTION

In recent years, growth in world production of biodiesel has been going exponentially (OPPE E. et al., 2007, J. Thompson, 2006). It is expected that by the end of 2010 in the United States this production will reaches more than 12 million tons per year (Behr et al., 2008). In the case of Brazil, with the government law 11.097/2005, the addition of 2% biodiesel is mandatory to petrochemical diesel between 2008 and 2012, and 5% from 2013. Similar laws are being implemented or are intended to apply in a short time in countries like Colombia, the United States or the European Union. Thus the production of biodiesel in Brazil for 2010 will be approximately 1.5 million tons per year (F. Batista, 2007), which represents about 160 thousand tons of crude glycerin annually.

Glycerin or glycerol (as commonly called in pure form) is 1,2,3-Propanotriol technical name. It is the main by-product of biodiesel production and is generated in an approximate ratio of 10% w/w or 25% molar. Crude glycerin is a mixture of glycerol, water, acids, esters, alkalis and alcohols (Quintella C., et al. 2009). It has typically 40% - 90% of glycerol, 1% - 50% of water, 2% - 8% of methanol and 0% - 10% of salts or other materials.

Although glycerol is a chemical well known for centuries and widely used in the food industry, beverages, cosmetics, plastics, paper, explosives, among others, in recent years is commercially significant increase in their availability. According to Mantovani H., (2006), in Brazil the conventional market usually gets to use approximately 40 thousand tons per year of this. Thanks to the biodiesel industry, this market is currently saturated and more than a half of the glycerol-producing industries have closed (Bonet J., et al., 2009). The oversupply of this product caused the price to fall in the international market (Oleoline, 2005), which can compromise the profitability of the biodiesel industry.

The main strategy used to try to resolve the problem has been finding new uses for glycerol, including animal nutrition, oils and fuels industry, materials, medicine, etc. (Sushil A., et al, 2008; O'Driscoll, C., 2007; Slinn et al., 2007).

This study presents a methodology to assess the feasibility of the direct combustion of crude glycerol as a promising option that can generate usable energy. Besides making an important contribution to the limited knowledge on this subject, especially as related to environmental performance. It's expected to contribute to improving the profitability and sustainability of the biodiesel industry, living conditions, social prospects and economical development of populations in remote areas with poor communication, limited access to energy from fossil fuels and use of wood as a main energy source. This probably is the case in large areas of Latin America, Africa and Asia, where just the transmission and distribution of conventionally generated power is difficult and expensive, so local production from a renewable and cheap energy can be a viable alternative, which helps to reduce deforestation and global warming.

It is a characteristic of biomass-derived fuels has high oxygen (O₂) content, resulting in a low production of particulate matter (PM), carbon monoxide (CO), total hydrocarbons (THC) and low sulfur oxides (SO_x). An example of this is the direct burning of beef tallow in a boiler that originally use diesel as fuel, as reported by Pagliuso, (2006). PM emissions were reduced 78% by mass, THC 77.5% and CO 80.4%. At the same time, it is necessary to investigate if other pollutants might occur. A frequently cited acrolein is an example, in connection with glycerol, which according to the Environmental Protection Agency (EPA) is potentially toxic (EPA, 2003).

2. MATERIALS AND METHODS

The procedures and equipment configurations described here were developed or adapted to assess the direct combustion of crude glycerin co-product of biodiesel manufacture of beef tallow. However, suggests also applicable to other types of combustion of crude glycerol, such as from soy biodiesel, palm and others. According to this methodology, this assessment will be performed comparing the performance observed for the crude glycerin with at least one fuel widely known under similar conditions. In this work, common brazilian diesel was used as test fuel for the methodology. This fuel was supplied by the Brazilian Petroleum Company (Petrobras S.A.) and therefore meets the specifications and standards of the Brazilian Association of Technical Standards (ABNT) and the American Society for Testing and Materials (ASTM).

2.1 Materials

Crude glycerin use for planning this methodology was supply by a commercial biodiesel plant located in Piracicaba, State of Sao Paulo (Brazil). It comes in solid state at room temperature and has the physicochemical characteristics listed in Tab.1.

Table 1. Physicochemical characteristics of Crude Glycerin

Parameters	Units	Value
	Density to 20°	1061
Sodium Chloride	mg/kg	190
pH	-	7.9
Sulfate	mg/kg	7200
Sulfur	mg/kg	2403
Acidity	mg KOH/g	0.86
Citrate	mg/kg	11
Silver Chloride	mg/kg	115
Phosphorus	mg/kg	395
Methanol	% m/m	7.6
Ash	% m/m	4.0
Water	% m/m	1.5
Glycerol	% m/m	48.5
MONG ⁽¹⁾	% m/m	46.4

⁽¹⁾: Matter (Organic) Non—Glycerol (MONG) represents by convention, the difference obtained by subtracting from 100 the sum of the content expressed as a percentage of glycerol, water and ash (IUPAC, 1980).

On the other hand, Fig.1 shows the Higher Heating Value (HHV) of this crude glycerin compared to other well-known fuels. As seen in this figure, the HHV of crude glycerin is comparable with that of ethanol.

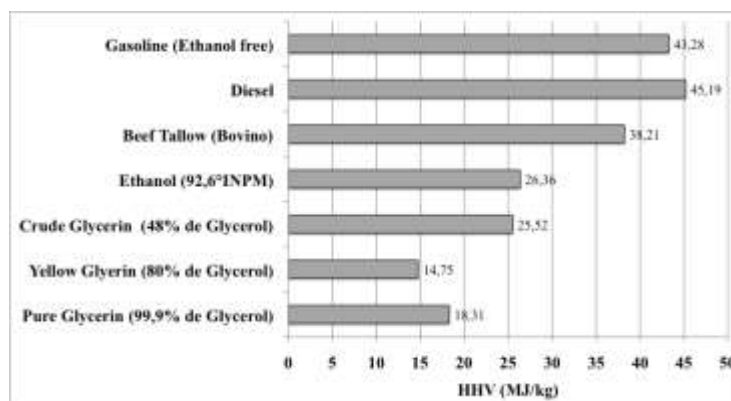


Figure 1. Higher Heating Value for Crude Glycerin compared with other fuels

2.2 Experimental Setup

Figure 1 shows an overview of the experimental configuration systems. Calorimetric flame tube furnace was used, which was built with 304 stainless steel in four modules, each a meter in length. This piece is composed of a central tube, overlaid by another that has larger internal diameter, forming a chamber for cooling water flow between the two tubes and a central cylindrical channel for the development of the flame and flow of the hot gases. Individual modules are divided into three calorimeters. Each calorimeter was instrumented with a temperature sensor for combustion gases (type k thermocouple) and cooling water. At the same time was measured in each case the water flow by individual orifice plates. This allowed further access to the characteristics monitoring of the combustion gases at different distances from the ignition point (equivalent to different residence times) and the heat transferred into the water. The control system of the combustion chamber was composed of a panel simulating the basic operating conditions and safety of a conventional boiler.

A swirl burner was used for the experiment. It was developed specifically for this study in the laboratories of the Center of Thermal and Fluids Engineering (NETeF) at the Sao Carlos School of Engineering School from the University of Sao Paulo. It is applicable to high-viscosity fuels, with low, moderate or high calorific value, including crude glycerin and beef tallow. It was coupled to a pump for highly viscous fluids manufactured by Hidrodinamica. It has air supply system using a conventional piston compressor, auto variable electric heating, ignition and auto power off. The measurement of air flow supplied to the burner was performed by previously calibrated orifice plates and needle control valves.

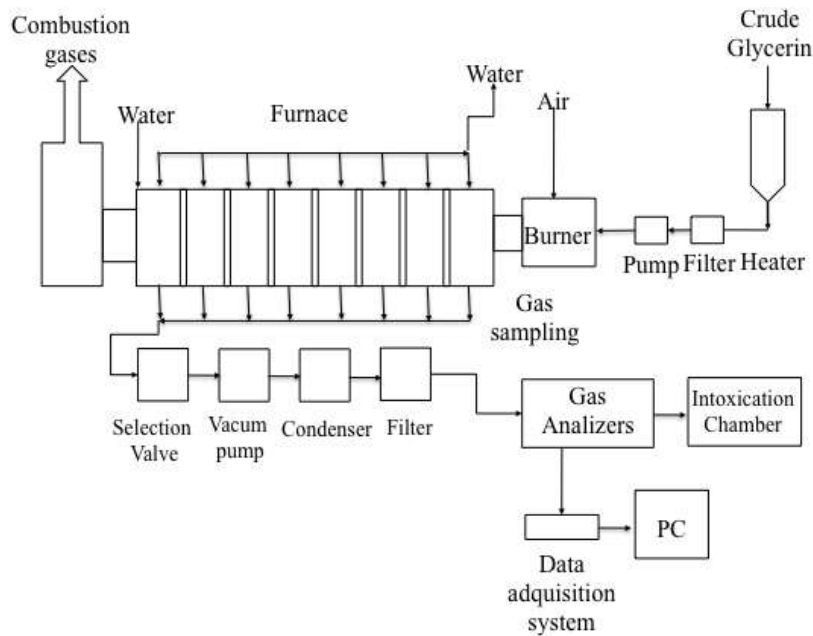


Figure 2. Overview of experimental setup for glycerol combustion



(a)



(b)



(c)

Figure 3. Calorimetric flame tube furnace: (a) general setup, (b) temperature measuring system, (c) detail of a water temperature sensor.

Whereas the crude glycerin from beef tallow comes in solid state at room temperature, the system integrated an adjustable electric heating unit and filtering which supplied this material to the burner in liquid state at a temperature above 70° C. This unit is showed in Fig.2 and Fig.3a. The crude glycerin supply to the heater is done manually. The diesel comes to the pump by gravity from a storage tank located two meters in height through a tube of 12 mm and passing through a filter and a burette coupled to a precision electronic balance, which allows determining the fuel consumption for weight difference. In the case of consumption of crude glycerin was planned that this would be measured by level difference on the tank that serves as heater. Milltronic 86122010 model ultrasonic was used for this purpose according to the calibration precision level.

The combustion gases were collected in each calorimeter using refractory probes connected to Teflon tubing of 3.2 mm, which carried the samples to a selector valve that allows the selection of a desired sampling point. From this point a vacuum pump sucks the gas and forces it to pass through a filter and a condenser, before to enter into the gas analyzers.

O₂, CO₂, CO, SO₂, THC and Nitrogen oxides (NO_x) from gas were continuously measured. Table 2 shows the specifications of the analyzers used, which were calibrated before each test with standard gases.

Table 2. Description of gas analyzers

	Parameters					
	O ₂	CO ₂	CO	THC	NO _x	SO ₂
Manufacturer	Horiba	Horiba	Horiba	Horiba	Horiba	Horiba
Model	MPA-510	VIA-510	VIA-510	FIA-510	CLA-510	VIA-510
Measuring principle	Paramagnetic	Infrared	Infrared	Hydrogen flame ionization	Infrared	Infrared
Range	0 -25 %	0 – 20 %	0 – 5000 ppm	0 – 3000 ppm	0 - 3000 ppm	0 - 1000 ppm
Error/Precision	±0.05%	±0.05%	±0.05%	±0.05%	±0.05%	±0.05%

The content of acrolein in combustion gases was determined by the procedure specified in the standard ABNT NBR 12026, which describes the analytic method for aldehydes and ketones determination contained in exhaust gas motor, liquid chromatography - Method 2.4 dinitrophenyl hydrazine (DNPH).

Furthermore, the methodology provides for measuring the mutagenic and toxic potential effects associated with fuel combustion, was the procedure name as KU20 Clone *Tradescantia* intoxication. This procedure is based on the Trad-SH test (*Tradescantia* Stamen Hair Mutation) to estimate the potential mutagenicity. The biomonitoring plant used is the clone KU-20 of *Tradescantia*. The Plants were grown outdoors in four different places (Controlled space, rural and urban area, and university's campus). During the test, the inflorescences of *Tradescantia* were exposed for one hour to the emissions produced from burning diesel in the flame tube furnace. It was used a test group and two control, the first set was directly exposed to the combustion gases in a chamber of intoxication made of transparent plastic. The second was placed next to the first, but exposed to ambient air and the third was put in a local outdoors, arbitrarily considered as little contaminated.

After the intoxication, all inflorescences were put in distilled water with mechanical ventilation for about 78 hours. The open flowers were removed and prepared for microscopic analysis. Hairs stem were observed with a Zeiss Stemi 2000-C model stereoscopic microscope coupled with a camera. Initially it was estimated as the average number of hairs for each stem flower. Then it went to count the number of mutational events in each yarn. A cell or Pink group between normal cells in purple characterized each mutagenic event. After, the count was estimated as the number of events for 1000 staminal hairs.

The acquisition of all data, except water and air flow, was performed by an acquisition system composed of a microcomputer with an acquisition board PCI-6023, coupled to a chassis module SCXI-1000 with SCXI-1100 multiplier equipped with 32 channels connected to a SCXI-1300 terminal block, all manufactured by National Instruments Inc. The signals transferred by the data acquisition board were processed in Lab View ® 7.1, with the interface shown in Fig.4. The automatic data acquisition time was set at one second and 60 s for manual acquisition. Total duration of each test was 70 min, with 15 minutes for the sampling time in the final calorimeter (which represents the output of gases to the atmosphere) and five minutes in the others.

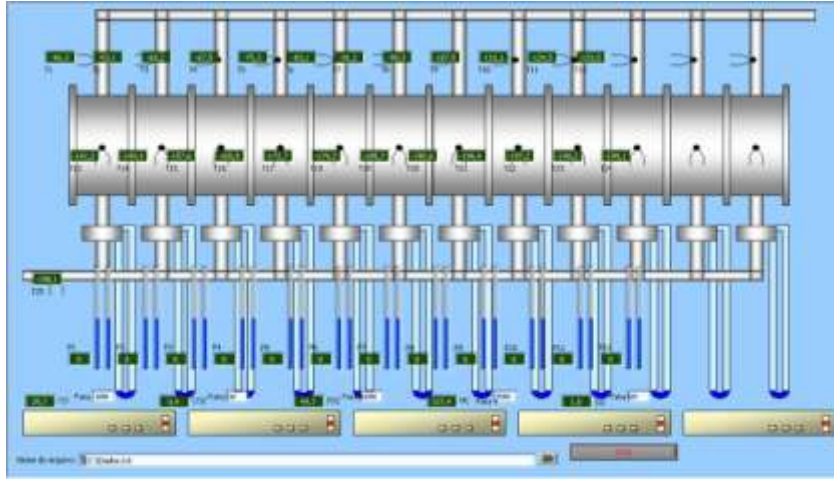


Figure 4. Detail of the interface in Lab View for data acquisition.

The air-fuel ratio for fuel used was calculated based on the equations of diesel and glycerin combustion writes in the form:



For glycerin, was used the equations of combustion of the main constituents of crude glycerin (glycerol, methanol, sulfur and Mong, assumed totally as sodium stearate). Thus combustion equations used for calculating fuel-air ratio were as follows, where the coefficients a, b, c, d and e were calculated by material balance.

Glycerol,



Diesel,



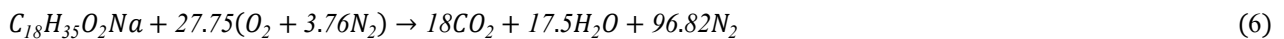
Sulphur,



Methanol,



Sodium stearate,



Therefore, the air-fuel ratio for combustion of crude glycerol will be approximately equal to the sum of individual values of the air-fuel ratio of each of its components, weighted by their content in the mixture of crude glycerin.

The adiabatic flame temperature was estimated using the principles of classical thermodynamics and others considerations describes by Moran and Shapiro (2002). Similarly the calculation for fuel-air ratio was assumed that for a combustible mixture, adiabatic flame temperature is approximately equal to the sum of the individual adiabatic flame temperature of each component, multiplied (weighted) by the mass fraction of each component in the mixture. Based on this, equation (7) was obtained. After replacing the values for the enthalpies of formation of products and reagents, according to the corresponding balanced combustion equation and using iterative calculation, the adiabatic temperature for a particular fuel was correlated as shown in equation (7).

$$\sum_P n_s \Delta h_s = \sum_R n_e h_{fe}^\circ - \sum_P n_s h_{fs}^\circ \quad (7)$$

3. RESULTS

The results for the air / fuel ratio are shown in Tab. 3. The analysis of Tab. 3 together with chemical formulas of the compounds included in the equations (2) to (6) shows that the amount of air required per unit of mass of considered fuel, is higher for combustible having lower oxygen content, which is completely consistent.

Table 3. Calculated values for the air-fuel ratio

Fuel	Air-Fuel ratio (kg air /kg fuel)
Diesel	14.92
Glycerol	5.22
Sulfur	6.44
Methanol	6.44
Tallow	12.40
MONG	11.55
Crude Glycerin	8.08

On the other hand, in Fig.5 was compared the results obtained for the adiabatic flame temperature for diesel and crude glycerin as a function of Excess Air Coefficient (λ), defined as the ratio of real air and the stoichiometric air. According to this figure, although the maximum temperature reached by the diesel stoichiometric conditions ($\lambda = 1$) is higher than that achieved by crude glycerin in the same conditions, this situation is different for higher air excess, finding a significant difference between the two fuels in favor of glycerin. At the same time is clear for crude glycerin a lower rate of temperature decrease with air increasing. This obviously reflects the physical and chemicals differences of each fuel.

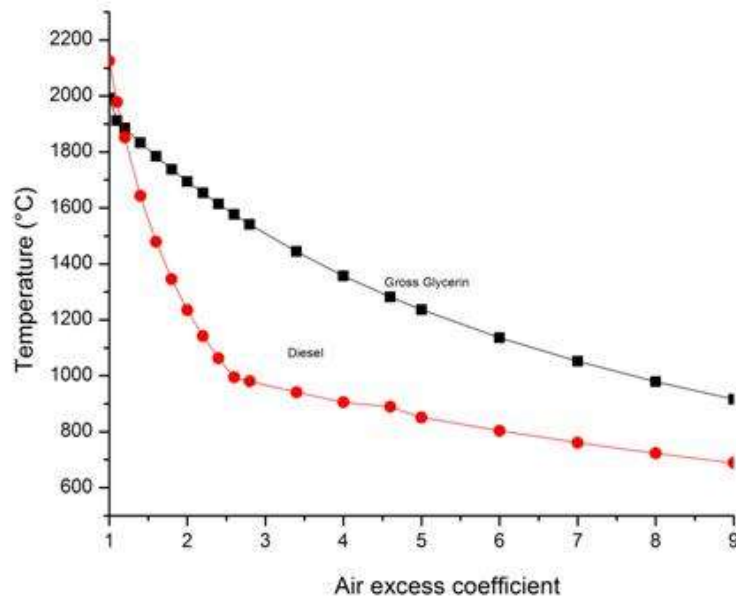


Figure 5. Comparison of adiabatic flame temperature for crude glycerin and diesel

Finally, Fig.6, 7 and 8 shows the results for emissions, cooling water temperature and temperature of gases during diesel combustion, which assessed the applicability of the procedures and described configuration.

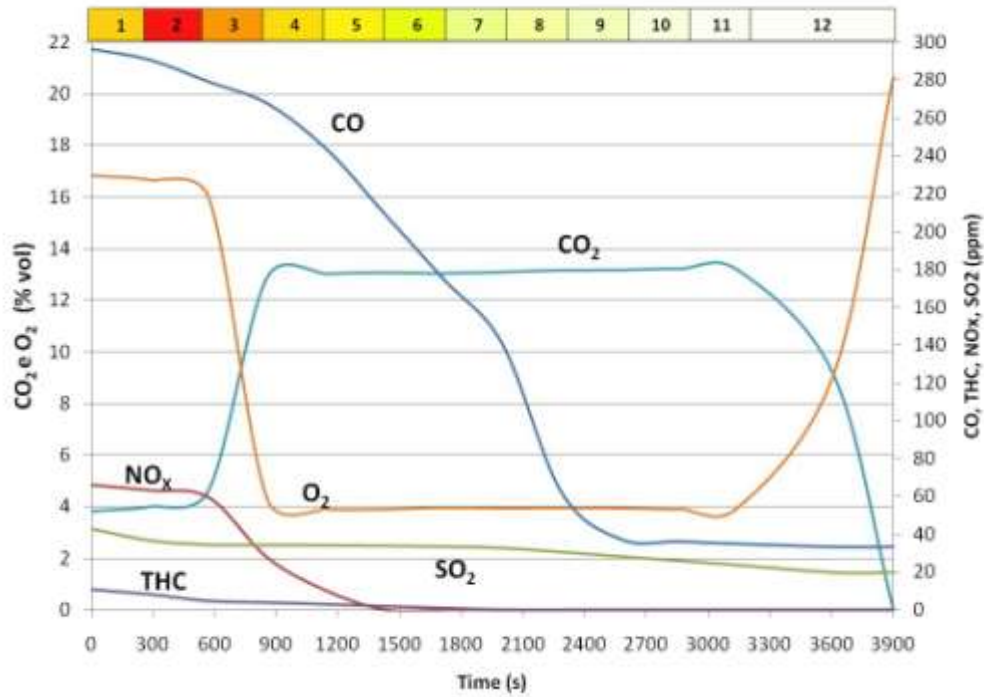


Figure 6. Temporal and longitudinal variation of O₂, CO₂, CO, SO₂, THC and NO_x in diesel exhaust

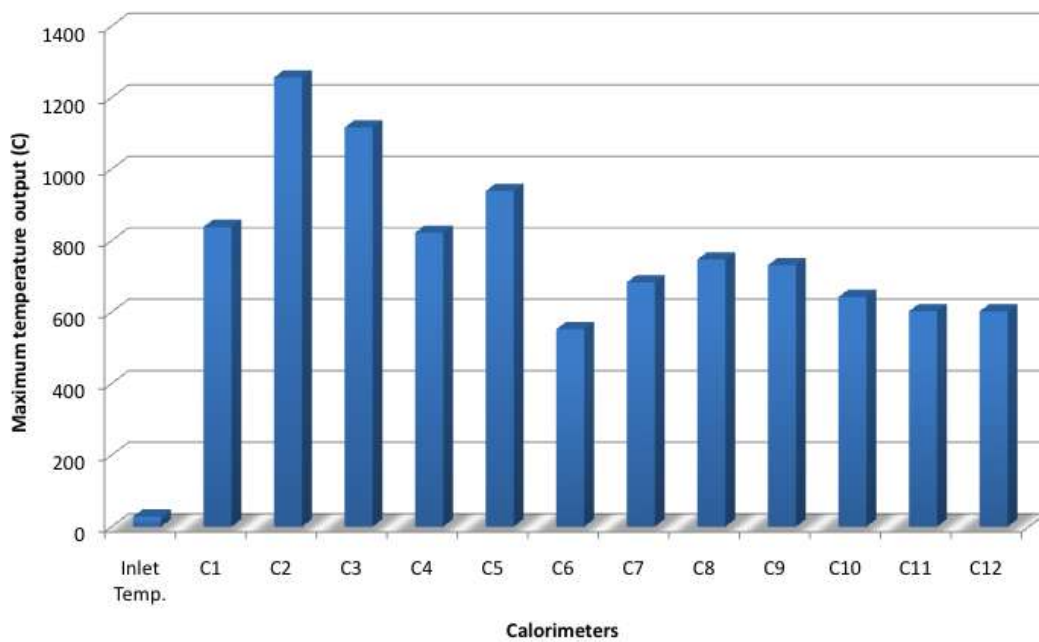


Figure 7. Temperature variation of gases

The results shown in Fig. 6 to 8 confirm that the system met the expectations for this fuel based in similar parameters reported by Rodrigues G., 2005. From Fig. 6 it was showed clearly the relations between the formations of some compounds associated with the destruction or transformation of another. This is one of the ways to show the progress of the reaction of combustion in the furnace. There is more different between the concentrations of O₂, CO₂ and CO. Fig. 8 register a sharp temperature increase in the calorimeter number five, that is replicated to the following modules, which was attributed to the burning of any combustible material accumulated inside the furnace.

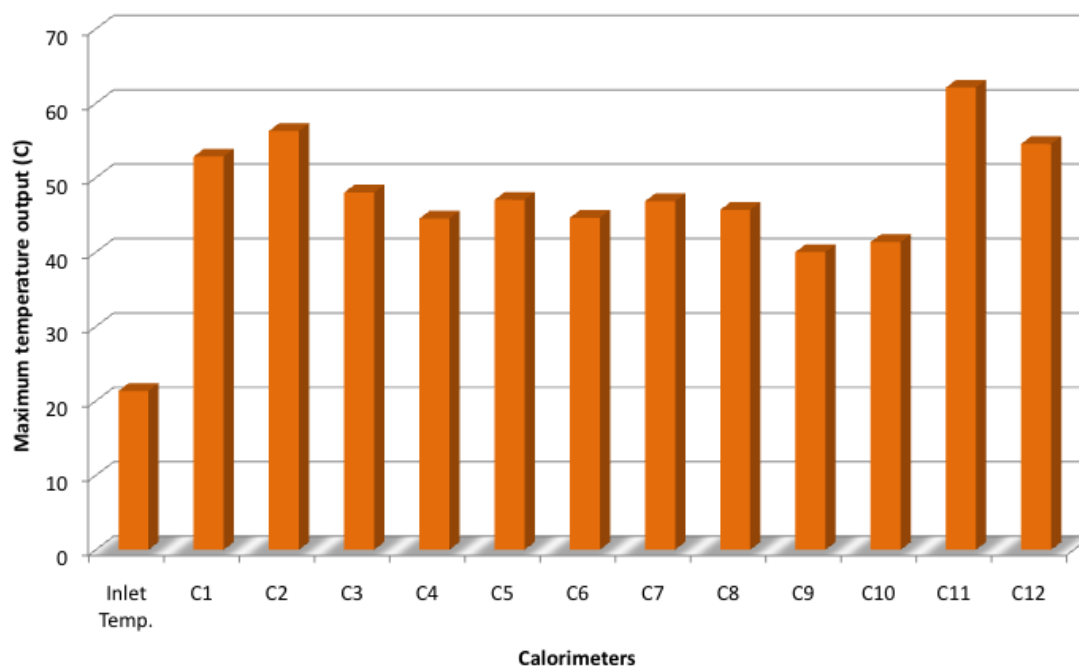


Figure 8. Temperature variation of cooling water

4. CONCLUSIONS

The methodology described is applicable to the evaluation of the combustion of crude glycerol in a flame tube furnace. The data can be collected by use, to assess a wide range of emissions and pollutants, the most suitable operational parameters and associated heat transfer. The main limitation that may occur is related to possible difficult control of process if an excessive number of variables are involved.

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