EVALUATION OF THE USE OF GLYCEROL FROM THE BIODIESEL PRODUCTION AS A CO-SUBSTRATE IN ANAEROBIC BIODIGESTOR FOR BIOGAS GENERATION

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Abstract. *In this work is evaluated the use of glycerol, resulting from biodiesel production, as co-substrate in anaerobic biodigestor with cattle manure to the biogas production. With the growth biodiesel production, the amount of glycerol increased and certainly the demand of currently applications on the market will not grow in the same proportion, so, it is necessary to find new uses for this biodiesel byproduct. The tests were made, in principle, in laboratory scale using two biodigestors of batch feed type (not continuous), and put in one of them 5% of glycerol and completing by equal parts of water and manure. Firstly, it was evaluated qualitatively the biogas production, and in later experiments it was possible to demonstrate quantitatively the efficiency of the use of glycerol in biodigestor with the same percentage by volume used previously. Preliminary results showed visually the capacity that the glycerol has to accelerate and to increase the production of biogas in an anaerobic biodigestor of batch feed type, which then, using a Bunsen burner, it was possible to check that it can be used in natura for direct burning. After fourteen days of experiment, it was concluded that the use of glycerol in the biodigestors improved the process of biogas production in approximately 60%.*

Keywords: *Glycerol; Biodiesel; Biodigestor; Biogas; Cattle Manure.*

1. INTRODUCTION

The guidelines of Kyoto Protocol encourage the use of less pollutant and renewable energy sources in developing countries. The target proposed in 1997 in the UN Conference of Climate realized in Kyoto, was the reduction of emissions of greenhouse gases between 2008 and 2012 (5.2% in average considering was base the values of the 1990). The way to encourage this reduction is the possibility of developing countries to negotiate their reductions with developed countries through the carbon credits sale by means of the Clean Development Mechanism (CDM).

New models of energy production and consumption are being developed based on renewable energy such as biomass, for example. One of the biggest challenges of this task is the introduction of various changes in environments tailored to traditional energy sources, not only from the technological aspect, but also from the human aspect of accommodation and comfort with existing installations, which is perhaps the most grave.

Among the renewable fuels is the biodiesel, a biodegradable fuel that can be obtained by different processes, such as cracking, esterification and transesterification. It can be produced from many types of raw materials, such as animal fats (bovine, swine and poultry) and/or vegetable oils (castor, palm, sunflower, babassu, peanuts, pine nuts and soybean, among others). The biodiesel can be used pure or mixed with diesel oil in diesel cycle engines, such as automotive or stationary (electricity generators).

Countries such as Germany, France and Italy already have well developed programs for the production and use of biodiesel. Brazil, which already has experience in the field of biofuels through the National Program of Alcohol (PROALCOOL), have again the collaboration of PETROBRAS company in the "National Program of Biodiesel Production and Usage" to meet growing demand due to the increase in addition the proportion of pure biodiesel in conventional diesel oil.

2. GLYCEROL UTILIZATION

Glycerol or propane-1,2,3-triol is an organic compound belonging to the alcohol function. It is liquid at ambient temperature (25°C), hygroscopic, odorless, viscous and sweet taste. The name originates from the Greek word "glykos", which means sweet. Glycerol is present in all oils and fats of vegetal and animal origin in their combined forms. Glycerol with purity above 95 % is the product in the commercial form, also designed as Glycerin.

As already happens with the production chain of sugar-alcohol sector, where, through the sugar cane processing, sugar and alcohol are produced with the bagasse as byproduct, which is burned in boilers producing energy (electricity and heat); in the biodiesel production chain, the glycerol, obtained as byproduct of oil processing plants, fats and used oils as raw material, can also be used, in addition to traditional forms, for the production of energy acting as co-substrate for some biodigestion process of organic matter. Due to its high content of easily degradable carbon, the glycerol has favorable properties in the anaerobic digestion biodigestor when associated with organic waste with high content of nitrogen.

For each liter of biodiesel produced between 100 and 200 ml of glycerol are produced. Part of this biodiesel byproduct is utilized in synthetic resins and esters, tobacco, paper, pharmaceutical applications, cosmetics and food, and part is discarded, since there is an higher offer than the demand. This imbalance may become higher due to the need of more production of biodiesel for addition to diesel, according to the government plan. Nowadays, the use of glycerin in market is distributed according to Fig. 1 (Purificação *et al.*, 2008).

A new application to the glycerol could be as an optimizer for production of biogas in anaerobic biodigestor, which can be burned in internal combustion engines or gas turbines for production of electric energy.

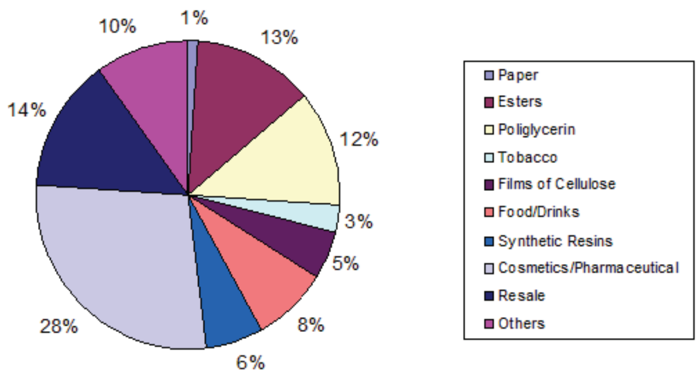

Figure 1. Glycerin use in various sectors (Purificação *et al.*, 2008).

In this context, this study has as main objective to evaluate qualitatively and quantitatively the introduction of the residual glycerol of the mini-pilot plant for biodiesel production that is being mounted in the Mechanical Engineering Department of UNESP at Ilha Solteira with the support of BIOCOM Biocombustível S.A., as co-substrate in the biodigestion process, with manure of animals (obtained in the experimental farm of the same university), evaluating the potential for the biogas production in laboratory scale and viability of the production of electricity, using an internal combustion engine converted for biogas and coupled to an electric generator.

3. BIOGAS UTILIZATION

The biogas produced is basically composed of methane (CH_4), which represents 60-70 %, carbon dioxide (CO_2), which represents the remaining 40-30 %, and small portions of other gases such as nitrogen, hydrogen and hydrogen sulfide gas (Comastri Filho, 1981). Before being burned in nature or even used as fuel in gas engines (Otto or Diesel cycle), gas turbines or gas micro-turbines, it is preferable that the biogas subjects to a purification process which will fix the natural properties and increase the calorific value, which is between 4,300 and 6,850 kcal/m^3 (Lima, 2005).

Some substances present in the biogas affect the burning process of making it less efficient, such as water and carbon dioxide from entering the place of the fuel in the combustion process and absorb energy generated. It can occur incomplete combustion, loss of power, failure of early feeding and corrosion caused by the presence of hydrogen sulphide (H_2S), reducing the yield and the life of the engine. To remove traces of sulfur, could be utilized a filter with iron oxide and to decrease the percentage of CO_2 could be use a tower with droplets of water, moreover, the decrease of humidity could be made through the cooling gas, which lead to water condensation (Costa, 2006). Another alternative to reduce the humidity would be the utilization of coalescing filters and refrigeration dryers and for reduce H_2S, can be using a filter of activated charcoal (Coelho *et al.*, 2006).

The internal combustion engines can use gaseous fuels (natural gas, propane, butane, biogas, synthesis gas, chemical naphtha and others), liquids (alcohol, gasoline, diesel, biodiesel and others) and mixtures of gaseous fuels with liquid in proportions that allow the self-ignition.

For use biogas as fuel, the Otto cycle is the most recommended. On these cases the biogas mixed with air in certain proportions and a pressure and temperature pre-set. However, it can be used the biogas in equipment Diesel cycle since the added fuel in the combustion chamber is a mixture of gas with 3 to 5 % of diesel. This equipment is known as bi-fuel or dual-fuel, depending how they are implemented the mixed fuel. In these systems, it is necessary to make use of high power compressors, to create the high pressures required for gas injection in this chamber/cylinder combustion.

4. MATERIALS AND METHODS

Currently the biodiesel which is utilized in the experiments is produced in a reactor donated by BIOCOM Biocombustível S.A., through an agreement with the UNESP at Ilha Solteira. The reactor is capable of producing 100 liters of biodiesel per batch through the process of transesterification of vegetable oils, using the methyl route. At this moment, just residual frying oil collected in Ilha Solteira city is being utilized for biodiesel production.

To evaluate the use of glycerol, the experiment was divided into two stages, being in both utilized two anaerobic biodigestors of batch feed type. These biodigestor have capacity of 5 liters, and the amount of manure diluted in water is about 1:1 by volume, totaling 3.5 liters of the mixture. In one biodigestor was utilized a ratio of 5% of the total volume of glycerol, as suggested by Robra *et al.* (2006).

The first stage shows qualitatively the capacity of glycerol to optimize the production of biogas, and check if it can be burned in natura. For storage of biogas, was connected to each biodigestor an air-chamber to serve as gasometer, allowing the burn of the gas.

The final stage shows quantitatively the production of biogas from each biodigestor through measuring cylinders linked to each other. One measuring cylinder served as equalization tank, allowing the confinement of biogas in the other, with constant pressure, in the case at room temperature.

The devices utilized in the experiments are shown in Fig. 2.

Figure 2. Representation of the devices utilized in the experiments.

The biodigestion process can be divided about three distinct phases: hydrolysis, acid and Methanogenic. In the hydrolysis stage, extracellular enzymes released by bacterias, have the responsibility to processing larger molecules (polysaccharides) in organic acids (lactic or butyl), alcohols, H_2 and CO_2, in addition to conducting the fermentation of proteins and lipids. In the acid phase, the bacteria that produce acids, transform the molecules of proteins, fats and carbohydrates in molecules of organic acids, ethanol, ammonia, hydrogen, carbon dioxide, among other compounds. In the third and last phase, the Methanogenic, methanogenics bacteria act on the hydrogen and carbon dioxide and processing methane. This is the longest part of the process, because over the course of chemical reactions occur the formation of micro-bubbles of methane and carbon dioxide around the methanogenic bacteria, isolating it from a direct contact with the mixture. For this reason, great importance was given to the biodigestor agitation to eliminate these micro-bubbles.

Table 1 shows the test description of biogas production. In tests, the biodigestors was maintained as local temperature (average 30 ºC), since the temperature is favorable for mesophilic bacteria to develop, as shown in Tab. 2 (Comastri Filho, 1981).

Table 1. Test description of Biogas production.

Biodigestor	% Manure	% Water	% Glycerol
A	50	50	0
B	47.5	47.5	5

Table 2. Types of bacteria and development temperature in biodigestors.

Type of Bacteria	Temperature Range for Development	Optimum Temperature
Psiciphilic	Less than 20 ºC	-
Mesophilic	Between 20 and 45 ºC	35 ºC
Thermophilic	Higher than 45 ºC	54 ºC

For determination of the mixture pH, was used a conventional indicator tapes and for determination of the levels of total solids (TS) present in the sample solution of cattle and water used in the experiments, it was used a method proposed by Arcuri (1986). First, it was measured the mass of an empty recipient in a precision balance, and then measured the mass of the recipient with 50 ml of sample, resulting in a wet weight (WW). This recipient was taken to an oven with a temperature of 105 °C until all the liquid evaporated, leaving only the solids. The recipient was weighed and determining their dry weight (DW). By Eq. (1) it was possible to determine the levels of total solids in the sample (TS). This procedure was performed for three different samples, as shown in Tab. 3.

$$TS = 100 - \frac{[(WW - DW).100]}{WW} \quad (1)$$

Table 3. Levels of total solids in the samples.

	Sample 1	Sample 2	Sample 3
Wet Weight (WW)	105.6 g	103.31 g	99.26 g
Dry Weight (DW)	59.1g	54.56 g	53.57 g
Total Solids (TS)	55.96	52.81	53.97

5. RESULTS AND DISCUSSIONS

In the initial stage, it was possible to check qualitatively the capacity of glycerol has to increase the biogas production in an anaerobic biodigestor of batch feed type. In seven days the air-chamber, used as gasometer of biodigestor that had glycerol (A), produced almost the total volume of biogas. The other gasometer (B) had a small production compared with the first, as shown in Fig. 3. The gasometer with biogas was connected to a Bunsen burner and can be verified that is flammable (Fig. 4).

Figure 3. Biodigestor and gasometer after seven days of biodigestion.

Figure 4. Biogas burning in a Bunsen apparatus.

The pH of the samples was found to be neutral (7-8), like as expected.

In final stage, it was possible to determine quantitatively the capacity of the glycerol has to increase the production of biogas. Table 4 presents the biogas daily produced by the biodigestors and the average temperature in the measurements. These temperatures were measured by an infrared thermometer of ICEL model TD 950. Moreover, all volumes were measured the same ambient pressure.

Table 4. Biogas production along the time.

Day	Average Temperature (ºC)	Biogas Production (ml)	
		With Glycerol	Without Glycerol
1	36.5	1,064	582
2	34.3	598	412
3	17.5	40	0
4	34.0	654	232
5	34.0	518	232
6	34.7	856	302
7	36.7	324	188
8	31.0	188	78
9	33.0	564	166
10	36	634	184
11	34	524	30
12	29	24	8
13	28	194	56
14	37	396	164
	Total:	6,578	2,634

It can be observed in Table 4 that the temperature on the third day of the experiment is outside the temperature range of development of the mesophilic bacteria, as shown in Table 2 (Comastri Filho, 1981), showing that the production of biogas was reduced or stopped for temperature less than 20 ºC.

Figure 5 shows the comparison of biogas production along the time, according to Table 4 data.

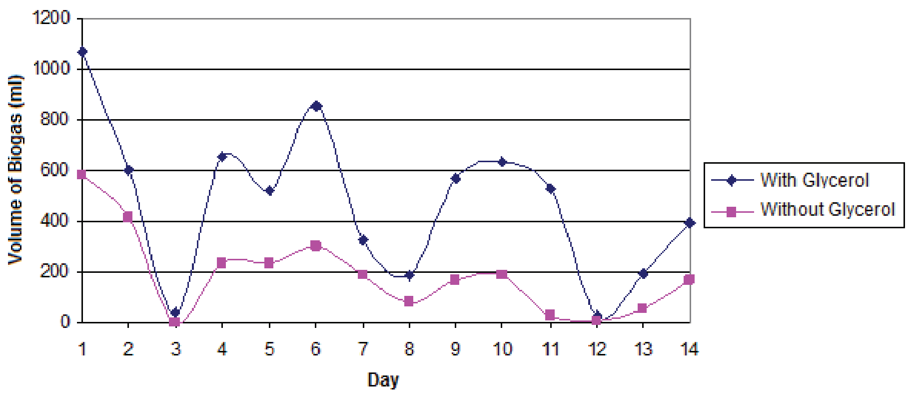

Figure 5. Comparison of biogas production along the time.

6. CONCLUSIONS

The study of biogas production using biodigestion of manure animals is already been done for some years, but is a recent and innovative initiative to study the effects generated by the use of glycerol for this purpose.

It was concluded that the use of glycerol from the biodiesel production as a co-substrate in anaerobic biodigestors of batch feed type with cattle manure improved, in fourteen days of experiment, the process of biogas production in approximately 60 %, which can be used in natura for direct burning and heat environments or used as fuel in internal combustion engines and electricity moto-generators, mainly in isolated rural areas that are breeding cattle.

Moreover, if an analysis on a larger scale be performed, considering, for example, the use of manure from a herd of 100 cattle, which could generate about 100 m³ of biogas (energy equivalent to three conventional LPG cylinders), will be obtained a financial return of approximately R$ 37,800.00 per year, considering that cylinders of LPG costs R$ 35.00.

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9. RESPONSIBILITY NOTICE

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