

THERMAL DECOMPOSITION BEHAVIOR OF CRUDE GLYCERIN

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Abstract. *The evolution of biodiesel generated an important increase in the supply of glycerin for industrial applications. A situation like this impels to develop additional rational and effective ways to use the glycerol byproducts of biodiesel. One of the most attractive ways is its use for energy needs. The present paper investigates the thermal decomposition of crude glycerin co-products of bovine tallow biodiesel by thermogravimetry (TGA/DTA). The main gaseous products are discussed and evaluated, and the mechanism of thermal decompositions was studied. The process revealed that the decomposition of crude glycerol is carried out in at least three distinct phases. The mechanism of decomposition of each phase is strongly associated with one or more components in the mixture. The occurrence of the first stage of decomposition and the observed behavior it is due to the presence of methanol and water mainly. The changes observed in the other stages are due to reactions of other components such as catalyzed glycerol decomposition, fatty acid methyl esters cracking and some residual salts transformations. The results and observed behavior were compared with glycerol thermal decomposition at the same conditions. The observed differences in some properties, mainly the activation energy reveals the role of some components in the kinetics of the decomposition process. Finally, was found that the thermogravimetry is an important and effective method to evaluate the partial feasibility and some combustion characteristics of potential fuels as crude glycerin.*

Keywords: *biofuel; biodiesel; thermogravimetry, energy, glycerol*

1. INTRODUCTION

In recent years, growth in world production of biodiesel has been going exponentially (Oppe E. *et al.* 2007, Thompson J., 2006). In 2010 global production will reach approximately 29 million tons per year (ENERS, 2010). 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 (Maturana A., 2008). Thus the production of biodiesel in Brazil for 2010 was approximately 2,7 million tons per year (MEN, 2010) that represents 9,1% of world's production and generates about 270 thousand tons of crude glycerin annually.

Glycerin or glycerol (as commonly called in pure form) is 1,2,3-Propanetriol in the technical nomenclature. 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).

Thermogravimetric analysis is an experimental approach to determine a fuel's thermal stability and/or its fraction of volatile components by monitoring the weight change as a specimen is heated (Panchasara H. *et al.* 2009), in addition is an interesting method for determining the kinetics of its decomposition (Caballero *et al.*, 1997). Heating rates in thermogravimetric experiments are low, and therefore this technique let to study the primary reactions in the decomposition of solids because their cracking is negligible (Conesa *et al.*, 1997).

A few authors have investigated in relation to thermal decomposition of crude glycerin. Dou *et al.* (2009) performed thermogravimetric analysis (TG/DTG) to determine basic kinetic parameters of crude glycerol, observing four phases of mass loss. Striugas *et al.*, (2009) investigates thermal decomposition of crude glycerol and your emulsions with

Russian heavy fuel oil in some proportions. They found similar thermal behavior than Dou *et al.* (2009) for crude glycerol and shows that the introduction of heavy fuel oil and other additives slightly affect the thermal stability of the mixture. In this case DTG and DSC curves of the glycerol emulsion with heavy fuel oil showed two additional endothermic reactions. As the same manner, Koch C. et al (2010) presented the determination of the activation energy through thermogravimetric analysis for the main region of the thermal decomposition for both glycerol and animal fat applying model-free kinetic.

This study investigates the thermal decomposition of crude glycerin co-products of bovine tallow biodiesel by thermogravimetry (TG/DTG), as a method to evaluate the partial feasibility and some combustion characteristics of crude glycerin as potential fuel involving your direct combustion 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 energetic and environmental performance.

Direct combustion is ancient process for energy producing. Biomass to energy conversion by pyrolysis and gasification are certainly not the most important options at present; combustion is responsible for over 97% of the world's bio-energy production (Demirbas, 2003). 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%.

2. EXPERIMENTAL

Thermal decomposition of crude glycerin and pure glycerol was analyzed. Crude glycerin derived from bovine tallow biodiesel 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. Glycerol USP grade (99,9 pure) was obtained from a local drugstore.

Table 1. Physicochemical characteristics of Crude Glycerin derived from bovine tallow biodiesel

Parameters	Units	Value
Density to 20°	kg/m ³	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 percentages of 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.

Thermogravimetric analyses were carried out utilizing a Shimadzu TGA-51H thermogravimetric analyzer. In each case the temperature increased from room temperature up to 900 °C with heating rate of 15°C/min. 10 mg of the sample was placed inside an aluminum crucible using an allowance of ± 0.5 mg. The reacting atmosphere was synthetic air at a constant flow rate of 100 ml/min over the sample. Additionally, to minimize factors that can generate errors in TG curves was performed a "white" under the same experimental conditions.

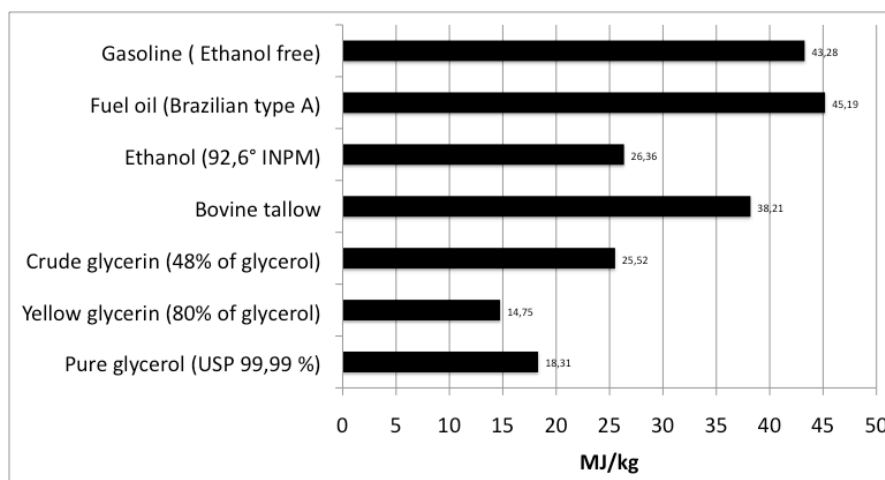


Figure 1. Higher Heating Value for Crude glycerin compared with other fuels

3. RESULTS AND DISCUSSIONS

The thermogravimetric curves (TG/DTG) for a temperature rate increase of 15°C/min are shown in Fig.1 and Fig.2. for crude glycerin and pure glycerol respectively.

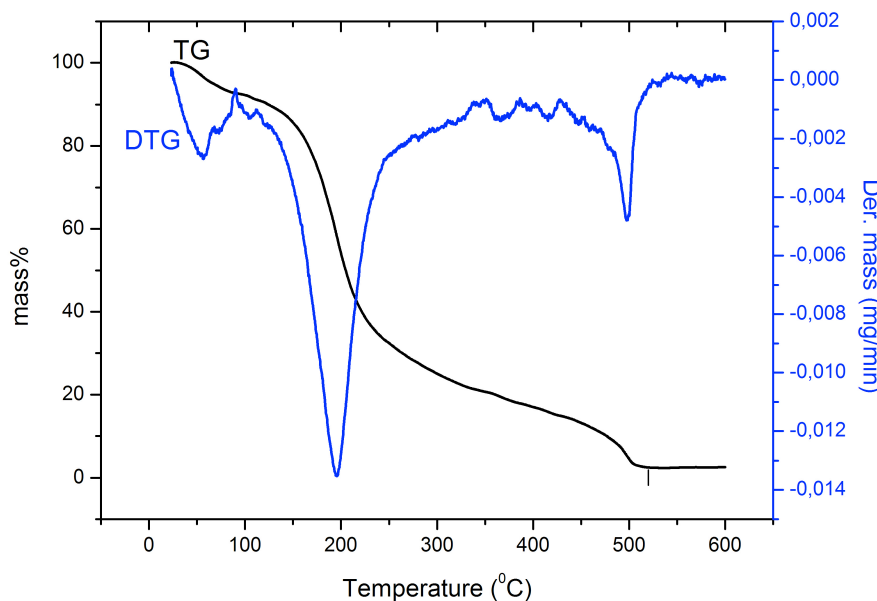


Figure 2. TG and DTG for crude glycerin

Figure 1 shows the TG and DTG mass loss curves of crude glycerin indicating three phases clearly differentiated and a probable fourth phase in the pyrolysis process.

The first mass loss for crude glycerin (phase 1) was approximately 12% starting at 23.78°C and ending at 89.8°C. Considering the crude glycerin chemical composition (see Tab.1) this loss is due to removal of the contents of water, methanol and probably some other volatile substance associated with biodiesel process manufacturing, such as residual catalysts, tallow or fatty acids. The volatility has an important effect on fuel vaporization, which affects fuel-air mixing and combustion processes.

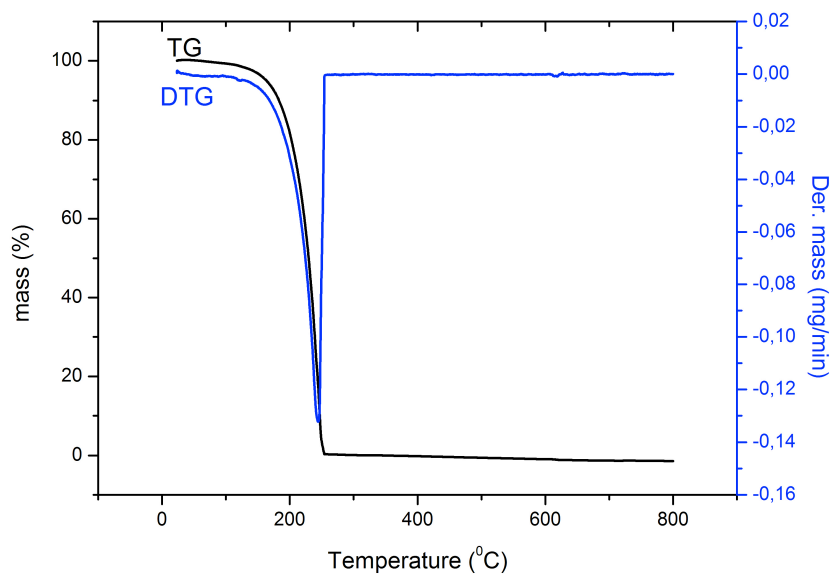


Figure 3. TG and DTG for pure glycerol

The main mass loss occurred in phase 2 for crude glycerin between 116°C and 320°C and corresponding approximately to 66% of initial mass. This extensive second mass loss may be explained by decomposition of the glycerol content. The transformation of glycerol content in crude glycerin may have generated part of the substances responsible for the third mass loss showed in phase three. This loss corresponds to a value between 9% and 10% occurring between 348°C and 389°C, probably was due to partial decomposition of some hydrated salts presents or formed in crude glycerin, especially sodium chloride, sodium phosphate.

The final phase reports the slower mass loss, approximately mass loss about 8% to 10% from 436°C to 527°C. This last mass loss may be due to the thermal decomposition or oxidation of coke produced from pyrolysis of glycerol and esters like biodiesel. Finally, about 2.5% of initial mass was the residue of crude glycerol decomposition.

In relation to thermal decomposition analysis of pure glycerol, the mass loss curve of this material was completely monophasic covering about 98% of its mass loss. This process was performed over a temperature range of 177°C to 231°C and leaving a final residue estimated in 1% of initial mass after the complete heating.

A resume including the mass loss, the initial, maximum and final temperatures for mass loss of pure glycerol and crude glycerin are presented in Tab.2 e Tab.3.

Table 3. Results for TGA pure glycerol at heating rate of 15°C/min

Phase	Parameter	Result	Probably due to
1	Mass loss	9%8	Thermal decomposition of glycerol content
	Initial mass loss	177°C	
	Maximum mass loss	211°C	
	Final mass loss	231°C	

Table 2. Results for TGA crude glycerin at heating rate of 15°C/min

Phase	Parameter	Result	Probably due to
1	Mass loss	12%	Removal of the contents of water, methanol and probably some other volatile substance associated with biodiesel process manufacturing, such as residual catalysts, tallow or fatty acids
	Initial mass loss	24°C	
	Maximum mass loss	56°C	
	Final mass loss	90°C	
2	Mass loss	66%	Thermal decomposition of glycerol content
	Initial mass loss	116°C	
	Maximum mass loss	196°C	
	Final mass loss	320°C	
3	Mass loss	9%-10%	Decompositions of some products of glycerol's transformation and partial decomposition of several hydrated salts presents or formed in crude glycerin, especially sodium chloride and sodium phosphate
	Initial mass loss	348°C	
	Maximum mass loss	353°C	
	Final mass loss	389°C	
4	Mass loss	8%-10%	Thermal decomposition or oxidation of coke produced from pyrolysis of glycerol and esters like biodiesel
	Initial mass loss	436°C	
	Maximum mass loss	499°C	
	Final mass loss	527°C.	

4. CONCLUSIONS

Thermal decomposition analysis of crude glycerol may play a significant role for planning direct combustion of crude glycerol and other technologies like gasification. The pyrolysis of crude glycerol co-product of bovine tallow biodiesel production process reports four clearly differenced phases. The main mass loss occur over the second phase due to glycerol decomposition, however water, methanol and salts contents play a key role for the combustion process because your influence on the design parameters.

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