ISSN 2176-5480

22nd International Congress of Mechanical Engineering (COBEM 2013)
November 3-7, 2013, Ribeirão Preto, SP, Brazil

GASIFICATION OF GLYCEROL IN POROUS REACTOR

William Magalhães Barcellos
João Igor da Rocha Leitão
Laboratório de Combustão e Energias Renováveis, PPGEM, Universidade Federal do Ceará, R. Humberto Monte s/Nº, BL. 715, Pici, CEP 60.455-970 (*)
william_barcellos@ufc.br and i_leitao@hotmail.com

Iago Lins Cavalcanti*
iago.lins@hotmail.com

Pedro Henrique Fonteles Dias*
Rafael Benevides Parente*
Francisco Nivaldo Aguiar Freire*
Selma Elaine Mazzetto*
pedrohfdias18@gmail.com, rafaelbp27@yahoo.com.br, nivaldo@ufc.br, and selma@ufc.br

Abstract. *This research refers to the development of a porous bed reactor for glycerol gasification, as an effective technology for syngas production from liquid fuels. Filtration Combustion (FC) is the base technology applied to develop this porous gasifier that has its reaction chamber filled by alumina spheres, which recirculate heat in the chamber and ensures self-sustainability of the process. FC allows operation at wide equivalence ratio range, with ultra-rich or ultra-lean mixtures (impossible to conventional reactors), providing operational stability. The prototype of porous gasifier built for this investigation presents certain design peculiarities, in terms of accessory systems, for example, the flamethrower ignition system. In the experiments, internal temperatures were measured through thermocouples distributed along the combustion chamber as well as the chemical composition of reaction products by chromatography. It was possible to carry out the glycerol conversion in relatively high reaction temperatures, between 1100 and 1800 K, inhibiting the formation of a highly toxic gas, the acrolein (C_3H_4O). Due to the porous medium, energy storage happens in the physical limits of the reactor, which avoids the formation of cold zones in the chamber and minimizes substantially the exhaust temperatures (below 350 K). Chromatography analyses have pointed out high hydrogen concentrations on syngas, applying the partial oxidation method to glycerol conversion.*

Keywords: *Glycerol, gasification, porous bed reactor, and filtration combustion*

1. INTRODUCTION

The possibilities to utilize renewable sources for energy production have become more appealing and practicable. For instance, vegetable oil fuels were not utilized once principally because they were more expensive than petroleum fuels. With recent increases in petroleum prices and uncertainties concerning its availability, there has been renewed interest toward these renewable fuels, especially to employ them in Diesel engines.

Through transesterification processes of vegetable oils to form methyl or ethyl esters (biodiesel), several outstanding advantages in using renewable fuels have been realized, among them: lesser emissions and operational costs. On the other hand, the transesterification process generates expressive amount of an important by-product, the glycerin, glycerol more impurities, in which its industrial recycling does not present economical feasibility. Or rather, under the point of view of market, glycerol allows applications for various industries (cosmetics, disposable diapers, resin, tobacco, food, etc.), however, impurities from transesterification reaction (water, salts, esters, alcohols etc.) limit its use (Mota *et al.,* 2009). Then, conventional industries are not able of consuming all this generated byproduct and, therefore, technological alternatives have been experimented to deal with that issue, table 1 shows some properties of glycerol.

property	value	property	value
Molecular weight	92.0938 g/mol	Phase	Liquid
Melting point	20°C	Boiling point	182°C
Density	1.25 g/cm^3	Solubility	Miscible in water
Vapor pressure	0.9998 mmHg	Dynamic viscosity	0.934 Pa.s
Surface tension	0.0648 N/m	Sound speed	6854 km/h
Refractive index	1.474	Specific Heat capacity	2.377 j/(gK)
Specific heat of vaporization	0.667 kj/g	Specific heat of combustation	18.06 kJ/g
Critical temperature	850 K	Critical pressure	7.5 MPa

Flash point	160°C	Autoignition point	370°C

Table 1 – Glycerol properties

An attractive and relatively simple reuse option of glycerol would be its application for liquid fuel boilers, targeting heating or electricity production. However, fireboxes of modern boilers operate on thermal stresses that make the direct utilization of glycerol unacceptable because of low combustion heat and adiabatic torch temperature. One of the possibilities to overcome this difficulty would be glycerol combustion in fuel emulsions or together with other types of fuel (Striūgas, 2009). In spite of that, when glycerol is heated to 280°C, it decays and produces a carcinogen specie, the acrolein (C_3H_4O), which always plays an important role in terms of security to justify the temperature control of gasification processes (Castro and Rust, 1961). Additionally, one promising technological alternative for the glycerol reuse is the gasification at high temperature in order to obtain synthesis gas and other gaseous products. The thermal decomposition of glycerol is viewed as an economical and environmentally friendly alternative in terms of final solution for the waste. However, it should be also highlighted that the oxygen contained in the composition of biomass fuels favors to the formation of particulate matter, carbon monoxide, and sulfur and nitrogen oxides when burned in conventional combustors (Cordoba, 2011).

Some reports have recorded the effort of the scientific community in creating new chemical routes to reuse of the glycerol in sustainable manner, i.e., with better conversion efficiencies through economically feasible processes. For instance, Martins (2009) have worked on steam reforming process of glycerol utilizing platinum catalyst supported on carbon. This system has been applied to syngas production at low temperature, integrated to other catalytic systems in order to produce hydrogen and liquid fuel in a single reactor. In this experimental investigation, effects of platinum particle size and PH of the feed solution on steam reforming reaction of glycerol have been studied. Similarly, other studies (Buhler *et al.,* 2002 and Eners *et al.,* 2010) proposing rotes to add value to glycerol have been performed, such as: selective oxidation and hydrogenolysis, dehydration, pyrolysis, reforming, etc.. Different compounds have been obtained since monomers for polymer materials up to high added value fuel, e.g., diesel and gasoline, through glycerol. Thus, chemical transformations of glycerol have resulted in some industrial interest compounds such as: acrolein, propilenglicol, dihydroxyacetone, syngas, etc. For most of them, researchers have then applied catalyst to lessen the reaction temperature and to increase the content of those mentioned species in reaction products. Anyway, catalytic process represents high operation cost and short period of uniform production regime based on catalyst activity time.

Then, there is need of developing technologies that allows efficient conversion of biomass in synthesis gas to be competitive with conventional methods, in especial dedicated to glycerol. In response to this issue, this paper proposes to employ Filtration Combustion (CF) to develop a non conventional reactor of glycerol gaseification (or any other liquid biomass). FC consists in carrying out combustion within the interstices of the porous medium, changing significantly the heat transfer phenomena in reaction, either at low or at high equivalence ratios. FC changes the characteristics of the conventional combustion due to the highly developed internal surface of the porous matrix, resulting in efficient heat transfer between gas and solid phases as well as in an intense mixing during the gas flow in the porous medium that enhances diffusion effective in the gas phase (Barcellos *et al.,* 2011 and Babkin, 1993). Due to the highly developed surface, the exchange of heat is favored inside the porous bed, i.e., heat recirculation between the gas phase and the porous medium. Therefore, most of the energy, normally discharged through the exhaust, is recirculated into the reactor causing the temperature rise needed to burning both ultra-rich and ultra-poor mixture.

Originally, FC has been applied to develop burners, furnace and boilers and heaters to be operated with a number of gaseous fuels, indistinctly. However, efforts have be dedicated to studies and researches to develop combustion thermal systems capable of burning solid and liquid fuels inside a porous medium, as technological advancements. For instance, mixtures of methane-air with equivalence ratios at the range between 2 and 3 have been employed in self-sustained reforming process by Toledo et al. (2011), using porous reactors. However, they have done effort to increase the equivalence ratio of reaction and to replace gas by biomass oil and solid fuels. Pedersen-Mjaanes *et al.,* (2005) have performed porous bed combustion by using a rich mixture of methanol, methane, octane and other fuels as a raw material and they have achieved conversions above 50%. Other works stand out themselves by the innovative methodologies that the authors have proposed for the production of syngas and energy, such as the hydrogen production from glycerol utilizing supercritical water (Guo *et al.,* 2011).

Recent articles referring to combustion of liquid biomass, more specifically about glycerol, have recorded the interest in meeting new methods of generating synthesis gas. (Valliyapan *et al.,* 2008) utilized a porous reactor with energy supply to thermally degradation (pyrolysis) of the glycerol and, therefore, his data have been utilized as reference to the present paper. In this context, although not treating of reaction in porous media, an important experimental work performed by Striugas (2009) has also served as data basis to develop this investigation. Striugas decomposed thermally the glycerin utilizing four sample types: pure glycerin (98%), glycerin average purity (88%), glycerin of low-grade (80-85%) and oil emulsion glycerol (27%). It was observed that the impurity level of the glycerin have not so much influence on the basic characteristics of products. However, high levels of impurities can cause damage to the equipment and result in high maintenance costs.

Objectively, this article aims to present a new concept of gasification/reforming reactor capable of processing any kind of liquid or gaseous fuel in a single porous reactor, where the fundamentals of FC were plentifully applied for the development of its conceptual and constructive designs. The reference biomass fuel for this study was the glycerol by the fact of this renewable fuel to be leading to environmental impacts and, still, due to its immense availability without a good practical destination, until then. Basically, the present paper is a kind of project enhancement of a previous porous reactor built and studied through scientific development performed by Parente (2012) at Laboratory of Combustion and Renewable Energies (LACER) of Federal University of Ceara - UFC (Brazil). It should be mentioned that although the gasifier's prototype has been developed to burn glycerin, the research group of UFC decided to test the glycerol firstly, as an initial phase of project developing, in order to diminish some variables in the performance analysis.

Thus, the thermal decomposition of glycerol in porous bed reactor has been studied, in which alumina (Al_2O_3) is used to fill up the combustion chamber. Through that reactor, Parente (2012) achieved to observe the rate of decomposition of the reactants, to indentify some operation and design parameters, to begin the studies about combustion/gasification of glycerol by the partial oxidation method. In this study, it is supposed that the porous matrix stores enough heat for the thermal decomposition of liquid biomass, and to create a proper thermal environment for its gasification, maintaining energetic sustainability of reaction. Despite it being a self-sustained process, external power is need only for starting up reaction, as a pre-heating process of the porous medium, where a new combustion ignition technique was employed, flame-thrower.

2. EXPERIMENTAL APPARATUS AND PROCEDURES

This experimental investigation about the glycerol gasification porous reactor (GGPR) had to fulfill a development and study methodology, considering that a novel technology has been created from concepts of a non-conventional combustion technology, Filtration Combustion, which has been applied to process liquid biomass by the partial oxidation method. Furthermore, the fact of the glycerol being selected to be the reference biomass for this study, some project care should be taken in account. Then, as this work is essentially experimental, prototypes had to be built in order to provide the necessary operation conditions that allow interpreting properly the phenomena present in the process. Therefore, the development of gasify prototype was preceded by a conceptual project, in which the working principles should be discussed previously in order to reduce time and cost of development. And, in sequence, the constructive project should be made, when design details are defined to prepare material and component specifications.

In parallel with experimental work, an analytical study has been performed as part of the conceptual project, in which reactions involved in the glycerol reformation are evaluated through a simplified model of simulation, concerning the syngas production. To decrease the number of variables to be considered in modeling, it was defined that as experiment well as simulation would treat of only pure glycerin, i.e., with concentration superior to 99,95%. Then, the reference fuel utilized for this study (experimentally and analytically) was the glycerol ($C_3H_8O_3$). Also, it was defined that the work would perform with base on only overall reactions, or rather, on combustion product and temperature analyses and theoretical reaction.

2.1 GGPR's Development

The core of the porous reactor (GGPR) consists of a steel tube of 0.075-m internal diameter and 0.50-m long, internally coated with refractory material and externally insulated with thermal insulation, so that, the effective internal diameter has only 0.05 m. In principle, all of its internal volume constitutes the reaction chamber, and it was prepared to work as a mechanically resistant device. The reactor as a whole is supported by a steel base which provides the necessary mechanical support for assembly of the reactor, including the process monitoring instruments. Also, it is well structured to deal with combustion gases in high temperature (until 1700 K) and with occurrence of unwanted pressure waves inside the reactor. The resulting reaction chamber, with 0.050-m diameter and 0.50-m length, is fully filled with spheres of alumina (Al_2O_3) with diameter of 0.0055 m, constituting an inert porous medium with porosity of approximately 40%.

The bottom end of the porous reactor is connected to air and glycerol supply systems through unidirectional flow valves (check valves), which only allows flow toward the reactor inlet. Then, three check valves were installed at bottom reactor's section: two valves for incoming process water and glycerol, and one third for the compressed air supply. At the top end of the reactor, there is an exhaust system to receive the combustion/gasification products (including toxic gases) to be taken out from the reactor toward gases analyzers (chromatography and others).

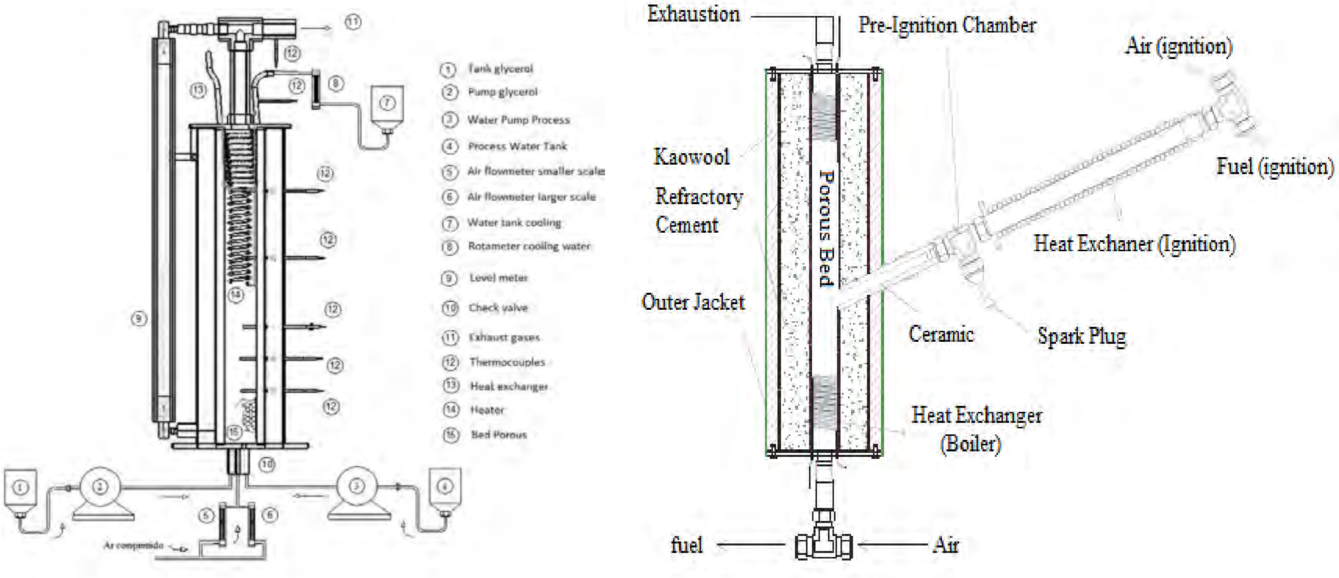
At the top section of the reactor chamber, there is a heat exchanger installed to extract energy from the combustion products from reaction zone. Removing energy from the exhaust, this heat exchanger also protects the reactor's components above it. Besides, the heat exchanger has the function of maintaining process stability and safe operation conditions because it work as a kind of thermal barrier to the upward flame-front propagation.

One of the principal design features that have required more worry and care is the ignition system, because it is assembled inside the chamber, participating of process. The original ignition system is to base of electrical resistance, utilized to pre-heat the porous matrix up to reach the spontaneous combustion temperature inside the reaction chamber. Basically, the first gasifier prototype was built with a resistive wire in coil shape, installed at the top section of prototype's reaction chamber. This resistive wire involves part of the porous matrix, occupying approximately 40% of the total length of the reactor, in order to heat the alumina spheres to lead to proper conditions for the spontaneous burning. Reached the operation temperature, the electric energy supply is interrupted and the air supply is initiated to start the combustion. This procedure has been the cause of some incidents occurred with the reactor, e.g., small explosions inside the reactor chamber due to the fact of the air to reach the region close to resistive wire, where there is a lot of fuel (glycerol plus gases from thermal degradation of glycerol) in gas phase. These undesirable events have demanded improvements of prototype's conceptual project and, thereby, a new ignition system was applied to this study.

This new ignition system consists of a flame-thrower that stands connected to the reactor chamber through the pre-chamber, where a flame-front is created for later being thrown to the principal chamber. The flame-thrower imposed the use of an auxiliary fuel (natural gas or syngas) to provide a flame inside the reactor chamber. When a great part of the porous medium reaches the spontaneous combustion temperature, the air is supplied at the bottom section of the reactor to be established a stable operation regime, only maintained by glycerol combustion (and derived compounds).

Still about the first prototype, it should be mentioned that there was an operational difficulty in relation to the glycerol pump applied to the project. The pump applied, initially, was a commercial device that had a lot of restrictions in terms of functionalism. Although this kind of pump is plentifully used in research laboratories, the fact of it works through pulses of diaphragm to inject glycerol into the reactor causes variations of the liquid surface level, which can result in instability. So this pump did not represent a good solution, which imposed an additional improvement to the GGPR's project. Then, it was necessary to develop a new pump conception feasible to this purpose, so that, the glycerol pumping could provide a constant flow, considering that glycerol has a relatively high viscosity (1.410 pc for 293 K).

In order to develop a pump exclusively dedicated to the GGPRT project, UFC's research group decided to build a new pump model, utilizing some commercial components normally used by the automobilist industry. As these devices are very robust, in general way, GGPR's pump was created based on the oil pump used in automobile engines, with certain design adaptations, such as: small glycerol reservoir, transmission system, electric motor of car windows, etc.. Due to the electric motor to allow variations in the voltage supply, applied to the motor, it was possible to provide different rotations and, thus, different glycerol flows, in steady state. The reservoir was made of stainless steel, which is a metal that is not attacked by the glycerol. This new pump has worked satisfactorily, until then, providing constant and low flow rates depending on the power of the electric motor. Figure 1 presents, schematically, a whole idea about reactor project features, including, this figure shows both the generations in terms of reactor development stage, i.e., the first prototype with resistive wire and second one with flame-thrower. It should be mentioned that the first reactor generation was plentifully used in the experimental investigation, becoming important for proving the project feasibility. Therefore, this first reactor was built in low-cost short-time manufacturing process, i.e., simple design and waste material employed in the initial development. Complementarily, Figure 2 shows the air and fuel (natural gas and glycerol) systems that assure the operation of GGPR's prototype.



(a) (b)

Figure 1: (a) Original GGPR (first development generation – heating by resistive wire)
(b) Optimized GGPR (second development generation – heating by flame-thrower)

ISSN 2176-5480

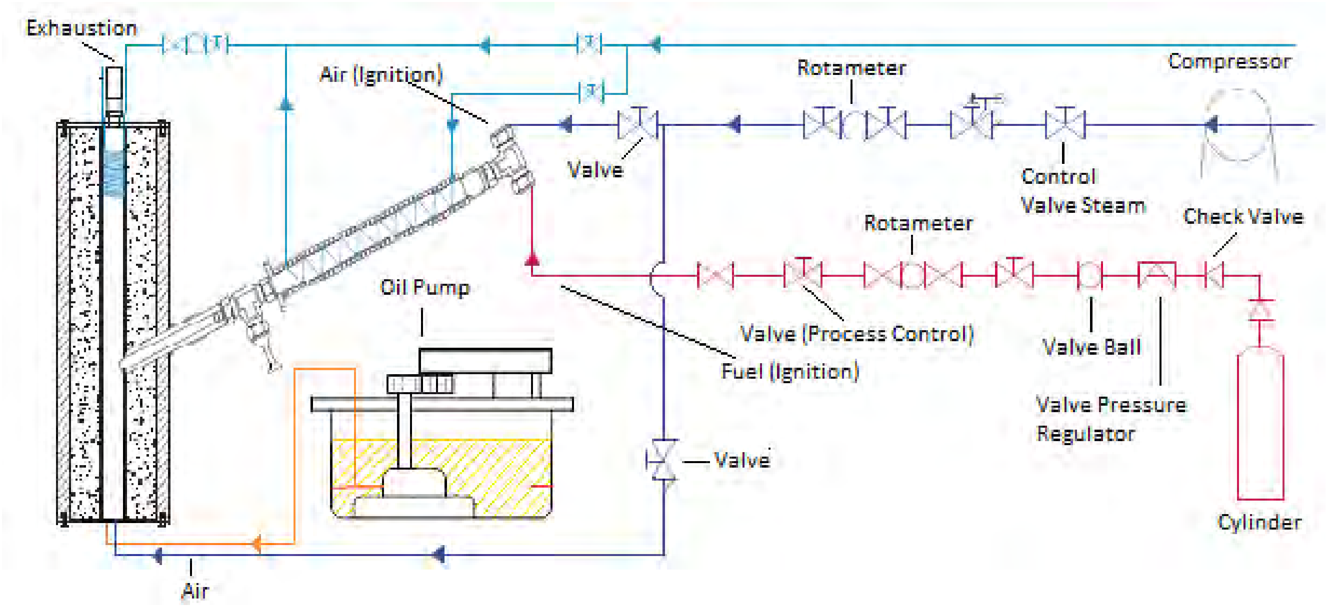


Figura 2 – Schematic diagram of operation supply system of GGPR

2.2 GGPR's Working Features

The development of this glycerol gasification porous reactor (GGPR) is to burn/gasify the glycerol (or any liquid biomass) directly in it reaction chamber without some auxiliary device to prepare fuel in terms of energy supply for vaporization. The working principle of this kind of reactor is based on the fundamentals of Filtration Combustion, in which a porous medium inside the reaction chamber participates of the process, storing and recirculating energy extracted from the own reaction zone to the fresh air-fuel mixture.

The important technological innovation involved in this project is the fact of the fuel maintaining itself in two phases (liquid and vapor) and equilibrium, i.e., together and in stable mode inside a same reaction chamber. The fuel, supplied in liquid state, takes into the reactor chamber in the same flow rate in order to maintain constant the level of the fuel quantity that is laid on the bottom of the reactor chamber. So, there is no complementary device to change the fuel state from the liquid to the vapor condition, which is done naturally by the heat transferred from the flame front to the fuel at the bottom. The flame-front propagates itself back and forth along a specific physical limit of the chamber, which is determined by the surface of liquid fuel at the bottom and by the heat exchanger at top. The flame front is supplied of air and fuel in gas phase to maintain itself and, on the other hand, the energy transferred from the reaction zone to fuel surface by radiation and conduction processes is enough to vaporize the fuel, remain a temperature gradient from the liquid surface toward the reactor chamber bottom. So, the operation of the GGPR can be handled easily from combustion to gasification (partial oxidation method), only depending on the equivalence ratio applied to reaction, which is controlled by the air flow rate supplied at the bottom end. A wide equivalence ratio range can be used in GGPR because of the porous medium that constitute de reactor chamber. In general way, porous burners have experimented with equivalence ratio varying from 0.1 to 10 for gaseous fuel, so that, if the equivalence ratio applied is lower than stoichiometry the reactor works as boiler/heater, and for superior values it work as a gasifier, producing syngas. It is expected that at equivalence ratio value higher than 5 a strong carbonization occurs on the walls and sphere surface, sometimes damaging. For the GGPR an equivalence ratio from 0.5 to 4 was employed in experiments and it has present great operational stability in all the range cited.

About reaction stability, it should be highlighted that the correct determination of energy extraction from the reactor is extremely important to control the operation. Water excess in the heat exchanger can affect significantly the reaction stability because of the energy extraction intensity. Strong energy extraction can interfere on reaction zone, so that the flame front can be quenched. Also, excessive energy extraction can cause condensation of combustion products that can mixture with glycerol and other compounds from vaporization, resulting from thermal degradation of glycerol at liquid surface, which interfere on the oxidation of the reactants through the reaction zone. On the other hand, if the water flow is too low, there may be sudden evaporation of the water circulating in the heat exchanger by creating areas of high pressure in the exchanger pipe, which can completely change the energy extraction system reaction and generate instabilities in the process and, particularly, jeopardize the operation. Similar effect can occur if the liquid glycerol level increases. In this case, the glycerol bulk works as a cold body, extracting more energy from the reaction zone than the necessary. So, if the level of liquid surface varies so much, this can result in instability. Furthermore, it should be noted that the consumption of fuel depends on the reaction temperature, consequently, it depends on the air flow rate employed in the process.

2.2 Monitoring and Operation Instruments

For the first GGPR prototype, the resistive wire used in the preheating of the porous matrix is a Fe-Cr-Al alloy with diameter of 1.3 mm, fed by a alternating current through autotransformer, varying the voltage from 0 to 240V (AC), with a maximum power of 2.2 kW. Aiming to isolate the wire from the porous body of the reactor and thermocouple joints, ceramic insulators were installed involving the resistive wire.

About the monitoring work, the reactor was instrumented to have five-point temperature measurement along its length, so as to allow monitoring the behavior of the reactor due to the variations of operation parameters. Through thermocouples of K-type nickel-chromium alloy with capacity limits the maximum temperature measurement around 1500 K, it was possible to identify peaks and distribution profiles of temperature throughout the porous matrix. It was also installed a point of temperature measurement in the water outlet of the heat exchanger in order to allowing monitoring and controlling the reactor through temperature of the water, which also served as the basis for calculating how much heat was extracted from the porous medium.

About the analysis of combustion products, a collection point was installed in the exhaust pipe in order to take samples to be submitted to a chromatography. Antecedent to the collection point for gas chromatography, it was installed a dehumidification system to allow an analysis on a dry basis. This system has also been developed in the laboratory as part of the scope of the reactor development, which was scaled exchange system through experiments and analysis of heat transfer.

Summarizing, a number of parameters are monitored during the reactor operation, such as: the combustion temperature; the water inlet and outlet temperatures at the heat exchanger; the exhaust gas temperature; and combustion products at exhaust stream end. The temperature inside the reactor's porous medium is measured through thermocouples, at 5 linearly spaced points along the reactor wall. In the following, it is given information about all instruments used in the experiments, including details about their uncertainties: i) Temperature distribution inside the reactor; the temperature of the exhaust gases; and the water temperature: J-type thermocouple, featured with a fine tip and presenting an error of 0.75% for the full scale; ii) Combustion Products: analyzer calibrated with reference gases, in which for the experiments the lowest scale available on the analyzer was selected: 0-20 ppm, presenting an error of ±4% for measurements lower than 125 ppm; iii) Gases Flowrate: Rotameters with 7% FS-accuracy, with calibration by comparison of their readings to the ones from two primary standard instruments. Using the calibration table to fit the readings, the error of the (corrected) measurements is supposedly reduced to the repeatability of the rotameters (~1%-FS) plus the error of the primary standard instruments (~1%-FS); iv) Water Flowrate: Frequency flow transducer and rotameters - Utilizing a 5-V power supply, it yields square wave pulse outputs, in which its precision linearity is approximately of ±1.5 % of full scale over a frequency range varying from 12 to 270 Hz (from 25 to 540 ml/min, respectively). The water rotameters have a nominal accuracy of 5%-FS. After the calibration the accuracy is estimated to be around 1%. Based on the accuracy of these instruments utilized on the burner experimental investigation, the uncertainties of the temperature, specific power and energy extraction efficiency were estimated in ±0.8%, ±5.4% and ±10.1%, respectively.

3. THERMODYNAMIC ANALYSIS

3.1 Energy Balance

In order to better understand the GGPR's working, an energy balance in the GGPR should be performed, considering the operation condition in steady state in which continuously happens oxidation of the glycerol that is laid on the reactor's bottom section, with the liquid surface maintained at the same level. In this condition, the glycerol supply rate to the reactor is similar to its vaporization rate from the liquid surface toward to reaction zone, as shown at Figure 3. Or rather, the energy supplied by the flame front by radiation and conduction processes (through the alumina spheres), toward the liquid surface, causes vaporization of glycerol on the first liquid layers, releasing latent heat in opposite direction to the sensible heat received from to the flame-front. The glycerol oxidation process takes place because air is supplied to reactor (also at the reactor's bottom section together with the fuel), in certain flow rate proper to determine the reaction type, combustion or gasification, i.e., at equivalence ratios lower or higher than stoichiometry, respectively. The Equation (1) is a simply global reaction that represents the possibilities of GGPR operation, in which the coefficients "b", "d" and "f" are reduced and "c" and "e" are increased, as the equivalence ratio is augmented and vice-verse.

$$C_3H_8O_3 + \left(\frac{3.5}{\Phi}\right)(O_2 + 3.76N_2) \Rightarrow bCO_2 + cCO + dH_2O + eH_2 + fO_2 + 3.76\left(\frac{3.5}{\Phi}\right)N_2 \tag{1}$$

Independent of the reaction type, the component variables of energy balance are always the same. In principle, the original energy source of the process is heat from the reaction zone (reaction enthalpy) that is released from total or partial oxidation of the fuel, represented by the flame front over the liquid surface, as shown at Fig. 3. From this available energy, a portion of it vaporizes the liquid glycerol (at the bottom) and the remaining energy is partially removed by the heat exchanger and lost through the reactor's wall and exhaust, as represented by following equations:

$$\dot{Q}_{Glycerol} = \dot{Q}_{Latent} + \dot{Q}_{Extraction} + \dot{Q}_{Products} + \dot{Q}_{Wall} \quad (2)$$

$$\dot{Q}_{Glycerol} = \dot{m}_{Glycerol}.\Delta H_{Combustion(Glycerol)} \quad (3)$$

$$\dot{Q}_{Latent} = \dot{m}_{Glycerol}.\Delta H_{Latent(Glycerol)} \quad (4)$$

$$\dot{Q}_{Extraction} = \left(\dot{m}.c_P.\Delta T\right)_{Water} \quad (5)$$

$$Q_{products} = \sum (\dot{m}_i.h_i)_{products} \quad (6)$$

$$Q_{Wall} = \int_{0}^{100} \dot{q}_{top-section}.dx + \int_{100}^{400} \dot{q}_{reaction-zone}.dx + \int_{400}^{500} \dot{q}_{bottom-section}.dx \quad (7)$$

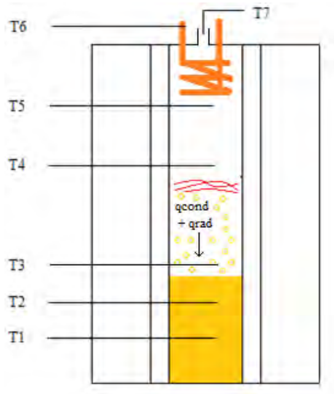


Figure 3: Schematic drawing of working principle of GGPR

For this energy balance, the considered reaction enthalpy and latent heat were respectively -1655.4 kJ.mol^{-1} and 89.69 kJ.mol^{-1}, where: i) $Q_{glycerol}$ is the total energy from glycerol oxidation, ii) Q_{latent} is the energy absorbed by glycerol vaporization process; iii) $Q_{products}$ is the energy removed by exhaust; iv) Q_{wall} is the energy lost through the walls; v) $Q_{extraction}$ is the energy extracted by the heat exchange.

3.2 Process Analysis

The purpose of this analysis is to attempt achieving elements that can help learning about the important reaction mechanisms resulting from the chemical kinetic involved in this process. Therefore, a pertinent bibliography has been consulted as well as a remote laboratory experience has been performed in order to joint information (at least preliminarily) about the intermediate reactions that might be participating in the process.

First of all, it is known that GGPR's reaction is maintained only whether the glycerol changes from liquid phase to gas phase, which takes place at approximately 540 K. However, it has not been clear if flame front is fed by only vaporized glycerol or there are others other chemical compound arising from thermal degradation of glycerol, when it is heated by the flame front. Based on the below Equation (8) and (9) (Lin, 2013), the energy enough to the complete glycerol pyrolysis is much higher than that one necessary to the phase change of this fuel.

$$(C_3H_8O_3)_{liquid} \Rightarrow (C_3H_8O_3)_{Vapor} \qquad \Delta H_{298.15} = 89.69 kJ.mol^{-1} \quad (8)$$

$$(C_3H_8O_3)_{liquid} \Rightarrow 3CO_{(g)} + 4H_{2(g)} \qquad \Delta H^{o}_{298.15} = 251 kJ.mol^{-1} \quad (9)$$

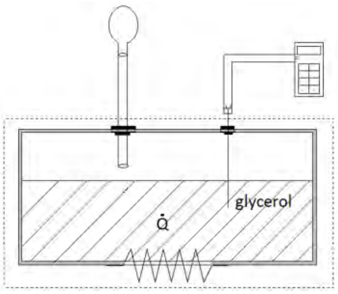


Figure 4: Auxiliary device for identifying gaseous compounds on the glycerol evaporation

Based on (Valliyappan *et al.,* 2008), the thermal decomposition of glycerol for producing syngas effectively occurs at temperature superior 950 K and in lower temperatures there is production of gases with high calorific value above that of the synthesis gas. Therefore a small and simple experiment in laboratory was performed to identify some intermediate compounds that are released when the glycerol is heated/vaporized by the energy from the flame front.

A simple experimental apparatus was used to make possible to study the reactions (8) and (9), through samples obtained from the exhaust at temperature similar to actual reaction such that occurs in the GGPR. Figure 4 presents a schematic drawing about this setup employed in the analysis.

Basically, the proposed system consists of a thermally insulated reservoir and filled with alumina spheres and liquid glycerol. It is electrically heated at its base in order to provide heat to glycerol to verify if there is thermal degradation or only change of state (from liquid to steam). In this reservoir, three bores were made to install thermocouple, exhaust tube and sample collect tube. Initially, the glycerol was gradually heated up to reach boiling temperature (around 540 K) and in this moment the gases over liquid surface were sucked by a vacuum pump to remove the gases from glycerol mixed with air. After, some gas samples were obtained from a point close to liquid surface and conducted to chromatography. Restricted results have pointed out that after the phase change there is the formation of intermediate compounds such as hydrocarbons, such as iso-propane and iso-butane, besides glycerol steam and small acrolein content.

Based on this complementary study through this small setup, it is possible to conclude that the process is much complex than it was expected, because in the reaction mechanism should included not only glycerol oxidation but also other reactions of these compounds obtained during the boiling process. It should be highlighted that the glycerol oxidation in itself is complicated a lot and few studies have dealt with chemical kinetic of this substance, and also it is very complex the reaction modeling about oxidation of glycerol and its aggregated compounds and in porous chamber, as occurs in the GGPR.

In this context, some proposals have arisen about glycerol oxidation, for instance, Lin (2013) has suggested a global mechanism to explain the partial glycerol oxidation, represented by Equation 10:

$$C_3H_8O_3 + \left(\frac{3-x}{2}\right)O_2 \Rightarrow xCO_2 + (3-x)CO_2 + 4H_2 \qquad \Delta H = (-598 + 283x).kJ.mol^{-1} \tag{10}$$

Also, it is essential to control the operating parameters of the process, due to the dehydration of glycerol produced is called the toxic acrolein (C_3H_4O), in which its production is inhibited at temperatures around 970 K (Wang, 2010). For the dehydration of glycerol, represented by Equations (11) and (12), the reaction energy value below presented encompasses both the reactions:

$$C_3H_8O_3 \Rightarrow C_3H_6O_2 + H_2O \tag{11}$$

$$C_3H_6O_2 \Rightarrow C_3H_4O + H_2O \qquad \Delta H = -24.9.kJ.mol^{-1} \tag{12}$$

The experimental results of the glycerol oxidation in the GGPR have pointed out a temperature range from 1150 to 1650 K, in which the reactor worked at equivalence ratio range from 0.5 to 5, respectively. So, it is supposed to find out a little concentration of acrolein in the products, as was proves by chromatography analysis. However, this reaction analysis should be better studied with more experimental investigations in order to achieve a more realistic comprehension about this process.

4. RESULTS AND DISCUSSIONS

4.1 Theoretical Results

It expected that the enthalpy and product concentration at the reactor outlet is a function of equivalence ratio of the air-fuel mixture. Based on that and utilizing the software *EES* (Engineering equation solver), it was performed a simulation, considering the chemical equilibrium condition, in order to infer the behavior of a variable in relation to another in a wide equivalence ratio range. Figure 5 shows the product composition by simulation of the glycerol oxidation as a function of equivalence ratio, in which when the mixture is rich (Φ>1), the predominant products are of an incomplete combustion (H_2 and CO). On the other hand, for lean mixtures (Φ<1) there are high content of CO_2 and H_2O and for the stoichiometric mixture (Φ=1) it was observed an inflection point on the graph.

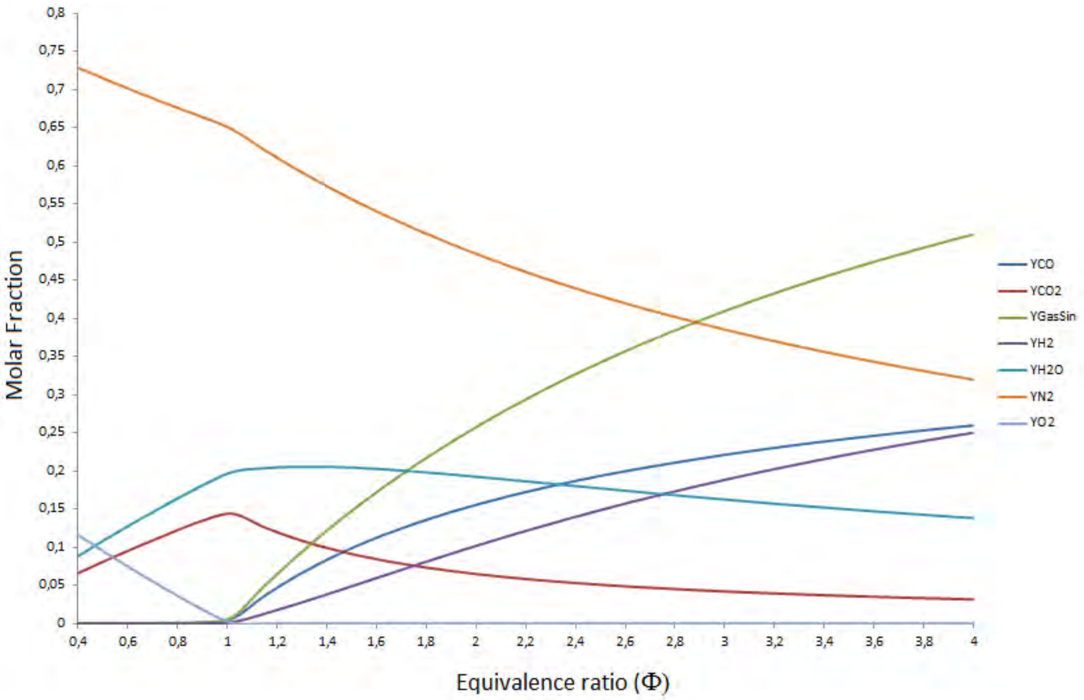


Figure 5 - Composition of the product stream as a function of equivalence ratio (Φ) in the state of chemical equilibrium.

4.2 Experimental Results

For a correct analysis of the data is necessary to choose a chromatographic method that will best represent the composition of the exhaust gases from the thermal decomposition of glycerol. For the glycerol decomposition, was used a portable-chromatograph, model CP-4900 Micro Gas Chromatograph manufactured by Varian. The chromatographic method TCD (thermal conductivity detector) was chosen as a method for achieving to represent a high precision the composition of gases from the glycerol. The method consists of varying the thermal conductivity of the carrier gas (helium) in the absence and presence of molecules of the gas to be analyzed. It is known the thermal conductivity of most gases, so just compare with the signal from the chromatograph and to infer the quality and quantity of gas powered.

For the partial oxidation, was used a chromatograph model 6098N, manufactured by Agilent, and the methods of chromatograph was the TCD and FID (flame ionization detector) methods. The FID method consists in the generation of an electric signal when the combustion of the samples is realized.

For the chromatographic analysis of the products of the glycerol decomposition test, the software used to interpret the signal emitted from chromatograph was Varian interprets and returns to the user a peak whose area represents a molar fraction of the given component of the mixture. Chromatograph's calibration allows to analyze components of the kind hydrocarbons and air (oxygen and nitrogen), which is very relevant since is known that hydrocarbons are intermediary to the production of synthesis gas. As expected on rich mixtures ($\Phi>1$) production of synthesis gas (hydrogen and carbon monoxide) is favored. It is observed that the fuel is almost completely consumed; then the reaction may achieve high conversions.

The assembled system, shown diagrammatically in Figure 4, confirms the hypothesis that hydrocarbons are formed during thermal decomposition of glycerol. Iso-propane and iso-butane are present in greater quantities in the chromatographic analysis shown in Table 2. There is absence of hydrogen and carbon monoxide when the temperature is lower than the temperature at which the synthesis gas is produced effectively (1100 K); and as already discussed short-chain hydrocarbons (iso-propane and iso-butane) are formed as intermediates in the production of synthesis gas. It is known that products shown in Table 2, after heating, will become other compounds. The product's analysis has been realized in function of the equivalence ratio at 800ºC temperature and 1 atm.

Table 2 - Weight fraction (X) of the product stream from the thermal decomposition of glycerol, without considering the presence of contaminants sampling as air, phenols and NO_x.

Sample	Time (min)	Temperature (K)	X_{CO2}	$X_{iso\text{-}C4H10}$	$X_{iso\text{-}C5H12}$
1	95	524	0.357883	0.450762	0.19135
2	100	533	0.078737	0.69240	0.228862
3	105	534	0.081318	0.731549	0.187133
4	110	541	0.081318	0.731549	0.187133
5	115	547	0.171777	0.648854	0.17937

Figure 6 aims to show the temperature distribution profiles inside the porous medium of the GGPR, working at wide equivalence ratio range ($0.5<\Phi<5$). Analyzing this figure, it is realized that peak of temperature in the porous chamber are placed at different positions. It can be explained by the high distance of flame front from the liquid surface that is function of equivalence ratio and energy stored in porous matrix.

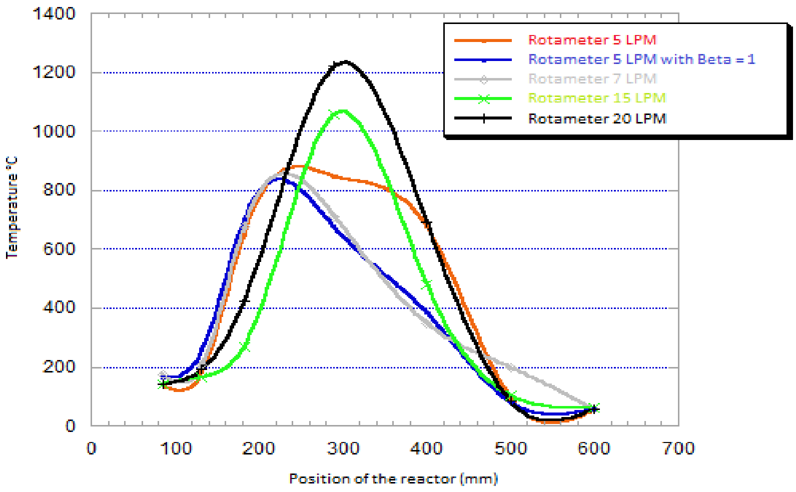


Figure 6: Temperature distribution profile along the GGPR's chamber for different air flow rate.

5. CONCLUSION

The development of this non-conventional gasifier (GGPR), designed and operated according to the principles of Filtration Combustion, proved the technical feasibility of using a porous medium for biomass gasification. The objectives defined in the research planning were reached, although to be dealing with originality in terms of gasification reactor. The syngas producion from glycerol partial oxidation in the GGPR has presented good reaction stability.

The experimental and theoretical studies helped understand the process of this new concept of gasification reactor, so that the parameters calculated analytically allowed reducing the time and cost of developing of the protopypes. In the experiments, important process phenomena could be observed, which have characterized the working principle of this gasifier, such as: i) the freely propagation of the combustion wave in porous chamber, maintaining a self sustained reaction a certain distance from the surface of the liquid; ii) the profile of temperature distribution in the porous medium; and iii) the stability of the reaction as a function of the ratio equivalence, among others.

The insertion of a heat exchanger at the top of the gasifier for simultaneous extraction of energy from the reaction zone proved to be an effective strategy for thermal control of the process, especially ensuring stability and security for the facility. On the other hand, the column of liquid (glycerol) at the bottom of the gasifier served with thermal barrier to propagation of the heat wave, while keeping a temperature gradient which protected its end.

Thus, this porous to liquid biomass gasifier presents itself as an economically viable alternative to mitigate the environmental impacts due to large current stocks of glycerin in transesterification plants of vegetable oils into biodiesel.

6. ACKNOWLEDGEMENTS

This work was supported by a Brazilian Government's Scientific and Technological Development Institution, CNPq - National Council of Technological and Scientific Development.

7. REFERENCES

Babkin, V.S., "Filtration combustion of gases, present state of affairs and prospects", Pure and Applied Chemistry, **65**: pp.335-344 (1993);

Barcellos,, W. M., Souza, L. C. E. O., Saveliev, A.V., and Kennedy, L. A., Ultra-low-emission steam boiler constituted of reciprocal flow porous burner, Experimental Thermal and Fluid Science, 35: p. 570–580, 2011;

Buhler , H.J., Ederer, A., and Kruse, C. M., "Ionic reactions and pyrolysis of glycerol as competing reaction pathways in near- and supercritical water" The Journal of Supercritical Fluids, 22: p. 37-53, 2002;

Castro, C.E., and Rust, F.F., Thermal Decomposition of Acrolein. The Attack of Methyl and t-Butoxy Free Radicals on Acrolein, *J. Am. Chem. Soc.*, 83 (24): pp 4928–4932, 1961;

Cordoba, A.Y.M., *Study of direct combustion of crude glycerin and blonde as alternative sustainable energy.* Doctor thesis, Federal University of São Carlos, São Carlos, 2011;

Eners, 2010. Production of Biodiesel in the world: 2007, 2008, 2009. Biofuels Plataform, Energy Concept, Lausane-Switzerland, v.1: p.1-3, 2010;

Guo, S., Guo, L., Cao, C., Yin, J., Lu, Y., Zhang, X., "*Hydrogen production from glycerol by supercritical water gasification in a continuous flow tubular reactor*" International Journal of hydrogen energy, 37: p.5559-5568, 2001;

Lin, Y.C., 2013. "*Catalytic Valorization of glycerol to hydrogen and syngas*" International Journal of hydrogen energy, 38: p. 2678-2700, 2011;

Martins, D.F., Contribuição ao estudo da reforma a vapor do glicerol em catalisadores Pt/c - efeito do tamanho da partícula de Pt e do Ph da solução de alimentação, MSc. Dissertation - Universidade Federal de Uberlândia (MG), 2009;

Mota, C.J.A., Silva, C. X. A., Valter L. C., 2009 "Gliceroquímica: Novos produtos e processos a partir da glicerina de produção de biodiesel". Quím. Nova, v.32, nº3: p. 639 – 648, 2009;

Striugas N., 2009 *Investigation Of Hydrogen Rich Gas Production By Thermal Glycerol Fraction Decomposition* Kaunas University Of Technology Lithuanian Energy Institute , Kaunas, thesis, 2009;

Parente R.B., *Reactor development of porous biomass gasification liquid applied for the partial oxidation glycerol.* MSc. Dissertation , Universidade Federal do Ceará, Fortaleza, 2012;

Perdersen-Mjaanes H., Chan L., Mastorakos E., "*Hydrogen production from rich combustion in porous media"* International Journey of hydrogen, 30: p. 579-592, 2005;

Toledo M., Vergara E., Saveliev A., "*Syngas production in hybrid filtration combustion"* International Journey of hydrogen, 39: p. 3907-3912, 2011;

Valliyappan T., Bakhshi N.N., Dalai A.K., "*Production of hydrogen and syngas via Steam Gasification of glycerol in a fixed-bed reactor"* bioresource technology, 99: p.4476-4493, 2008;

Wang W. Thermodynamic analysis of glycerol partial oxidation for hydrogen production. Fuel Process Technol 2010; http://www.wolframalpha.com/input/?i=glycerol

8. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.