Syngas from Glycerine by Electric Arc

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Abstract

This article reports the advance in the research that is being followed in the Universidad Industrial de Santander, within the framework of the Alternative Energies research line, we attempt to give an additional value to residual glycerine (1, 2, 3-propanetriol) from the industrial production of bio-diesel in Colombia, by generating synthesis gas (Syngas) through molecular breaking by means of electric arc generated plasma. To reach this goal there is being followed a set of lab tests, kinetic-chemical simulation, energy efficiency and environmental impact evaluation have been obtained in research.

Keywords: Biodiesel, Glycerine, Syngas, Plasma, Electric Arc, Gasification

1. Introduction

Within the frame work of the global energy crisis that has been intensifying in recent decades, arises the need to find alternative sources to provide the energy needed to operate the world in the short, medium and long term.

As a response to this pressing need arise, the so called bio-fuels, originating from plant sources and biomass, in which the biodiesel is an alternative that has had a widespread use and a wide range of applications and developments.

The biodiesel manufacturing process currently comes along with a large-scale production of a by-product called glycerine or glycerol (1, 2, 3-propanetriol), the total quantity of glycerine is the sum of those produced by this process and the direct production from industry, this has maintained a growth in the glycerine offer that has led to a gradual saturation of the glycerine market in the world. It is worth noting that the rate production of glycerol related to biodiesel is estimated at around 1 kg of glycerol per 10 kg of biodiesel produced. [1]

Thus comes up the need to find new ways to use and commercialize glycerine as a by-product of biodiesel.

With this perspective the present research seeks to establish perspectives and to offer alternatives to be modelled and simulated for the generation of synthesis gas (Syngas) from the glycerol, as a base material or precursor of the subsequent acquisition of methanol, using at first instance, the arc generated plasma.

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2. Conceptual framework

2.1 Glycerol

Glycerol or glycerine, is a poly-alcohol, is nontoxic and is one of major products of digestive degradation on lipids, is a prelude to the Krebs cycle. It is also produced as an intermediate product of alcoholic fermentation. Glycerol, along with fatty acids, is one of the components of simple lipids such as triglycerides and phospholipids.
Glycerine has thousands of applications, with large quantities used for the manufacture of medicines, cosmetics, toothpaste, urethane foam, synthetic resins, gums and other applications. The production of snuff and food also consumes large amounts of glycerol.

2.2 Syngas

The synthesis gas (Syngas) is a mixture of hydrogen (H2), carbon monoxide (CO) and other minor gases. This gas is used as the main intermediate for the production of hydrogen and other hydrogen-based chemical compounds with high added value as ammonia, liquid fuels and solvents, among other products. In the industry, Syngas production from methane or low molecular weight hydrocarbons can be carried out in various ways: Refurbished Catalytic Reforming Thermocatalytic, Partial Oxidation, etc. The Syngas formed by endothermic reactions (steam and CO2 amended) requires high energy inputs. The most simple and efficient conventional method for production of Syngas could be the hydrocarbons oxidation in air, as described by the ideal equation:

$$\begin{aligned} & C_nH_mO_p + x(O_2 + 3.76N_2) \rightarrow \\ & nCO + m/2H_2 + 3.76(n/2 - p)N_2 \qquad [1] \\ & Para\_x = (n/2 - p) \end{aligned}$$

The increase in x from (n/2-p) for rich mixtures increases the heat of the reaction, but at the same time, produces carbon dioxide and water vapour, thereby reducing the amount of Syngas generated. The oxygen to fuel ratio (x) determines the heat of reaction and the amount of Syngas generated. For this process, it has been traditionally used as a catalyst the nickel supported on gamma-alumina (Ni/γ-Al2O3), but the problems relating to the volume of the catalyst, catalyst poisoning and high maintenance costs have limited application to large-scale industrial operations.
The use of high activity electric shock (plasma) for this conversion has been tested and studied numerically in the last decade, but the traditional plasma systems cannot simultaneously provide high power density for large-scale industrial applications with high outputs, and at the same time a selective chemical conversion process. More broadly, understanding the physics of electric shock has brought, as a result, the development of a new class of discharge systems, which fall into the category of transition shock, still very attractive for the applications sought.
These are discharges with plasma parameters between heat and cold non-thermal transition called thermal shock / no-heat, where the gas temperature significantly increases (2000 - 3000 K), but downloads are still not in thermal regime. Gliding Arc Reactor is an example of such systems [2 and 3].

2.3. Plasma generation by electric arc

Plasma is an ionized gas, for which nature has been called the fourth state of matter. "Ionized" means that it has lost at least one binding electron on the molecule of precursor gas. When the temperature is increased the molecules become more energetic and transform the sequence of matter solid, liquid, gas and finally, plasma. This is why it is called the "fourth state of matter."

The free electric charges, electrons and ions, plasma give a high electrical conductivity (an index of greater than gold or copper), an internal interactivity and a strong response to electromagnetic fields.
The plasma state occurs naturally but can also occur intentionally in a laboratory or in industry, allowing many opportunities for many applications, including thermonuclear synthesis, electrolysis, laser, fluorescent lamps, and many more.
For processes of technological development such as this, the plasma provides three main features that are particularly attractive:
The temperature and energy can significantly exceed those seen in more conventional technologies.
In the plasma state there can be obtained very high concentrations of energy and active substances (electrons, ions, atoms and radicals, excited states, and photons of different wavelengths).
In a state of plasma there are essentially conditions far from equilibrium, providing very high concentrations of active substances and maintaining the temperature as low as molar environment has.
These features allow a significant intensification of traditional chemical processes, increasing efficiency, and usually allowing the successful simulation of chemical reactions, something impossible in conventional chemistry.
When a voltage source coupled to a set of electrodes (with a mutual distance of relative closeness) is able to generate a voltage large and long enough, it might cause the overcoming of the dielectric strength of the medium in which the electrodes are immersed, allowing the electric conduction of the medium and generating the electric arc between the electrodes and a consequent rise in temperature in the vicinity thereof, thereby raising the temperature of the medium to levels that can induce the formation of plasma.
Typically in these procedures is used what essentially consist in an arrangement of two electrodes, for which it is possible to vary their separation, these electrodes are subjected to a potential difference which produces an electric field between them by subjecting the material to dielectric stresses and eventually causing a discharge into the material by altering their electrical and chemical characteristics as seen. [5]

2.4 Plasma chemical processes

Each plasma chemical reaction is characterized by factors and components, including: The reactants, products, pressure, temperature, heat of reaction (H-enthalpy-constant pressure, U-internal energy, constant volume) and the conversion factor ρ. There action rate coefficient for electron reactions (described in Table 1) can be calculated once we have two important relationships:

- The distribution of electronic energy.
- The "cross section" σ for the process.

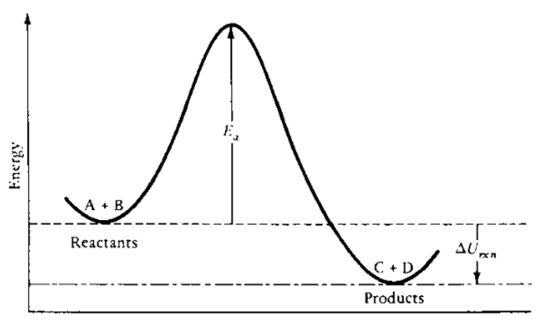

Figure 1. Reaction A + B + C + D: If one of the reactants is brought to an excited state B = M *, it can overcome the activation energy, initiating the reaction [Eliasson, p1069].

Given that the cross section is known as a function of energy or velocity and the electronic distribution function is calculated by solving the Boltzmann equation, the conversion factor can be calculated by solving the integral:

$$\rho = \langle v\sigma \rangle_f = \int_0^\infty v \cdot \sigma \cdot f(\varepsilon) d\varepsilon \qquad [2]$$

Where the function of electronic energy distribution has been normalized as:

$$\int_0^\infty f(\varepsilon) d\varepsilon = 1 \qquad [3]$$

In the case of a reaction between two atoms or molecules, the procedure for calculating the energy of the process is basically the same. For this case it is necessary to take into account the movements of both species involved A and B, which have their distribution functions for each species.
Table 1 shows the main chemical reactions generated by the plasma effect (s) of reagent (s). In this case the excited species are marked with an asterisk (*), ions are marked (+ or -), M is an intermediate time of collision, A and B are atoms.

Table 1. More common types of Plasma-chemical reactions. [4]

Electronic/Molecular Reactions	
Excitation	$e + A_2 \rightarrow A_2^* + e$
Dissociation	$e + A_2 \rightarrow 2A + e$
Linking	$e + A_2 \rightarrow A_2^-$
Dissociative Linking	$e + A_2 \rightarrow A^- + A$
Ionization	$e + A_2 \rightarrow A_2^+ + 2e$
Dissociative ionization	$e + A_2 \rightarrow A^+ + A + e$
Recombination	$e + A_2^+ \rightarrow A_2$
Detach	$e + A_2^- \rightarrow A_2 + 2e$
Atomic / Molecular Reactions	
Closure decoupling	$M^* + A_2 \rightarrow 2A + M$
Closure ionization	$M^* + A_2 \rightarrow A_2^* + M + e$
Load Transfer	$A^{\pm} + B \rightarrow B^{\pm} + A$
Ionic recombination	$A^- + B^+ \rightarrow AB$
Neutral recombination	$A + B + M \rightarrow AB + M$
Decomposition	
Electronic	$e + AB \rightarrow A + B + e$
Atomic	$A^* + B_2 \rightarrow AB + B$
Synthesis	
Electronic	$e + A \rightarrow A^* + e$
	$A^* + B \rightarrow AB$
Atomic	$A + B \rightarrow AB$

To describe the family of volumetric discharge electrons out of balance, the majority of the 4 families of above reactions are important. In stationary situations, the loss of electrons by coupling and recombination must be balanced by ionization processes and disengage. For the treatment of these systems require computers with enough processing power to solve the Boltzmann equation in the generated systems as well as the differential equations that describe the main reactions. [4]

3. Materials and equipment used

• Igniter with tests container.
• Reactor plasma arc made up of: container, electrodes, power supply, circuit, and voltage transformer (12V, 24000V).
• IR Thermal Imaging Camera.
• Multimeter FLUKE brand (2)
• Oscilloscope FLUKE brand.
• Gas Chromatograph with TCD sensor Agilent 5973N.
• Gas analyzer LAND
• Patterns of H2 and CO provided by AGA.
• Samples of glycerol from ECODIESEL Bidets Ltda.
• High purity glycerol, Merck.

4. Results and discussion

4.1 Dielectric stiffness determination for glycerol

To study the formation of Syngas in plasma reactors, there were determined experimentally the break over voltage of glycerol samples from bidets, using a dielectric meter in insulating oils (igniter), from tests following the standard for testing insulating oils, NTC 3218.

Figure 2. Test vessel for the igniter coupling

For this purpose there were performed a set of tests prescribed by the standard then there were verified the match criterion statistics. The result of the break over voltage with electrode gap of 1cm was as follows:

$$V_{sample_{break}} = 3640.1[V]$$

4.2 Determination of the energy efficiency of glycerol conversion in syngas

The next step performed was to determine the energy efficiency of glycerol conversion process shown in Syngas, breaking through molecular action of plasma produced by the arc.
To do this, it was designed a test reactor that consists of:

- Pulse generator with high current power supply.
- Booster transformer with optimum insulation.
- Acrylic airtight container for carrying out the reaction.
- Stainless steel electrodes for arc generation.

Figure 3 shows the complete assembly of testing prototype and, Figure 4 shows a detail of the electrodes arranged within the container.

The measurements were made taking into account the experimental design. Based on what is said above, there were taken measurements of the input electrical power and the amount of Syngas produced was sensed by a gas analyzer coupled to the reactor. The relationship H2/CO of Syngas generated was determined by gas chromatography in samples selected at the end of each run of the process. The tracking variables were the running time of the process, the frequency of the voltage, distance and shape of the electrodes.

Figure 3. Complete assembly of testing prototype

Figure 4. Details of the reactor ready for testing

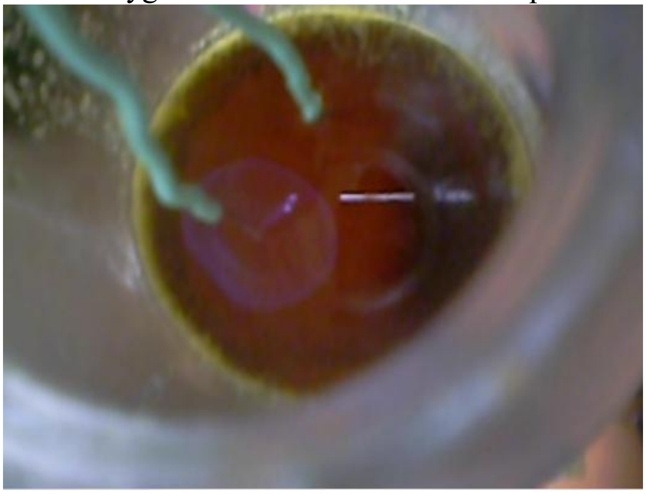

Figure 5. Details of combustion from gas generated by gasification of crude glycerol with electric arc

Figure 6. Detail of gas production from electric arc generation in USP type glycerol

Using the partial oxidation glycerol can be reformed into Syngas without extra oxygen.
Preliminary results show the generation of gas for USP glycerine samples (Figure 6), and combustion for gas generated from crude glycerol samples, after applying a high voltage between electrodes immersed in the sample.
Moreover, the preliminary monitoring of temperature in the plasma yields average values between 600 °C and 900 °C for different input voltage levels.

5. Research development

The preliminary stages of the research project is focused on identifying and establishing the real potential of the proposed idea, for which there is being conducted a series of processes of experimentation and simulation that will meet the conditions and technology and energy requirements of a procurement process Syngas arc. From these data there shall be a general map of the process that will take into account the physical, chemical and economical variables, thus providing with a sufficient margin of confidence, the viability and benefits of the proposed technological development. For this purpose, there are being developed the following research topics:

5.1 Determination of the energy efficiency for the process

For this topic it is expected to quantify the Syngas produced by gasification of crude glycerol In the plasma reactor of Figures 3 and 4, correlating with the energy of the process input. The general scheme of data collection is shown in Figure 7.

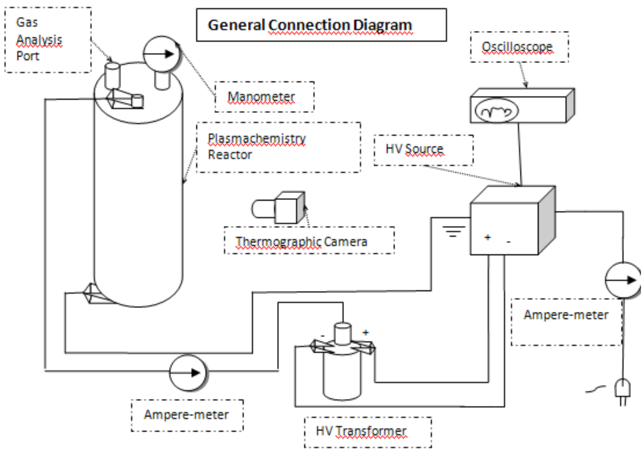

Figure 7. General scheme for experiments made in order to determine the energy efficiency of the process.

5.2 Economic efficiency for the process

This topic discusses the economic efficiency of the process, taking into account the cost of electrical energy input in the process and the cost of Syngas generated and by this way to determine the efficiency of the process.

5.3 Simulation

In addition to laboratory tests that have been performed, there are performing simulations of processes with the help of specialized software such as CHEMKIN ® and COMSOL®, which take into account the physical and chemical variables of the process, and with reference counting and a source of information regarding the experimental data and literature.
The process will allow more detailed description of the process, taking into account the energy factors, the characteristics of the prototype and the raw material and first-level considerations of thermodynamic processes developed in the process. The data used in the simulation come from the developed experimental tests, as well as those reported in the literature and similar investigations were carried out.

6. Conclusions

Via plasma reforming of raw materials and waste products is a promising alternative to obtain energy as hydrogen and products of interest from a source with added value, such as Syngas.
The results obtained in tests show the generation of combustible gas from crude glycerol samples and quality USP samples, allowing to preliminarily conclude that the feasibility of the process of obtaining Syngas from glycerol remaining in the production of biodiesel, via gasification witch plasma generated by electric arc. This type of process is noted for its low requirements on equipment and less drastic conditions, in terms of pressures and temperatures compared to other forms of plasma generation.
Results were obtained threshold voltage disruption of crude glycerol of 3640 V, allowing projecting the necessary equipment for the generation of electric arc plasma in the test material.

References

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