Hydrogen Production from the Oxidation of Human Excretion Products

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Abstract An electrochemical system was developed to produce hydrogen from organic compounds present in the products of human excretion. The electrochemical reactions were separated into two compartments: the oxidation of organic matter in an anodic half-cell and the production of hydrogen by the reduction of hydronium ions present in the chemical equilibrium of the water in a cathodic half-cell. A membrane system separates the half-cells and a system of electric bridges compensates the current flow generating two perpendicular to each other electric fields and establishing experimental load/mass balance, generating a selective ion flow cell (SIFC) which produces hydrogen with values higher than 90% purity, also, it is energy efficient because it produces 79% of the electrical energy applied to the system. In this work was used as reference molecule urea, which is the most abundant organic compound in the urine.

1. Introduction

The harmful climatic effects have been increasing throughout the history by the handling of the polluting emissions mainly towards the atmosphere, being the emissions caused by the fossil fuels the most forceful [1]. The study of molecular hydrogen (H_2) as an alternative energy source has shown significant advantages to reduce pollution, because it produces clean combustion producing only water after the reaction, in addition it emits more energy than the first mentioned, comparing the heat of combustion Of gasoline (47 MJ kg^{-1}) and hydrogen (142 MJ kg^{-1}), It is evident that the latter is 302% more energetic [2]. According to the so-called hydrogen economy, its use is limited by the difficulties in storage, transport and relatively high energy consumption to produce it [3].

In order to solve energy problems in the production of H_2 it has been found that this gas can be produced by electrolysis of urea [4]. Studies show that by modifying electrochemical conditions and in general chemical conditions it is possible to carry out the oxidation of urea (by urea / urine electrolysis) in such a way that it is carried out with energy viability [4 – 9]. In addition it is known that urine is the most abundant residue of the planet and it is part of the charge Pollutant of the waste water because it is part of the excrements. The urine contains 22 g of urea per liter and it can be a direct source of urea [10], therefore it is feasible to produce hydrogen from the PHE, however, although the urine electrolysis systems reduce the potential required with respect to water electrolysis [4] (main H_2 source), because of the complexity of the matrix they generate several by-products in the process of obtaining of H_2; There are many undesirable reactions within which the formation of solids, foam and different gases are present which can be present in higher concentrations than hydrogen gas, also the high presence of salts with alkaline and alkaline earth cations change the electrochemical properties in a system affecting the production of H_2 cause electrode position phenomena in the electrodes of an electrolytic cell.

Due to the above it is necessary to separate the oxidation process of the products from the human excretion of the reduction (hydrogen production) in such a way that H_2 is obtained as clean as possible avoiding the presence of undesirable electrochemical reactions and reducing the energy consumption for that reason.

Separating the anodic reaction from the cathodic process involves taking into account charge and mass transport mechanisms through the electrolytic system ensuring that the mass/charge transfer between an anodic compartment and a cathodic compartment is selective and efficiently dynamic. For that it is necessary to use the system designed in this research, a selective ionic flow cell (SIFC). This system is unique and completely new, therefore, the first studies about its operation and its energy efficiency are reported here.

Materials and Methods

Reagents

Merck Ammonia solution 32% - 105426

Merck Sodium hydrogen carbonate - 106323

Merck Nitric acid 20% - 100456

Pearly urea Iagro

ASTM A240 316 stainless steel electrodes

Materials

Cast Acrylic thickness 100 mm

Protek DC Power Supply 3003B

AMS-HPS-100 percentage of hydrogen sensor

HoneywellAWM3300Vairflow sensor calibrated for H_2

Method

The electrolyzer is a system of steel electrodes configured in such a way that two electric fields are generated (Figure 2). In the cathode compartment as well as in the anodic stainless steel plates are formed which make up the electrodes and the electric bridge (figure 1). In the anode occurs mainly urea oxidation in presence of water generating gaseous nitrogen, carbon dioxide, hydronium ions and electrons (semi-reaction 1a), in the cathode hydroniums that pass through a cation exchange membrane are reduced producing molecular hydrogen (semi-reaction 1b).

The conditions of the electrolytic cell when only working with urea pattern are: at the anode it requires water, urea and a conducting electrolyte as a salt (in this case sodium bicarbonate) and the cathode only needs water and small amounts of HNO_3 a Electrolyte carrier; And when the system works with urine: at the anode the urea and the conductive salt are replaced by urine as it provides the 2 substances mentioned, while at the cathode the conditions are kept constant.
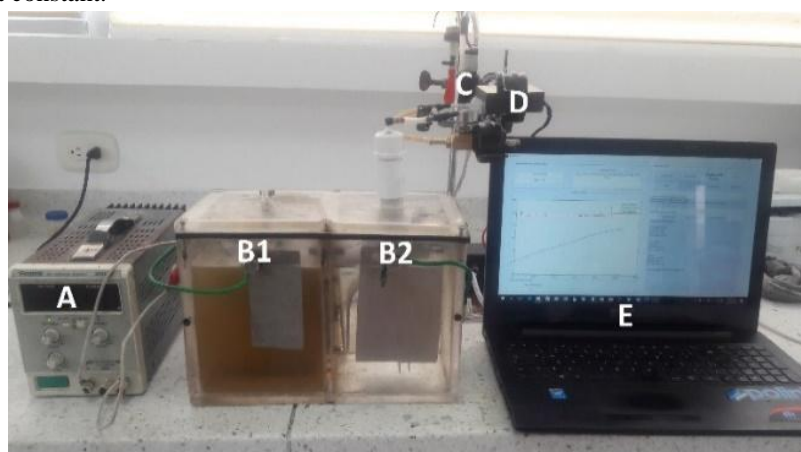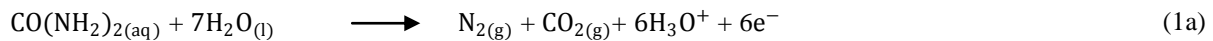

Figure 1: Photograph of the electrolyser with the measurement system. A. Power Source, B1. Anode containing urine, B2 Cathode containing acid water, C. AMS-HPS-100 sensor, D. Honeywell AWM42150VH sensor, E. Registration MhydrosSystem.
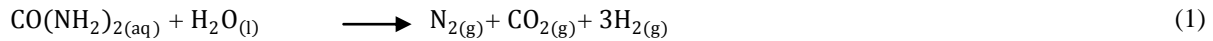
Anode

$$CO(NH_2)_{2(aq)} + 7H_2O_{(l)} \longrightarrow N_{2(g)} + CO_{2(g)} + 6H_3O^+ + 6e^-$$ (1a)

Cathode

$$6H_3O^+ + 6e^- \longrightarrow 3H_{2(g)} + 6H_2O_{(l)}$$ (1b)

Cell

$$CO(NH_2)_{2(aq)} + H_2O_{(l)} \longrightarrow N_{2(g)} + CO_{2(g)} + 3H_{2(g)}$$ (1)

The H_2 produced by the cell is quantified by a monitoring system that allows the measurement of the amount of this gas in line and continuously. The H_2 produced at the cathode is monitored by the Mhydros system, which is composed of a HPS-AMS-100 concentration sensor that measures the percentage of hydrogen, another airflow sensor calibrated for H_2 (Phidgets sensor that is based on Pressure differences) that measures the total volumetric flow, another sensor that measures the current applied to the system [11]. Knowing that the heat of combustion of H_2 is 286 kJ mol^{-1}, it is established the energy generated by the electrolytic cell that compared to the energy applied allows to calculate the energy efficiency of the system.

Results and Discussion
It was possible to construct the electrolyzer (in patent process according to call PIPM-17 of iNNpulsa Colombia) that allows the production of hydrogen from urine with a high degree of purity, values ranging from 63 to 92% H_2 are recorded in Table 1.

Table 1: Relation between the amount of hydrogen produced and the energy of the system: From the concentration of H_2 produced (% H_2) and gas flow measured in milliliters per second (mls^{-1}), the energy produced by the system in Joules per second (J s^{-1}) and comparing with the energy applied to the cell by means of a power source it was determined that high energy efficiency is obtained.

Applied Energy (J s^{-1})	Gas Flow (ml s^{-1})	Percent H2 (%)	Produced Energy (J s^{-1})	Energy efficiency
0.92	0.09	92	0.73	0.79
0.92	0.09	76	0.60	0.65
0.92	0.09	63	0.50	0.54

By adjusting values of 4 Volts (V) and 0.23 Amperes (A) that represent 7.5 J s^{-1} with a power source and a flow of 0.09 mls^{-1} various values of H_2 concentration were obtained, each value varies according to the internal configuration of the electrolytic cell. It is observed in Table 1 that the highest percentage of H_2 is 92% which is expressed with the value of energy efficiency of 0.79; Ie, the energy in the form of heat that would be obtained by burning the hydrogen produced in those conditions would be 79% of the energy applied (percentage energy efficiency).The value of 63% represents a lower energy ratio, with an efficiency of 0.54. The table 1 shows three representative values which report that there are variations in the products without varying the applied energy, in fact, lower values of %H_2 have been obtained, this is due to the configurations of the system of membranes, of the system of electric bridge, to the electrode system and to the electrolytes that in the suitable concentrations allow the passage of current through the solutions.

The electrolytic cell has hoses through which gases emerge. These ducts go to the atmosphere, therefore the system initially operates at atmospheric pressure, when a pressure difference (small vacuum) is applied, the reaction in the cathode is increased due to the displacement of the physical equilibrium H_2 Liquid-H_2 Gaseous. In all cases, when the gas produced by the electrolyser is extracted with the low vacuum system, the concentration sensor shows a higher percentage of hydrogen at the same potential and current conditions, therefore it was necessary to establish adequate extracted flows with a low vacuum system so that the water does not vaporize, as for example, in table 1 for 0.92 J s^{-1} applied, a flow of 0.09 mls^{-1} was established.

As for the membrane system, an assembly was carried out in which two ionic transport routes are generated within the solutions, negative charge ions cross the upper zone membrane (figure 2) (hydroxyl ions of the cathode towards The anode), while positively charged ions cross by the lower space (hydronium ions from the anode to the cathode). That facilitates the flow of charges throughout the all system generally improving the dynamic efficiency of the cell (migration load transport). The figure 2 shows how the electric fields are arranged which fix the paths following the ions.
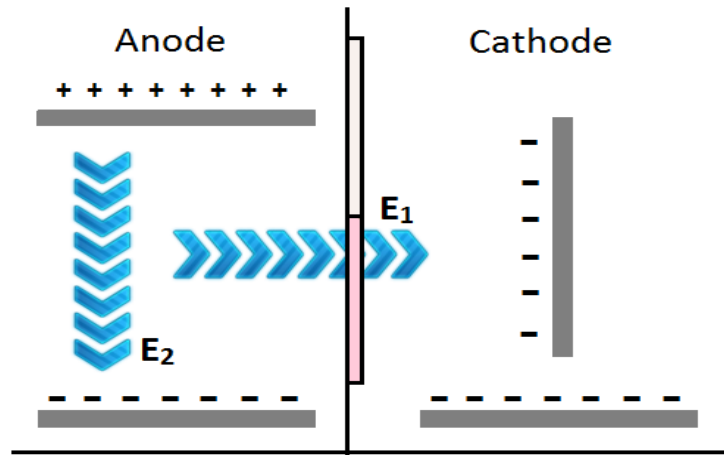

Figure 2: In this figure the electric fields that affect the system are represented in a general way, one with horizontal orientation and one with vertical. "E_2" directs positive ions in the anode from the positive plate to the negative plate, in a vertical manner, however, "E_1" having a horizontal direction deflects the path thereof through the membrane from the anode to the cathode because "$E_1 > E_2$".
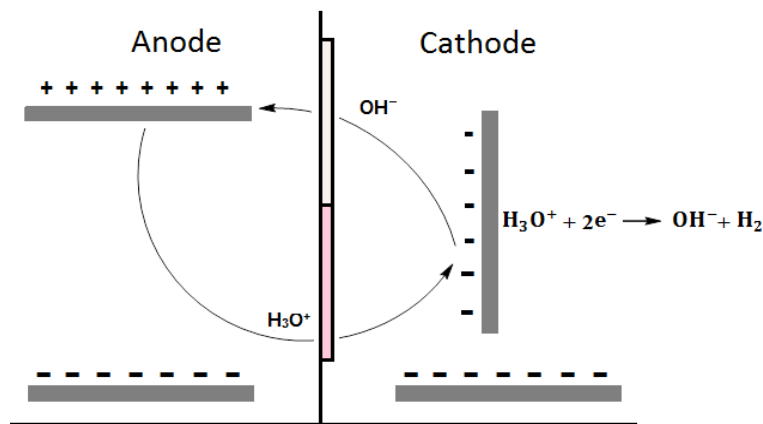
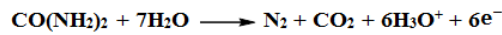$$CO(NH_2)_2 + 7H_2O \longrightarrow N_2 + CO_2 + 6H_3O^+ + 6e^-$$
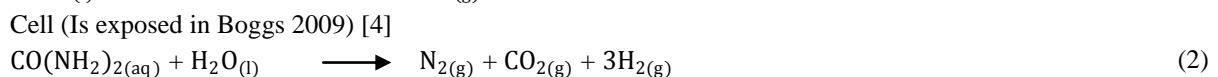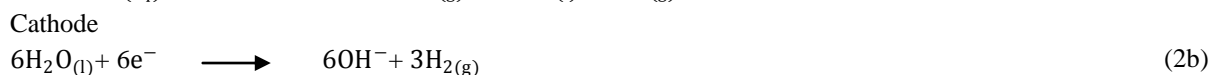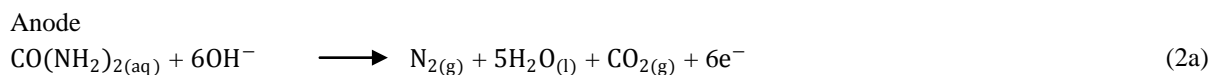

Figure 3: Schematic representation of the movements of the ions through the membranes. The hydronium produced in the anode crosses the lower membrane, while the hydroxyls that are generated in the cathode cross to the anode through the upper membrane.

Anode
$$CO(NH_2)_{2(aq)} + 6OH^- \longrightarrow N_{2(g)} + 5H_2O_{(l)} + CO_{2(g)} + 6e^- \qquad (2a)$$
Cathode
$$6H_2O_{(l)} + 6e^- \longrightarrow 6OH^- + 3H_{2(g)} \qquad (2b)$$
Cell (Is exposed in Boggs 2009) [4]
$$CO(NH_2)_{2(aq)} + H_2O_{(l)} \longrightarrow N_{2(g)} + CO_{2(g)} + 3H_{2(g)} \qquad (2)$$
In the anode, urea undergoes two types of reactions (1a) and (2a). "Reaction 1a" is the predominant one, which occurs initially when the anodic medium is neutral and the "reaction 2a" that can occur in small proportions when the medium becomes basic [4] after the time of electrolysis and/or when adding NH_3OH. In figure 3 is

observed that the urea is oxidized in neutral medium, with presence of water, producing nitrogen, carbon dioxide and hydronium ions; In the electrolysis of urea in addition to cations electrons are produced, which continue their route through the electric circuit while the H_3O^+ cross the selective membrane and are reduced in the cathode because of the electrons coming from the anode by means of the electrodes and of the electric bridge; in the cathode in the reduction according to reaction 1b hydrogen and water are generated and with respect to reaction 2b the products are hydrogen and hydroxyl ions which cross the membrane migrating to the anode.

It should be noted that there are different phenomena of charge transport, the main ones in these experiments are: First; of diffusion, which is due to the concentration gradient of species in the two compartments of the cell. Because the acid (greater acid constant than water) is added in the cathodic half-cell, the concentration of the protons would be higher there, so the tendency due to this phenomenon is that the protons move from the cathode to the anode. Second; Of migration, that is due to the electric field applied; As there is a potential difference between the electrodes, the positive charges migrate to the negatively charged plates, that is, the protons migrate from the anode to the cathode (to the tasting). In this system the transport by migration predominates for cause the applied electrical potentials, because in the cathode the hydronium ions are reduced to molecular hydrogen implying the electrodynamic attraction of more positive charges in such a way that there is electric current in the system, besides the movement by diffusion loses effect since the concentration of H_3O^+ tends to decrease in the cathode due to the proton consumption.

A flow of hydroxyl ions is shown in the Figure3. OH^- ions can be generated either from the reaction of the chemical equilibrium of the water (reaction 3) by the Le Chatelier Principle or from a second half-reaction produced on the cathode electrodes (reaction 2b). Initially hydrogen is generated with the protons that the acid provides and with the protons migrate from the anode, but if in the cathode the potential with respect to the electric bridge increases more than the cathodic half-reactions need,then, the H_3O^+ produced in The reaction 3, can also be reduced and therefore the chemical equilibrium of the water is displaced towards the products, mainly increasing the basic medium by the free hydroxyls.

$$2H_2O_{(l)} \rightleftharpoons OH^- + H_3O^+ \tag{3}$$
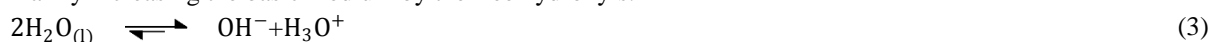
Because of the diffusion and migration phenomena, the hydroxyl anions produced at the cathode are displaced towards the anode by means of a generic membrane where they participate in the oxidation reaction of the urea which occurs in basic medium according to the half-reactions 2a and 2b and to reaction 2. In the anodic compartment, in the half-reaction 2a water is produced but not hydronium ions are generated; while in the cathodic half-cell, semi-reaction 2b, water is consumed from this compartment and no hydroniums are consumed, here also hydroxyls are produced, which in combination with hydroxyls dissociated by water move through the membrane system towards the anode.

It should be noted that reactions 1 and 2 have the same stoichiometric proportions, indicating that they are the same reaction but coming from different routes. In general, for each mole of urea, 3 moles of hydrogen, 1 mole of nitrogen and 1 mole of carbon dioxide are produced.

Figure 3 is based on the migration of hydronium and hydroxyl ions because the system generally works with respect to these phenomena. These migrations are always due to the electrical potential supplied to the cell and on account of the system need there must be sources of ions, the anode and the cathode respectively. Then, if the cathode requires protons, in the anode these must be generated in some ways including the reaction of the water balance (reaction 3), which mostly tends toward the products, the same happens in the cathode, where the tendency is to move the reaction 3 to the right to supply the amount of hydroxyl the potential demands. Therefore, and in general terms, the phenomena have as one of their main bases the chemical balance of water. Now, the main purpose of the cell is to generate hydrogen and for this the hydroniums are reduced also producing hydroxyls, and this is way like described the cathodic process in figure 3.

Analysis about Percentage Energy Efficiency

Although the CFIS is a system that combines several processes such as the oxidation of organic molecules present in the urine (mainly urea) and the chemical balance of water, it is a system that works with the application of electrical energy, therefore it is electrolytic, then, the comparison of the final result (its maximum

energy efficiency) should be based on other types of electrolysis cells of urine or urea that report values of energy efficiencies.

First in the work Kim et al., 2013 a cell was studied to produce hydrogen and to carry out water treatments with an anode of TiO_2 doped with bismuth oxides and stainless steel cathode and using as electrolytes $LiClO_4$ or Na_2SO_4 when it works with urea and without electrolytes when it works with urine, that cell works with 3 V and 0.03 A and generates an energy efficiency of 10%. That cell is coupled to a photovoltaic cell in such a way that the energy that is used for electrolysis is solar energy [12]. The increase in energy efficiency of CFIS (79%) is very considerable compared to the 10% reported for that cell, this means that CFIS is much more viable in energy terms.

In Park, Vecitis, & Hoffmann, 2008 was carried out a work to generate hydrogen from the electrolysis of organic compounds and not for urine, but taking into account that urine contains different organic compounds this comparison is appropriate. In that work they used an electrolytic cell in which the organic molecules are oxidized in an anode of TiO_2 doped with bismuth oxides and water is reduced in a stainless steel cathode; NaCl electrolyte was used. Although in that investigation they applied potentials of up to 10 V, finally they worked voltages of 3.7 to 4.1 V and currents of 0.7 to 0.9 A, obtaining energy efficiencies between 30 and 70%. That process is appropriate for the degradation or oxidation of organic compounds mainly present in wastewater [13]. Regarding the previous study, the efficiency is considerably higher, however it does not reach the 79% achieved by the CFIS.

The difference in the CFIS efficiency compared to the electrolysis of water is not much. According to the Department of Energy (DOE) of the United States, the energy efficiency of water electrolysis currently in alkaline medium is 76% [14], 3 units less than the CFIS efficiency.

The reports referenced in this section allow to determine that the energy efficiency of the CFIS is really good. This assumes that the cell described in this paper is a suitable system for energy applications such as hydrogen production and water treatment in a more viable way than the jobs reported in this section. Additionally, CFIS can be easily coupled to photovoltaic cells in such a way that the energy used for electrolysis is totally solar, allowing the production of hydrogen using CFIS to be a very ecological process.

The CFIS in vehicular applications

The fact of having separated the half-reactions in different compartments, allowed to establish a system that is much more efficient dynamically and energetically than the electrolysis of urine made in a single container because according to the above, there are different ways to reach the same end product, but improving and/or increasing the amounts of hydrogen produced.

1 liter of urine has about 22 g of urea equivalent to 0.37 moles, which in this system produce 1.12 mol H_2, this, taking into account that the stoichiometric ratios between urea and hydrogen are 1:3. Table 2 presents energy data for hydrogen produced from 1 liter of urine and 1 liter of gasoline. Although the heat of combustion is greater for hydrogen these values express that 1 liter of urine generates much less energy than 1 liter of gasoline, which would be approximately what 90 liters of urine would produce. In spite of the above, it is possible to work in a car with a hybrid system in order to study proportions and try to reduce the consumption of fossil fuel and therefore reduce pollution, according to a research at the University of Nariño - Colombia in a car Hybrid "H_2 (from urine) -gas-domiciliary-gasoline", in which has been installed the electrolytic system described in this work using raw urine, this study has significantly reduced (50%) gasoline consumption and production of greenhouse gases and acid rain more than 50%.

Table 2: This table compares the energy produced by 1 liter of gasoline and 1 liter of urine equivalent to 1.12 mol of H_2.

Substance in liters	Heat of combustion ($MJ\ kg^{-1}$)	Energy per liter ($KJ l^{-1}$)
1 l de Orina ó 1.12 mol de H_2	142 (H_2)	350 (orina)
1 l Gasolina	47	32000

In this research the energy production of hydrogen from the urea in the urine has been analyzed. According to the reactions that have been raised in this article, it is possible to say that urea is the main producer of hydrogen, therefore when the urine is enriched with urea, there is more organic matter in the anode for the production of hydrogen, producing more energy in the form of hydrogen, which indicates that including stool will increase the amount of hydrogen by taking advantage of total excreta.

Conclusions

By replacing the electrolysis of the urine in a single vessel by the split electrolysis (separating the two half-reactions) hydrogen was obtained with values that exceed 90% of purity, that is to say, a high purity of hydrogen was obtained cause this gas is released without Gaseous by-products produced by urine in the anode compartment, In addition the dynamic production efficiency of this gas is improved because two reaction forms (reaction 1 and reaction 2) are present to generate H_2 with the same molar ratios allowing the system to remain in electrical and mass balance.

An electrolyser (CFIS) was constructed which oxidizes the urea present in the urine with a maximum energy efficiency of 0.79 (or 79%); this causes that the electrolytic process in the CFIS is economically and energetically viable. In addition, CFIS can be used in a viable way for wastewater remediation

Although this system produces H_2 energetically efficient, it amount generated by the urine is low in relation to the energy that the motor vehicles need because the urine contains little amount of urea. However, it is possible to enrich the urine with more urea and easily oxidizable organic compounds present in the excrement in order to increase energy production in such a way that it is possible to realizate mixtures of gasoline- H_2(from urine) In order to reduce fossil fuel consumption.

Acknowledgments

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