Technology

STUDY ON THE DISPOSAL OF WASTE FROM THE HYDROGEN GENERATION BY ALUMINUM OXIDATION IN ALKALINE SOLUTION

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ABSTRACT

In face of the current high energy consumption and demand worldwide, a change to a sustainable energy matrix became one of the pillars for global sustainability. The use of renewable energy has been one of the most attractive subjects in recent years. Several public policies in this matter have been suggested and there are ongoing efforts toward their implementation. The United Nations (UN) proposed what is called the 2030 Agenda, which considers 17 Sustainable Development Goals (SDG) to be achieved by the year 2030. In support of the 2030 Agenda, research on the production of fuels from clean and sustainable sources is being conducted by the scientific community around the world. Fossil fuels are finite and also a major source of environmental pollutants, therefore the choice of using renewable sources of energy tends to be an increasingly growing and attractive alternative. Hydrogen is a fuel with a high heating value and is known as the most abundant gaseous element and simplest in chemical structure. The scientific community researching fuel cells has given much attention to the generation and storage of hydrogen. Besides the electrolytic hydrogen production and the reforming of fossil fuels (e.g., natural gas), hydrogen can be generated by metallic means, for example, by oxidation of aluminum in an alkaline solution. The use of recyclable metals, such as aluminum in this study, is an option for sustainable hydrogen generation processes. Nevertheless, like any chemical reaction, part of the products generated are waste, and some are even harmful to the environment, which makes the production of sustainable fuels unfeasible in case of not finding an appropriate technological industrial destination for such waste. The herein study comprises the investigation of the industrial and technological applications of the products of the hydrogen generation reaction from aluminum. Mastering the chemical reaction parameters of that reaction is paramount for the optimal design of a hydrogen generation system. The disposal of the waste is relevant since it makes the energy supply chain complete and sustainable.

Keywords: Hydrogen Generation; Chemical Waste; Sustainability; Renewable Energy; Sustainable Energy Chain.

INTRODUCTION

Fossil fuels have been widely used since the first industrial revolution, due to their easy availability and wide range of applications. The use of coal followed by oil provided unprecedented industrial growth, which ended up generating a strong dependence on these types of fuels (Furlan, 2020). However, in the 70s after the first oil crisis, the need for alternative energy sources was highlighted, given that fossil fuels are finite and highly polluting to the environment (Lorenzi and Andrade, 2014).

The use of renewable energy sources started to stand out around the world in recent decades, such as wind, biomass, geothermal, and even nuclear energy. They clash with each other in terms of profitability and suitability for use. The International Energy Agency - (IEA) compares that in 2018, more than 30% of the world's energy was derived from oil and fossil sources, while more than 45% was derived from mineral coal and natural gas. And less than 20% came from renewable sources, such as hydroelectric, biomass, and nuclear.

Much has been studied about the migration of the energy matrix, mainly due to the richest deposits of fossil sources and oil wells in the Middle East region, which constantly conflicts with the West, particularly with the USA. Such political and ideological conflicts of interest also interfere with the good management and generation of global energy.

HYDROGEN AS A SUSTAINABLE FUEL SOURCE

The use of hydrogen as an energy carrier and ultimately as a fuel emerged as an attractive alternative to produce electricity and heat in a cleaner way. Hydrogen is the simplest and most abundant element in the universe. In addition, in its gaseous form, its calorific value is extremely superior when compared to other fuels, making its use much more profitable in this regard, since smaller amounts of fuel would be needed to generate the same energy values (Wanghon, 2018). Added to this, there is the fact that the burning of hydrogen gas produces only water vapor, not emitting any of the greenhouse gases that are considered to be major contributors to global warming, thus characterizing it as a friendly gas to the environment.

Despite the many benefits that the use of hydrogen as a fuel provides, it presents some difficulties regarding its production and storage. Some of the main ways to produce this fuel are through electrolysis or hydrocarbon reforming, processes that require an item of high energy expenditure. In the case of hydrocarbon reform, there is also the emission of greenhouse gases (Jacob-Furlan, *et. al.,* 2020). In addition, the issue of storage and distribution of this type of fuel is one of the greatest challenges, given that hydrogen is not very dense and has a low boiling temperature, which makes its storage difficult (da Silva, 2020). In order to store it then, high pressure and continuous monitoring are required, as it is a highly reactive gas.

In this scenario, hydrogen presents itself as a very promising alternative in discussions about changes in energy matrices. Regardless of the scientific and technological difficulties, different modes of producing hydrogen in a clean and sustainable way can be explored, and the mathematical modeling of such methods will complement existing fuel cell models (dos Santos, 2019).

Fuel Cells

Fuel cells are devices that use mechanisms that convert chemical energy into electricity through electrochemical reactions producing water and heat. The process of energy conversion of fuel cells does not imply the generation of pollutants derived from burning at high temperatures. The O_2 enters the fuel cell as the oxidizing agent and reacts with the H_2 that enters from the opposite side of the oxygen entry in the fuel cell. The reaction produces water and electric current (due to the flow of electrons). Which makes this form of sustainable energy conversion one of the most environmentally attractive, as it does not release polluting emissions into the atmosphere (Júnior, 2019).

Henceforth, aiming at the continuous generation of hydrogen to feed the fuel cells, the present research intends to study the chemical reaction of aluminum (from industrialized beverage cans) with an alkaline solution of sodium hydroxide. Inside the reactor, aluminum undergoes an oxidation-reduction reaction with the alkaline solution, and from that, it generates a complex called sodium aluminate and pure hydrogen gas.

Mastering the hydrogen generation reaction is a great challenge, mainly because it is an exothermic reaction, so one of the main technological challenges to be overcome is to quantify the hydrogen generated and control the reaction temperature as a function of the concentrations of the alkaline solution and the amount of aluminum (Furlan *et. al.,* 2020).

Aluminum

Being considered one of the most popular metals on the face of the Earth, aluminum stands out for being present in most human activities (Greenwood, 1997). Although it constitutes only about 1% of the Earth's mass, it is the most abundant in the Earth's crust, which partly explains its popularity. It does not co-exist in an elemental way in nature - Al^0-, as it has a high affinity for O_2, from the atmosphere, so its main form is for the Al^{3+} ion (Constantino *et. al.,* 2001).

In Antiquity, aluminum was widely used as a mordant by the Egyptians, while the Romans used it as an astringent (Kauffman and Adams, 1990; Evans, 1995). Before Charles Martin Hall and Paul-Louis-Toussaint Héroult in 1888 discovered the chemical process of obtaining aluminum via metallurgy, - which was a historic and economic advance -, aluminum was seen as a precious metal equated with a jewel, in addition to being considered rare and noble. It had a high added value for merchants, being acquired only by the nobility, in addition to being displayed alongside the crown jewels, and often used in place of gold, in 19th-century royal dinners (Martin, 2011).

Moreover, Brazil stands out in the recycling of aluminum, evidencing the relevant role in the economic, social, and environmental sphere of the metal (Constantino *et. al.*, 2001). Industrialized beverage cans have 99% aluminum in their composition. The widespread use of aluminum, and the fact that its recycling process is well understood and applied worldwide (Cassanelli, 2016), make it possible for the aluminum used in the hydrogen production chemical reaction to be obtained from reuse, promoting sustainability, and making the process attractive (Reinert *et al.*, 2021).

Chemical Reaction

There are several chemical reactions that generate hydrogen as a product, however, aiming at the development of a sustainable hydrogen system, aluminum was chosen as a reactant (Bolt *et al.*, 2020; Haller *et al.*, 2021; Hurtubise *et al.*, 2018). It is found in the literature records of experimental results in which aluminum was cut into small strips with dimensions of about 2 x 2 cm^2, in order to maintain a good contact surface, convenient for the reaction to occur (da Silva, 2020). Reactions with large pieces of aluminum are not optimal, since the contact surface area of the reaction is small making the reaction produce a low amount of H_2. (Furlan *et al.*, 2020*)*.

Another highlight is the economic aspect, which is feasible because the reagents used in the chemical reaction are easy to obtain, in this case, water and aluminum stand out, which, coupled in an alkaline medium with an aqueous solution of sodium hydroxide, react generating hydrogen gas and a gelatinous complex called sodium aluminate. In addition, the fact that aluminum hydroxide has considerable industrial importance, and the system does not need very expensive equipment to operate, further reduces the cost of the process as a whole (Hiraki, 2007; Akiyama, 2009).

The reaction is highly exothermic, causing the release of heat energy, in which about 853 kJ/mol is produced. (Cassanelli, 2016). Aluminum in contact with atmospheric air oxidizes forming aluminum oxide as a thin layer that ends up isolating aluminum from the external environment. Thus, it is necessary to use a catalyst to minimize the reaction time, which naturally takes place after many hours. This increases the production efficiency in the system. The catalyst used in this study was the hydroxide (alkaline) solution - NaOH, due to its wide use in the industry which facilitates its acquisition, but other basic catalysts and chemical hydrides can also be used.

The sodium hydroxide present in the solution dissociates forming OH^- ions that prevent the formation of aluminum oxide, exposing the metal to contact with water and starting the reaction (Hsieh; Her; Chen, 2012). The global reaction is characterized by Eq. (1), below:

$$Al_{(s)}+NaOH_{(aq)}+3H_2O \rightarrow 32H_{2(g)} + Na[Al(OH)_4]_{(aq)} \quad (1)$$

From a chemical point of view, it is interesting to keep the reaction well controlled, so that there is a good performance, wherein the reactants and products can be easily consumed and generated. The reactions described in Eqs. (2) - (4) exemplify the interaction between O_2 and H_2. It is an oxidation-reduction of oxygen with hydrogen and, therefore, the cell adopted for this study is an alkaline membrane cell (AMFC). A cellulose-based membrane is immersed in an aqueous and alkaline solution of potassium hydroxide which acts as a liquid electrolyte, allowing the better passage of ions (OH^-). Known concentrations of 20% to 40% of KOH are needed in order to guarantee the transport of ions from the anode to the cathode (Sommer, 2009).

$$\text{anode:} \quad H_{2(g)} + 2OH^-_{(aq)} \rightarrow 2H_2O_{(l)} + 2e^- \quad (2)$$

$$\text{cathode:} \quad \tfrac{1}{2}O_{2(g)}+2H_2O_{(l)}+2e^- \rightarrow 2OH^-_{(aq)} + H_2O_{(l)} \quad (3)$$

$$\text{global reaction:} \quad H_{2(g)} + \tfrac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)} \quad (4)$$

When the reaction described in Eq. (1) starts to generate a lot of H_2 and there is little O_2 reacting, it must be stopped abruptly - before its spontaneous termination - taking into account that if it doesn't, inside the cell the alkaline membrane starts to burn, and the electrons and ions are no longer mobile, and income is also starting to fall. For this, acids are added, usually acetic acid. Under these circumstances, residual aluminum comes into contact with the acidic medium, with a tendency to produce a gelatinous complex with the remaining hydroxide, which is often difficult to remove from the reactors if left idle for a long time.

Furthermore, when the reaction has its spontaneity respected, and by itself, it comes to an end, the complex is also generated, however, it does not come into contact with the acidic medium. Sodium aluminate is then dispersed in an aqueous solution inside the reactor. The solution can then contain the ionizable complex, that is, with aluminum in the form of ions (Al^{3+}), in the presence of OH^- ions in an aqueous medium.

DISPOSAL OF WASTE FROM ALUMINUM

Sodium aluminate, also obtained in the reaction, has several industrial applications and, therefore, can be reused. It is used in the manufacture of refractory bricks and added as an additive in concrete intended for very cold weather, facilitating the drying process, but also has applications in the pharmaceutical and textile industry (Wang et al., 2009).

Correspondingly, aluminate can be dissociated to obtain sodium hydroxide again, reused in future reactions, and form the aluminum hydroxide, which is used in the manufacture of makeup, skin cleansers, and all kinds of cosmetics. It can even be used in the treatment of some diseases and vaccine preparation, such as anti-tetanus, hepatitis A and B (Pereira, 2017). The dissociation reaction of sodium aluminate is given by Eq. (5):

$$Na[Al(OH)_4]_{(aq)} \rightarrow NaOH_{(aq)} + Al(OH)_{3(aq)} \qquad (5)$$

The chemical equilibrium of any reaction can be direct and indirect, depending only on the spontaneous direction of the reaction, and the factors that can affect the equilibrium (Atkins, 2006). In Eq. (5) above, the direct equilibrium when it is in an acidic medium, that is, when there is an excess of H^+ ions, there is a tendency for the formation of sodium aluminate, although when the medium has an addition of OH^- ions so that the equilibrium is shifted towards alkalinity, aluminum hydroxide is generated.

The Eq. (1), is a spontaneous reaction from the thermodynamic point of view, that is, generating the sodium aluminate complex - $Na[Al(OH)_4]$, consequently, in an extremely alkaline medium - pH 14. Due to pH 14, care must be taken in the container where this solution is standing. If it is in glass reactors, such as the Erlenmeyer flask, the extremely basic solution in high concentration can start to attack the glass, in such a way that the silicon starts to dissociate in the solution. When the hydroxide in high concentration begins to attack the glass, a whitish surface begins to be noticed, and even depending on the intensity of the attack, the glass becomes more fragile, in addition to mentioning an aluminate crust that is very difficult to remove. after the reaction has cooled down completely.

If the reactor where the tailings are stored is made of steel, the alloys that compose it, such as Nickel and Copper metals, can also begin to react with the basic medium, so that they generate interferences. When the hydroxide attacks steel, the behavior is similar to that of glass, and there may be whitening of the contact area where the attack took place, and also if the reaction cools, the aluminate will stick to the surface so that it is difficult to remove afterward.

Beyond that, care must be taken as the reaction described by Eq. (1) - generating reaction - is extremely exothermic, so that, combined with the high concentration of hydroxide present in the medium, it ensures a more efficient attack on the reactor's resting surfaces.

In order to avoid these interferences in the reaction, some care must be taken, such as:

1. The rapid removal of the tailings at the end of the reaction;
2. pH adjustment to acid, with the use of hydrochloric acid, since chlorides are soluble, in order to prevent the formation of solid compounds under the surface, and if an attack occurs, it is quickly neutralized;
3. Storage of the tailings solution must be done in plastic containers.

Ensuring the above steps are carried out, the chemical treatment without interference can be effective so that the aluminum hydroxide extraction or even the reaction to generate alumina is productive (Kirk-Othmer, 1992), such as Eq. (6) demonstrate below:

$$2\ Al(OH)_{3(s)} \rightarrow Al_2O_{3(s)} + 3H_2O_{(l)} \qquad (6)$$

Alumina also has great industrial potential, as the Bayer Process uses it for the production of metallic aluminum. Thus, it is another product that interests the industrial market along with aluminum hydroxide.

CONCLUSION

Hydrogen is categorized as a good alternative energy carrier and fuel for renewable purposes, mainly taking into account its high calorific value and the multiplicity of pathways to its generation. It is also clear that there are still several mishaps regarding the storage of H_2 fuel, however, when it is scientifically mastered, the future will be promising. Even when the political and economic progress of some potentials around the world is observed, an analysis is made that a change in the energy matrix is urgently needed so that the environment is no longer harmed by fuels from fossil sources.

A key element in the development of strategies that can support sustainable development involves not just thinking about the generation (in this case of hydrogen) but taking into account that the disposal of some by-products is also necessary. Therefore, this work consists precisely of having a look at the disposal of residual aluminum from the reaction that is being studied for hydrogen generation in fuel cells. The generated aluminate can go to industries and when it has its pH adjusted to the basic medium again, it will dissociate in a way that will shift the chemical equilibrium towards the formation of aluminum hydroxide, which has wide industrial application.

In this way, the energy chain is fed in a sustainable way, and the industry may have one of its main products being offered in greater demand, since the energy matrix migrates, the production of aluminum tailings will be greater, so that the industry will benefit both in financial cost and in energy expenditure.

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