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SUSTAINABLE HYDROGEN PRODUCTION FROM RECYCLED ALUMINUM

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Abstract. *The Chemical Industry has been increasingly looking for clean, renewable and sustainable technologies. The automotive industry, in particular, has been looking for solutions that make the vehicles of the future no longer dependent on fossil fuels. One of the technologies that has been developed is related to fuel cells that use hydrogen as fuel. Currently, the forms of Hydrogen production in the chemical industry continue to use fossil fuels such as natural gas and naphtha or production from electrolysis of water. This work will present the production of Hydrogen from the spontaneous chemical reaction between recycled aluminum and sodium hydroxide. The system takes in consideration the knowledge of heat and mass transfer, mass and energy balances, heterogeneous reactors, thermodynamic of solutions, refrigeration and science of materials. The reaction is exothermic and the reactor will be operated isothermally. From data obtained by conductometric method and mathematical modeling of the system will be possible to predict the behavior of the reaction. The expected results are the hydrogen production and the validation of the kinetic proposed. Graphs of conductivity x time and the consumption of sodium hydroxide x time will be obtained to analyze and to confirm the order of the reaction.*

Keywords: *Reactor, Aluminum, Sodium, Aluminate, Hydrogen.*

1. INTRODUCTION

The Chemical and automotive industries have evolved to a new level of technology because the world needs to be less and less dependent on fossil fuels. Arguably, the industry has the necessity to produce Hydrogen in a renewable and sustainable way. The chemical industry will continue to use hydrogen in its formulations and vehicles have been developed to use hydrogen, but the world needs a new form of large-scale production.

It is important to add to this analysis that recycled aluminum will be used. Aluminum is a material that can be recycled infinitely without losing its thermo-mechanical properties, in other words, it can be recycled and used for the same purposes as many times as necessary and this is the main motivation to use the recycled aluminum in this work and it is important to take in consideration that the cost of obtaining recycled aluminum is less than 10 % of the total cost of aluminum production from bauxite.

This work has the objectives of Hydrogen production firstly in a small laboratory scale so that the kinetic proposed for this analysis can be tested and proved and secondly in a semi-batch reactor from the reaction between recycled aluminum and an aqueous solution of sodium hydroxide, as well as the accomplishment of a mathematical modeling for future development and design of a continuous reactor.

In order to achieve the goals of this work, the degree of isothermicity of the reactor must be taken into account so that the data obtained from the reaction system can be reliable. Studies will be conducted to analyze mainly the order of the reaction (and the conversion as a consequence), and if possible the amount of Hydrogen produced. The main method to be used so that the reaction can be observed accurately is the conductometric method, where the conductivity can be measured and gives reliable results which ones after some mathematical manipulations can provide values of concentration of products and indicate the order of the reaction. If the reaction system has electrolytes in solution, the conductivity can be measured as a function of time and when there is no more variation in its values of conductivity, this is a strong indication the reaction has achieved the end of running. Even so, as the reaction of this study is strongly exothermic, the relation between conversion and temperature must be studied in parallel to the reaction order analysis because the maximum yield of the reaction between aluminum and aqueous solution of sodium hydroxide will be achieved only if the knowledge of how the temperature influences the reaction is to be perfectly dominated. In additional studies, but not objective of this current work, gas chromatography is to be used to characterize the quality of the gas produced for subsequent use in fuel cells. With the mathematical model, practical data and theoretical data obtained from reliable sources, the project for a continuous reactor will be possible and this is what the industry really needs.

The performance calculation of any reactor for heterogeneous non-catalytic reactions involves the combination of intrinsic transport processes and kinetics where there are ion-exchange reactions between a solid phase and a liquid/aqueous phase generating in this present case liquid/aqueous phase and a gas phase.

When a component of a fluid reacts with a solid, the sequence of steps is similar to that of the fluid-solid reactions of the catalytic type. The reaction at an active center of the solid must occur by adsorption of the reagent fluid at that active center followed by a surface reaction in which the adsorbed molecule participates. Such reactions are also known as topochemical reactions. It is really important to emphasize the fact that the rate of reaction regarding a solid phase may be determined by the available surface area A of the solid particles (Upadhyay, 2006). This implies that in this study, particles of solid aluminum to be used must have a regular geometry so that the effects of all variations of concentration in solution regarding sodium hydroxide can be observed accurately. Therefore, for an irreversible reaction, the rate (velocity) of the reaction is determined by the following four steps:

- Mass transfer of the global fluid to the external surface of the particle;
- Intergranular diffusion in a particle;
- Adsorption in an active center of the solid reagent;
- Intrinsic reaction in the active center.

The way as the solid particles of aluminum are to be consumed during the development of the reaction can be explained by the Shrinking Core Model (Levenspiel, 1999).

The main kinetic study that has been considered in this work is what was presented by Aleksandrov et al. (2003). It is a work consistent with the theory of Shrinking Core Model for non-catalytic chemical reactions between solids and liquids (aqueous phase).

The main reaction investigated and object of interest in this work is the following:

$$2Al_{(s)} + 2NaOH_{(aq)} + 6H2O_{(l)} \rightarrow 2Na[Al(OH)_4]_{(aq)} + 3H_{2(g)} \quad \Delta H=-832,4\ kJ/mol \tag{1}$$

The structure of aluminate ions in solution is among the most important problems of aluminum chemistry (Tossell, 1999).

Another emphasized factor in the study of NaOH/ $Na[Al(OH)_4]$ solutions is that the thermodynamic model of Pitzer (Pitzer, 1973) is adequate to predict the coefficient of activity of the solution and consequent thermodynamic behavior. This is because the Pitzer model has shown highly satisfactory results in ion behavior studies in solutions with Na^+/ $Al(OH)_4^-$ (Königsberger et al., 2006) .

In order to understand the behavior of the solution, it has been used viscosity studies (Sipos et al., 2001), density studies (Reynolds et al., 2006) and specific heats and enthalpies (Chen et al., 1991).

2. METHODOLOGY

For the purposes of this current study there has been conducted two methodologies in order to get a better understanding of how the reaction between recycled aluminum and an aqueous solution of sodium hydroxide works. The first method has been studied until the present moment only for qualitative purposes but the methodology to be described in order to prove the kinetic has been used not only for qualitative but also mainly for quantitative purposes.

Firstly, for the qualitative method in order to make Hydrogen production feasible in the laboratory, it has been used as the primary source square particles of recycled aluminum of 0,5 cm^2 (particles with regular geometry) and 0,20 mm thickness.

The mass of aluminum needs to be weighed in an electronic balance. A diluted NaOH solution has been prepared in a Beaker, which one contains the required stoichiometric mass of NaOH to react with the pre-weighed aluminum. Then the mass of aluminum and the NaOH solution are add to the semi-batch reactor which can be an Erlenmeyer in a small laboratory scale or a small semi-batch reactor (constructed in stainless-steel 304). The sketch of the system is presented according to Fig. 1.

The reacting solution should be kept under very low stirring ($\leq$ 150 rpm) in order not to allow the settling of aluminum particles (Aleksandrov et al., 2003). For qualitative purposes it has been run reactions with a NaOH aqueous solution of 2,5 mol/l which is a little concentrated, but it provides the information about the power of the reaction regarding enthalpy variation and the improvement of the temperature. The system must be kept at 321,15 K with a cooling system, considering the fact the reaction is highly exothermic. The cooling system is a thermic machine, with a closed system using a refrigerant fluid in the coil.

Subsequently the Hydrogen production, the resulting solution should be withdrawn from the reactor and filtered so that the insoluble impurities contained in the recycled aluminum can be removed from the resulting solution. The solids retained by the filter element must be dried in a kiln at 333,15 K for further calculation of the impurities.

To the filtrate, nitric acid concentrated (HNO_3) must be added until the pH achieves 9.0. White and insoluble crystals are formed, more commonly known as aluminum hydroxide $Al(OH)_3$. After this procedure, the solution should be filtered again, by vacuum filtration system so as to separate the resulting solution from the white crystals of aluminum hydroxide. The solid material should be dried also in a kiln at 333,15 K for later weighing and calculation of reaction conversion.

During the reaction, the flow of Hydrogen can be measured though a sensor and is to be pumped by a small compressor to a cylinder in order to make possible a future characterization by gas chromatography.

Regarding the quantitative method and the main purpose of this work that is to prove the kinetic of the reaction between aluminum and a diluted aqueous solution of sodium hydroxide which is the real necessity of a new renewable chemical industry, and according to the results and discussions to be presented in the item 3 of this work, it has been run reactions between square particles of aluminum of 0,5 cm^2 (superficial area) and 0,2 mm thickness and a diluted aqueous solutions of sodium hydroxide (98 % purity). The quantitative method is called conductometric method and basically it uses an electrical conductivity meter which one measures the electrical conductivity. At the same time, while running the reactions, three variables have been measured that are temperature, pH and the electrical conductivity. This kind of method gives the most reliable information because during the course of the reaction there has been strong formation of aluminate ions ($Al(OH)_4^-$) which ones acting together sodium(Na^+), aluminum (Al^{+3}) and hydroxyl (OH^-) ions, improve the electrical conductivity of the solutions. The behavior of the electrolytes in the solutions have been perfectly studied (Chen et al., 1986; Chen et al., 2009) and the behavior of the aluminate solution have been strongly studied in the aluminum industry (Belitskus, 1970; Magalhães et al., 2002; Königsberger et al., 2006; Tossell, 1999). The data about aluminate solution in the literature give confidence to scientists in order to produce Hydrogen from this kind of solution. This is a perfectly new way of Hydrogen production from a renewable and sustainable method because not only the NaOH but also the Aluminum can be recovered in the proposed Hydrogen production way.

During the tests with conductometric method it has been tested solutions with 0,25 mol/l, 0,5 mol/l, 0,75 mol/l and 1,0 mol/l respectively. Stoichiometric amount of aluminum for each solution has been weighed in an electronic balance so that the stoichiometric relation of the reaction could be respected. Basically, the method indicates the end of the reaction when there are no more changes in the electrical conductivity and the values measured in μS/cm (conductivity) can be perfectly converted in ppm and then in concentration (mol/l) of products. This is what really proves the order of the reaction regarding the reactant NaOH. All the data regarding these tests are to be presented and discussed in the item 3. Another important observation in this method is the fact there are an amount of water used to prepare the aqueous solutions and an amount of water which reacts according to the equation (1). From the aqueous solutions it is known there is formation of H_3O^+ and OH^- ions and they influence the amount of electrolytes in the solution, but in the reactions in which the order and the molecularity are not the same because one of the reactants is in excess is called pseudo-order reactions. Thus, the rate of the reaction regarding the concentration of water has no dependency because the water is the solvent and besides it is in excess. Then, the order and the concentration of water is substituted by the value 1 and it does not appear on the rate of the reaction. The rate is only function of the superficial area of the aluminum particles and the concentration of NaOH solution. This is important to emphasize because the conductometric method gives answers about Al and NaOH consumption and how the amount of water is directly related to the reaction has been given by the mass balance of the reaction and it can be measured as a function of time, so the equation (5) to be presented in the item 2.1 is only representative.

2.1 Mathematical equations

The mathematical model developed in this work takes in consideration the principles of mass (equations 3 to 8) and energy (equations 11 to 18) conservation and the kinetic of the reaction (equations 9 and 10) in a semi-batch reactor. The presentation of the equations starts by the design equation (2) of a batch reactor which takes in consideration the conversion X_e of the reaction.

Design equation :

$$-r_A V = N_{A0}.dX_e/dt \tag{2}$$

According to Aleksandrov et al. (2003) the kinetic of the reaction between solid aluminum and an aqueous solution of sodium hydroxide is represented by the equations (9), (10). It is important to emphasize the fact that the solid phase is represented in the equation (9) by the superficial area. The equation (10) represents the constant of the reaction. One of the objectives of this current work is to test and to prove that the equation (9) represents properly the behavior of the reaction between aluminum and sodium hydroxide. The equations (3), (4), (5), (6), (7) are the rate laws which show the consumption of reactants and the formation of products during the running of a reaction as a function of time. The symbol C has been used to represent the concentration of different species in solution. Inside the small reactor while the reaction is running there are solid, liquid and gas phases besides the electrolytes in solution which ones give important information about the reaction. This shows how the mass balance varies until the end of the reaction. The equation (8) shows the relation among the rate laws of reactants and products. The equation (4) is only representative because the concentration in solid state reactions there is no meaning. How the aluminum influences the reaction can be measured and studied by the shrinking-core model.

Rate law:

$-r_{NaOH}= dC_{NaOH}/dt$ (3)

$-r_{Al} = dC_{Al}/dt$ (4)

$-r_{H2O}= dC_{H2O}/dt$ (5)

$r_{Na[Al(OH)4]}= dC_{Na[Al(OH)4]}/dt$ (6)

$r_{H2}= dC_{H2}/dt$ (7)

$-r_{NaOH} /2 = -r_{Al} /2 = -r_{H2O} /2 = r_{Na[Al(OH)4]}/2 = r_{H2}/3$ (8)

$r_{NaOH}= k_{app}S[OH]^{-}e^{-E/RT}$, $[s^{-1}]$ (the kinectic of the reaction) (9)

$lnk=(12,26\pm0,5)–(51,7\pm1,3).10^3/RT$, $[mols/s.m^2]$ (the first-order constant rate) (10)

So that a perfect understanding of the reaction can be achieved, undoubtedly it is necessary to study and to dominate the energy balance of the reaction and it is mandatory to analyze the behavior of the reaction regarding the conversion while the temperature increases, considering the reaction is strongly exothermic. This can be understood by the study of the adiabatic conversion X_{EB} (15) which shows how the temperature increases until the end of the reaction and gives an important information about how the temperature could be controlled during any running so that a maximum conversion could be achieved. The Van't Hoff law (13) shows how the equilibrium constant of the reaction K_e decreases for an exothermic reaction while the temperature increases. For the purposes of this article, the effects of temperature upon the reaction behavior is to be analyzed only by using mathematical equations. The practical tests were conducted to analyze the Hydrogen production and to prove the kinetic for a diluted aqueous solution of sodium hydroxide. From the equation (16) to (18) it is possible to predict a semi-batch system for Hydrogen production considering the temperature control by removing heat from the reactor with a coil (using a fluid refrigerant).

Energy balance:

$\Delta G^0=-RTlnK_e$ (Free Energy of Gibbs at T_0=298,15 K) (11)

$\Delta H_R(T)= \Sigma H_{products} – \Sigma H_{reactants}$ (Entalpy of reaction) (12)

Van't Hoff law:

$dlnK_e/dT=- \Delta H_R^0/RT$ (13)

$\theta_i=N_i^0/N_{NaOH}^0$, where Ni_0= initial mols of species i (14)

Adiabatic Conversion:

$X_{EB}= \Sigma\ \theta_i C_{pi}(T-T_0)/\Delta H_R^0$ (15)

Generated Heat in a Batch Reactor:

$Q_g= N_{NaOH}{}^0.\Delta H_R(T).dXe/dt$, where Xe is the real conversion of the system (16)

Removed Heat in a Batch Reactor:

$Q_r=m_cC_{pc}(T_{a1} – T_{a2})= m_cC_{pc}(T_{a1}-T)[1-exp(UA/ m_cC_{pc})$ (17)

$T_{a2}= T-[(T-T_{a1})[1-exp(UA/ m_cC_{pc})$ (18)

Where the variables $m_c(kg/h)$, $C_{pc}(KJ/kg\ {}^oC)$, T_{a1} and T_{a2} are related to the fluid refrigerant.

2.2 Sketch of the system

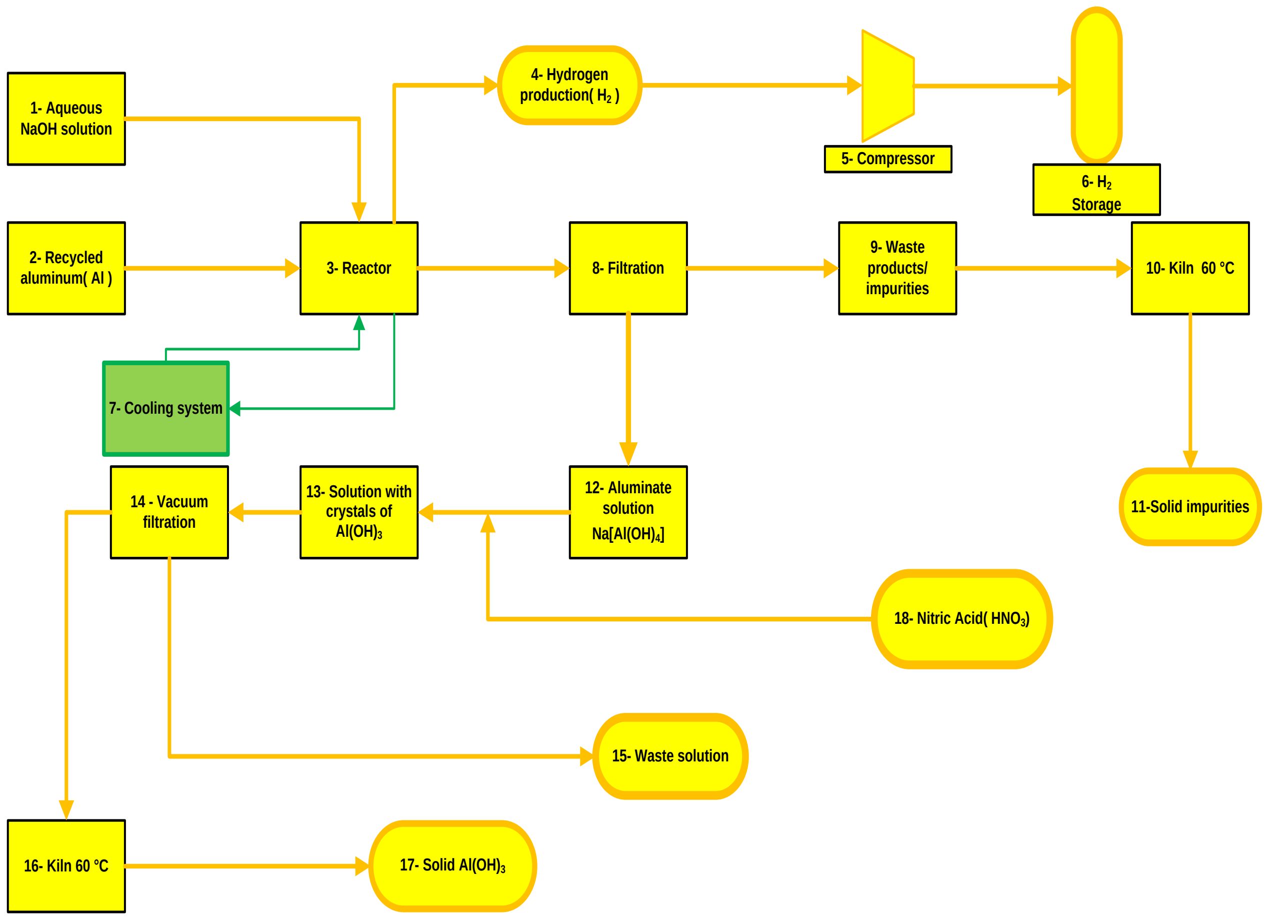

Figure 1. Sketch of Hydrogen Production from Recycled Aluminum and Sodium Hydroxide

3. RESULTS AND DISCUSSION

Firstly, after getting from the theoretical studies for aqueous solutions of NaOH (concentration 2,5 mol/l) the graphs between adiabatic conversion x Temperature (K) (Fig. 2) and ln Ke x (1/T) (Fig. 3) where Ke is the equilibrium constant, it is possible to observe that the maximum conversion obtained for the system in a semi-batch reactor is 50 %, what is called equilibrium conversion (Xe). It is necessary to emphasize the fact that the cooling system must be reliable, otherwise the reaction would achieve high temperatures but no more conversion. From the Fig. 3 it is possible to observe how strong is the decrease of the equilibrium constant while the temperature of the reaction increases. On practical terms, the phenomenon has been observed during the qualitative studies because for an aqueous solution of NaOH of 2,5 mol/l (concentration) the temperature rises until 333,15 K in about 5 min of reaction. For the purposes of this current work, this qualitative analysis is just to keep clear how important is to control the temperature of the reaction in order to maximize the final conversion and Hydrogen production. Just as an additional information, the current reaction is not a chemical equilibrium because the reaction runs in only one way but the equilibrium constant shows how is the behavior of the conversion while the temperature increases and it is an important evidence of how quickly the reaction reaches the stabilization.

Another fact observed while conducting the procedures according to Fig. 1 was the formation of white crystals of aluminum hydroxide after the addition of concentrated nitric acid in the solution. After the end of each running with no more formation of Hydrogen gas, the procedure described in the item 2 was conducted so that all the steps could be observed. The main step after the reaction was the obtainment of the white crystals because this proves with very good reliability the fact that aluminum can be recovered in this process, likewise it happens on aluminum industry. The qualitative method has given a strong indication of all the tests conducted in a laboratory scale can be perfectly scaled up to an industrial scale in the future.

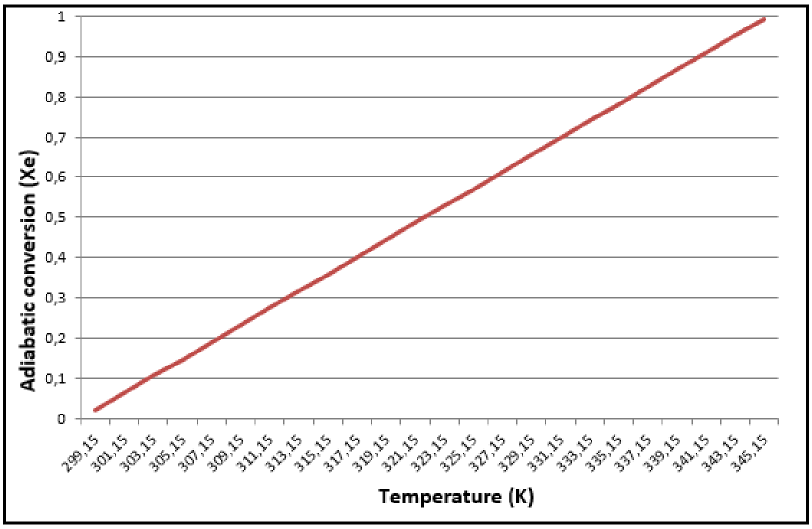

Figure 2. Adiabatic conversion (Xe) x Temperature (K)

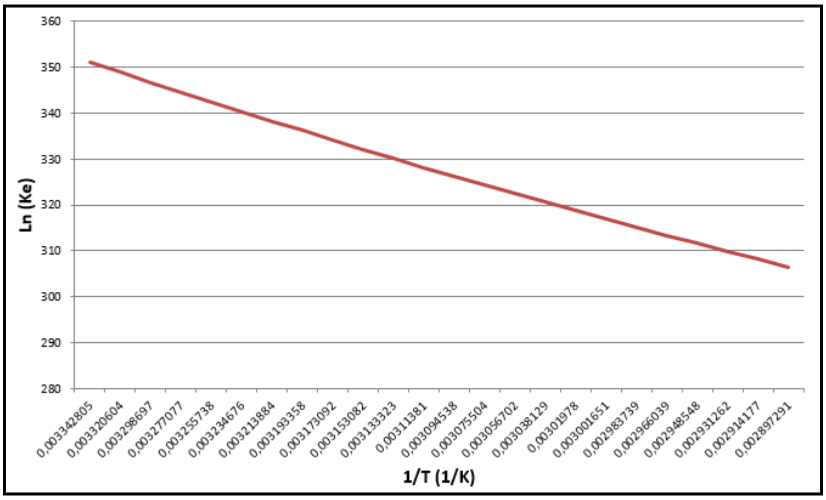

Figure 3. Ln (Ke) x 1/T (1/K)

From the quantitative tests the following results of conductivity x time are given in the next Figures, as follows:

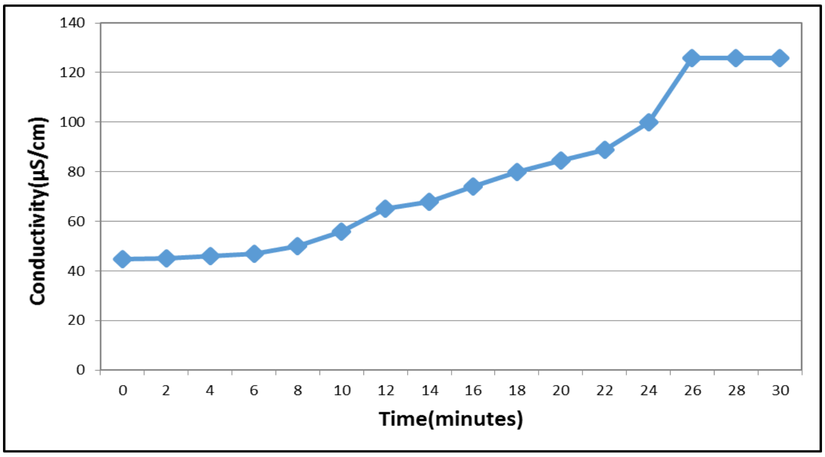

Figure 4. Experimental results of Conductivity (µS/cm) x Time (min) for reaction between 0,25 mol/l NaOH solution and solid recycled aluminum (0,5 cm^2 and 0,2 mm thickness). The temperature T and the pH remained constant during the tests at 299,15 K and 12,4 respectively.

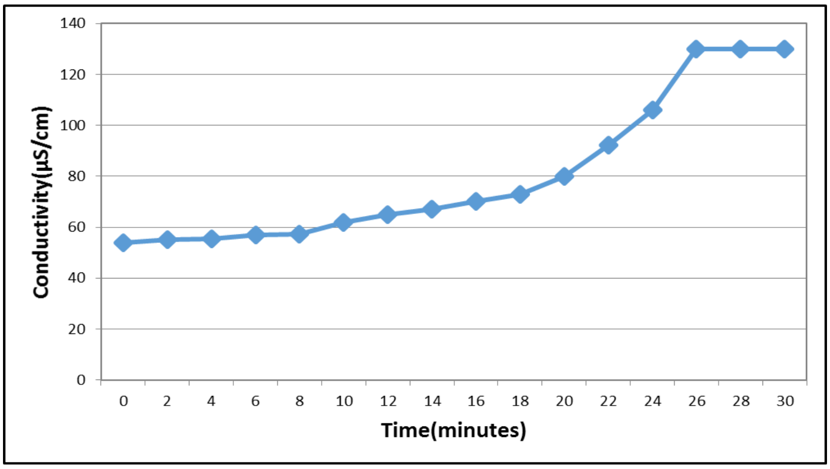

Figure 5. Experimental results of Conductivity (µS/cm) x Time (min) for reaction between 0,50 mol/l NaOH solution and solid recycled aluminum (0,5 cm^2 and 0,2 mm thickness). The temperature T and the pH remained constant during the tests at 300,15 K and 13,0 respectively.

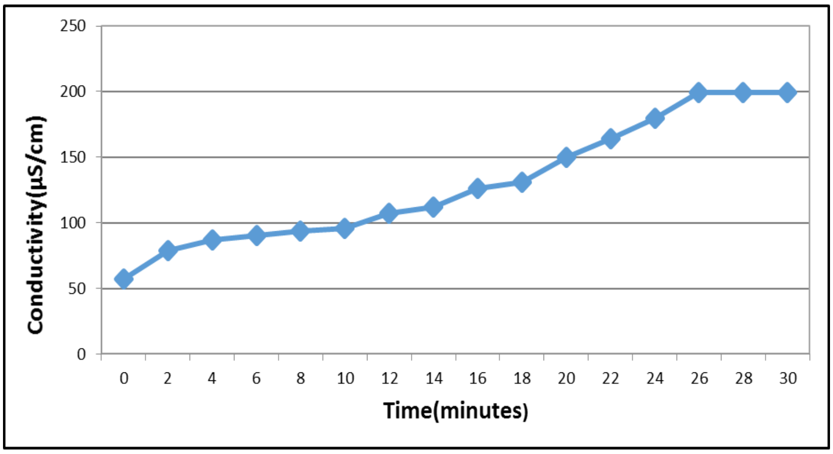

Figure 6. Experimental results of Conductivity (µS/cm) x Time (min) for reaction between 0,75 mol/l NaOH solution and solid recycled aluminum (0,5 cm^2 and 0,2 mm thickness). The temperature T and the pH remained constant during the tests at 300,65 K and 13,5 respectively.

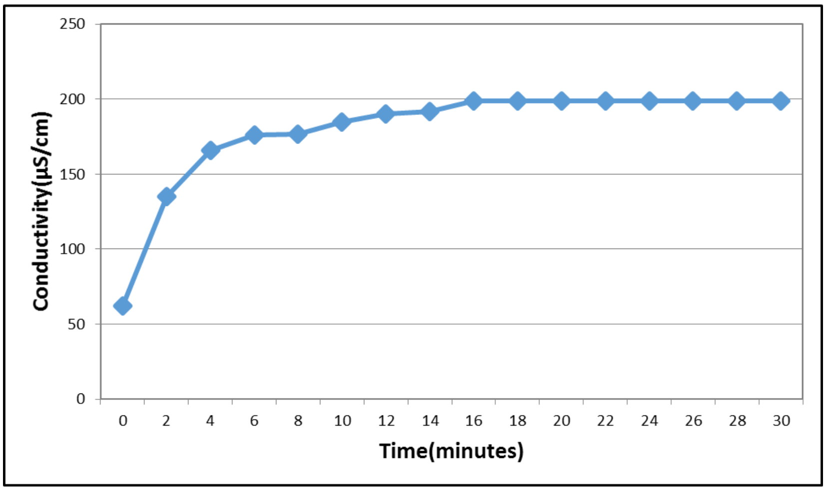

Figure 7. Experimental results of Conductivity (µS/cm) x Time(min) for reaction between 1,0 mol/l NaOH solution and solid recycled aluminum (0,5cm^2 and 0,2mm thickness). The temperature T and the pH remained constant during the tests at 303,15 K and 13,5 respectively.

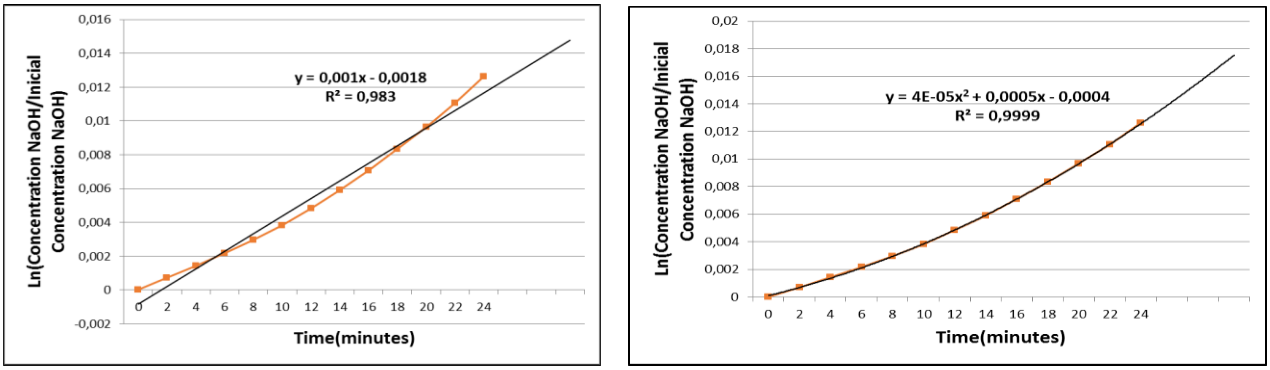

Figure 8. Relation between Ln (concentration of NaOH/Initial concentration of NaOH) x Time (min) for reaction with 0,25 mol/l of NaOH solution. For the same graph has been shown the linear trend with R^2 and polynomial trend with R^2.

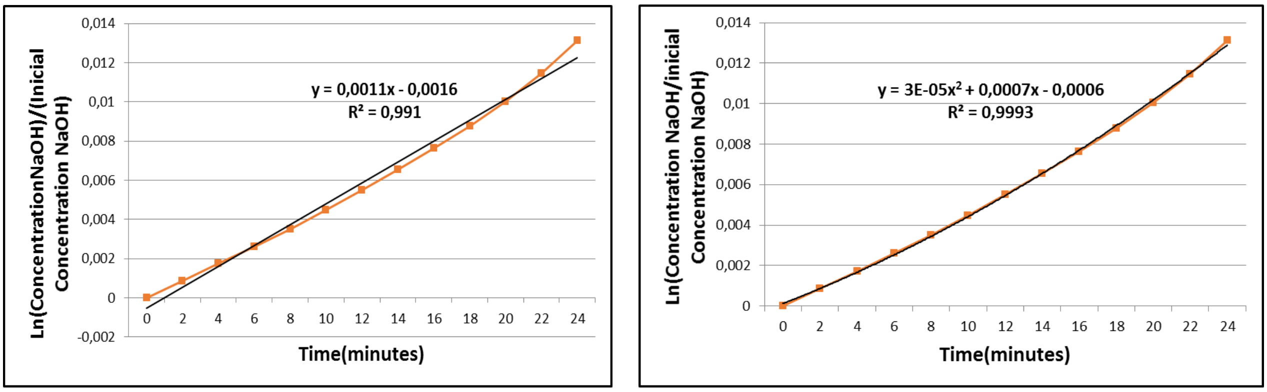

Figure 9. Relation between Ln (concentration of NaOH/Initial concentration of NaOH) x Time (min) for reaction with 0,50 mol/l of NaOH solution. For the same graph has been shown the linear trend with R^2 and polynomial trend with R^2.

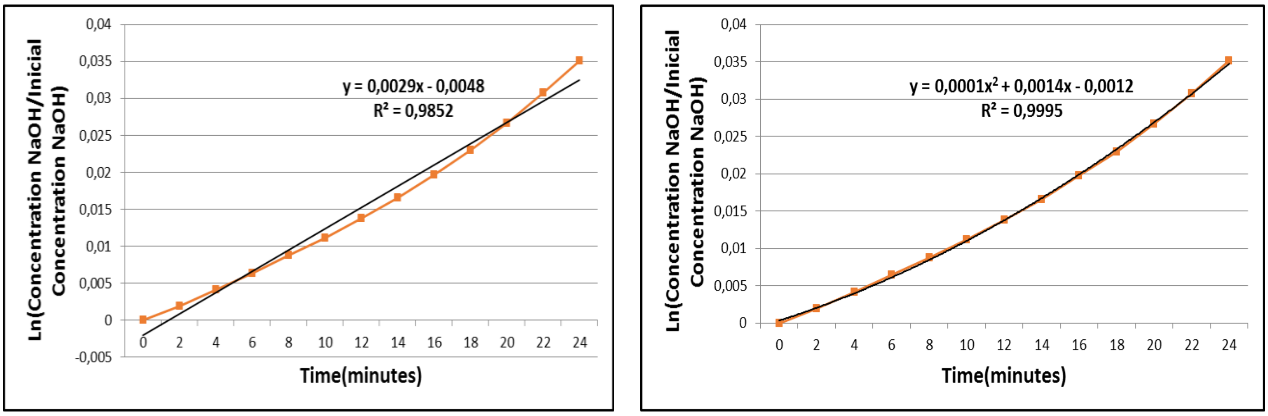

Figure 10. Relation between Ln (concentration of NaOH/Initial concentration of NaOH) x Time (min) for reaction with 0,75 mol/l of NaOH solution. For the same graph has been shown the linear trend with R^2 and polynomial trend with R^2.

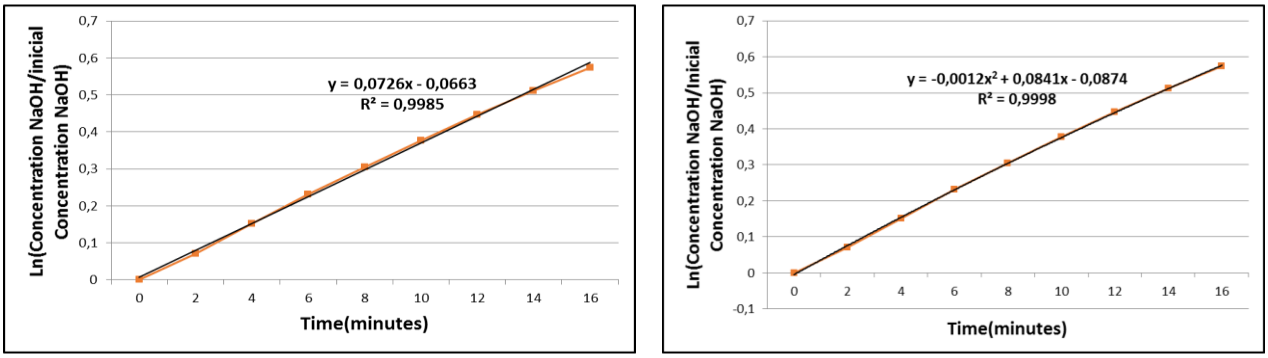

Figure 11. Relation between Ln (concentration of NaOH/Initial concentration of NaOH) x Time(min) for reaction with 1,0 mol/l of NaOH solution. For the same graph has been shown the linear trend with R^2 and polynomial trend with R^2.

Firstly, for a better understanding regarding the tests using the conductivity meter, it was coordinated a series of reactions for each concentration and an average of the results were obtained before making the graphs.

According to the Fig. 4, Fig. 5, Fig. 6 and Fig. 7 it is possible to observe how is the behavior of the reaction while producing a solution of sodium aluminate and Hydrogen gas. During the reaction the values of conductivity increased as predicted and at some moment there were no more variation. As mentioned in this work this represents the end of the reaction.

Considering the fact that all the tests were conducted with diluted aqueous solutions of NaOH, the temperature and pH were measured for each running, but no significant variation was observed regarding these two variables. This is an important conclusion because despite the reaction is extremely exothermic, isothermal conditions were kept so that only the variations in conductivity could be observed and analyzed.

As expected, while increasing the concentration of the solutions, the reactions occurred faster. After some mathematical manipulations of the results, different concentrations of sodium aluminate were obtained while running the reactions and based on the mass balance it was possible to get the results regarding the consumption of NaOH. These were the most important data obtained because according to Fig. 8, Fig. 9, Fig. 10 and Fig. 11 it was possible to get the graphs related to the consumption of NaOH against time. For each concentration of NaOH solution it was created graphs for testing if the reaction is really a first-order reaction in relation to the NaOH consumption or not.

For each concentration and analysis of the order of the reaction there are two graphs with the same results but different trends and equations. There are linear trends and polynomial trends indicating how close to a first-order the reaction is. The R-squared has showed a linear trend as high as 0,98 but even so it seems the results must be better evaluated and more tests must be conducted. As a result, it is not possible to conclude in this current work with assertivity if the kinetic proposed is correct or if it is a second order rate regarding the consumption of NaOH.

Another point to suffer an optimization is related to time, because all the measures of conductivity were made considering each two minutes. This must be more accurate and other tests will be done considering measures in each minute so that better graphs can be obtained.

Regarding the Hydrogen production until this time of the current research it hasn't been possible to measure the amount of Hydrogen gas produced because the focus was to prove the kinetic and by a qualitative method to understand step by step if a renewable process is feasible. More tests with a bigger volume of solution must be run so that a considerable amount of Hydrogen gas can be produced and bottled for further characterization by gas chromatography.

Besides the kinetics analysis, there are another point to be discussed in further works regarding the phenomenon of mass transfer, because in the reaction between solid aluminum and a diluted aqueous solution of NaOH, the mechanism of reaction is governed by the reaction itself and not by the mass transfer but as the solution becomes more concentrated in relation to products, from literature it is known the aluminate ions make it difficult the production of Hydrogen.

The recycled aluminum must be as pure as possible because the purer is the aluminum, the best will be the results of the reaction and of the Hydrogen production.

4. ACKNOWLEDGEMENTS

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