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Electrolysis process analysis by using low carbon content additives: a batch test study

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Abstract

Biomass ash, especially, wood ash has a high degree of alkalinity. As the wood ash has an alkaline environment and similarities to zeolites structure, it may be used in the electrolysis process as a solid electrocatalyst to reduce or replace chemical catalysts. Design of Experiment and Statgraphics software were used for the research. The goal of the experiment was to analyze possibilities of ash use as an electrolyte component. The statistical analysis was performed using the Statgraphics statistical data analysis tool and the empirical models with correlation equations describing the pH value of analyzing samples. The results were validated using the effects of variables, the half-normal probability plot, Standardized Pareto chart, main effects plot for pH and estimated response surface for variables. The used validation methods show that there is strong correlation between pH value and used sample mixture in the experiment. Further research needed to prove the theory about possibilities of ash use as an electrolyte component.

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Keywords: electrolysis process, biomass ash, batch test, ash additives, alternative electrocatalysts, design of experiment

1. Introduction

The principle of electrolysis was discovered in 1800 by two English scientists. "Electrolysis is the process in which a direct electric current passing between two electrodes through an ionic substance that is either molten or dissolved in a suitable reaction product" [1].

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The reaction of water electrolysis can be written [2]:

$$H_2O + electricity + heat \rightarrow H_2 + \frac{1}{2} O_2 \quad (1)$$

There are three types of water electrolysis [2, 3]:
- alkaline water electrolysis;
- proton exchange membrane (PEM) water electrolysis;
- solid oxide (SO) technology.

There are three differences between water electrolysis. The main and the first difference between three technologies relates to electrolyte type used in process OH^- ions in alkaline water electrolysis, H^+ ions in proton exchange membrane water electrolysis and O_2^- ions in solid oxides water electrolysis. The second difference between technologies relates to the site water consumption: it is a cathode with alkaline water electrolysis and solid oxides water electrolysis and consumed water at anode with proton exchange membrane water electrolysis. The last difference between technologies is the temperature at which these technologies operate. For alkaline water electrolysis and proton exchange membrane water electrolysis, temperature is under 100 °C, but for solid oxides, the water electrolysis temperature is between 650 °C and 1000 °C [2].

Alkaline water electrolysis is a mature technology [1, 2]. The reactions at the electrodes are as follows [4]:

Anode: $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$ (2)

Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (3)

Overall reaction: $H_2O \rightarrow H_2 + \frac{1}{2}O_2$ (4)

The meaning of catalyst is that a catalyst is a substance which alters the rate of chemical reactions without involving itself in the reaction. There are positive and negative catalysts. The positive catalyst or catalyst increases the rate of the reaction, but the negative catalyst delays the rate of a reaction [5]. Catalytic processes are heterogeneous (the catalyst, typically a solid, is in a different phase from the reactants) and homogeneous (the catalyst is in the same phase, typically liquid, as the reactants) [6]. The homogeneous and environmentally hazardous catalysts are mineral and Lewis acids, organic and inorganic bases and toxic metallic compounds. Also there are groups of solids catalysts like metals, oxides, sulfides, carbon and bulk materials or those supported on a more or less catalytically active support like silica, alumina, zirconia, titania, ceria, carbon and others. The catalysts mentioned have specific chemical properties, such as acid-base or redox or dehydrogenating or hydrogenating or oxidizing, and physical properties like porosity, high surface area, thermal and electrical conductivity and attrition resistance. There are large groups of catalysts which correspond to oxides, mixed oxides, zeolites, clays and mesoporous materials [7].

Biomass ash, especially wood ash has a high degree of alkalinity [8]. As the wood ash has an alkaline environment and similarities to zeolites structure it may be used in electrolysis process as solid electrocatalyst to reduce or replace chemical catalysts. Zhang (2011) mentioned that some improvements are still possible in alkaline water electrolysis. One scientific publication provides attempts to identify alternative electrocatalysts and develop alternative separators [1].

There are also scientific researches according ash use as catalysts in [9, 10], but there were no publications found where biomass ash use as a catalyst in the electrolysis process.

2. Methodology

2.1. Design of Experiment

Design of Experiment (DOE) and Statgraphics software were used for this research. Pinciples from Design of Experiment and Statgraphics software were adapted. The experimental planning began with setting a goal. The goal of the experiment was to analyze possibilities of ash use as an electrolyte component. The second step included definition of factors, where the experimental results can be affected by quantitative and qualitative factors, which can be controlled or uncontrolled. There are four factors, which are chosen for the experiment plan: temperature, composition of sample (mixture, %), sample diameter and moisture content. Through the pilot experiment it was ascertained that the analyzed sample creation depends on the selected temperature and sample composition. There are also two factors which affect the subject of the experiment: moisture and diameter of the sample. In experimental planning, these two factors will be taken as controlled factors. So, the analyzed samples will be prepared with equal dry mass and also moisture will be with the same proportions for all analyzed samples.

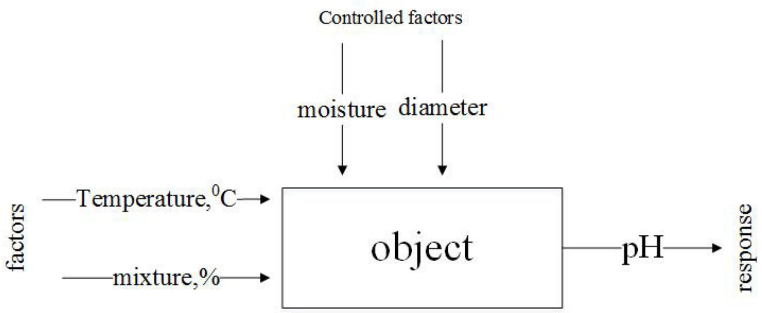

Fig.1. Factors and response in experiment plan.

Factors which will be used in experiment planning are temperature and sample composition. In DOE factors are defined as low, high and center point values, but in DOE factor definition include definition of factor type, factor role and also low, high and center point value definition. There are chosen low and high values for chosen factors. The temperature is taken 700 °C and 900 °C, but the sample content will be the low 20 % and the high 75 %. The response in experimental planning will be pH level.

The third step is the selection of an experimental design, where a two – level factorial design experiment with two levels and two factors was developed. With two levels and two factors there are four factor combinations. Combinations for two – level factorial design are high – high, low – low, high – low and low – high.

The fourth step in DOE is used to select the type of model that the user anticipates will fit the results of the experiment once it has been performed. The model in DOE Wizard can be selected from five types of process factors models.

In the fifth step, a selection of runs is made. This step is useful for the experiment where more than three factors were analysed. In this experiment seven runs were conducted.

The sixth step in DOE is evaluation of design, the experimental design can be evaluated using tables, graphs and equations. Tables give analysis summary, design worksheet, ANOVA table, model coefficients, alias matrix, correlation matrix, etc. The main graph in the DOE is design points, prediction variance plot, prediction profile, fraction of design space plot, etc.

2.2. Ash mixture preparation

In the experiment, the bottom ashes are used and they consist of different sizes of solid particles. Different mixtures of wood biomass and straw biomass ashes are used (25 %, 50 % and 75 %). Between collecting and the experiments, the ashes were kept in separate plastic bags that were hermetically sealed. The first step to prepare the sample was ash crushing in a pestle. After crushing, samples were prepared for burning in a muffle furnace. Distilled water was used as a binding agent. Samples were made in the shape of a sphere, because it provides a larger surface area and less chance of the sample sticking on the laboratory equipment. Samples were heated to 900 °C temperature for 2 hours. Samples were then cooled and placed in hermetically sealed bags again until later use in electrolysis batch tests.

2.3. Experimental equipment

Based on alkaline water electrolysis, a principle electrolysis apparatus was built for the experiment. The principal scheme of electrolysis is seen in Fig. 2

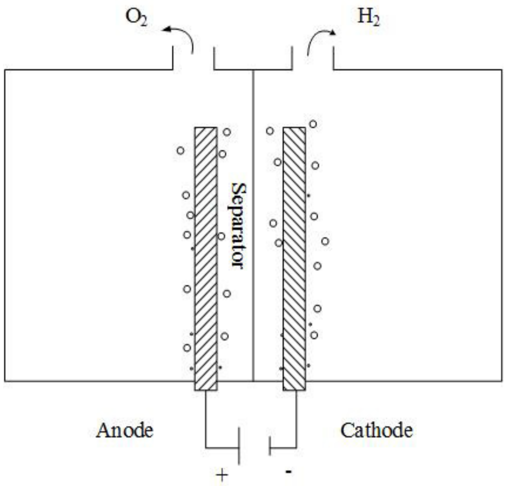

Fig. 2. Scheme of electrolysis (left side).

3. Results and discussion

Using experimental planning four experiments with three center points were carried out. In the experiment biomass ashes were used to analyze possibilities of ash use as an electrolyte component. . The main factors in the experiment were temperature and ash mixture ratio (moisture and diameter of the sample as controlled factors, where for the all samples they are equal).

The experiment was conducted with the aim to produce hydrogen without chemical catalyst use in the electrolysis process. Three hydrogen measurements were taken with different weight of samples, voltage and time for the experiment.

Two methods for hydrogen measurement were used. The first method was a hydrogen production measurement using mass change (weighting before and after experiment). The experimental apparatus was left for a 24h period on scales to determine mass changes, where 4 measurements were done in a 3 hour period. There were no measurements made from the evening of the first day evening until the morning of the next day. After 24h there was no mass change and hydrogen measurements could no longer be conducted.

The second method was bubble measurement. The experimental apparatus was connected with a glass tube which was filled with soap. Measurements started when the first bubble crossed the first section measuring line. With the second method it is not possible to measure hydrogen because of low hydrogen production (no bubbles in experimental period comparing to reference experiment). There may be several reasons why it was not possible to measure hydrogen from the electrolysis process. The first reason is the sample's characteristics, whereby the sample may not have enough of an alkaline environment which deters the reaction from accelerating. The second reason can be the technical specifics of the apparatus used which was experimental and based on the theory of electrolysis. There also have been problems with the anode and cathode materials used in the electrolysis process.

The correlation between factors is determined using the Statgraphic software. After calculation, results are gathered that show no correlation between pH and temperature. The equation:

$$pH = 13.4286 - 0.0025 \cdot temperature \tag{5}$$

Characterizes correlation between pH and temperature. Since the P-value in the ANOVA table is greater or equal to 0.05, there is not a statistically significant relationship between pH and temperature at the 95.0 % or higher confidence level. The R-Squared statistic indicates that the model as fitted explains 6.73 % of the variability in pH. The correlation coefficient equals −0.26, indicating a relatively weak relationship between the variables. The standard error of the estimate shows the standard deviation of the residuals to be 0.83.

The correlation between pH and mixture is strong. Since the P-value in the ANOVA table is less than 0.05, there is a statistically significant relationship between pH and mixture at the 95.0 % confidence level. The R-Squared statistic indicates that the model as fitted explains 60.57 % of the variability in pH. The correlation coefficient equals −0.78, indicating a moderately strong relationship between the variables. The standard error of the estimate shows the standard deviation of the residuals to be 0.54.

Another test to validate the effects of variables is the half-normal probability plot for variables (see Fig. 1.). The preference of the probability plot is in the arrangement of effects from variables on the variability ("noise" line in software). The more distant variable is from the variability line, the greater effect on the pH value with higher accuracy can be obtained.

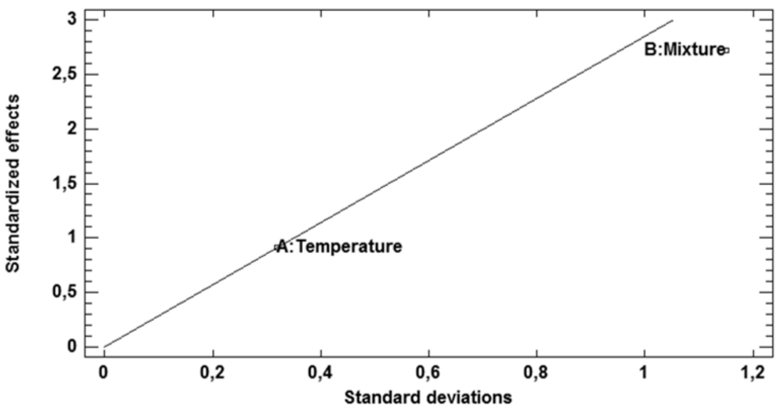

Fig. 3. Half – Normal Plot for pH.

Fig. 3. shows that more distance from the variability line is for mixture, where temperature point is on the line. Mixture has greater effect on the pH value than temperature.

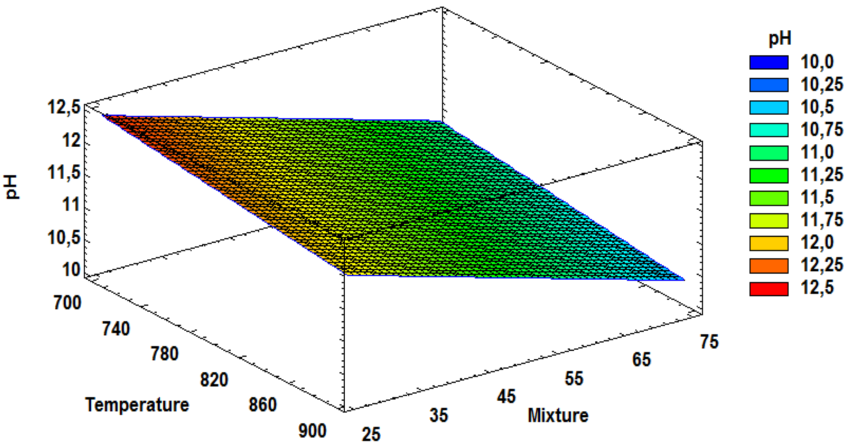

Fig. 4. Estimated response surface

Fig. 4. shows an empirical equation (5) in 3-dimensional space. The data validation lets us analyze the factor correlation. It is necessary to conduct data analysis and model validation for factors which are used in the experiment. From the data it is seen that the factor with the biggest impact is the mixture type used in sample preparation.

Prepared samples have an alkaline environment, so they can be used as catalysts in electrolysis process to reduce or replace chemical catalyst in electrolysis process. The best sample for electrolysis was determined to be with 25 % mixture (with closeness to the ideal solution of 87, where 1 is the ideal solution). The experiments did not yield any results due to technical problems, so the hypothesis for the best solution was not experimentally proven. More experiments are needed.

The statistical analysis was performed using the Statgraphics statistical data analysis tool and the empirical models with correlation equations describing pH value of analyzing samples. The results were validated using the effects of variables, the half-normal probability plot, Standardized Pareto chart, main effects plot for pH and estimated response surface for variables. The used validation methods show that there is strong correlation between pH value and used sample mixture in the experiment.

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