Analysis of use of bioenergy production by-products to enhance electrolysis process

Dace Lauka[a], Julija Gusca[b], Silvija Nora Kalnins[c], Edgars Vigants[d] and Dagnija Blumberga[e]

[a] *PhD student, Institute of Energy Systems and Environment, Riga Technical University, Riga, Latvia, dace.lauka@rtu.lv*
[b] *Associated Professor, Institute of Energy Systems and Environment, Riga Technical University, Riga, Latvia, julija.gusca@rtu.lv*
[c] *Researcher, Institute of Energy Systems and Environment, Riga Technical University, Riga, Latvia, silvija-nora.kalnins@rtu.lv*
[d] *Senior researcher, Institute of Energy Systems and Environment, Riga Technical University, Riga, Latvia, edgars.vigants@rtu.lv*
[e] *Professor, Institute of Energy Systems and Environment, Riga Technical University, Riga, Latvia*

Abstract:

Besides positive effects to the climate change mitigation and greenhouse gas reduction, the use of bioresources in the energy production sector also generate additional environmental load associated with management of combustion process waste. Effective use of such wasted materials as biomass by-products might improve life cycle environmental performance of the biobased fuels and energy. In this study, bioenergy production by-products were proposed as electrocatalysts for H_2 generation via water electrolysis process. To analyse the suitability of the by-products (biomass ash) as electrocatalysts, a technique for order preference by similarity to ideal solution (TOPSIS) is applied. Catalysts formed from the wood and straw briquette ashes were analysed within the study in the following proportions: (1) 25 % straw and 75 % wood; (2) 50 % wood and 50 % straw; (3) 75 % wood and 25 % straw and (4) 100 % straw ash. A standard water electrolysis unit was used for the experiment; hydrogen production rate was identified using a soap flowmeter. Results of the study shows that the catalysts based on the proportion 25 % of straw ash and 75 % of wood ash are evaluated as the most efficient for hydrogen production through water electrolysis (generating the higher H_2 volume), however additional efforts need to be done for improvement of H_2 production efficiency if compared with traditional metal based catalysts.

Keywords:
Electrolysis, Biobased catalysts, Biomass, pH, TOPSIS.

1. Introduction

Production of energy from renewable resources takes a specific role in climate change mitigation actions. Hydrogen is considered as clean energy for future energy demands. In recent years the role of electrolysis has increased due to its application as an intermediate element for production of methane in the integrated renewable energy resources systems, thus emphasizing sustainable energy generation [1,2]. Water electrolysis is a well-known technology for hydrogen production with an environmental performance of zero direct emissions. Despite the fact, that electrolysis is considered as a clean energy production process, efficient use of electrolytes and water plays an important role for the environmental performance of the system. By now, a major part of water electrolysers are based on alkaline electrolytes or protone exchange membrane units, which are primary produced for the needs of electrolytic processes [3,4]. Use of noble metals (Pt, Ru) and different alloys, as electrocatalysts generates environmental pressures in resource consumption category and due to its limited geographical availability – in transportation category. Besides, high efficiency of the noble metal based electrocatalysts is offset by its high costs. Use of energy production by-products as electrolytes can improve the overall environmental and also economic performance of the integrated system. In this paper, a green, locally available and sustainable alternative for utilising electrocatalysts for H_2 generation, namely biomass ash, is proposed.

Biomass as a renewable energy source is coming increasingly popular. Although biomass fuel combustion is a CO_2 neutral process, it creates a considerable amount of bottom ashes which contributes to another environmental issue – waste and its disposal. Biomass ash is a complex inorganic – organic mixture with polycomponent, heterogeneous and variable composition. It contains closely associated solid, liquid and gaseous phases with different origin. The ash constituents depend on type of biomass, type of soil and biomass harvesting. Ash content in wood and wood products depends on type of biomass which is used in combustion process [5].The main components in biomass ash are Ca, K, Na, Si, and P. Some type of biomass ash can contain silicones or alkali metals [6-8]. The amount of biomass ash depends on various factors: biomass type, soil and biomass cultivation, climate and geographical location, concentration of fertilizers, industrial process and harvesting techniques [5, 9].

The ash content in biomass ash varies from 0.1–46 % (mean 6.8 %) for 86 types of biomass [10], that is also proven in other studies [5, 9, 11]. As concluded by Vassilev et al. [12] and Beloborodko et al. [13], woody biomass has alower ash content than herbaceous and agricultural biomass. Summary of the data on ash content in biomass fuels is given in Fig.1.

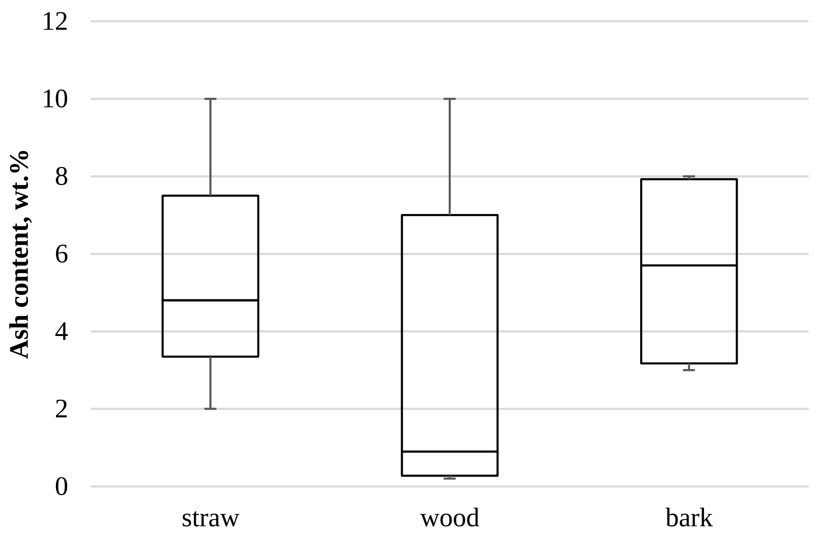

Fig. 1. Ash content in biomass fuels [5,9-11].

The research [10] shows that there is a strong correlation between biomass ash yield and other fuel characteristics. There is a positive correlation if biomass consists of Cl, S, N, Si, P and Ca in case of straw, but negative correlation – C, Cl, O, H, N and S for wood. Ash yield correlates with such factors as pH, electrical conductivity, dry water – soluble residue, cellulose and Mn and MgO elements in the fuel, lignin and volatile matter [10].

According to European Union goals, future production of biomass ash increase and ash utilization may cause serious environmental problems and thus its recycling become more important [6]. Approximately 480 million tons of biomass ash is generated worldwide annually [10]. For example in Finland, power and heating plants produce 150 000 tonnes of biomass ash annually, but in Australia – around 100 000 tonnes [14,15].

Despite the fact, that biomass ash is categorised as industrial waste, its physical and chemical properties allow to use biomass ash as an important raw material for a variety of applications [5, 6, 12, 16]. An overview of the biomass ash recent applications is given in Fig. 2.

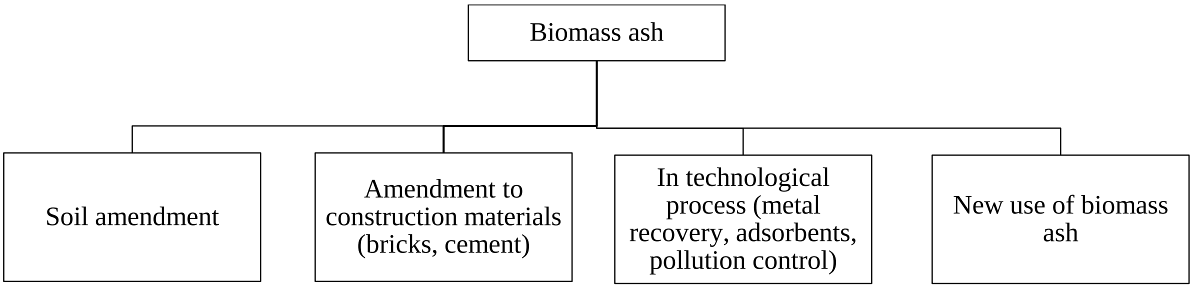

Fig. 2. Possibilities of biomass ash application.

Biomass ash, especially wood ash, has high level of alkalinity [18]. As wood ash has alkaline characteristics simlar to zeolite structure, it may be used in electrolysis process as solid electrocatalyst to reduce or replace chemical catalysts. Zhang, et al. [19] mentioned that some improvements are still possible in alkaline water electrolysis. Most scientific publications resulted in use of biomass for hydrogen production in gasification process. However some scientific studies [20, 21] analysed use of coal ash as catalysts, but no studies were found on use of biomass ash as catalyst in water electrolysis process.

The aims of the current study are: (1) within a design of experiment to perform a mathematical analysis on definition of the most suitable composition of bioenergy production by-products as catalysts in water electrolysis process; (2) to prove the results of mathematical analysis with experimental data.

2. Methods and materials

2.1. Preparation of ash catalysts

Bottom ash from wood and straw briquette combustion is used for preparation of catalysts. Different sizes of solid particles appeared in the bottom ash samples, thus to ensure consistency, the ash was crushed to powder, weighted and sampled; each sample included 2 g of dry mass ash powder and 2.5 g of distilled water used as a binding agent. To ensure larger surface area and reduce sedimentation of the ash at the electrolysis unit, sphere shaped ash catalysts are proposed (see. Fig.3). To get harder consistence of the sample, sphere catalysts were heated in a muffle furnace for more than 2 hours in 1000 ºC.

Fig. 3. Wood – straw ash catalysts before and after heating (1st - 25 % straw; 2nd - 50 % straw; 3rd - 75 % straw; 4th - 100 % straw).

Four sample sets with different wood ash and straw ash proportion were developed: the proportions of straw and wood ashes were selected randomly, however it was mathematically assumed that 25 % step can show the potential changes in the results.

- 1st – 25 % wood ash and 75 % straw ash (S25);
- 2nd – 50 % wood ash and 50 % straw ash (S50);
- 3rd – 75 % wood ash and 25 % straw ash (S75);

- 4th – 100 % straw ash (S100).

2.2. Description of experimental hydrogen production unit

An experimental alkaline based water electrolysis unit, made of glass, was developed for the study. Two steel electrodes, the working electrode and the counter electrode, were fixed on acrylic resin block with epoxy resin bond and the potential of both controlled. Distilled water was used as an aqueous solution and spherical ash catalysts added in each chamber. A principal scheme of the unit is given in Fig. 4.

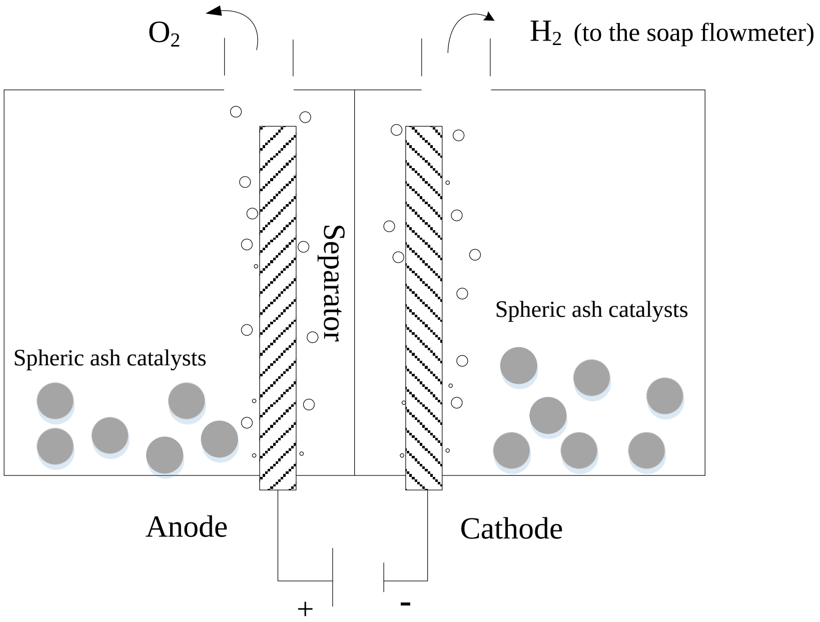

Fig. 4. Principal scheme of the experimental water electrolysis unit.

The amount of hydrogen (gas bubbles) produced was observed with a soap flowmeter [22]. The concept of the flowmeter is given in Fig. 5.

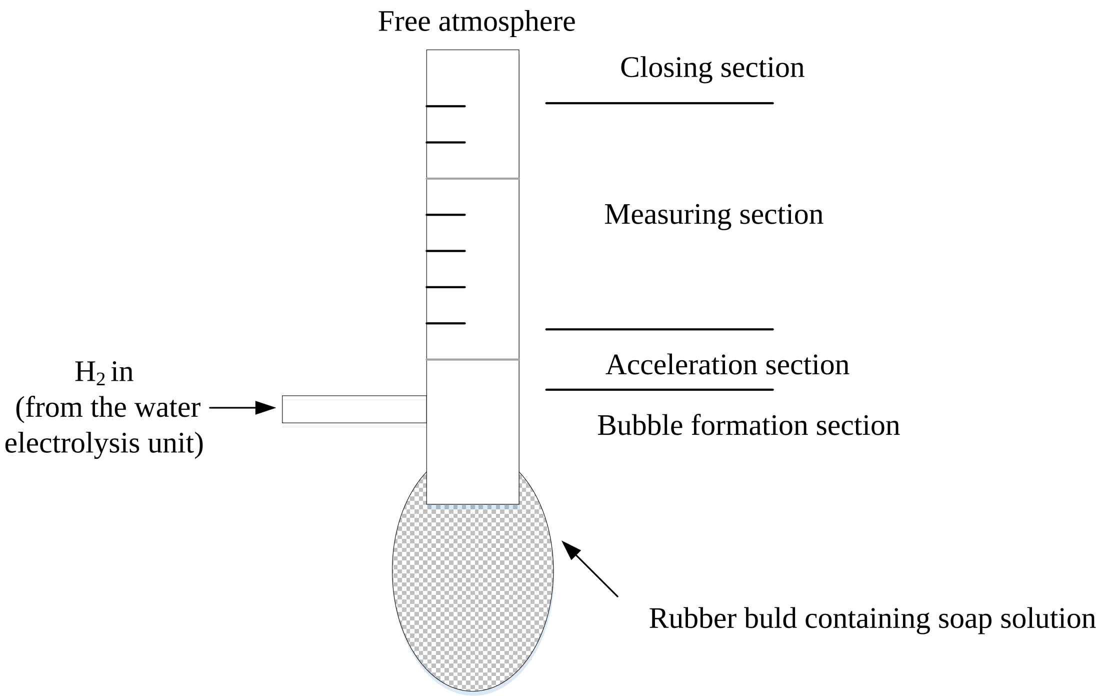

Fig. 5. Scheme of H_2 production flowmeter (based on [23]).

The soap flowmeters are widely applied for the manual measurements of gas flow rates, especially for low flow rates [23] – thus corresponding to the hydrogen flow rate in the traditional water electrolysis unit within the current study.

2.3. Analysis method

To analyse the suitability of the wood ash as catalysts, a technique for order preference by similarity to ideal solution (TOPSIS) is applied. TOPSIS accords to a classical multi-criteria (MCA) decision making method [24, 25] to solve a multiple attribute decision making problem. The method allows selecting the best of a finite number of alternatives against their performance of a selected set of criteria [25]. The selected alternative should be as close as possible to the ideal solution and as far as possible from the negative ideal solution [24-26]. The suitability of the TOPSIS method for evaluation of energy production processes and environmental sustainability are proven by many authors [27-30]. Within a current study, the TOPSIS method is applied at the level of experimental design – to define the best alternative of the catalyst sample. The application of the TOPSIS method as an experimental design approach is reported by Tiwary et al. [31] and Tansel [32] – they have demonstrated the usability of the multi-criteria decision making method for selection of optimal process parameters in manufacturing industry. Anupam et al. [33] proposed the TOPSIS method for the selection and ranking of raw materials for the pulp and paper industry: chemical and morphological characteristics of biomass varieties were evaluated according to preference for the industry.

In the current study, the samples are evaluated with three criteria: pH value, diameters of catalysts and sample surface characteristics. Criteria weights are determined based on expert assumptions and are as follows: pH – 0.6, diameter (in mm) – 0.1 and surface – 0.3. Table 1 summarises a decision matrix for assessment of biomass by-products catalysts.

Table 1. Desicion making matrix for biomass by-products catalysts assessment

		pH	Diameter, mm	Surface
		x_1	x_2	x_3
Optimal values		max	min	max
Criteria weight, q		0.6	0.1	0.3
v_1	S25	12	20	2
v_2	S50	11	17	1
v_3	S75	10	16	1
v_4	S100	11	17	1
	min	10	16	1
	max	12	20	2

The first step of TOPSIS analysis includes normalization of values: it will help to obtain non-dimensional parameters that are comparable in easier way. The normalisation matrix can be reached with different normalization models: vectorial, linear, non-linear and logarithmic [33]. Within the current study, the Witendorf linear normalization model is used (see Eq.1 and Eq. 2).

$$b_{ij} = \frac{\max a_{ij} - a_{ij}}{\max a_{ij} - \min a_{ij}} \quad \text{, if max } a_{ij} \text{ is preferable;} \tag{1}$$

$$b_{ij} = \frac{a_{ij} - \min a_{ij}}{\max a_{ij} - \min a_{ij}}, \text{ if min } a_{ij} \text{ is preferable.} \tag{2}$$

The second step in TOPSIS is the development of a normalized and weighted matrix by multiplying criteria weight (w_i) with normalized criterion values (b_{ij}) (see Eq.3).

$$v_{ij} = b_{ij} \cdot w_i \quad (3)$$

The third step in MCA is the definition of a positive-ideal (Eq.4) and negative-ideal solution (Eq.5).

$$A^+ = \mathrm{Max}_i\, v_{ij} \quad (4)$$

$$A^- = \mathrm{min}_i\, v_{ij} \quad (5)$$

Then ideal-positive separation (Eq.6) and negative-ideal separation (Eq.7) needs to be calculated.

$$S^+ = \sqrt{\sum_{j=1}^{n}\left(v_{ij} - v_j^+\right)^2},\ \ i = 1,2,..,m \quad (6)$$

$$S^- = \sqrt{\sum_{j=1}^{n}\left(v_{ij} - v_j^-\right)^2},\ i = 1,2,..,m \quad (7)$$

The final step in MCA is calculation of the relative closeness to the ideal solution:

$$\boldsymbol{C_i^*} = \frac{\boldsymbol{S_i^-}}{(\boldsymbol{S_i^+} + \boldsymbol{S_i^-})},\ \ i = 1,2,..,m \quad (8)$$

If $C_i^* = 1$, the alternative is the ideal solution and if $C_i^* = 0$, the alternative is the negative-ideal solution. The coefficient of closeness is used to rank the alternatives in a preference decreasing order. The alternative with the maximum utility value is the most preferable solution [24, 25].

3. Results and discussion

The aim of the paper was to define the best alternatives for use of biomass ash as catalysts in water electrolysis processes for hydrogen production. The multi-criteria analysis TOPSIS method was selected for assessment of defined alternatives. Using multi-criteria analysis four wood fuel ash catalyst alternatives with different composition were evaluated: S25, S50, S75 and S100. Three criteria with specific weights were defined – pH, diameter of catalytic spheres and surface characteristics of the spheres.

The weighted normalized decision matrixes were used to find the positive-ideal solution and negative-ideal solution with respect to the specific physical parameters of the developed catalysts. The distance of each catalyst from these solutions was obtained and the results are shown in Fig. 6.

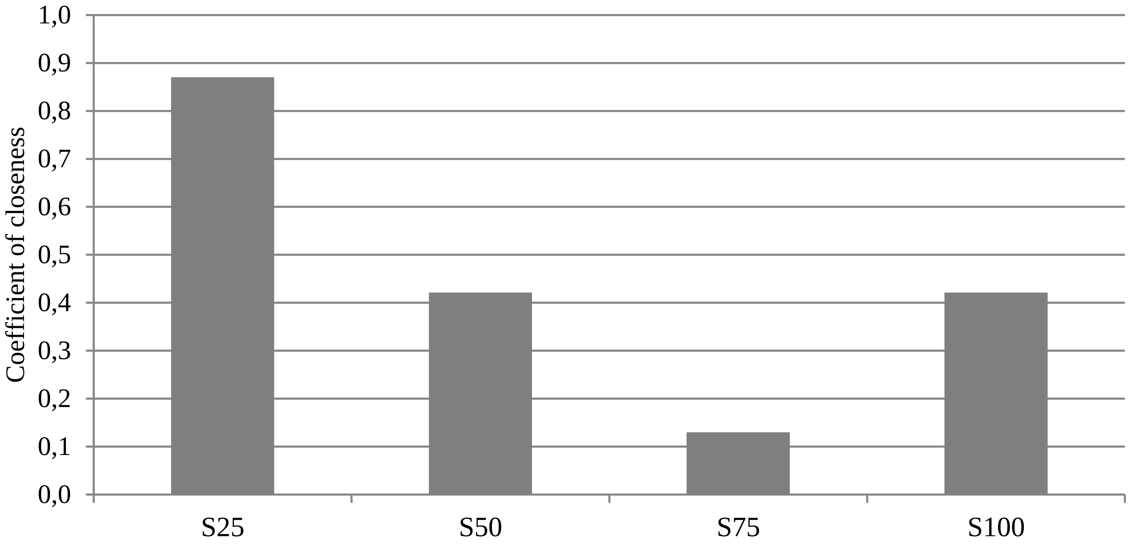

Fig. 6. Results of TOPSIS analysis: comparison between wood and straw ash samples.

The MCA analysis performed showed that S25 can be defined as an appropriate sample for the electrolysis process: the coefficient of closeness for this alternative is 0.87 to positive-ideal solution. To find the reasons of such distribution of the results, the chemical composition of the samples were analysed (see Figure 7).

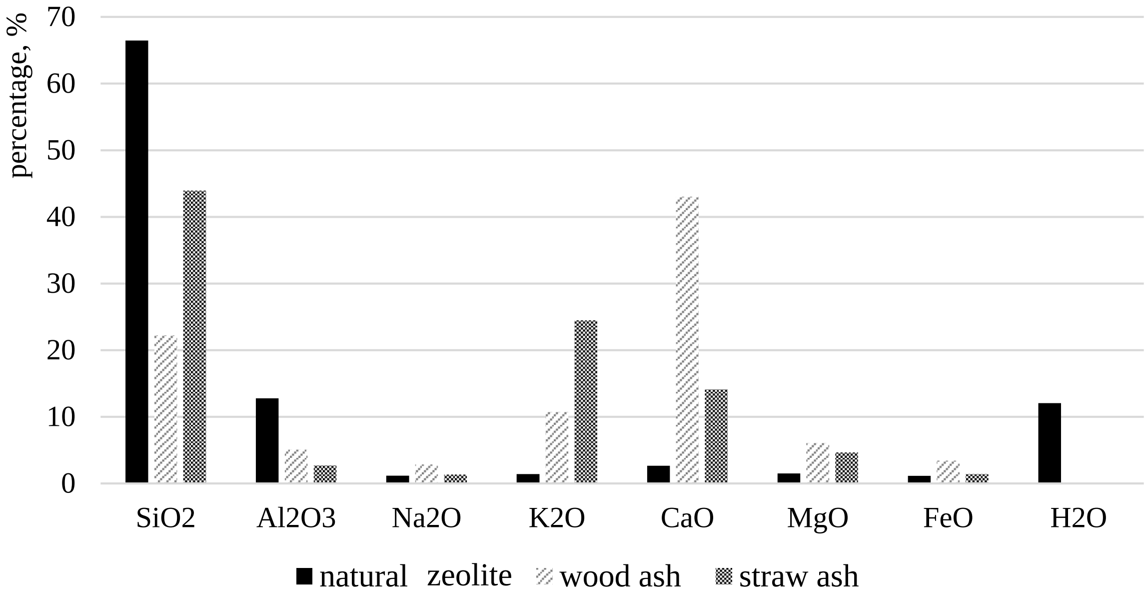

Fig. 7. Comparison of natural zeolite and biomass ash chemical composition [34].

As seen from Fig.7, the wood ash by it chemical composition is rich with chemical elements like CaO, K_2O, MgO, Al_2O_3 and SiO_2; straw ashes mainly consist of SiO_2, K_2O and CaO that makes it similar to the natural zeolites parameters. The main difference between natural zeolite and straw ash is in Al_2O_3, where natural zeolites have 30%, but straw ash only 3%, but from the other side, wood ash has higher amount of Al_2O_3 than straw ash. It might be concluded, that from the chemical composition perspective, the straw is more favourable product to substitute the natural zeolites. However, S25 has the highest pH level between the samples (pH=12) and the surface area – the parameters significant for the catalytic properties of ashes.

It was also found that a combination of straw ash and wood ash in the samples S50 and S100 have similar results in hydrogen production rates. This might be an important factor when experiments are implemented: if there is a lack of the wood ash as a raw material for production of the catalysts, the wood ash might be effectively substituted with 100 % straw ash catalyst. Additionally, this substitution might be considered from economic perspectives as well.

To validate the TOPSIS results, a laboratory experiment was performed as described in Chapter 2.2. The results of the experiment confirmed that hydrogen production via water electrolysis if biomass ash catalysts are used is more effective if the proportion of the ash is 25 % straw ash and 75 % wood ash. However additional hydrogen production monitoring, based on direct continuous measurement method with a gas analyser, might be useful to reduce uncertainty associated with use of the soap flowmeter.

Conclusions

Suitability analysis of biomass combustion ash use in the water electrolysis process as catalysts was researched in the study. The MCA TOPSIS method was used to compare various parameters of the catalysts in terms of getting a higher H_2 production rate. Four wood fuel ash catalyst alternatives with different compositions were evaluated: S25, S50, S75 and S100. Three criteria that are necessary for performance ranking were selected within the study: pH, diameter of catalytic spheres and surface characteristics of the spheres. Weights of the criteria were based on literature analysis and also the opinion of the field experts was taken into account. The results of the TOPSIS analysis showed that S25 sample (25 % wood ash and 75 % straw ash) is ranked as the most optimal catalyst for hydrogen production in the water electrolysis unit; the analytical results were also confirmed with the experimental results showing a good perspective to use the bio-by-products (biomass ash) as the catalysts in the water electrolysis processes. Environmental performance of such substitution might be significant – reduction of use of chemical catalysts is obtained. However, detailed calculation of technical, environmental and economic effectiveness (for example hydrogen production rate per material economy and resource effectiveness) is required.

The study proved that the TOPSIS method can be successfully employed for design of experiment phase to choose better alternative for further experiments.

Acknowledgements

This work has been supported by the European Social Fund project "Involvement of Human Resources for Development of Integrated Renewable Energy Resources Energy Production System" (project No. 2013/0014/1DP/1.1.1.2.0/13/APIA/ VIAA/026).

ESF EIROPAS SOCIĀLAIS FONDS

EIROPAS SAVIENĪBA

IEGULDĪJUMS TAVĀ NĀKOTNĒ

References

1. Bhandari R, Trudewind C, Zapp P. Life cycle assessment of hydrogen production via electrolysis – a review. Journal of Cleaner Production 2013;85:151-63.
2. Agbossou K, Chahine R, Hamelin J, Laurencelle F, Anouar A, St-Arnaud J-M, et al. Renewable energy systems based on hydrogen for remote applications. Journal of Power Sources 2001;96:168-72.

3. Barbir F. PEM electrolysis for production of hydrogen from renewable energy sources. Solar Energy 2005;78:661-9.
4. Carmo M, Fritz DL. A comprehensive review on PEM water electrolysis. International Journal of Hydrogen Energy 2013;38:4901-34.
5. Siddique R. Utilization of wood ash in concrete manufacturing. Resources, Conservation and Recycling 2012;67:27-33.
6. Ahmaruzzaman M. A review on the utilization of fly ash. Progress in Energy and Combustion Science 2010;36:327-363.
7. Tortosa Masiá A., Buhre B., Gupta R., Wall T. Characterising ash of biomass and waste. Fuel Processing Technology 2007;88:1071-81.
8. Thy P., Jenkins B.M. et al. High temperature elemental losses and mineralogical changes in common biomass ashes. Fuel 2006;85:783-95.
9. Schmitt V. E., Kaltschmitt M. Effect of straw proportion and Ca- and Al-containing additives on ash. Fuel 2013;109:551-8.
10. Vassilev S. V., Baxter, D., Andersen, L. K., Vassileva, C. G. An overview of the composition and application of biomass ash. Part 1. Phase–mineral and chemical composition and classification. Fuel 2013;105:40-76.
11. Nordgren D., Hedman H., Padban N., Boström D., Öhman M.Ash transformations in pulverised fuel co-combustion of straw and woody biomass. Fuel Processing Technology 2013;105:52-58.
12. Vassilev S. V., Baxter D., Andersen L. K., Vassileva, C. G. An overview of the composition and application of biomass ash. Part 2. Potential utilisation, technological and ecological advantages and challenges. Fuel 2013;105:19-39.
13. Beloborodko A., Klavina K., Romagnoli F., Kenga K., Rosa M., Blumberga D. Study on Availability of Herbaceous Resources for Production of Solid Biomass Fuels in Latvia. Agronomy Research 2013;11;2:283-94.
14. Emilsson S., Swedish Forest Agency. International handbook: from extraction of forest fuels to ash. Sweden: Swedish Forest Agency, 2006.
15. Kuba T., Tscholl A., Partl C., Meyer K., Insam H. Wood ash admixture to organic wastes improves compost and its performance. Agriculture, Ecosystems and Environment 2008;127:43-9.
16. Campbell A. Recycling and disposing of wood ash. TAPPI Journal 1990;73(9):141-3.
17. Kalembkiewicz J.,Chmielarz, U. Ashes from co-combustion of coal and biomass: New industrial wastes. Resources, Conservation and Recycling 2012;69:109-21.
18. Demeyer A., Voundi N. J., Verloo, M. Characteristics of wood ash and influence on soil properties and nutrient uptake: an overview. Bioresource Technology 2001;77:287-95.
19. Zhang J., Zhang L.,Lei Liu, H. Electrochemical Technologies for Energy Storage and Conversion, 1st ed. Somerset, NJ, USA: Wiley-VCH, 2011.
20. Musyokaa M., Petrika F., Humsb E., Baserc H., Schwiegerc W. In situ ultrasonic monitoring of zeolite A crystallization from coal fly ash. Catalysis Today 2012;190:38-46.
21. Babajide O., Musyoka N., Petrik L., Ameer F. Novel zeolite Na-X synthesized from fly ash as a heterogeneous catalyst in biodiesel production. Catalysis Today 2012;190:54-60.
22. Lauka D., Blumberga D. Electrolysis process analysis by using low carbon content additives: a batch test study. Energy Procedia 2015; *In Press*.
23. S. Lashkari, B. Kruczek. Development of a fully automated soap flowmeter for micro flow measurements. Flow Measurement and Instrumentation 2008; 19:397-403.
24. Hwang C.L., Yoon K.P., Multiple attribute decision making: Methods and applications. New York: Springer-Verlag; 1981.

25. Behzadian M., Khanmohammadi S. O., Yazdani M., Ignatius J., A state-of the-art survey of TOPSIS applications. Expert Systems with Applications 2012;39(17):13051-69.
26. Zenonas T., Edmundas K., Zavadskas F. P. Multi-criteria Optimization System for Decision Making in Construction Design and Management. Engineering Economics 2009;7-17.
27. Xi B.D., Su J., Huang G.H., Qin X.S., Jiang Y.H., Huo S.L., Ji D.F., Yao B., An integrated optimization approach and multi-criteria decision analysis for supporting the waste-management system of the City of Beijing, China. Engineering Applications of Artificial Intelligence 2010;23(4):620-31.
28. Dace E., Rusanova J., Gusca J., Blumberga D. Selecting a Catalyst for Methanation Process: Technical and Economic Performance Based TOPSIS Analysis. In: Zevenhoven R. editors. ECOS 2014: Proceedings of the 27th International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems; 2014 June 15-19; Turku, Finland. Åbo Akademi University: pp.1-9.
29. Ziemele J., Vigants G., Vitolins V., Blumberga D., Veidenbergs I. District Heating Systems Performance Analyses. Heat Energy Tariff. Environmental and Climate Technologies 2014;13:32-43.
30. Kuznecova T., Romagnoli F., Rochas C., Energy Metabolism for Resilient Urban Environment: A Methodological Approach. Procedia Economic and Finance 2014;18:780–8.
31. Kalnins S.N., Blumberga D., Gusca J. Combined methodology to evaluate transition to low carbon society. Energy Procedia 2015; *In Press*.
32. Tiwary A.P., Pradhan B.B., Bhattacharyya B. Application of multi-criteria decision making methods for selection of micro-EDM process parameters. Adv. Manuf. 2014; 2:251–8.
33. Tansel Y. An experimental design approach using TOPSIS method for the selection of computer-integrated manufacturing technologies. Robotics and Computer-Integrated Manufacturing 2012; 28: 245–56.
34. Anupam K., Lal P.S., Bist V., Sharma A.K., Swaroop V. Raw Material Selection for Pulping and Papermaking using TOPSIS Multiple Criteria Decision Making Design. Environmental Progress & Sustainable Energy 2014; 33(3):1034-41.
35. Inglezakis, V. J., Zorpas, A. A. Handbook of Natural Zeolites. SAIF Zone, Sharjah: Bentham Science Publishers; 2012.