Development of Technology and Installation for Biohydrogen Production

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Abstract. The article discusses the method for hydrogen production and the device this method application. The relevance of the use of renewable fuels and the positive impact of renewable energy on the environment and the economy is also considered. The presented technology relates to a method for hydrogen production from organic materials subject to anaerobic fermentation, such as the components of solid municipal waste, sewage sludge and agricultural enterprises wastes, sewage waste. The aim of the research is to develop an effective eco-friendly technology for hydrogen producing within an industrial project. To achieve the goal, the following issues have been addressed in the course of the study:
- development of the process schemes for hydrogen producing from organic materials;
- development of the technology for hydrogen producing;
- optimization of a biogas plant with the aim of hydrogen producing at one of the fermentation stages;
- approbation of the research results.

The article is recommended for engineers and innovators working on the renewable energy development issues.

1. Introduction

According to the theory of techno-economic paradigm (innovative waves), Russia is now located at the junction of the fifth and sixth. The fifth innovative wave is based on the development of biotechnology, genetic engineering, new energy sources, etc. The sixth innovative wave will be based on the development of robotics, nanotechnology related to genetic engineering and molecular biology, artificial intelligence systems, etc. [1] Therefore, new technological solutions are more important today than ever before.

Russia currently faces serious problems concerning the issue of global sanctions, import substitution, dependence of its economy on hydrocarbon resources. It’s important for Russia to make a transition to the sixth innovative wave, not fully finishing the preceding fifth. This will allow catching up with the technologies of the leading countries and providing the opportunity to solve existing problems. Russia spends seven times less than Japan and 20 times less than the United States on science today. It is recognized that the continuous development of economy and industry creates an increasing demand for energy resources and makes it necessary to develop renewable and alternative energy sources [2].

The framework of the sixth techno-economic paradigm implies further development of nuclear energetics, expanding the use of hydrogen as a clean energy source in addition to natural gas, and significantly broadening the use of renewable energy sources [3].
In the period of global instability and falling prices for hydrocarbons the dependence on fossil fuels is especially pronounced. This can be noticed both on the consumer market and in industrial and commercial sector.

Non-renewable fuels are a limited source of stored energy, which can be released during the combustion process, thus a considerable amount of toxic substances, pollutants gets into the atmosphere. Therefore, developing renewable and alternative energy technologies is very significant for the development of the country, both an environmentally and economically.

For example, Italian Ministry of Economic Development has adopted a new program for the development of biogas companies and transport biogas to the different areas of the country. At the moment, the development of bioenergy inhibit the following factors: increased demand for compressed natural gas transport, local limitations of the raw material base, low prevalence of filling stations for this type of fuel. Besides, since biomass is available in a limited amount, the largest contributions to renewable energy systems are originated in wind and solar power. Nevertheless, the high proportion of fluctuating renewable energy present challenges, especially regarding the need to balance the energy to the electrical grid [4]. The developed program increases the profitability of enterprises for the production of biogas and opens new opportunities for use of agricultural biogas [5].

The development of bio-energy solves two problems: energy recovery and disposal of different types of waste. The use of renewable energy, biogas in particular, is very promising for the developing countries, as in small settlements there is currently no centralized power supply or sewage system, which is leading to serious environmental problems [6]. Biogas consists of 65% methane, 30% carbon dioxide and 1.5% hydrogen sulphide [7]. Hydrogen sulphide is toxic and corrosive [8], with an unpleasant odor. For these reasons, it must be removed from the resulting biogas. A salak fruit seeds packed bed reactor with sulfur oxidizing bacteria as biofilm [9], and trickling biofilter [10] showed good results in this.

A method for producing hydrogen rich gas from the blast furnace sludge is promising for the large industrial cities with developed production. Blast furnace slag generates hydrogen-rich gas via the endothermic reactions of sludge pyrolysis. Blast furnace slag as catalyst can greatly increase H2 and CO contents of gas by improving tar degradation and reforming of biogas (CO2 and CH4) [11].

Biohydrogen is the only carbon free fuel, which ultimately oxidizes to give water as a by-product, and it is a flexible and safe energy resource that can be utilized in all sectors globally. Biohydrogen can be converted into energy through either combustion or fuel cells to generate electricity, and further it releases explosive energy in heat engines [12].

Hydrogen is an ecologically clean fuel, which upon combustion forms no toxic substances. Hydrogen is also widely used in the production of fertilizers, dyes, plastics, fats, and in other industrial areas. Blends of biogas with methane or propane and hydrogen make it possible to achieve high fuel characteristics and resistance to detonation for use in various engines [13].

The ability to produce hydrogen in anaerobic reactors and the identification of factors affecting the hydrogen-producing bacteria has been shown in the research [14].

In addition, there have been conducted studies on the possibility of obtaining biohydrogen from a brewery wastewater [15] in anaerobic reactors with mixed microbial consortia [16].

Table 1 shows the conventional methods for producing hydrogen on an industrial scale.

| Methods:                    | Disadvantages methods                                      |
|-----------------------------|------------------------------------------------------------|
| Steam reforming of hydrocarbons | Spent fossil hydrocarbon fuel                             |
| Partial oxidation of coal   | Spent fossil hydrocarbon fuel                             |
| Electrolysis of water       | Despite the ecological compatibility of technological process is very expensive and economically inefficient for most industrial enterprises. The amount of energy used for electrolysis of water exceeds the amount of energy produced by burning the resulting hydrogen |
| Photovoltaic method         | Limited use due to lack of access to solar energy for most countries of the world |
On the basis of the evaluated methods for producing hydrogen, it is possible to draw a conclusion about the absence of organic industrially applicable method of hydrogen production.

2. Problem statement
Our proposed technology relates to a method for producing hydrogen from subjected to anaerobic fermentation of organic materials, such as components of solid municipal waste, sewage sludge and wastes of agricultural enterprises, sewage waste.

3. Research questions
The following questions have been addressed in the course of the study:
- development of process schemes for producing hydrogen from organic materials;
- development of technology for producing hydrogen;
- optimization of biogas plant with the aim of producing hydrogen on one of the stages of fermentation;
- approbation of research results.

4. Purpose of the study
Because the known ways of producing hydrogen have a number of significant deficiencies the relevance of the topic causes no doubt. The aim of our research is the development of an effective eco-friendly technology for producing hydrogen for industrial project.

5. Research methods
The technology is based on the possibility to process organic materials, subjected to anaerobic digestion in a biogas plant, to a discrete low voltage electric current in order to increase hydrogen and reduce methane production. It is experimentally proved that the formation of hydrogen decreases with increasing acidity of the treated material and the environment of methanogenesis.

Such a process allows obtaining hydrogen from materials of municipal solid waste, wastewater, sewage waste and agricultural waste in such quantities, that the energy of the hydrogen produced exceeds the energy required to generate the electrical current needed to maintain the continuity of the process. At the same time reducing the mass of waste and the reduction of time required for treatment and disposal of the material in use.

The proposed technology of producing hydrogen does not require the use of fossil energy sources, nor is it dependent on the presence of sunlight and can be used to provide decentralized electricity supply systems and systems with other energy infrastructure, at the same time providing useful energy from collected wastes.

The ability to process the waste of livestock farms, which solves the problem of disposing of animal waste, obtaining additional useful energy and high quality organic fertilizers for agriculture is of particular interest for it.

The technology is to process the organic material undergoing anaerobic fermentation in a biogas plant with the electric current. The electric current enhances the performance of hydrogen producing bacteria and reduces the activity of methanogenic microorganisms.

The received hydrogen can be used directly for obtaining energy to maintain operation of the process equipment.

The considered technology can be implemented by the means of biogas plant.

The generation of electric current can be produced by the application of electric potential between the electrodes that are in contact with the processed organic material. The electrodes can be made of different materials, such as lead, copper, brass, steel.

Processing is carried out by application of electric potential in the range from 1.0 to 7.0 volts, treatment with 3.0 to 4.0 volts shows the best result. Voltage, the average distance between electrodes and the number of electrodes can vary depending on the size and composition of the processed organic material.

Electric current is generated intermittently, with intervals chosen to minimize the consumption of electrical power and to maximize the production of hydrogen.

For example, the magnitude of the electric potential can be adaptively adjusted according to the information obtained through feedback from the gas analyzer and an associated controller.

Figure 1 shows a three-stage digester of a biogas plant to produce hydrogen.
Figure 1. The digester of a biogas plant: 1 - pump feed; 2 - anaerobic digester; 3 - mixing device; 4 - raw material discharge pump; 5 - manometer; 6 - electric heating device; 7 - pH sensor; 8 - the temperature sensor; 9 - container under sludge; 10 - psychrophilic fermentation camera; 11 - mesophilic digestion camera; 12 - thermophilic digestion camera; 13 - controller; 14 - relay operated by the controller; 15 - voltage source; 16 - electrodes; 17 - gas analyzer.

Voltage supply depends on the analyzer on the output valve. The voltage is intermittently fed to suitable concentric electrodes 16, to influence the anaerobic fermentation of organic biomass located between the electrodes with the aim of producing hydrogen. In working condition, voltage is supplied from source 15 in accordance with the working cycle, controlled by relay 14, which is constantly operated by controller 13 to facilitate hydrogen generation and to prevent substantial methane formation. Controller 13 is supplied with feedback information from gas analyzer 17. Upon the occurrence of trace quantities of methane between the electrodes 16 a voltage is applied for a recorded time period until the suppression of methane formation. Controller 13 notes the time before the new formation of methane. It is used by duty cycle, including the application of the voltage between the electrodes 16 for a bit longer time than the time marked for the suppression of methane formation and subsequent neutral electrode operation for a lesser time than the time noted previously, corresponds to the determination of trace quantities of methane.

The working cycle is a subject to adaptive change to reduce the application time of the voltage and lengthen the time between applications of voltage to minimize the formation of methane, while maximizing the formation of hydrogen with the least application of voltage to the electrodes 16. The voltage decrease with the emergence of another variable and adaptive adjust in accordance with the application time of the voltage to reduce energy consumption. The algorithm of adaptive adjustment quickly adapts to changes in the composition of organic waste, moisture content, temperature and other variables.

6. Findings
The experiments were carried out on the laboratory biogas plant, which was supplied to the electrodes attached in parallel to a 1.5 volt battery, with the result that the supply capacity reached 3 volts. In the result
of the process, the formed product stands out through a branch pipe. The branch pipe joins the gas analyzer to monitor the output of hydrogen and methane.

**Example 1.**

Fresh manure obtained from the farm with 90% humidity was taken as a control sample. It was placed in the laboratory biogas plant and subjected to anaerobic digestion without applying electric current. The composition of biogas is given in table 2.

| Table 2. The experimental results of biogas without the use of electric current. |
|---|---|---|---|
| Day | %CH₄ | %CO₂ | %N₂ |
| 13  | 55  | 40  | 5   |
| 16  | 60  | 35  | 4   |
| 19  | 65  | 30  | 5   |
| 22  | 70  | 25  | 5   |
| 25  | 70  | 25  | 5   |

Based on the experimental data, the active process of biogas starts on day 13 from the beginning of the technological process, and reaches a maximum at 22-25 day. Biogas consists mainly of methane and carbon dioxide, the hydrogen is released in small quantities.

**7. Conclusions**

Thus, the experiment allows evaluating the possibility of obtaining biohydrogen in the reactor of a biogas plant. In the experiment, passing an electric current through the biomass reduces methane concentration to values of less than 10% and increases hydrogen concentration in the material up to 65%. These results confirm the possibility of using the proposed technology for producing hydrogen, followed by its use as an alternative source of energy.

At the same time, we must not forget about the safety of all technological processes in the development of both biogas and hydrogen, as the generated substances are explosion and fire-hazardous substances. Exchange of experience between different companies, feedback and announcements of results of the investigation of accidents can provide the safety of technological processes [17-20].

The situation in the global economy today suggests that it is time to pay more attention to the scientific potential of the proposed technologies. The conclusion that can be drawn from the above is the fact that the technologies of the sixth innovative wave are potentially promising for science and require more careful and detailed study. The Potential of application of hydrogen technologies is unlimited. In relation to agriculture, this technology can be relevant in connection with the constant lack of energy resources and high-quality biological fertilizers.

**References**

[1] Bojanova I 2014 The Digital Revolution: What’s on the Horizon? *IT Pro: Published by the IEEE Computer Society* pp 8–12

[2] Perez C 2010 Technological revolutions and techno-economic paradigms *Cambridge Journal of Economics* 34 pp 185–202

[3] Mathews J A 2013 The renewable energies technology surge: A new techno-economic paradigm in the making? *Futures* 46 pp 10–22

[4] Ertem F C, Martínez-Blanco J, Finkbeiner M, Neubauer P and Junne S 2016 Life cycle assessment of flexibly fed biogas processes for an improved demand-oriented biogas supply *Bioresource Technology* 219 pp 536–544

[5] Patrizio P and Chinese D 2016 The impact of regional factors and new bio-methane incentive schemes on the structure, profitability and CO2 balance of biogas plants in Italy *Renewable Energy* 99 pp 573–583

[6] Le T H, Tran V T and Le Q V, Schnitzer H and Brauneeg G 2016 An integrated ecosystem incorporating renewable energy leading to pollution reduction for sustainable development of craft villages in rural area: a case study at sedge mats village in Mekong Delta (Vietnam: Energy, Sustainability and Society) 6(1) 21
[7] Syed M, Soreanu G, Falletta P and Beland M 2006 Removal of hydrogen sulfide from gas streams using biological processes—a review Can. Biosyst. Eng 48 pp 2.1–14
[8] Lastella G, Testa C, Cornacchia G, Notornicola M, Voltasio F and Sharma V K 2002 Anaerobic digestion of semi-solid organic waste: biogas production and its purification Energy Convers. Manage 43(1) pp 63–75
[9] Lestari R A S, Sediawan W B, Syamsiah S and Sarto Teixeira J A 2016 Hydrogen sulfide removal from biogas using a salak fruit seeds packed bed reactor with sulfur oxidizing bacteria as biofilm Journal of Environmental Chemical Engineering 4(2) pp 2370–2377
[10] Vikromvarasiri N and Pisutpaisal N 2016 Hydrogen sulfide removal in biotrickling filter system by Halothiobacillus neapolitanus International Journal of Hydrogen Energy 41(35) pp 15682–15687
[11] Luo S and Feng Y 2016 The production of hydrogen-rich gas by wet sludge pyrolysis using waste heat from blast-furnace slag Energy 113 pp 845–851
[12] Bharathiraja B, Sudharsanaa T, Bharghavi A, Jayamuthunagai J and Praveenkumar R 2016 Biogas and Biogas – An overview on feedstocks and enhancement process Fuel 185 pp 810–828
[13] Gómez Montoya J P, Amell A A and Olsen D B 2016 Prediction and measurement of the critical compression ratio and methane number for blends of biogas with methane, propane and hydrogen Fuel 186 pp 168–175
[14] Vasconcelos E A F, Leitão R C and Santuella S T 2016 Factors that affect bacterial ecology in hydrogen-producing anaerobic reactors Bioenergy Research pp 1–12
[15] Zhang J and Zang L 2016 Enhancement of biohydrogen production from brewers spent grain by calcined-red mud pretreatment Bioresource Technology 209 pp 73–79
[16] Vijaya Krishna S, Kiran Kumar P, and Chaitanya N, Himabindu V and Lakshmi Narasu M 2016 Biohydrogen production from brewery effluent in a batch and continuous reactor with anaerobic mixed microbial consortia Biofuels pp 1–7
[17] Casson Moreno V, Papasidero S, Scarponi, G E, Guglielmi D and Cozzani V 2016 Analysis of accidents in biogas production and upgrading Renewable Energy 96 pp 1127–1134
[18] Heezen P A M, Gunnarsdottir S, Gooijer L and Mahesh S 2013 Hazard classification of biogas and risks of large scale biogas production Chem. Eng. Trans. 31 pp 37–42 Retrieved from http://www.aidic.it/cet/13/31/007.pdf.
[19] Riviere C and Marlair G 2010 The use of multiple correspondence analysis and hier-archical clustering to identify incident typologies pertaining to the biofuelindustry Biofuels Bioprod. Biorefining 4 pp 53–65 Retrieved from http://dx.doi.org/10.1002/bbp.
[20] Salzano E, Di Serio M and Satacesaria E 2010 Emerging safety issues for biodiesel production plants Chem. Eng. Trans. 19 pp 415–420