Methanization of Lemna Minor for the Purpose of obtaining Hydrogen

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Abstract— *The article discusses the theoretical possibilities of using biomass produced on open water bodies by growing the Lemna minor plant for hydrogen production. The process of obtaining hydrogen is solved primarily in two stages, including the methanization of biomass and the subsequent transformation of methane into hydrogen and carbon dioxide. It deals with current technologies of methane oxidation to form hydrogen using water vapor, such as WGSR, SMR, MPS and PSMR technologies. It indicates various methods of purifying hydrogen from unwanted elements with their subsequent applicability in small local hydrogen production plants in decentralized hydrogen economy.*

***Keywords*— hydrogen, Lemna minor, methane, biomass.**

I. INTRODUCTION

Globally increasing requirements for obtaining hydrogen using technologies that do not use fossil resources for their operation nor for the production of hydrogen, are increasing with the rising prices of fossil sources and gradual reduction of the number of their abundant deposits. The production of green hydrogen by the means of the electrolytic decomposition of water using renewable sources of energy currently faces obstacles with the lack of renewable sources of electric energy. One of the ways to decrease the dependence on fossil sources during the hydrogen production process is the use of organic biomass, the processing of which produces the so-called blue hydrogen. However, the use of biomass also encounters problems with land, when large volumes of arable land intended for growing food are occupied at the expense of the cultivation of biomass that can be used for energy. This problem is solved by growing biomass on water bodies. The advantage of producing biomass on open water surfaces is the reduction of arable land required for the cultivation of energy recoverable biomass. Another advantage is the increase of yields due to the faster growth of aquatic biomass compared to its terrestrial equivalent. Lemna minor is one of the smallest and fastest-growing flowering plants on the earth. It´s an extremely reduced floating freshwater plant. The growth rate of Lemna minor in the wastewater in an open uncontrolled environment is at the level of 29 $g \cdot m^{-2} \cdot day^{-1}$, as it is dry biomass, which corresponds to 104 $t \cdot ha^{-1} \cdot year^{-1}$. During experiments with new types of fast-growing biomass, such as sun hemp (Crotalaria juncea L.), yields were achieved only at the level of 11 $t \cdot ha^{-1} \cdot year^{-1}$. [2] In the case of fast-growing trees such as willow, the yield can be in the range of 16 – 17 $t \cdot ha^{-1} \cdot year^{-1}$ and in the case of poplar in the range of 18 – 16 $t \cdot ha^{-1} \cdot year^{-1}$. [3] The use of fast-growing herbs such as bamboo can represent of the possibilities of fast and efficient biomass cultivation for energy purposes, but even in this case there are limitations caused by bamboo's requirements for growth conditions. In ideal conditions for growth in an uncontrolled environment, the bamboo reached a maximum yield of 47 $t \cdot ha^{-1} \cdot year^{-1}$. [4]

II. ORGANIC DECOMPOSITION OF LEMNA MINOR INTO METHANE

When producing hydrogen from organic biomass it is possible to use several methods of its processing. Among the simplest methods of processing biomass is the thermal decomposition of organic substances with the simultaneous production of synthesis gas, oils, ash, or solid residues. The thermal recovery process of Lemna minor produces large amounts of carbon dioxide at the expense of the production of hydrogen, carbon monoxide and methane. This problem is caused by the presence of a high proportion of oxygen in the basic biomass, which results in a high production of carbon dioxide, as shown in Fig. 1 from the research of N. Muradov et al.

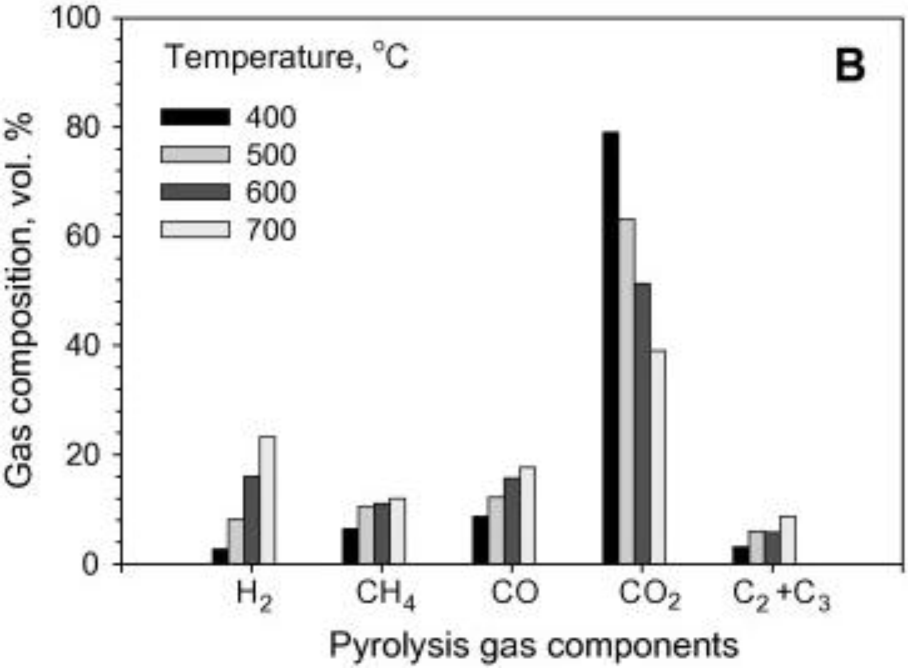

FIGURE 1: Composition of pyrolysis gas produced by Lemna minor pyrolysis depending on pyrolysis temperature at Ar flow rate 60 ml·min^{-1} [5]

One of the variants in which it is possible to increase the yield of hydrogen obtained from Lemna minor biomass is its conversion into methane using methanogenic organisms. By subsequent technological treatment of methane, it is possible to obtain hydrogen to produce carbon dioxide. For the process of converting Lemna minor into methane, it is necessary to carry out the initial pre-treatment of the biomass to increase the efficiency of its recovery. The basis of the pre-treatment is drying and grinding of biomass, which improves the access of substances in the following processes into the organic structure and increases the efficiency of the processes. Grinding is followed by a hydrolysis process, during which the polymeric organic substances (polysaccharides, fats, proteins) with the help of aerobic bacteria are broken down into monomers – alcohols and fatty acids, releasing hydrogen (H_2) and carbon dioxide (CO_2). The produced gases can be captured and added to the treated biogas to increase the yield of hydrogen from the overall process.

After hydrolysis, the treated biomass is transferred to the reactor, where the initial preparation for the direct production of biogas takes place. The first step is acidogenesis, during which the residual oxygen in the air is consumed. An anaerobic environment is created, and higher organic acids are formed. This transformation is carried out by facultative anaerobic microorganisms, which are capable of existing in both environments. During the following process of acetogenesis, higher organic acids and alcohols are converted into acetic acid H_2 and CO_2. The final phase of the entire fermentation process is methanogenesis. It takes place in an environment without access to air and the decomposition of acetic acid into methane CH_4 and CO_2 occurs. Hydrogenotrophic bacteria create methane from H_2 a CO_2 that are dissolved in water. [6] The yield of a mixture of hydrogen and methane can reach the level of 33 mol·kg^{-1} when appropriate procedures are used and if additional equipment is used, the total yield can rise to the level of 38,76 mol·kg^{-1}, as stated by K. Manpreet et al. [7]

III. OBTAINING H_2 FROM BIOGAS RICH IN CH_4

To obtain hydrogen from biogas rich in methane, its technological treatment is necessary. For the purposes of technological treatment of biogas, it is advisable to use systems in which methane is converted by merging with water vapor into hydrogen and carbon dioxide. Such devices include, for example, steam reformers (SMR), in which methane is combined with water vapor according to the equation (1):

$$\mathrm{CH_4 + H_2O \leftrightarrow CO + 3H_2}\ \Delta H_{\mathrm{SR}} = 206\ \mathrm{kJ \cdot mol^{-1}} \tag{1}$$

Subsequently, the gas is treated using WGS reactors, in which carbon monoxide is combined with water vapor in the presence of catalysts according to the equation (2):

$$\mathrm{CO + H_2O \leftrightarrow CO_2 + H_2}\ \Delta H_{\mathrm{WGSR}} = -41\ \mathrm{kJ \cdot mol^{-1}} \tag{2}$$

In addition to changing the ratio of individual incoming components, temperature also has a significant effect on the efficiency of the conversion of carbon monoxide into hydrogen. As was proven in the study created at the Ohio State University, under the leadership of prof. Liang-Shih Fan, in the case of high-temperature conversion, there are significant changes in the efficiency of the whole process by changing the temperature. An increasing tendency to increase CO conversion efficiency can be observed with increasing temperature in the reaction chamber, while the break occurs in the critical temperature region (550-650 °C), after which a gradual decrease in efficiency occurs (Fig. 2). In the case of atmospheric pressure and steam:CO mixing ratio, the conversion increases from 45,8 % at 450 °C to 83,2 % at 600 °C. Subsequently a decrease occurs and at 800 °C the conversion efficiency is at the level of 69,4 %. This phenomenon occurs as result of a decrease in the equilibrium constant, [3] which decreases with increasing temperature. The increase in conversion value can be observed with the increasing steam:CO ratio. While at a 1:1 steam-carbon dioxide mixing ratio and a temperature of 650 °C, the conversion efficiency is 63,5 %, in the case of 2:1 ratio the efficiency reaches a value of 71,6 % and at 3:1 ratio a value of 80,28 %.

$$K_{WGS}=\frac{[CO_2][H_2]}{[CO][H_2O]}=812{,}9-\frac{6{,}628e+5}{T}+\frac{1{,}001e+8}{T^2} \tag{3}$$

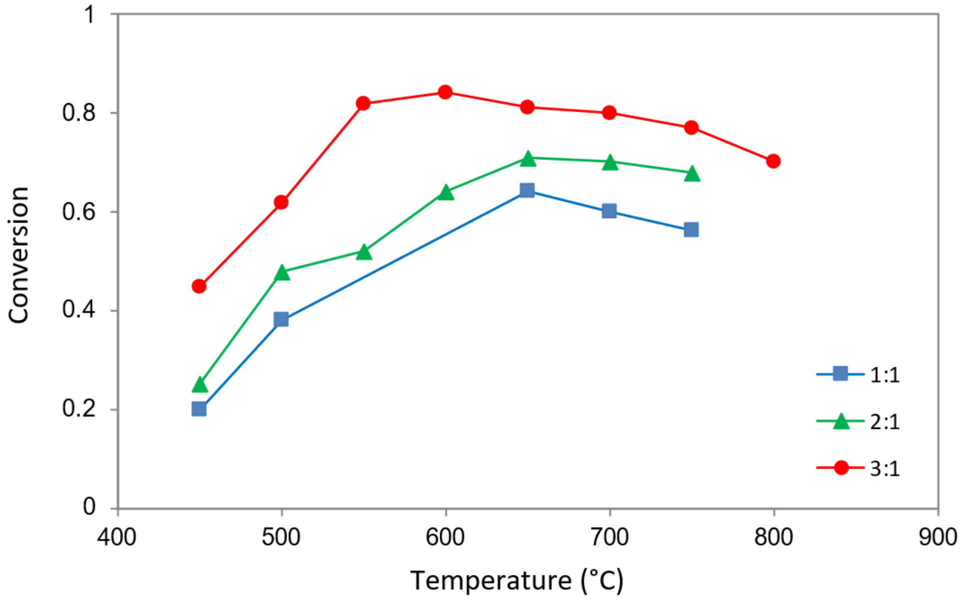

FIGURE 2: Effect of reaction temperature on CO conversion at 0 kPa pressure

Another option that can be used, is the microwave plasma sources (MPS) method, in which methane is combined with water vapor at high temperatures, just like in SMR processes. However, in this case, unlike SMR processes where catalysts are needed, the plasma supplies the necessary energy and free radicals to the process of combining the input raw materials to form H_2 and CO_2 in one step. High energy electrons generated by nonthermal plasma speed up chemical processes leading to the conversion of the methane produced by Lemna minor into hydrogen and carbon dioxide. Significant advantages of nonthermal plasma are its high reactivity and low energy consumption while being able to operate in the low temperature range. Catalysts are usually required in nonthermal plasma to speed up the conversion process. In the area of the discharge, the nonthermal plasma is internally heterogeneous, which leads to a reduction of the reaction surface. As a result, the conversion rates and permeability are low. [7]

Another option for methane valorisation by converting it into hydrogen and carbon dioxide is the plasma steam methane reforming (PSMR) process. During this process, unlike MPS, catalysts are not required for the reaction of methane with water vapor, which results in hydrogen and carbon dioxide. The advantage of microwave plasma is the absence of catalysts, in which clogging occurs during the process of converting methane to hydrogen. Due to clogging of the catalysts, the efficiency of the entire process decreases, and the costs associated with their replacement are increasing. In the paper Plasma steam methane reforming (PSMR) using a microwave torch for commercial-scale distributed hydrogen production, Olugbenga Akande et al. described the process, in which more than 90% conversion of methane to hydrogen and carbon dioxide occurs. In some cases, the over-all conversion efficiency exceeded 99 %.

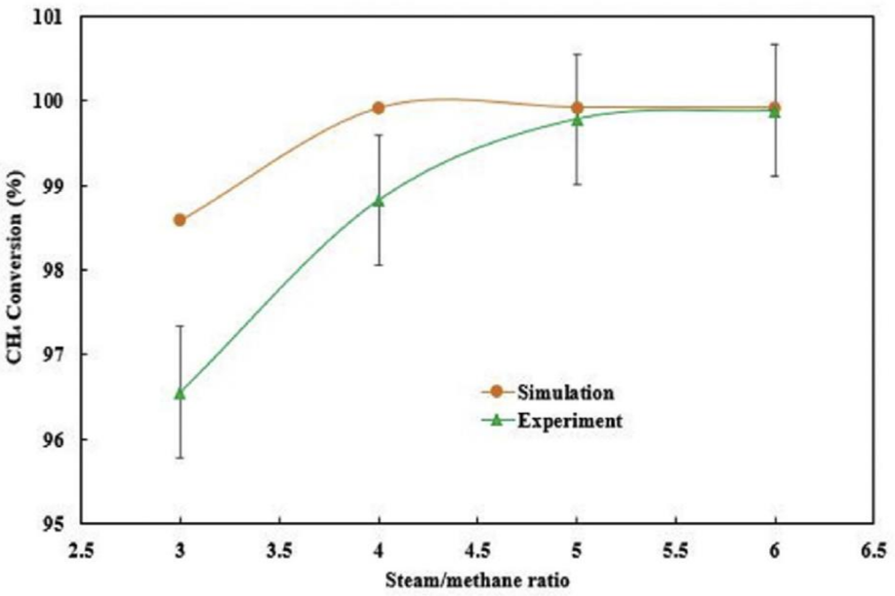

FIGURE 3: Methane Conversion as a function of Steam/Methane Ratio [8]

IV. SEPARATION OF HYDROGEN FROM BINARY MIXTURE OF H_2 AND CO_2

One of the most used methods for the separation of hydrogen from the mixture of gases is the PSA process. It is a process of separating hydrogen from the remaining components using pressure fluctuations in the storage tank (Pressure Swing Adsorption – PSA). The PSA process consists of adsorption unit, in which pressure changes occur and, together with the use of a bed of solid adsorbent, the separation of impurities from the hydrogen stream occurs. The result of this process is a high-purity high-pressure hydrogen and a low-pressure mixture of the remaining gas components containing impurities and part of the hydrogen. The adsorbent beds are regenerated by depressurization and flushing. Part of the hydrogen (up to 20%) can be lost in the waste gas. Adsorption technology during pressure fluctuations is based on the physical binding of gas molecules to the adsorption material. The force acting between the gas molecules and the adsorption material depends on the gas component, the type of adsorption material, the partial pressure of the gas component and the operating temperature. The separation effect is based on the differences in binding forces to the adsorbent material. Highly volatile, low-polarity components such as hydrogen are practically non-adsorbable, unlike molecules such as nitrogen, carbon monoxide, carbon dioxide, hydrocarbon derivatives, and water vapor. Consequently, these impurities can be adsorbed from the hydrogen-rich gas stream. With this method, highly pure hydrogen is obtained. The pressure swing adsorption process works essentially at a constant temperature. It uses the effect of alternating pressure and partial pressure to carry out adsorption and desorption. Due to the absence of cooling and heating devices, which are not necessary in a constant temperature process, the entire process of one cycle can take place in the range of minutes.

In addition to PSA methods, there are also membrane methods in which hydrogen is separated from the remaining components of the gas using a semi-permeable membrane that enables the hydrogen molecules to pass. However, bigger molecules are unable to pass through the membrane. There are generally two classes of membranes for production and purification of hydrogen, both of which are organic: dense phase metals and metal alloys and porous ceramic membranes. Porous ceramic membranes are commonly prepared by sol-gel or hydrothermal methods and have high stability and durability in high-temperature, harsh, polluted and hydrothermal environments.

Membrane systems do not contain any moving parts or switching valves and achieve potentially very high reliability. The main threat are components in the gas (such as aromatic substances) that attack the membranes, or liquids that clog them. The membranes are produced in relatively small modules. For a larger capacity of the device, more modules connected in parallel are added to increase the area of the membranes. Costs increase linearly with capacity, making them more competitive at lower gas capacities being processed. [9]

Many other methods such as cryogenic freezing processes or the use of metal-hydride alloys for hydrogen separation currently represent an expensive or energy-intensive solution for use in decentralized hydrogen production in small local operations.

V. CONCLUSION

Current state of hydrogen production from renewable sources is not currently sufficient for the full competitiveness of green or blue hydrogen against grey hydrogen. The possibilities of producing blue hydrogen using fast-growing biomass appear to be promising in the near future. As proven by the research at the beginning of this article, fast-growing aquatic plants, primarily Lemna family, represent non-negligible source of biomass for the production of the blue hydrogen. Their yields significantly exceed those of terrestrial crops grown for energy purposes. However, the technology of biomass valorisation during the process of hydrogen production from water biomass must take place in less conventional ways due to the high proportion of oxygen in the feed. The consequence of this high proportion is an unacceptable proportion of carbon dioxide during thermal processing of biomass. The possibilities of valorising biomass through its transformation into methane with the use of methanogenic bacteria represent the possibility of increasing the yield of hydrogen compared to thermal decomposition. The subsequent processing of methane using conventional treatment methods, such as SMR and WGSR or new MPS and PSMR methods represents a good basis for improving hydrogen yield. After the subsequent treatment of hydrogen necessary to increase its purity, either by using membrane purification or the PSA process, it is possible to obtain more competitive blue hydrogen compared to grey hydrogen. The processes of hydrogen production from aquatic biomass could enable its decentralization into smaller local enterprises and thereby improve the availability of this fuel for ordinary users.

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