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INVESTIGATIONS OF HYDROGEN PRODUCTION FROM LIQUID SUBSTANCES IN PLASMA OF MICROWAVE DISCHARGE

Abstract

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The subject of this doctoral thesis is an investigation of producing hydrogen from liquid substances containing hydrogen atoms in their molecules (liquid hydrogen carriers) in plasma of microwave discharge. The motivation of this thesis was the global demand for an efficient and cost-effective method of hydrogen production.

The goal of was to gather experimental results to determine an efficiency of hydrogen production from selected liquid hydrogen carriers in plasma of microwave discharge. The efficiency of hydrogen production is characterized by the following parameters: hydrogen production rate (expressed in g(H₂)/h), percentage of hydrogen in the working gas after plasma treatment (expressed in %), energy yield (expressed in g(H₂)/kWh), conversion degree of liquid substance (expressed in %), and selectivity of conversion into hydrogen (expressed in %). The selected liquid hydrogen carriers were ethanol, isopropanol and kerosene. These liquid hydrogen carriers represent an attractive source of hydrogen due to their high number of hydrogen atoms in their molecules. Other advantages include low cost and wide availability. The investigations was aimed to confirm or reject the thesis of this work, which was formulated as follow: optimization of microwave plasma generation conditions through appropriate selection of the geometry of the plasma device, microwave frequencies and power, as well as the components and parameters of the working gas (i.e., a mixture of plasma gas and liquid hydrogen carrier in a form of vapors) leads to efficient hydrogen production from selected liquid hydrogen carriers.

In the investigations, two waveguide-supplied metal-cylinder-based nozzleless microwave (2.45 GHz and 915 MHz) plasma sources (MPSs) were used. Both sources allowed for plasma generation at atmospheric pressure. Gas chromatography and IR spectroscopy were used to determine the volumetric composition of the working gas after plasma treatment. These two methods allowed for determination the parameters of the efficiency of hydrogen production.

The optimization of the electrodynamic characteristics of the MPSs was the first stage in the investigations of hydrogen production. The electrodynamic characteristics is defined as the dependence of $P_R/P_I(l_s)$, where P_R is the power of the microwave wave reflected from the MPS, P_I is the power of the microwave wave supplied to the MPS, and l_s is the distance between the MPS and the movable plunger. This dependency represents the efficiency of microwave wave absorption by the plasma generated in the MPS. To optimize the MPS electrodynamic characteristics, a minimum of the $P_R/P_I(l_s)$ need to be found. The minimum corresponds to the position of the moveable plunger, where the most efficient absorption of the P_I power by the generated plasma takes place. The experimental measurement of the

electrodynamic characteristics of the MPS allowed to determine the minimum of the $P_R/P_I(l_s)$ dependency. Experimental optimization of the electrodynamic characteristics was supported by computer simulations of the distribution of the electromagnetic field inside the MPS. The computer simulations have confirmed that, for the experimentally determined optimal position of the movable plunger, the calculated electromagnetic field is focused precisely at the location of the microwave plasma generation. The simulations allowed for the estimation of electron concentration n_e and collision frequency ν in the considered cases of generated microwave discharge.

Next, experimental optimization of the method of introducing liquid hydrogen carrier vapors into the MPS was carried out. Two methods of introducing vapors into the plasma source were tested: the swirl method and the axial method. The ethanol was used as an example for the tests, and its vapors were generated using an induction vapor generator with a capacity of up to 2.4 kg/h of ethanol vapors. The aim was to achieve stable microwave discharge with the maximum amount of introduced ethanol vapors in the discharge area. The work indicated that axial introduction of ethanol vapors fulfilled the intended purpose. In the swirl method, above the amount of 0.8 kg/h of introduced vapors, intensive carbon deposit formation occurred inside the MPS. In the longer-term perspective, this effect was leading to the disappearance of the microwave discharge.

Under these optimized conditions, with the axial introduction of ethanol vapors, investigations of hydrogen production were conducted using thermal decomposition, dry reforming, and steam reforming methods in the MPS 2.45 GHz and the MPS 915 MHz. The highest efficiency of hydrogen production at the 2.45 GHz MPS was achieved using the steam reforming method. In this method, the rate and energy yield of hydrogen production were 62.5 g(H₂)/h and 21.4 g(H₂)/kWh, respectively. At the MPS 915 MHz, the highest energy yield was achieved using the steam reforming method (26.9 g(H₂)/kWh), while the highest hydrogen production rate was obtained using the dry reforming method, 116.2 g(H₂)/h. The obtained results indicated that hydrogen production was more efficient in the MPS 915 MHz than in the MPS 2.45 GHz. As a result, further investigations were conducted only using the MPS 915 MHz experimental setup.

The next stage of the investigations consisted of experiments using isopropanol and kerosene as sources of hydrogen. Despite using the axial method of introduction, both the thermal decomposition and steam reforming methods resulted in intense carbon deposition inside the MPS 915 MHz. Therefore, research on hydrogen production using the above-mentioned methods was not continued. The investigations were only carried out using the dry

reforming method. In the process of dry reforming of isopropanol, the highest rates of hydrogen production and energy yield achieved were 93 g(H₂)/h and 18.5 g(H₂)/kWh, respectively. While, in the case of kerosene, the corresponding values were 39.1 g(H₂)/h and 7.4 g(H₂)/kWh, respectively.

As part of the investigations on hydrogen production, the emission spectra of microwave discharge were recorded with the use of optical emission spectroscopy (OES) technique. The OES technique enables the identification of excited atoms, molecules, and ions in the generated plasma. The OES technique allowed for the determination of the vibrational temperature T_{vib} and rotational temperature T_{rot} of the recorded molecules and molecular ions. The OES analysis led to the conclusion that the introduction of the vapors of the liquid hydrogen carrier into the plasma region caused a decrease in the T_{vib} and T_{rot} temperatures of plasma particles. On the other hand, an increase in the absorbed power by the plasma led to an increase in the T_{vib} and T_{rot} temperatures. This increase in temperature has a positive effect on the kinetics of the conversion process of ethanol into hydrogen.

The investigations showed that the conversion of ethanol, isopropanol, and kerosene was over 99%. The method of steam reforming of ethanol vapors in the MPS 915 MHz achieved the highest energy yield of hydrogen production, reaching 26.9 g(H₂)/kWh. However, in order to meet the 2030 target set by the US Department of Energy (DOE), which is 60 g(H₂)/kWh, the obtained energy yield of hydrogen production needs to be improved. Nevertheless, it is worth noting that the economic landscape is changing, and new criteria for evaluating hydrogen production may appear, as a result the DOE recommendation is not the only criterion for accepting the hydrogen production method. With the evolution of the industry, other criteria like raw material extraction, manufacturing and processing, transportation, usage and retail, and waste disposal may severe influence the final implementation of the method. A method with worse energy performance, expressed by the energy yield and production rate, can be competitive and worth implementation when the others factors vail.

By comparing the energy yield of steam reforming of ethanol with the results of hydrogen production using other methods, it can be concluded that the hydrogen production method from ethanol is efficient enough to be used for distributed hydrogen production. Therefore, it can be said that the obtained results have met the goal set out in the thesis and confirmed the validity of the thesis statement.