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RESEARCH ARTICLE

An autonomous hydrogen production system design based on the solid chemical hydride

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Abstract: This paper develops a hydrogen generator prototype that is for fuel cell systems used in portable applications. This generator is designed based on the use of solid-state hydrides with high hydrogen storage capacity in the catalytic hydrolysis reaction. Some using problems such as unstable hydrogen production, one-off service life, heavy or large-volume storage system, and short duty time can be avoided in moveable applications when the use of the produced prototype. In addition, A simulation model and an autonomous control algorithm, which evaluates the hydrogen generation and temperature responses of the prototype, are developed. The results confirm that the performance of a portable and autonomous prototype with 4 parts and 1-hour hydrogen production capacity is enough for small fuel cell applications. As a result; the tightness and performance tests of the prototype were investigated using different catalyst samples for 1 hour, and the results were investigated in depth. The average flow rate of this 4-part autonomous generator is approximately 3.00 L/min.gcatalyst during 1 h. In the working cycle, the soft ripples have spied on the hydrogen-produced amount from time to time.

Keywords: Sodium Borohydride, Hydrogen Production, Autonomous System, Power Generator, Portable Application.

1. Introduction

Conventional fossil fuel sources, such as coal, oil, and natural gas, which meet most of the world's energy demand, are being consumed rapidly. Additionally, their combustion products are causing global problems, such as the greenhouse effect and pollution. Therefore, many countries have published their strategic plans to achieve net zero-emissions targets by 2050. Thus, there is a movement towards renewable energy sources, which are environmentally friendly, more efficient power production, zero emissions, over the world. Renewable energy technologies such as solar, wind, hydropower, and heat pumps are widely preferred for increasing energy demand [1]Co, Bi, CoBi, and CoBi/CNT catalysts are prepared via co-precipitation method and sodium borohydride (NaBH4. Today, battery technologies have been more popular to be used in applications that have a large share of carbon emissions such as portable applications and transportation applications. However, the batteries fail to satisfy the energy required for developing technologies, their weights increase the energy consumption of the systems and create transport problems. One of the developed systems, which is based on renewable energy sources, to supply the required energy is the fuel cells. The fuel cells have the potential of achieving much higher specific energy densities than any advanced battery system. Fuel cells, which can operate in light, quiet and grid-independent environments, have high energy conversion efficiency, high power density, and zero pollutant emission, providing an alternative way to obtain the energy required by portable applications [2]. At this point, alternative energy sources appear as a solution. Hydrogen is an excellent alternative to meet the growing demand for efficient and clean energy sources [3]. As an energy carrier, hydrogen is expected to play an important role in future energy systems. As the lightest element, hydrogen has many advantages such as environmental friendliness and the highest energy capacity per unit weight [4]in industry, working, cleaning, transportation and commuting from one place to another. The majority of energy being used is obtained from fossil fuels, which are not renewable resources and require a longer time to recharge or return to its original capacity. Energy from fossil fuels is cheaper but it faces some challenges compared to renewable energy resources. Thus, one of the most potential candidates to fulfill the energy requirements are renewable resources and the

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most environmentally friendly fuel is hydrogen (H2.

Besides, hydrogen is a very difficult gas to store. The most common method of hydrogen storage is to obtain compression and storage of hydrogen gas in high-quality tanks (at least 200 bar), but this method increases costs and causes high energy consumption. In addition to cost, hydrogen is a volatile and flammable gas, which creates disadvantages in terms of safety [5]. Nowadays, research is being done to use hydrogen stored in different chemical compounds to reduce these disadvantages. For example, various hydrides such as Lithium Hydride (LiH), Calcium Hydride (CaH_2), Magnesium Hydride (MgH_2), Lithium Borohydride ($LiBH_4$), Lithium Aluminum Hydride ($LiAlH_4$), Sodium Borohydride ($NaBH_4$), Ammonia Borane (NH_3BH_3) are used sources of hydrogen [6]. Among the borohydrides defined as reducing substances and used in the formation of many hydrolysis reactions, $NaHB_4$ is the most known. $NaHB_4$ is a strong reductant and can react with many organic and inorganic compounds. $NaBH_4$ is considered a potential candidate for hydrogen storage due to its high hydrogen storage density and controllable hydrogen release through hydrolysis at room temperature. As a result of the reaction of $NaBH_4$ with water, hydrogen is released and $NaBH_4$ can be synthesized again from Sodium Metaborate ($NaBO_2$), which is a by-product. In this case, it reveals that $NaBH_4$ is a renewable product. The reaction of $NaBH_4$ with water (Eqn.1) progresses very slowly under room conditions. A catalyst needs to be used to accelerate this reaction and increase the yield [7]. In hydrolysis reactions, when $NaBH_4$ is used in high concentrations, it can cause the by-product ($NaBO_2$) to crystallize and change the structure of the catalyst that used in the reaction [8]. In the hydrolysis reactions of $NaBH_4$, conventional catalysts containing noble metals such as Ru and Pt [9,10]simple, convenient, and safe chemical process generates high purity hydrogen gas on demand from stable, aqueous solutions of sodium borohydride, NaBH4, and ruthenium-based (Ru are replaced by Co or Co-B [11] supported, lower-cost catalysts.

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \quad (1)$$

The average hydrogen flow rate required for a 500 W PEMFC is about 5 standard liters per minute (SLPM) [12]. However, 1.2 kW output can be obtained from the system with the highest hydrogen production rate of 16 SLPM that using at 3 kW PEMFC [13]. Therefore, the increase in the amount of NaBH4 concentration causes an increase in the hydrogen flow rate. In the results of the experiments conducted in the literature, an increase in the hydrogen production rate was observed as the concentration increased. The maximum hydrogen flow rate was measured as 120/16/2.4 SLPM in reactions using 15/10/5 wt% solutions, respectively [8].

In the literature, there are studies on PEMFC supported by NaBH4. Of those; Murooka et al. proposed a nickel-catalyzed solution as a catalyst for a 100 W PEMFC fed with NaBH4 [14]. At the Toyota Research Lab, Kojima et al. developed a NaBH4 assisted hydrogen production system with a hydrogen production rate of 120 SLPM to produce the hydrogen required for a 10 kW PEMFC [15].

In a hydrogen production system study by Kim et al., the system produced hydrogen at a rate of 6.5 SLPM for 120 minutes [16]. They have integrated this hydrogen generation system with a 400 W PEMFC. Sprayed Co-B catalyst was preferred as a catalyst in the system. In the microreactor study pioneered by Kim and Lee, a micro-reactor with an average hydrogen production rate of 5.6 ml/min was developed for Micro-PEMFC applications using Co-B catalyst [17]. Kim used Co-P-B catalyst, which has a higher efficiency than Co-B, as a catalyst in his last micro-reactor study [18]. He integrated the micro-reactor system he developed into a micro fuel cell with a maximum power output of 157 mW at a current of 0.5 A.

Li and Wang, developed a hydrogen generation system that hydrolyses NaBH4 with a conversion rate of over 90%, which can continuously supply hydrogen to power a 3 kW PEMFC. NaBH4 concentration of 15% by weight was used in the system. In addition, the system is controlled by a microcontroller [19].

In this study by Kim, solid-state NaBH4 particles were used. NaHCO3 solution with a concentration of 8.8% by weight at 25 °C was used as a catalytic solution. As a result of the study, a 100 W fuel cell system can be operated with the hydrogen produced from the developed system [20].

Avrahami et all, developed a hydrogen generation system powered by solid-state NaBH4 with a hydrogen density of 4.5% by weight and a hydrogen flow of about 400 mL/min, and an energy density of 1400 Wh/kg for long and short-run times [21]. In the hydrogen generator system experiments conducted by Zakhvatkin et al., they recorded that 110 L of hydrogen was produced for 6.3 hours with an average flow rate of 290 mL/min and fuel conversion efficiency of 98%. The energy density obtained from the system components is 1300 Wh/kg for the fuel, 540 Wh/kg for the generator, and 377 Wh/kg for the fuel cell with a power capacity of 30 W, respectively [22].

In this study, a new design of the hydrogen generator prototype, which has been developed for fuel cell systems used in portable applications, is focused on. The base of this prototype is designed as an autonomous hydrogen generator, that is using solid chemical hydrides for hydrogen/fuel cells applications. This design provides high energy density, inexpensive design, low cost, high applicability, and fast use, refilling, or cleaning. As a result of the study, a small prototype design was built, examined, and characterized, details about the operating system and performance of a portable and autonomous prototype with 4 parts and 1-hour hydrogen production capacity are given.

2. Materials and Experimental Methods

2.1. Materials

The Cobalt (Co) Micron powder was supplied from the Nanografi company. The Cobalt (Co) Micron Powder is 99.99% pure and has a size of 1 µm. $NaBH_4$ chemical powder was supplied from the Tekkim company. $NaBH_4$ is 98.5% pure and contains 0.05% Si and 0.005% Fe.

2.2. Experimental Setup/ Test Rig

Firstly, the catalytic activity performances of the Co Nanopowder were investigated on a reaction model which includes the hydrogen gas generation from the catalytic hydrolysis is being carried out in a 250 mL four-necked round-bottom reaction vessel. The precisely weighed solid $NaBH_4$ and the catalyst samples are loaded from one of the four necks. The water is being contacted with the solid powder in the reaction vessel using a dropping funnel. Then, the working performance of the hydrogen generator is tried with Co Nanopowders. The water + catalyst mixture was be added with the help of a pump to on the $NaBH_4$ particles that are in the fuel reservoir. The reaction is expected to occur rapidly at room temperature. The reaction temperature is measured with a thermocouple integrated from the second neck and connected with the microprocessor in both experiments. The hydrogen gas is passed through a dehumidifier to remove water vapor. The produced hydrogen gas volume was measured and recorded by a high-precision Alicat Flowmeter. Simultaneously measured data was transferred to the microprocessor and recorded in the host computer. The hydrogen gas produced as a result of the hydrolysis reaction taking place in the reactor was transferred through the humidifier to the flow meter. The pressure, temperature, and production amounts are taken from the flow meter collected by the microcontroller were being monitored and were be realized with an automatic control system for sustainable electricity generation.

The developed reactor is intended to be made of plexiglass material. All connections of the generator were pasted with chloroform adhesive to prevent possible hydrogen leakage, providing a high sealing environment. The fuels will be discharged from their respective chambers into the reservoir where the reaction takes place. The 20 ml water + catalyst mixture will be added with the help of a pump to on the $NaBH_4$ particles that are in the fuel reservoir. The reaction is expected to occur rapidly at room temperature. The hydrogen gas produced as a result of the hydrolysis reaction taking place in the reactor was transferred through the humidifier to the flow meter. The pressure, temperature, and production amounts are taken from the flow meter collected by the microcontroller will be monitored and will be realized with an automatic control system for sustainable electricity generation. The test rig of the hydrogen generator system is shown in Figure 1. The algorithm of the autonomous control system will be designed depending on the changes in reactor pressure. A test station will be installed in this way; the system tests such as pressure, temperature, and the performance of hydrogen production are planned in this system. The electronic operating performance of systems and autonomous systems requirements of the system will also be evaluated. After optimal results were obtained from these experimental tests, a prototype of the size that will be integrated into a stack of the fuel cell was prepared.

3. Prototype Design

In this study, a four-chamber generator was designed. The design of each of the rooms; consists of 4 sections, namely the control unit, the water reservoir, the auxiliary equipment section, and the $NaBH_4$ reservoir. The control unit is positioned above these 4 reaction chambers. The water reservoir consists of a chamber with a conical structure as a mixture of catalyst powder and water. It is aimed to provide the necessary water pressure for the water pump due to the shrinking structure of gravity and the conical structure. The water pump, sensors, and other auxiliary equipment are kept away from water and moisture contact in the auxiliary equipment section. Water and catalyst solu-

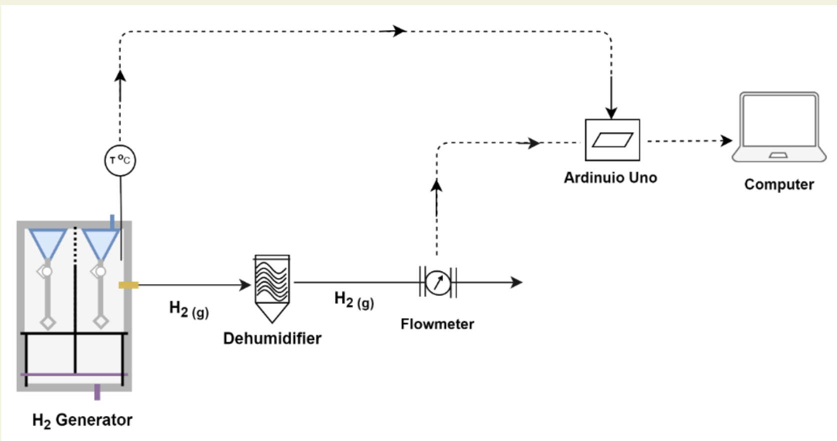

Figure 1. The test rig of the hydrogen generator system

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tion, which is the flow of it controlled by a water pump, will be sprayed on the $NaBH_4$ powder with the help of nozzles, and a homogeneous distribution is achieved. The fuels are discharged from their respective chambers into the reservoir where the reaction takes place. The hydrogen generator prototype 3D design is shown in Figure 2. The hydrogen generator, whose size and volume, was determined, was manufactured using plexiglass material. All connections of the generator were pasted with chloroform adhesive to prevent possible hydrogen leakage, providing a high sealing environment.

<u>Autonomous Control Card Design and Writing Control System Algorithms:</u>

The basis of this project is to ensure the continuity of the energy source required for the duty period of the system, depending on the decrease in the gas level in the system. The gas sensor placed in the prototype of the gas sensor measures the hydrogen gas level, activates the water pump when the gas level starts to decrease depending on the situation and enables the reaction in the second reaction vessel to start. The autonomous control system flowchart and equipment connection of the hydrogen generator prototype is shown in Figure 3.

A temperature and humidity sensor has been added to the prototype to take into account other environmental conditions that may affect the operating performance of the system. With this sensor, it works independently of the system's autonomous control, but they are programmed to shut down the system when high values are measured. A reference value has been entered for the operation of the system. When the value measured by the gas sensor falls below this reference value, the next water pump will be activated and the reaction will be activated. According to the data coming from the gas sensor, a system mechanism that works automatically by triggering the 220 V water pump with DC 5V has been established.

The sensors are connected to the analog input of the Arduino. When the gas level drops according to the values between 0 and 255 read from our sensors, it activates the relay and controls the water flow. Since the water pump works with 12 volts (it can work a minimum of 6 volts), it is controlled with the help of a relay. The purpose of the relay is to prevent the Arduino used in the system from being burned due to the current. Since this process has a unidirectional working principle, a transistor can also be preferred. Values and important information read from the sensors can be read from the LCD screen.

<u>*Control System Algorithms:*</u>

The working algorithm written for the simultaneous monitoring of the autonomous operation and working parameters of the hydrogen generator is implemented using the Arduino board. The system is programmed using the 1.6.3 version of the Arduino software and the ATmega328 programming language. Figure 4 shows part of the Arduino software that contains the program's instructions.

For the required energy needed during the first operation, since the Arduino should be fed with at least 6 volts and the valves should be working at around a minimum of 6 volts, Lithium-Polymer batteries with a capacity of 7.4 V and 2-cell were preferred.

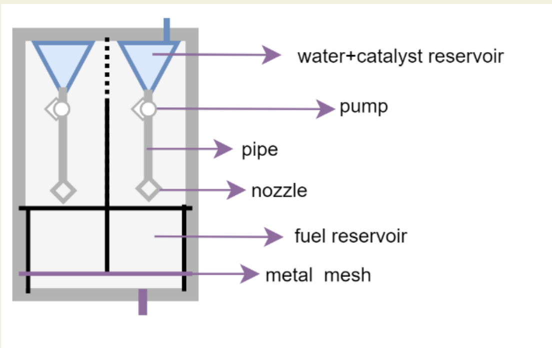

Figure 2. The design of the hydrogen generator system

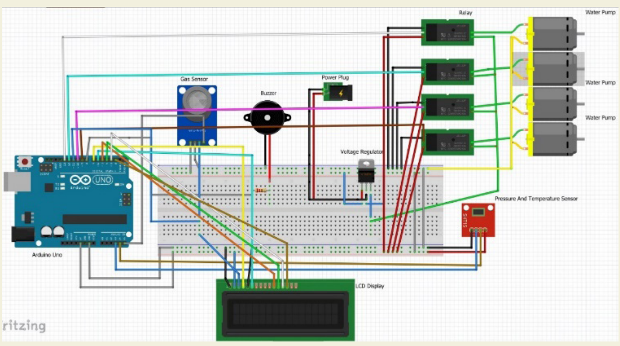

Figure 3. The design of the autonomous control system

4. Results

Firstly, manual experiments have been carried out to record hydrogen production and reaction conditions such as hydrogen flow, generator' temperature, generator' pressure, and to evaluate the prototype's feasibility, sealing, efficiency and performance. The sealing and the performing experiments were made using Co nanopowder. After then, the Co-BFSs catalyst samples [23], that are synthesized in our previous study, were used in autonomous experiments of this prototype.

4.1. Manual performance experiments

The manual experiments of the prototype were carried out using 2 g of $NaBH_4$, 20 ml of distilled water, and, Co nanopowder as a catalyst that was used in 2 different amounts as 0.2 g and 0.5 g. A series of experiments were carried out until the sealing of the prototype was optimized. That is, the sealing of the prototype was increased until the amount of hydrogen gas produced by the Co nanopowder in the glass reactor vessel and the amount of hydrogen gas produced in the prototype were approximately the same.

In the experiments with 0.2 g and 0.5 g of Co nanopowder, the total hydrogen productions that are given in Figure 5, are approximately 340 L and 360 L, respectively. The total hydrogen amounts of the 0.2 g and 0.5 g Co powders are very close to each other, but the reaction using 0.5g of Co powder ends 2 times faster, can be shown. As can be seen in Figure 6, the reaction time shortened with the increase in the amount of catalyst, however, the hydrogen production rate decreased. Also, the hydrogen production average flow rates are approximately 80.95 and 55.38 L/min.$g_{catalyst}$, respectively. The hydrogen production rate of the hydrolysis reaction at 25 °C using 1 wt % $NaBH_4$ and Co powder is 0.13 L/min.$g_{catlayst}$ [24]. In this study, it is 500 times higher using 10 wt% $NaBH_4$ at 50 °C. Figure 6 is showing relatively constant hydrogen flow (of about 17.5 L/min) along 20 min. As a result, when the amount of Co catalyst sample was increased, the reaction times were shortened, but the high amount of hydrogen production observed in the use of different amounts of catalyst in the literature did not decrease. In the literature studies, it is stated that the reason is due to the maximum saturation of the reaction [23,25]. The reduction in this study is negligible. Manual experiments of the 4-segment prototype were performed in both catalyst amounts. As can be seen in Figure 7 and Figure 8, the next system segment was activated when the hydrogen flow rate for 0.5 g was about 3 L/min.$g_{catalyst}$, while in the experiment using 0.2 g catalyst, it was manually activated when the hydrogen flow rate was about 2.40 L/min.$g_{catalyst}$. In the hydrolysis reactions of the Co nanopowder end, it is difficult to produce stable hydrogen because the Co nanopowder hydrolysis reaction ends suddenly. Therefore, using Co nanopowder was not efficient in manual 4-segment experiments. Depending

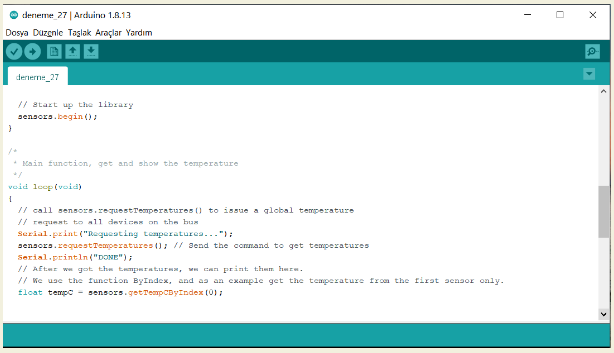

Figure 4. A part of the autonomous control system working algorithm

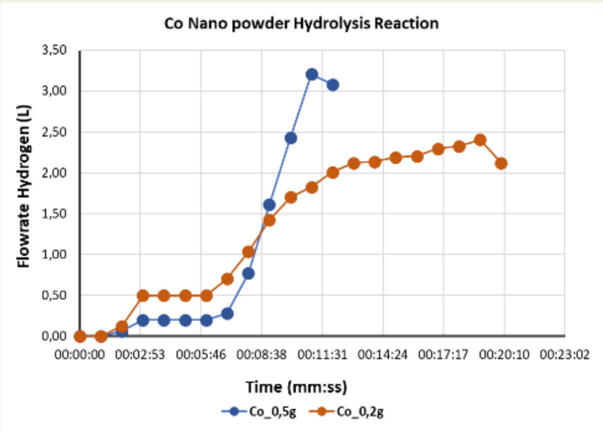

Figure 6. The flowrate hydrogen production of the Co nanopowder catalyst sample that is different amounts

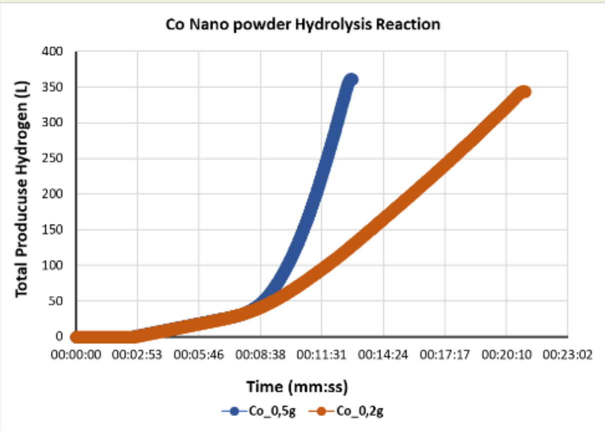

Figure 5. The total hydrogen production of the Co nanopowder catalyst sample that is different amounts

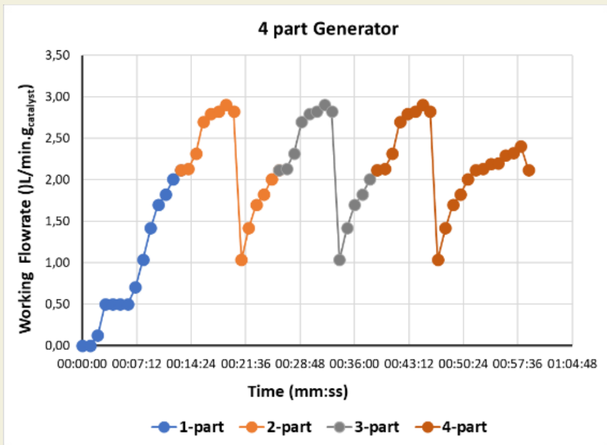

Figure 7. The performance of Manuel Hydrogen Generator Prototype with 0.2 g Co nanopowder catalyst for 1-hour

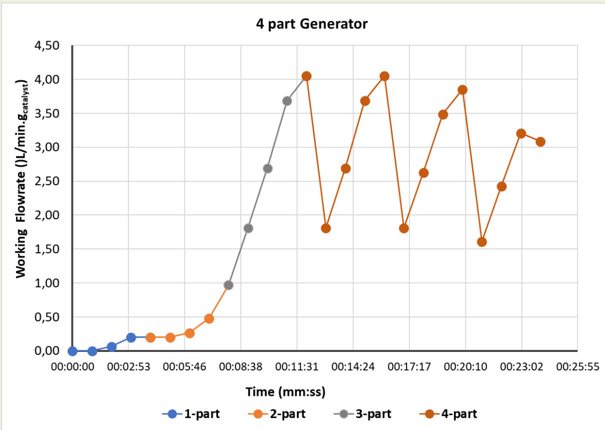

Figure 8. The performance of Manuel Hydrogen Generator Prototype with 0.5 g Co nanopowder catalyst for 24-min

on the decrease in hydrogen gas in the system, it may be considered to change the algorithm to be used for activating the next segment for some special cases. This working cycle is designed to have a maximum instantaneous hydrogen production of 3 L / min.gcatalyst continuously for 1 hour. In this working cycle, the amount of hydrogen produced instantaneously decreases to 1 L / min.$g_{catalyst}$ from time to time. This situation can be adjusted by increasing the amount of $NaBH_4$ used according to the instantaneous hydrogen requirement of the system to which the generator will be connected.

4.2. Autonomous performance experiments

The autonomous experiments of a prototype were carried out using 2 g of $NaBH_4$, 20 ml of distilled water, and 0.5 g Co-BFS$^+$ catalyst powders were used. Hydrogen production performance and flowrates graphs of Co-BFS$^+$ catalyst powders are given in Figure 9 and Figure 10. In the experiment where 0.2 g Co-BFS$^+$ (%20, %30, %40, and %50) catalysts were used, the reaction times were 22, 24.41, 25.20, and 25.45 minutes, the maximum flow rate of the reaction were 1.93, 1.95, 1.86, and 1.92 L/min.$g_{catalyst}$, the instantaneous flow rates of the reaction were 12.30, 12.28, 13.27 and 13.03 L/min, and the total flow rates were 270.8, 307, 331.82, and 388.45 L, respectively. A series of experiments were carried out until the autonomous controlling and performance of the prototype were optimized. The results of the experiments were shown in Figure 11. Each part of the 4-segment generator was started when the rate of the previous segment's hydrolysis reaction decreased. A working time is designed to have a maximum instantaneous hydrogen production of 2.5 L / min.$g_{catalyst}$ continuously for 1 hour. In this working cycle, the amount of hydrogen produced instantaneously decreases to 1 L / min.$g_{catalyst}$ from time to time. This situation can be adjusted by increasing the amount of $NaBH_4$ used according to the instantaneous hydrogen requirement of the system to which the generator will be connected.

The result of this study, since it has an autonomous control and a segmented structure, hydrogen production can be done according to the needs of the system. This innovative hydrogen production method from directly solid chemical hydride has improved the reliability, and durability of the hydrogen generator system. Hydrogen gas produces sufficient amounts when needed, not compressed, and liquefied in the system. Thus, the use of excessive chemicals in the system is prevented and its safety is increased. Hydrogen gas can also be produced via a catalytic reaction from the liquid chemical hydride, but, this method supplies production that is lower than the solid chemical hydride. Also, the $NaBO_2$ chemical powder, which is released as a by-product as a result of the reaction, causes a decrease in the performance of the system, unstable hydrogen production, and low reliability. By-products released in the prototype system produced can be discharged from the system through the drainage channel. In addition, it does not need cartridge replacement and cleaning as in other hydrogen generators using solid chemical hydride.

5. Conclusions

As a result, this study was focused on a hydrogen generator prototype that can be used efficiently in hydrogen/fuel cells portable applications. The energy required for applications was provided from hydrogen gas which is produced with the use of hydrides that have high hydrogen

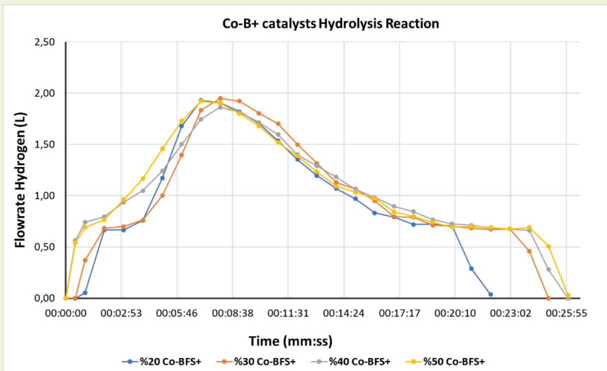

Figure 10. The flowrate hydrogen production of the Co-BFS+ catalyst sample that are different amounts of Co

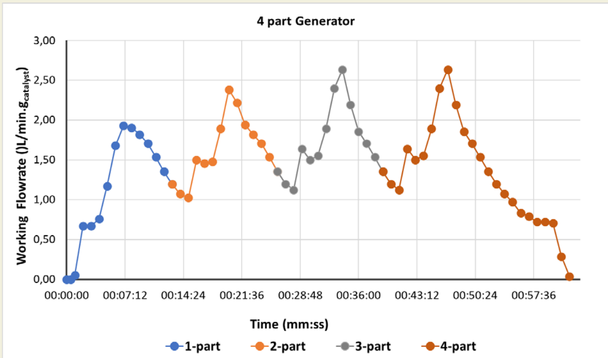

Figure 11. The performance of Autonomous Hydrogen Generator Prototype with %20 Co-BFS catalyst for 1-hour

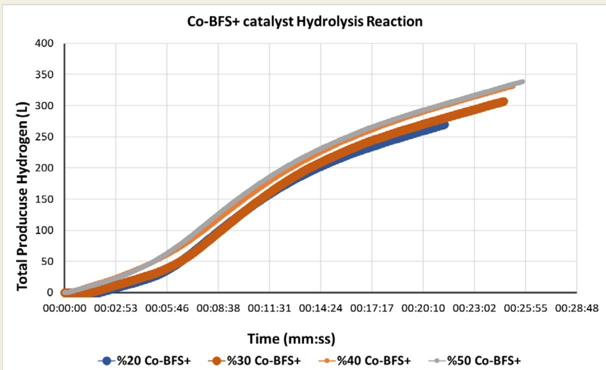

Figure 9. Hydrogen production performance graphs of Co-BFS+ catalyst powders

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storage capacity in the catalytic hydrolysis reaction which occurs between water, the sodium borohydride, and the catalyst. According to the findings obtained from other studies in the literature, a new prototype was designed. This design provides high energy density, inexpensive design, low cost, high applicability, and fast use, refilling, or cleaning. However, this study shows the hydrolysis performance of pure Co nanopowder that is satisfactory fuel conversion and high hydrogen production rate at ambient temperature. With this study, it is aimed to close the gap related to the use of solid-state NaBH4 hydride in studies where hydrogen generator design and the use of pure Co powder as a catalyst in experiments in the literature. A new field of research has been opened regarding the use of by-products with high metal content and different pure nanopowders. The average flow rate results of the %40 Co-B-BFS(+) catalyst performance in the 4-part autonomous generator were almost 2.33 L/min.gcatalyst continuously for 1 hour.The maximum instantaneous hydrogen production flowrate the Co nano powder performance in the 4-part autonomous generator were almost 3 L/min.gcatalyst during 1 hour. Each part of the 4-part generator was started when the rate of the previous segment's hydrolysis reaction to decrease. In these working cycles, the soft ripples are spied on the hydrogen produced quantity from time to time. These ripple situations can be adjusted by increasing the quantity of NaBH4 used according to the instantaneous hydrogen requirement of the system to which the generator will be connected. So, new studies can be done to provide more stable hydrogen production by using different parameters.

In addition to these results, the energy needed by portable systems used in defence technologies is supply by traditional energy storage technologies, which are large in volume and heavy in mass. For these systems, it is of great importance to develop lighter and more efficient alternative applications such as hydrogen generators instead of heavy energy storage technologies. With the outputs obtained as a result of the prototype work, the problems in the insufficient energy capacity of the batteries used as the traditional method have been solved. The weight and volume of the systems have been reduced, thus increasing their duty times. Given the requirements in military or civilian life worldwide, it is important both academically and commercially to lead the development and manufacture of these systems, which are of high strategic importance due to the large gaps that exist in this market.

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