



Pressurized diesel fuel processing using hydrogen peroxide for the fuel cell power unit in low-oxygen environments

Kwangho Lee^{a,1}, Gwangwoo Han^{a,1}, Sungbaek Cho^b, Joongmyeon Bae^{a,*}

^a Department of Mechanical Engineering, KAIST, 291 Gwahangno, Yuseong-gu, Daejeon 305-701, Republic of Korea

^b Agency for Defense Development, Bugyuseong-daero 488 Beon-gil, Yuseong-gu, Daejeon, Republic of Korea

HIGHLIGHTS

- Novel concept of diesel fuel processing with hydrogen peroxide was developed.
- The core parts are diesel ATR reactor, WGS reactor, H₂ separation membrane.
- Diesel ATR, WGS characteristics were analyzed at pressurized condition.
- The permeation experiments of H₂ separation membrane were carried out.
- Design points that can maximize the efficiency of the fuel processor were suggested.

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ABSTRACT

A novel concept for diesel fuel processing utilizing H₂O₂ is suggested to obtain the high-purity H₂ required for air-independent propulsion using polymer electrolyte membrane fuel cells for use in submarines and unmanned underwater vehicles. The core components include 1) a diesel-H₂O₂ autothermal reforming (ATR) reactor to produce H₂-rich gas, 2) a water-gas shift (WGS) reactor to convert CO to H₂, and 3) a H₂ separation membrane to separate only high-purity H₂. Diesel and H₂O₂ can easily be pressurized as they are liquids. The application of the H₂ separation membrane without a compressor in the middle of the process is thus advantageous. In this paper, the characteristics of pressurized ATR and WGS reactions are investigated according to the operating conditions. In both reactors, the methanation reaction is enhanced as the pressure increases. Then, permeation experiments with a H₂ separation membrane are performed while varying the temperature, pressure difference, and inlet gas composition. In particular, approximately 90% of the H₂ is recovered when the steam-separated rear gas of the WGS reactor is used in the H₂ separation membrane. Finally, based on the experimental results, design points are suggested for maximizing the efficiency of the diesel-H₂O₂ fuel processor.

1. Introduction

Fuel cell power units are energy conversion devices that directly convert chemical energy into electrical energy, and they have the advantages of a high energy conversion efficiency and environmental friendliness [1–5]. In addition, because the noise emission and oxygen consumption of fuel cell power units are considerably lower than those of other combustion-based power engines, they have attracted considerable attention as air-independent propulsion (AIP) systems for submarines and underwater unmanned vehicles (UUVs) [6–15]. In particular, polymer electrolyte membrane fuel cell (PEMFC) power units have been applied to German HDW 214-type submarines as AIP systems. After the PEMFC AIP system was introduced, the continuous

diving time increased from a few days to two weeks for conventional diesel submarines, which had been operated using lead-acid batteries during submergence [6,10,15]. The hydrogen storage density of the hydrogen source is an important factor that determines the continuous diving time. Currently, diesel submarines are equipped with huge metal hydride cylinders that supply H₂ to the fuel cell module. However, due to the heavy weight and limited volume of these cylinders, the loading capacity of the metal hydride cylinders is limited, which restricts the continuous diving time. Furthermore, hydrogen charging is only possible in ports that have a hydrogen charging infrastructure, and it takes a long time to charge hydrogen. Therefore, it is necessary to improve the hydrogen storage density and provide logistic support [16–20]. In addition, the low hydrogen storage density of metal hydride cylinders

* Corresponding author.

E-mail address: jmbae@kaist.ac.kr (J. Bae).

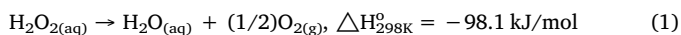
¹ Both authors contributed equally to this work, Co-first author.

limits their application in small UUVs [11,12,14].

To overcome these limitations, various fuel processing technologies that are applicable to AIP systems have been studied [16–18,21–23]. Krummrich et al. reported a 480 kW-class onboard methanol fuel processor that can replace metal hydride cylinders in large German submarines [16]. In addition, Hynergreen, a Spanish company, developed a 300 kW-class onboard ethanol fuel processor and applied it to the Navantia-constructed S-80 submarine [21,22]. Submarines equipped with fuel processors can use liquid fuel with a high hydrogen storage density, and this setup increases the continuous diving time. In addition, it is advantageous to acquire and resupply the hydrogen sources instead of using the metal hydride method.

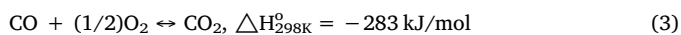
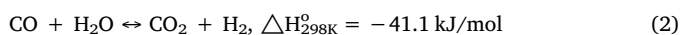
Diesel fuel may be the most promising hydrogen source for mobile applications. In particular, diesel fuel has significantly higher specific volumetric and gravimetric hydrogen densities than those of the hydride forms of hydrogen sources or other hydrocarbon fuels. In addition, the infrastructure around the world is well-equipped for diesel fuel, and it is easy to transport and store in a liquid state [19,24–32]. However, in order to reform diesel fuel, oxygen, as well as water, is required as an oxidizing agent, and the oxygen supply is critically limited in low-oxygen environments [33,34]. To solve this problem, our research team developed a reactor for autothermal reforming (ATR) that utilizes diesel fuel and hydrogen peroxide (H₂O₂) for the AIP fuel cell power units used in submarines or UUVs [35,36].

H₂O₂ has relatively high volumetric oxygen storage density because oxygen could be chemically stored in hydrogen peroxide. Since H₂O₂ is in a liquid state at room temperature, unlike liquid oxygen, there is no need for additional facilities for insulation and cooling, which can enhance oxygen storage efficiency. In addition, H₂O₂ has the decisive advantage of being able to supply water and oxygen required for the diesel autothermal reforming reaction as well as heat through the decomposition reaction as shown in Eq. (1) [37–39]. Utilizing the advantages of diesel and hydrogen peroxide, H₂-rich gas was effectively produced in low-oxygen environments.



Until now, a reformer that produces hydrogen-rich gas, which is part of the diesel-H₂O₂ fuel processor, has been developed. However, in order to apply this fuel processor to PEMFC modules, additional processes must be introduced for removing the CO fraction in the reformat gas. In particular, to prevent CO poisoning in the Pt-based anodes of PEMFC modules driven at temperatures between 60 and 80 °C, the CO fraction of the inlet gas should be maintained at the ppm level [25,40,41].

The fuel processor for mobile PEMFC applications generally consists of the following parts: a fuel reformer, multi-stage water-gas shift (WGS) reactors, and a preferential oxidation (PROX) reactor [24,25,31,40,42–47]. In addition, a sulfur trap must be installed when sulfur is present in the fuel. The fuel reformer converts the hydrocarbon fuel into hydrogen-rich reformed gases, while the WGS and PROX reactors convert CO into another gas [48–50]. The WGS and PROX reaction equations are shown in Eq. (2) and Eq. (3), respectively. In the PROX reactor, CO is selectively oxidized, by supplying additional oxygen to reduce the CO fraction to several tens of ppm [47–49]. PROX requires oxygen during the reaction, which is a disadvantage in low-oxygen environments. In addition, since the PROX reaction is strongly exothermic ($\Delta H_{298\text{K}}^\circ = -283 \text{ kJ/mol}$), a cooling load is required to maintain an appropriate reaction temperature, thus increasing the complexity of the system.



In this study, we proposed a diesel-H₂O₂ fuel processing concept that uses a hydrogen separation membrane instead of a PROX reactor to solve the CO removal problem that exists in current fuel processors. The

hydrogen separation membrane can selectively transmit only hydrogen without consuming oxygen during the final stage [51–53]. An important aspect of hydrogen separation is utilizing the appropriate pressure conditions. Therefore, when using a conventional fuel processor that requires the supply of gaseous reactants, a compressor must be introduced for pressurization. However, in this study, the liquid diesel fuel and hydrogen peroxide are advantageous because using liquid reactants can significantly reduce the energy consumption of pressurization and the noise emissions because a compressor is not required. Therefore, employing a hydrogen separation membrane, which requires pressurized environments, could be much easier in the proposed system than in conventional diesel fuel processing systems, which use air as the oxidant. Moreover, the high-purity hydrogen obtained from the membrane separation can be used in the PEMFC. Additional WGS reactors and oxygen-consuming PROX reactors, which have been used to lower the CO concentration, can be replaced with compact hydrogen separation membranes that do not require an additional oxygen supply.

Studies on diesel fuel processors using ATR, WGS and PROX reactors have been conducted at several institutes [24,25,40,41,46,54–57]. However, hydrogen membranes have rarely been applied in diesel fuel processors because they require high pressure, resulting in undesired effects such as methanation and parasitic power to pressurize [58–61].

In this paper, comprehensive studies were carried out for each reactor to develop a pressurized diesel-H₂O₂ fuel processing technology with a hydrogen separation membrane. First, the characteristics of ATR and WGS reactions were investigated under various operating conditions. Second, hydrogen separation membrane permeation experiments were performed according to temperature, pressure differences, and inlet gas composition. Finally, based on the experimental results, the design points of the diesel-hydrogen peroxide fuel processor were analyzed to maximize efficiency.

2. Fuel processing system outlook

The proposed fuel processor aims to apply diesel fuel to PEMFCs in low-oxygen environments. Therefore, high-purity hydrogen is required that has a carbon monoxide fraction less than several tens of ppm and free of sulfur compounds. The components of the fuel processor proposed in this study, as shown in Fig. 1, include 1) an ATR reactor, 2) a hydrogen peroxide decomposer, 3) a sulfur trap, 4) a WGS reactor, and 5) a Pd-based alloy membrane for hydrogen separation.

Hydrogen peroxide is vaporized during heat exchange with the ATR reactor reformat gas. Subsequently, vaporized gas is decomposed into steam and oxygen through a hydrogen peroxide decomposer and supplied to the ATR reactor. This oxidant preparation process was proposed and validated in a previous study [36]. In the ATR reactor, the diesel fuel and oxidants are converted to H₂-rich gas through catalytic reforming reactions. When using a commercial diesel source, the sulfur compounds must be removed because they can have a deleterious effect on the subsequent stage involving the WGS reactor and hydrogen separation membrane (in addition to the possible degradation of the PEMFC anode) [25]. In the WGS reactor, the fraction of the carbon monoxide is decreased, and the fraction of hydrogen used as the fuel of the fuel cell is increased. Finally, the hydrogen at the WGS rear gas is separated through the hydrogen separation membrane into a high-purity form (99.99% or more) and residual gas, which includes CO₂, H₂O, CO and H₂ [52].

The hydrogen recovery performance in the hydrogen separation membrane is an important factor that determines the entire fuel processing efficiency. The definitions of the hydrogen recovery and efficiency are shown in Eqs. (4) and (5), respectively.

$$\text{H}_2 \text{ recovery } [\%] = \frac{\dot{n}_{\text{H}_2, \text{separated to the permeate side}}}{\dot{n}_{\text{H}_2, \text{feed to the membrane}}} \times 100 \quad (4)$$

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