



# Development of a thermally self-sustaining kW<sub>e</sub>-class diesel reformer using hydrogen peroxide for hydrogen production in low-oxygen environments



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## HIGHLIGHTS

- Novel technology of a kW<sub>e</sub>-class diesel reformer with hydrogen peroxide was developed.
- Thermally self-sustaining operation is possible without any heating devices.
- Reforming characteristics were analyzed when operated with hydrogen peroxide.
- Hydrogen peroxide decomposer was newly introduced to resolve side effects.
- Reformer design points were suggested when hydrogen peroxide is used as an oxidant.

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## ABSTRACT

A novel technology of a diesel reformer that uses hydrogen peroxide is developed to obtain the hydrogen required for fuel cell air-independent propulsion for underwater applications, such as submarines and unmanned underwater vehicles. Diesel fuel could be a promising hydrogen source for underwater applications due to its high hydrogen density and its globally well-equipped infrastructure. An alternative oxidant, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), is applied to supply not only oxygen but also the water required for diesel autothermal (ATR) reforming. The proposed reformer does not require an additional heating device to supply heat for the vaporization of diesel or oxidant due to the exothermic nature of the ATR reaction and the heat of decomposition of H<sub>2</sub>O<sub>2</sub>. The effects of H<sub>2</sub>O<sub>2</sub> on diesel reforming were confirmed based on operating the engineering-scale (kW<sub>e</sub>-class) diesel-H<sub>2</sub>O<sub>2</sub> reformer. Undecomposed H<sub>2</sub>O<sub>2</sub> caused an excessively high temperature in the mixing zone and a corrosion effect in the reformer wall. To overcome these phenomena, we introduced a catalytic H<sub>2</sub>O<sub>2</sub> decomposer to fully decompose hydrogen peroxide into steam and oxygen. From this important step, we essentially eliminate side effects from undecomposed H<sub>2</sub>O<sub>2</sub> and retain a high reforming efficiency by utilizing the heat of decomposition of H<sub>2</sub>O<sub>2</sub>.

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## 1. Introduction

Fuel cell power units are attracting considerable attention because of their high efficiency and environmental friendliness in various applications, including automobiles, auxiliary power units and distributed power plants [1–6]. Furthermore, the area of fuel cell power units has been extended to specific applications in low-

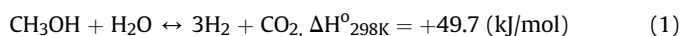
oxygen environments, such as submarines and unmanned underwater vehicles (UUVs), because of their significantly low level of noise emission and oxygen-consuming characteristics [7–12]. Air-independent propulsion (AIP), which rarely requires oxygen, is essential for submerged operations in low-oxygen environments. Among the AIP technologies, the fuel cell power unit is considered to be the most attractive solution due to its high specific energy density and low oxygen-consuming characteristics [13,14]. The continuous diving time of submarine applications, for instance, has been significantly increased from a few days to two weeks by introducing fuel cell AIP [9,15]. However, the hydrogen source still

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remains an obstacle for enhancing underwater operations. Small- and medium-sized diesel submarines currently store hydrogen in hydride form with metals contained in large storage cylinders [16]. Unfortunately, there are some restrictions regarding the loading amount of such metal hydride cylinders, such as their high weight and volume. In addition, such metal hydrides limit the continuous diving operation of submarines because it takes a long time (~33 h) to charge hydrogen, in addition to the fact that charging is only possible in ports that possess a hydrogen charging facility [15–17]. Moreover, this metal hydride with a low hydrogen storage density has been a restriction for applications to small-sized UUVs [12,14].

Consequently, studies on applying alternative hydrogen sources for applications in low-oxygen environments to replace metal hydrides were conducted to overcome the drawbacks of metal hydrides [15,16,18–20]. Such studies specifically focused on overlooking the main characteristics and the hydrogen storage densities of gaseous hydrogen, liquid hydrogen, hydrocarbon fuel and chemical hydride, in addition to metal hydride, as a hydrogen source and the feasibility for actual applications. P.C. Ghosh et al. investigated the optimum combination of hydrogen sources, including metal hydrides, chemical hydrides and other storage sources, for obtaining a substantial enhancement in the submerged endurance in a 3000 ton-class submarine [19]. Among the various hydrogen storage or production technologies onboard, supplying hydrogen via hydrocarbon reforming stands out as the most developed study at an actual system level [15,16,18]. The Spanish Navy via the Navantia factory introduced ethanol reforming technology as an onboard hydrogen production method for a 300 kW-class PEMFC in a submarine AIP [18]. Moreover, Krummrich et al. recently reported that field and final testing for applying a 480 kW-class onboard methanol reformer as a hydrogen source in a larger German submarine were completed [16]. The methanol reforming process was highlighted as an adequate onboard hydrogen production method because of its mature technology and high H/C ratio. However, because an endothermic reaction is required in the steam reforming reaction for methanol (Eq. (1)), an additional load of oxygen is required to supply a heat source through a burner [21].

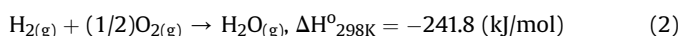


Diesel fuel may be the most ideal hydrogen source for low-oxygen environments. The specific volumetric and gravimetric hydrogen densities of diesel fuel are considerably higher than those of other hydrocarbon fuels, chemical hydrides and metal hydrides [22,23]. Furthermore, the infrastructure is well equipped worldwide, and due to the liquid form of diesel, its storage and transportation could be considerably more convenient [24,25]. Consequently, generating hydrogen through onboard diesel reforming could lead to the efficient operation of fuel cells, which will maximize the substantial enhancement in the submerged endurance.

Factors that are important for diesel reforming in subsea applications are a simple system configuration for a compact system size, fast start-up time, dynamic response, and, most importantly, the activity and stability of the reforming catalyst. In this respect, the autothermal reforming (ATR) method, in which both steam and oxygen are used as an oxidant, can be considered to be the most suitable reforming method among the available reforming methods (partial oxidation and steam reforming) because this method can guarantee the catalytic performance and other dynamic characteristics [26–32]. Steam suppresses coke formation on the diesel ATR catalyst, and oxygen effectively decomposes aromatic compounds in diesel fuel. Yoon et al. succeeded in the long-term operation of 2500 h of diesel ATR by controlling the operating conditions related to steam and oxygen and introducing a fuel

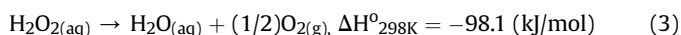
injection method to improve the reactant mixing performance [31,32]. Pasel et al. also reported that they ran the autothermal reformer with a 10 kW<sub>e</sub> class for 10,000 h using BTL diesel and GTL kerosene [30].

However, diesel ATR is impossible in low-oxygen environments without an additional supply of oxygen. Because the underwater environments lack in oxygen, oxygen should be supplied through additional facilities. The primary type of oxygen storage used in AIP is liquid form in a cryogenic tank (liquid oxygen boiling point: –183 °C). This liquid oxygen (LOX) tank is known as the key component that increases the system complexity [11,16]. This is because both regular purging due to its high evaporation pressure and continuous cooling are essential for LOX, which makes the efficient storage of oxygen difficult. Currently, LOX is primarily used for fuel cell driving. Therefore, to operate diesel ATR, additional LOX is crucial for the continuous oxygen demand. For fuel cell operation, at least stoichiometric amount of oxygen which satisfies overall fuel cell reaction of Eq. (2) is required. The minimum amount of oxygen is allocated to half times of amount of hydrogen loaded (except for metal hydride cylinder) in mole base and eight times of amount of hydrogen loaded in mass base [8].



However, if hydrogen is supplied using diesel ATR with LOX, the minimum loading amount of oxygen (only oxygen amount) should be increased almost two times larger (This value is calculated based on typical diesel ATR experimental results [33–35]); consequently, expanding overall LOX facilities is essential for driving a diesel ATR, which is extremely difficult for applications in low-oxygen environments. For these reasons, diesel reforming has not been highlighted as a hydrogen source for submarine applications [16,22].

Our research team has suggested an innovative concept of using hydrogen peroxide as an alternative oxidant for effectively applying diesel reforming in low-oxygen environments [33]. Storing hydrogen peroxide onboard does not require additional insulation or cooling energy because it is in liquid form at room temperature, unlike LOX. Furthermore, its volumetric oxygen storage density is relatively high because oxygen could be chemically stored in hydrogen peroxide, which enhances the oxygen storage efficiency [36]. Additionally, not only oxygen and water, which are oxidants required for diesel ATR, but also additional decomposition heat can be acquired from the decomposition of hydrogen peroxide according to Eq. (3) [36–38]:



Our previous study confirmed that hydrogen peroxide could be used as an alternative oxidant for diesel ATR by comparing experiments performed using conventional oxidants in a micro-reactor. In addition, studies on designing operating conditions and evaluating the catalytic performance were successfully conducted at the micro-reactor scale. In the previous study, the flow rate of reactants, including hydrogen peroxide, was so low that the effect of the heat of decomposition was negligible [33].

Because feasibility was demonstrated in the previous study, we developed an actual kW<sub>e</sub>-class diesel autothermal reformer with hydrogen peroxide. In this paper, the scientific and technical issues that occurred during the development of this reformer are comprehensively discussed. First, the temperature profile and reforming performance were analyzed when the engineering-scale reformer was operated using hydrogen peroxide. Second, a design modification to introduce an additional hydrogen peroxide decomposer was conducted to resolve problems that occurred when the unmodified reformer was used. Finally, we suggest a

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