



Diesel autothermal reforming with hydrogen peroxide for low-oxygen environments



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HIGHLIGHTS

- The concept of diesel reforming using hydrogen peroxide was newly proposed.
- Characteristics of hydrogen peroxide was experimentally investigated.
- Thermodynamically possible operating conditions were analyzed.
- Catalytic performance of Ni–Ru/CGO for various diesel compounds was evaluated.
- Long-term testing was successfully conducted using Korean commercial diesel.

ARTICLE INFO

Article history:

Received 19 March 2015
Received in revised form 26 May 2015
Accepted 15 June 2015

Keywords:

Diesel
Hydrogen peroxide
Autothermal reforming
Hydrogen
Low-oxygen environments

ABSTRACT

To operate fuel cells effectively in low-oxygen environments, such as in submarines and unmanned underwater vehicles, a hydrogen source with high hydrogen storage density is required. In this paper, diesel autothermal reforming (ATR) with hydrogen peroxide as an alternative oxidant is proposed as a hydrogen production method. Diesel fuel has higher hydrogen density than metal hydrides or other hydrocarbons. In addition, hydrogen peroxide can decompose into steam and oxygen, which are required for diesel ATR. Moreover, both diesel fuel and hydrogen peroxide are liquid states, enabling easy storage for submarine applications. Hydrogen peroxide exhibited the same characteristics as steam and oxygen when used as an oxidant in diesel reforming when pre-decomposition method was used. The thermodynamically calculated operating conditions were a steam-to-carbon ratio (SCR) of 3.0, an oxygen-to-carbon ratio (OCR) of 0.5, and temperatures below 700 °C to account for safety issues associated with hydrogen peroxide use and exothermic reactions. Catalytic activity and stability tests over Ni–Ru (19.5–0.5 wt.%) $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-x}$ were conducted using various diesel compounds. Furthermore, long-term diesel ATR tests were conducted for 200 h using Korean commercial diesel. The degradation rate was 3.67%/100 h without the production of ethylene.

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1. Introduction

Fuel cells are energy conversion devices that convert chemical energy into electrical energy with relatively high efficiency and low pollutant emissions. Moreover, fuel cells have less noise emission and require lower oxygen supply than traditional combustion-based power systems [1,2]. Therefore, there has been much interest in applying fuel cells to low-oxygen environments such as submarines, UUVs (unmanned underwater vehicles), and other applications [3–6]. For submarine applications in particular, fuel cells can be the most attractive option for APUs (auxiliary power units) or AIP (air independent propulsion) due to their silent

and lower oxygen-consuming characteristics and high efficiency [7,8]. To drive fuel cells, a continuous hydrogen supply is required. Metal hydride is currently the main hydrogen source for submarine applications. However, metal hydride has a low hydrogen storage density and requires a relatively longer recharge time. Therefore, the mission range and underwater endurance of submarines (or UUVs) has been limited [9]. Some studies have sought to apply hydrocarbon reforming to supply hydrogen into fuel cells effectively in low-oxygen environments [10,11].

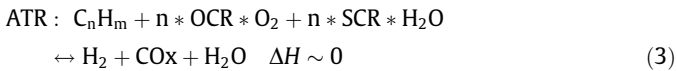
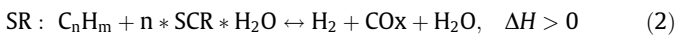
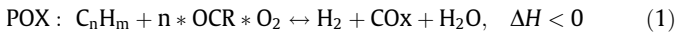
Diesel fuel has a higher hydrogen density than other hydrocarbon fuels, suggesting diesel reforming as a promising hydrogen source for fuel cells [12–16]. Diesel fuel also has advantages in terms of storage and accessibility for low-oxygen environment applications due to its liquid phase and well-equipped infrastructure [17–19]. If hydrogen production via diesel reforming could

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be performed in low-oxygen environments, diesel reforming could be applied to submarine applications for successful missions and objectives.

The three available reforming methods are classified by the types of reactants: POX (partial oxidation, Eq. (1)), SR (steam reforming, Eq. (2)) and ATR (autothermal reforming, Eq. (3)) [20].



SCR (steam-to-carbon ratio) and OCR (oxygen-to-carbon ratio) are each defined by the ratio of steam, and oxygen to carbon number n .

By varying SCR, OCR and the reaction temperature, the reaction sets can be net exothermic as in POX, net endothermic as in SR, or thermally neutral as in ATR [21]. There are advantages and disadvantages of each reforming method that must be considered when selecting the most suitable method for the desired application. ATR combines POX and SR; fuel, water, and oxygen are fed to the reactor simultaneously. ATR shares several advantages with both POX and SR, such as rapid thermal response and relatively high hydrogen yields. Furthermore, ATR requires no external heat source due to its slight exothermic reaction, enabling simple reformer configurations [21–23]. Based on these advantages, ATR may be the most suitable method for subsea submarine applications.

ATR has been considered the most appropriate method for diesel reforming because the steam supply suppresses coke formation over the catalyst and aromatic compounds in the diesel fuel can be effectively decomposed by oxygen [24–29]. Yoon et al. successfully suppressed carbon deposition by controlling SCR and OCR and successfully tested long-term operation of ATR for 2500 h by considering the fuel delivery method [30,31]. Samsun et al. developed 5 kW_e high-temperature polymer electrolyte fuel cell system operated with diesel ATR and other components for an auxiliary power unit [22]. However, in low-oxygen environments such as the subsea, conventional diesel ATR using oxidants such as water and air (or oxygen) could not be used without additional oxygen sources.

In this study, aqueous hydrogen peroxide solution (H₂O_{2(aq)}) was proposed for diesel ATR in low-oxygen environments. H₂O_{2(aq)} is used not only as a source of oxygen but also as a source of water; both are acquired by decomposition of hydrogen peroxide according to the following Eq. (4):



In subsea applications, both high oxygen density and safety issues should be considered. Hydrogen peroxide is in liquid form, and the oxygen per unit volume is high, which could reduce the required size of storage tanks. The oxygen density of pure hydrogen peroxide is approximately 21 mol O₂/liter at 1 bar and 25 °C. In comparison, pure O₂ gas has to be stored at 485 bar and 5 °C to attain comparable oxygen density [10]. According to Eq. (4), during decomposition, heat is released due to the exothermic nature of the reaction. If the concentration of H₂O_{2(aq)} is 67 wt.% or greater, all decomposition heat is used to vaporize water included in the

solution, increasing the potential for spontaneous decomposition [32]. Decomposition of a high concentration of H₂O_{2(aq)} would be hazardous in extreme situations such as submarine applications and should therefore be prohibited. In addition to decomposition heat, purchasing commercial H₂O_{2(aq)} as a solution more concentrated than 50 wt.% is difficult. For these reasons, the concentration should be less than 50 wt.%.

In this paper, diesel ATR using H₂O_{2(aq)} as an alternative oxidant was comprehensively studied. First, experiments comparing different oxidants (H₂O_{2(aq)}, water, and air) were conducted to assess the characteristics of hydrogen peroxide as an oxidant for diesel reforming. Second, operating conditions such as SCR, OCR, and the reaction temperature were analyzed using thermodynamic calculations to discover which enables ATR reaction, when H₂O_{2(aq)} is less than 50 wt.%. Third, the reforming catalytic activity and stability of our in-house prepared catalysts were evaluated for various diesel compounds. The catalytic performance assessment was performed for ATR with n-dodecane and two synthetic diesels that each contained sulfur and aromatics. Finally, long-term testing was conducted using Korean commercial diesel.

2. Experimental

2.1. Catalysts

For the experiments comparing different oxidants, the ATR reforming catalyst of platinum (Pt) on gadolinium (Gd)-doped CeO₂, Pt (0.5 wt.%)/CGO (Ce_{0.8}Gd_{0.2}O_{3-δ}) was used. This catalyst was synthesized using combustion spray method, and it was supplied by Praxair Co. in the form of fine powder. To test diesel reforming performance, Ni–Ru (19.5–0.5 wt.%)/CGO (Ce_{0.9}Gd_{0.1}O_{2-δ}), which was originally developed for diesel pre-reforming, was used [33,34]. Ni–Ru (19.5–0.5 wt.%)/CGO catalyst was synthesized using glycine nitrate process (GNP). Synthesized powder type catalyst was calcined in air at 800 °C for 4 h. Information on the catalysts is summarized in Table 1. BET and chemisorption measurements were conducted as previously described [33,35]. CGO-based catalysts are generally highly resistant to carbon deposition because the oxygen vacancies generated by the Gd dopant produce a reactive lattice oxygen in CeO₂ that can enhance the reforming activity of CGO-based catalysts [17,36].

All catalysts were pelletized using a uniaxial press and crushed into small granules with sizes ranging from 250 to 500 μm for the reforming tests.

2.2. Experimental setup

2.2.1. Hydrogen peroxide characteristic tests as an oxidant

A schematic diagram of diesel–H₂O₂ micro-reactor system is shown in Fig. 1. In this section, the characteristics of hydrogen peroxide as an oxidant in diesel reforming were compared with those of the conventional oxidants, water and air. When hydrogen peroxide was used as an oxidant, the same amount of N₂ included in air was additionally supplied to the reactor. SCR, OCR, GHSV (gas hourly space velocity), reaction temperature, and fuel used were the main experimental operating parameters. All operating

Table 1
Catalysts used for diesel–H₂O₂ reforming.

	Bet surface area (m ² /g)	Active metal surface area (m ² /g)	Fabrication method	Supplier
Pt/CGO (0.5 wt.%)	35.11	0.96	Combustion spray method	Praxair
Ni–Ru/CGO (19.5–0.5 wt.%)	25.01	12.73	Glycine nitrate process (GNP)	In-house catalyst

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