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Short communication

Diesel fuel processing for fuel cells—DESIRE[☆]

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Abstract

The advantages of fuel cell systems on naval surface vessels are generally based on their low emissions, high comfort and high efficiency. Today the NATO-logistic fuel for naval ships is F76 marine diesel fuel. Because of its availability and the fact that the use of hydrogen onboard ships would require a much higher storage volume, the reforming of F76 diesel fuel is essential for the implementation of fuel cell systems on naval surface vessels. The DESIRE-project has been performed from 2001 until 2004 to demonstrate the feasibility of the reforming of F76 diesel fuel into a hydrogen-rich gas suitable to be utilized in PEM-fuel cells. A steam reformer system has been realized in the project. A small PEM-fuel cell has been coupled to the reformer system and operated successfully.

Keywords: Diesel reformer; Naval ship; Marine application; Desulphurization

1. Introduction

For electric power generation on board of naval ships it is clear that the application of fuel cells provides several potential advantages over combustion engines. Today commercially available diesel generator sets onboard ships supply the ships network system with the required electrical energy. These generators are sophisticated technology, but the operation of these systems comprises several disadvantages for naval ships. Especially the signatures of these generators, in being noise, vibrations and their high exhaust gas temperatures, lead to impacts on the ship's design. Because of this the main benefits of fuel cell systems in initial naval ship applications (2010–2020) will be the very low signatures of the energy generation units. Furthermore, the increase of importance for distributed power generation in future naval ship concepts, e.g. the All Electric Ship, lead to further benefits of fuel cell systems compared to diesel generator sets [1,2]. On the long-term (after 2020) also reduced life cycle costs of fuel cells are expected. However, since hydrogen is the 'natural' fuel for most types of fuel cells, but will not be a logistic NATO fuel, there is a need for the conversion of logistic NATO F76 marine diesel fuel to a hydrogen rich gas, suitable for fuel cells.

2. Background

Today the application of fuel cell systems in the maritime market is mainly focused on niche applications. The latest class of conventional submarines developed by Howaldtswerke-Deutsche Werft (HDW) is equipped with an air-independent propulsion system (AIP-System) for submerged operation based on fuel cells. This system had been developed during the last two decades, until it was ready for production. The first two fuel cell equipped submarines U31 and U32 have been set into service in October by the German Navy.

The main difference between the AIP-System for submarines and a fuel cell system for a surfaceship, naval or commercial, is the choice of the reactants. Whereas in a submarine pure oxygen is stored in liquid oxygen tanks (LOX), a surfaceship's fuel cell system would of course utilize the aerial oxygen. The hydrogen in a submarine is stored in metal hydride storage cylin-

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ders. Onboard a surfaceship the use of pure hydrogen would result in very large storage volumes, because the required power level is high, as well as the time of operation between refueling. Because of this fact the use of pure hydrogen in ships will be limited to niche application. In naval ships the operation on logistic fuels is mandatory for a widespread implementation of fuel cell systems. Today's naval ships are operating on F76 diesel fuel, a NATO-specified diesel fuel that is available worldwide.

The main objective of the DESIRE project was to investigate, evaluate and demonstrate the technology to convert F76 diesel fuel into a hydrogen rich gas suitable to be utilized in a fuel cell system. The project duration was from 2001 to 2004, and has been performed under the umbrella of the Western European Union, a union of all NATO-countries in Europe. The participating countries in the DESIRE project were The Netherlands, Germany, Turkey and United Kingdom. The development of fuel cells was not considered in the project.

3. System evaluation and studies

In the first phase of the DESIRE-project the focus was on studying the technical and economical feasibility of diesel fuel processing for fuel cells in naval ships. The performance of the system has been compared to diesel generator sets, with the objective to achieve a customer benefit with the system. The focus was a system with an electrical power output of 2.5 MW, to be realized by 2010. Therefore, trade-off rules have been defined to evaluate different routes of fuel processing and also different types of fuel cells. These trade-off rules were:

- cost;
- signatures;
- efficiency;
- size and weight;
- strength of the system/modularity;
- start-up time and dynamics;
- ARM (availability, reliability and maintenance);
- development status;
- safety;
- environment/emissions.

Based on these criteria each partner had to rate several considered systems for the electrical energy generation with F76 diesel fuel onboard a naval ship:

- gas turbine (as state-of-the-art system);
- partial oxidation + SOFC + gas turbine;
- partial oxidation + SOFC + PEM-FC;
- partial oxidation + PEM-FC;
- steam reforming + SOFC + gas turbine;
- steam reforming + SOFC + PEM-FC;
- steam reforming + PEM-FC;
- autothermal reforming + PEM-FC.

Especially the requirement to realize the system by 2010 had an influence on the scores of the partners. It is of course expected that the system efficiencies of solid oxide fuel cells (SOFC) will be higher than efficiencies for PEM-fuel cells, but the availability of SOFCs by 2010 is not ensured. This expectation led to low scoring of the SOFC-Systems at the development status. In contrast PEM-fuel cells were considered to be available, even for the desired higher power outputs.

For the diesel fuel processing system three different designs have been considered: partial oxidation, autothermal reforming and steam reforming. The steam reforming system has been considered to be the most promising system because of the highest efficiency of the fuel processing unit. The reformate produced in a partial oxidation or an autothermal reformer is diluted by the aerial nitrogen, a further disadvantage compared to a steam reformer. The main disadvantage of the steam reformer was identified to be the slow response to load changes, but this was not considered to be that important for naval applications.

Taking into consideration the trade-off rules and especially the time schedule for the realization, the system consisting of a steam reformer and a PEM-fuel cell has been chosen for the conceptual design on the 2.5 MW scale. Also the design of the demonstrator system to be realized in phase 2 of the project has been performed by ECN on the basis of this conceptual design.

In Fig. 1 the system of the 2.5 MW diesel fuelled fuel cell system is shown. The heat integration of the process is not shown in detail.

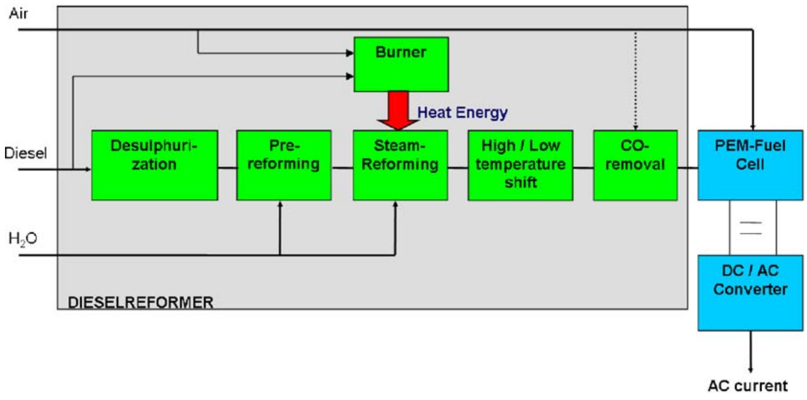


Fig. 1. System design for diesel-fuelled fuel cell system based on steam reforming and PEM-fuel cells.

The process consists of the following key components:

- the evaporators, one for diesel fuel and another for the water (both not shown);
- the desulphurization unit, consisting of sections for hydro-desulphurization and adsorption of the hydrogen sulphide;
- the pre-reformer unit, a catalytic reactor;
- the steam reformer, heated by a diesel burner;
- the adiabatic high temperature shift (HTS) and low temperature shift (LTS);
- the preferential oxidation unit;
- the PEM-fuel cell;
- the hydrogen recycle stream (not shown);
- the anode offgas that is fed to the burner of the steam reformer (not shown);
- the water recycle system (not shown).

Additionally an electrical power conditioning system has been considered.

The calculated electrical efficiency of the system is 35–40%, depending on the current density of the fuel cell applied.

During the evaluation and consideration of all components required for a diesel-fuelled fuel cell system it became clear that it is not possible to meet all requirements with available components. Especially the volume and weight requirements are not met with the existing technology. Priorities should be defined for the different criteria when such a system is realized on a short- or medium-term [3].

Further developments in the next years are needed to bring this technology towards commercialization. A very important point is the development of robust and cost-effective fuel cells. For the operation of a PEM-fuel cell on reformate it would be very beneficial to increase the fuel cell temperature above 120 °C (high temperature PEM-FC), because the CO-tolerance increases at higher temperatures.

For systems with power outputs in MW-range, as considered in the studies, systems with solid oxide fuel cells offer much higher efficiency potential than PEM-fuel cells. Therefore, a continuously consideration of the availability of these fuel cells is mandatory in the following years.

For the realization of a demonstrator unit consisting of all fuel processing components in phase 2 of the project it has been decided for cost reasons to build up a system without heat integration. This shows the feasibility of the reforming process, the heat exchangers are not necessary for this purpose.

4. Demonstration of diesel fuel processing system

In phase 2 of the project the aim was to demonstrate the fuel processing technology for F76 diesel fuel as evaluated in phase 1. Therefore, conceptual designs have been performed for each subsystem on a scale equivalent to 25 kW electrical power output of the PEM-FC. The PEM-FC itself has not been considered.

The evaporation of the diesel fuel has been considered because of the risk of formation of carbonaceous material (carbon, char, coke, soot, etc.). This risk occurs because of the different constituents in the diesel fuel that have boiling temperatures from 180 to 360 °C. This can cause thermal cracking of single constituents in the diesel fuel. Tübitak MRC in Turkey has performed several studies on different evaporator designs. The experimental studies showed that this thermal cracking could be minimized by a proper evaporator design and operating conditions. The evaporator that has been realized is heated by hot gases, to simulate the operation on reformer offgas. To investigate the change of the diesel fuel properties during the evaporation process the diesel fuel has been condensed completely after evaporation, and the distillation curve is compared with the curve for the initial diesel.

The result of the experiments performed for the evaporation unit showed that the evaporator design is very important for the reliable operation of a F76 fuel processor.

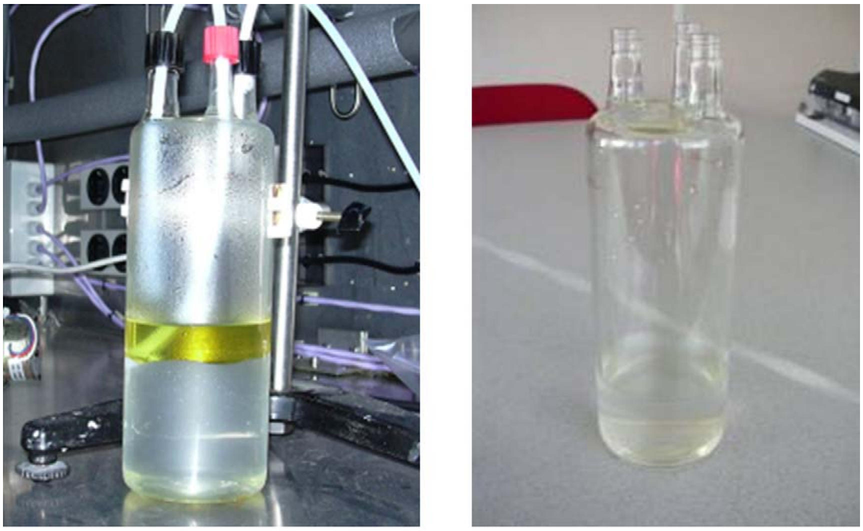
According to the NATO specification F76 diesel fuel worldwide contains up to 1 wt.% sulphur, in Europe up to 0.2%. The complete desulphurization of the diesel fuel is of utmost importance to protect the catalysts of the subsequent units from sulphur poisoning. The evaporated diesel fuel is fed with hydrogen to the desulphurization unit consisting of fixed beds for ultra-deep hydro-desulphurization (HDS) on NiMo and adsorbtion on ZnO. Downstream a special adsorber has been installed that should selectively remove the remaining traces of sulphur containing hydrocarbons.

In the HDS unit hydrogen is added to force the formation of hydrogen sulphide (H_2S), which can be removed inside the ZnO-bed by forming ZnS. In the subsequent special adsorber the last traces of bonded sulphur in higher hydrocarbons should be removed.

These reactors have been designed, manufactured and tested by ECN in The Netherlands on a 25 kW_e scale, using F76 diesel with a sulphur content of 0.13 wt.%. Prior to commissioning the NiMo catalyst was ex situ presulphided by a third party. The testing of the desulphurization unit showed that the HDS with the ZnO-adsorption removed approximately 75% of the sulphur in the diesel feed. The special adsorber had to be removed after a few hours of operation, because a strong exothermic hydrogenation reaction occurred, making it impossible to operate the unit in stable operation.

Therefore, the fuel conversion in the desulphurization unit did not meet the requirements for the subsequent units. One major reason for that was the operation of the HDS at very low pressure (approximately 4 bar abs.). Conventional HDS units, as applied in refineries, operate at elevated pressure above 40 bar and reduce sulphur levels to typically 300–500 ppm, whereas ultra-deep hydro-desulphurization units can achieve sulphur levels even below 10 ppm nowadays [4]. After these results it has been decided to operate the system on city diesel, containing less than 10 ppm of sulphur. Additionally some tests have been performed on Hydroseal, a nearly sulphur-free aliphatic solvent that could be regarded as a diesel substitute.

The desulphurized diesel fuel is mixed with steam and fed to the pre-reformer unit. The hydrocarbons of the diesel fuel should be fully converted mainly into methane and hydrogen at temperatures of 400–550 °C. The implementation of a pre-reformer unit simplifies the design of the steam reformer, because no higher



Source: ECN

Fig. 2. Condensed samples of pre-reformer experiments performed with precious metal-based catalyst (left sample) and nickel-based catalyst (right sample).

hydrocarbons have to be converted in the steam reformer, which minimizes the risk of coke formation.

Two pre-reforming catalysts have been tested at ECN at 25 kW_{el} scale. The tests showed that nickel-based catalysts are most suitable for the conversion of diesel fuel. A possible drawback is that nickel-based catalysts might have a stronger sensitivity against sulphur impurities than precious metal-based catalysts. For the demonstrator unit an adiabatic pre-reformer has been realized.

In Fig. 2 the results of the pre-reformer experiments performed with different catalysts is shown. The product gas from the pre-reformer has been condensed. If the fuel is completely converted, no diesel condensate can be found on top of the condensed water. The left sample shows the result applying a precious metal pre-reformer catalyst. A poor conversion of the feed diesel of only 25% was achieved, whereas with the conventional, nickel-based catalyst the total conversion of diesel was >98% (sample shown on the right). The reaction conditions were equal for both tests.

After the pre-reformer the gas enters the steam reformer. The gas mixture of hydrogen, methane and steam is converted into a hydrogen and carbon monoxide-rich gas mixture in a highly endothermic reaction. A diesel fuel burner supplies the heat energy that is required for the reaction. The steam reformer is operated at a reaction temperature of approximately 800 °C.

The test results showed that the steam reformer designed by Stork PE in The Netherlands worked very well at the chosen operating conditions. The chemical equilibrium was reached for the outlet gas composition. Furthermore, the steam reformer showed the ability to convert higher hydrocarbons resulting from the pre-reformer.

In the subsequent units medium temperature shift, low temperature shift and the preferential oxidation the carbon monoxide (CO) content in the reformate gas is reduced from about 16% (dry) to below 10 ppm. CO impurities affect the performance of PEM-fuel cells, therefore it is essential for a reformer system to provide a gas mixture with a very low CO content. These reactors have been designed and manufactured by HDW/HFCS in Germany and tested by the University Duisburg-Essen.

The results of the tests were very promising. The gas mixture at the outlet of both shift reactors nearly reached chemical equilibrium, the CO content could be reduced below 0.3%. The preferential oxidation reactor was a two-stage design with intercooler and two separate air supplies. The inlet temperature of the preferential oxidation reactor had to be controlled very carefully in order to avoid peaks in the CO content.

The results of the demonstrator testing performed on a test rig at ECN in The Netherlands showed that the system produced a very good gas quality. Therefore, a small PEM-fuel cell has been successfully coupled to the system. The performance of the fuel cell operated on reformate from Hydroseal is shown in Fig. 3.

Additionally the CO-content of the reformate fed to the fuel cell is shown. The peaks have been detected during load changes of the reformer.

The overall efficiency of the fuel processor unit was 82% at full load. The basis for this calculation is the lower heating value (LHV) of produced hydrogen compared to the LHV of the diesel fed to the reformer and burner section.

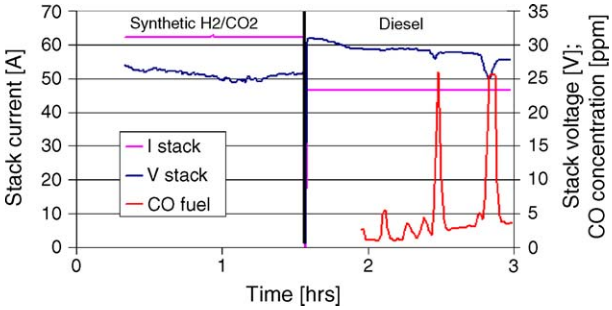


Fig. 3. Operation of PEM fuel cell stack on synthetic anode gas up to 1.6 h and reformate from diesel fuel processor from 1.6 to 3 h (*Source*: ECN).

Generally the operation of the demonstrator system has been successful, despite the problems at the desulphurization unit. City diesel as well as Hydroseal has been processed successfully. The use of precious metal catalysts for all components resulted in an easy handling of the single units.

Endurance tests have not been performed with the demonstrator unit. In continuous operation the unit has been running for 18 h. After this period a failure in auxiliary equipment occurred that forced the operators to run down the demonstrator.

5. Conclusions and recommendations

The studies have shown that it is basically possible to convert NATO F76 diesel fuel into hydrogen-rich gas suitable to be used in fuel cells. Further developments in the next years are needed to bring this technology to commercialization and to meet all requirements of today’s energy generation onboard naval ships.

The 25 kW demonstrator successfully showed the conversion of diesel fuel to a hydrogen rich gas, suitable for use in a PEM-fuel cell. With the results of the demonstrator operation and the studies performed in the first phase of the project, a broad basis has been generated for the further developments in this technology.

The key components are the desulphurization and the pre-reformer. Therefore, improvements are necessary in both units: The desulphurization must reduce the sulphur content to the required level of the pre-reformer, because the pre-reformer has been identified to be most sulphur-susceptible unit of the system. Additionally the catalyst for the pre-reformer unit should be improved with respect to its sulphur tolerance.

Furthermore, the lifetime of the catalysts in all units has to be investigated. A demonstration of a system with heat integration and the required power conditioning system should be realized, to assess the interdependencies between all units.

The development of a power pack system, consisting of fuel processor, fuel cell, power conditioning system and additional energy storage (e.g. batteries or ultra-capacitors), capable to be installed onboard, is recommended. The design of the additional energy storage depends a lot on the requirements for the power generation system. Generally load changes could be handled with such energy storage, to prevent the reformer system from being operated a lot in load changes.

The results of the DESIRE-project lead to directions for improvements of the system, especially with respect to the use of high sulphur diesel fuel for fuel cell systems.

Acknowledgement

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