

Supplementary material for “A Comparative Review of Alternative Fuels for the Maritime Sector: Challenges for Clean Energy Implementation in Economic, Technology and Policy”

Fuel cell

Hydrogen can be consumed by gas turbines and internal combustion engines, however, electricity production with the use of intermediate mechanical energy conversion may result in a low efficiency. The fuel cell is currently recognised as the most efficient way to consume hydrogen onboard ship due to the electrochemical kinetics of hydrogen [1]. Utilising hydrogen onboard with fuel cell systems is already commercially available, with examples of hydrogen-powered ships including Nemo H₂, FCS Alsterwasser and SF-BREEZEas [2][3][4]. When consuming pure hydrogen in a fuel cell, both fuel cells show a similar efficiency of approximately 40–60% depending on the fuel purity, with water the only by-product generated from the process in addition to heat [5][6][7][8]. Hydrogen is a compatible fuel with the major fuel cell systems excluding DMFC. PEMFC is an ideal solution for consuming hydrogen onboard due to the low operating temperature (65–85°C) and maturity in application [9][10][11][12]. However, PEMFC can only be operated with pure hydrogen which limits the use of PEMFC to small size ferry ships and yacht. Regarding the low energy density issue brought by the challenges in storage of hydrogen onboard, the application of MCFC and SOFC systems with higher energy density fuels is currently under investigation and has been seen as a solution for long-distance shipping [13].

Among all hydrocarbons, natural gas is one of the most attractive fuels for direct operation on fuel cells, because it is one of the most widespread alternative fuels, cheap, and its simple molecular structure poses lesser challenges than heavier hydrocarbons. Direct-methane SOFCs have been the focus of considerable attention in the 21st century. Nickel-based anodes are currently the most common anode used for SOFC due to its low cost and excellent catalytic properties for the reforming and electrochemical reactions [14]. Experimental research has indicated that SOFCs with Ni-based anodes can be operated stably with methane at intermediate temperatures (600–800°C) [15][16][17]. The most critical challenge arising from direct feed of methane to SOFC is the faster cell degradation due to carbon deposition at the anode. Surface carbon can largely reduce the efficiency of the system by blocking the access of reactants to reaction sites [18]. In recent years, effort has been devoted to improving the anode activity and stability of SOFC with natural gas fuel including incorporating an additional functional layer on Ni-based anodes [19][20][21], incorporating Sn addition to the nickel-based anode [22][23], and alternative anodes for direct-methane SOFCs [24][25][26].

Methanol can be consumed as a direct fuel or raw material for hydrogen production. In fuel processor–fuel cell systems, methanol will be first converted into hydrogen rich gas through steam reforming, or partial oxidation, or autothermal reforming. The converting process can be conducted either in a separate processing system or integrated within the fuel cell system. Then, the H₂ rich gas will be fed to the fuel cell to generate electricity after remove impurities present in the source fuel. High-temperature fuel cells, such as HT-PEMFC and SOFC, are more suitable for the application of methanol in the fuel processor–fuel cell systems [27][28][29][30]. The high-temperature fuel cells have a better capability of thermally integrated methanol reforming and more manageable tolerance against fuel contaminants with a high efficiency (30–50%). In addition, methanol can also be directly consumed in the direct methanol fuel cells (DMFCs) without reforming. However, the problems that occur in DMFC including unfavourable methanol crossover, poor oxidation kinetics and low activity catalysts lead to a poor efficiency of the system (20-30%) [31][32].

The last selected alternative fuel tested with FC is ammonia. Ammonia is easy to be cracked into hydrogen at high temperature. The thermal decomposition of ammonia is starting at 405°C and almost complete conversion can be achieved at temperatures above 590°C [33][34]. Therefore, one of the main options for the direct use of ammonia as fuel is the SOFC. The normal working temperature of SOFC is in the range of 650°C to 850°C and the decomposition of ammonia can take place in the fuel cell. Another advantage of utilising ammonia with SOFC is no high cost catalysts are required to reach high conversion of ammonia. Numerous studies have been conducted on the thermal decomposition of ammonia with different catalysts. Nickel and yttria stabilised zirconia (YSZ) has been proven to be a very efficient catalyst and over 90% ammonia cracking can be achieved for ammonia SOFC at a working temperature of 800°C [35][36][37][38]. Experimental test results also indicated that NO_x emissions in the off-gas of ammonia SOFC can be prevented when the iron-based catalyst has been used as anode in SOFC [39][40]. Another FC that attract attention from researchers is alkaline electrolyte direct ammonia fuel cells, it is reported that one of the earliest alkaline electrolyte direct ammonia fuel cells were investigated in the 1960s [41]. Alkaline electrolyte direct ammonia fuel cells can be operated at low or medium level temperatures because the ammonia in the anode is reacting directly with hydroxide ions through the alkaline membrane instead of cracking ammonia into hydrogen. However, the issues of low catalytic activity of the electro-catalysts and the difficulty of ammonia oxidation at low temperatures are the key barriers for alkaline electrolyte direct ammonia fuel cell to consume ammonia at a high efficiency [42]. Up to date experimental results indicated that the performance of alkaline electrolyte direct ammonia full cell (15-30%) is worse than SOFC (30-60%) [43][44][45][46]. Recent studies showed the possibility of improving the efficiency of membrane electrolyte direct ammonia full cell, a newly designed anion conducting electrolyte based 5-cell direct type fuel cell stack has been reported to reach the energy efficiency of 52.4% with ammonia [47].

Internal combustion engine

To consume LNG fuel, ships are required to have a gas-powered energy system which generally composed of the fuel storage system, the engine system, the bunker station, the pipe system and

generator sets. Depending on the working principle and the fuel type consumed by the main engine, its systems used by LNG-fuelled vessels can generally be classified into two groups dual-fuel systems and pure gas system. One main characteristic of the dual-fuel energy systems used on board is the two independent fuel storages and supply systems. The concept behind this design is to allow the ship to switch flexibly between consuming conventional fuel oil and LNG fuel. The dual-fuel system can run in either diesel or gas mode. In gas mode, fuel oil is used only as 'pilot oil' and the total amount of fuel oil in this mode is less than 1 per cent of total fuel [48]. A pure-gas system is today commonly used by inland waterway or costal working vessels. The design of low-pressure four-stroke pure-gas engines is very similar to that of the four-stroke dual-fuel engine, but it can operate only in gas mode. The cycle Otto/Miller is the basis for the operation of this engine. In the pure-gas system, the pure-gas engine system uses a spark plug to ignite the fuel gas in the combustion chamber [49].

One of the most attractive advantages of biodiesel as an alternative fuel is that it can be consumed directly in existing diesel-based internal combustion. However, the challenges and difficulties are also associated with the use of biodiesel like cold start problems, low calorific value, difficulty in fuel pumping lead by high viscosity [50]. These problems can be solved by mixing biodiesel with diesel fuel. Currently, primary marine engine makers, such as MAN, Wärtsilä, Yanmar, Cummins, Caterpillar, etc., have claimed that their engines can use 5-30% and even up to 100% biodiesel blends with or without engine modifications [51].

Existing studies showed that ammonia can be implemented as fuel along or blended with other fuels in either spark-ignition (SI) or compression-ignition (CI) combustion schemes. However, the combustion properties of ammonia have led to some technological barriers to effectively consuming ammonia in engine systems, such as high auto-ignition temperature, narrow flammability limits, low flame speed and toxicity [52]. Experimental results from [53] indicated that limited by the low flame speed utilising ammonia independently in SI engine will result in deterioration in engine performance due to incomplete combustion. There are several studies investigated the use of pure ammonia in CI engine, for example, [54], [52] and [55]. However, the outcomes of the studies were disappointed. Compressions ignition of pure ammonia in existing diesel engines is difficult to achieve since the high auto-ignition temperature and narrow flammability limits. The test results showed that successful ammonia compression ignition operation could only be observed under extremely high compression ratios from 35:1 to 100:1 [56]. To circumvent the challenges associated with the unfavourable combustion properties of ammonia, the combination of ammonia with combustion promoters has been adopted to improve the combustibility of ammonia. Hydrogen and diesel are the most commonly used combustion promoter blend with ammonia [57][58][59][60][61]. [62] investigated the performance of ammonia/hydrogen mixtures as a fuel in an SI-engine system. The authors reported that blended 10 vol.% hydrogen with ammonia has significantly lowered the ignition compression ratio to 8.9:1 from 35:1 for pure ammonia at the engine speed of 1200 rpm. Ammonia fuelled marine engine has not been commercialised yet, Wärtsilä is planned to test the world first full-scale ammonia engine in Stord, Norway during the first quarter of 2021[63].

Battery-powered system

Battery as the main source of power is the key of pure battery-powered vessels. The Nickel manganese cobalt oxide (NMC) based Li-ion cell, Lithium iron phosphate (LFP) cell, Nickel Cobalt Aluminium (NCA) cell are considered as the most suitable types of battery for full electricity ships with compromise between the most important parameters of energy density, costs, safety, availability and lifetime [64]. Recent studies and attempts made by the industry indicated that the implementation of battery storage technologies onboard can be technically and economically feasible [65][66][67][68][69][70][71]. Nevertheless, energy storage capacity and recharging speed of electricity storage systems have been and continues to be the limiting factors for large ships. For large ocean-going vessels, batteries are currently only used as backup power or supplementary in the hybrid system [72]. An increasing number of studies are currently taking place and looking deeply into solid-state battery technology [73][74]. The combination of solid-state battery with metal-air could dramatically improve the specific energy, energy density and safety of the cell [75]. We have reason to believe that when these technologies have matured, vessels will be able to sail longer distances with pure electricity supply and increase ship size for pure battery power application.

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