

Studies on In-Engine Combustion of Low and Zero-Carbon Fuels

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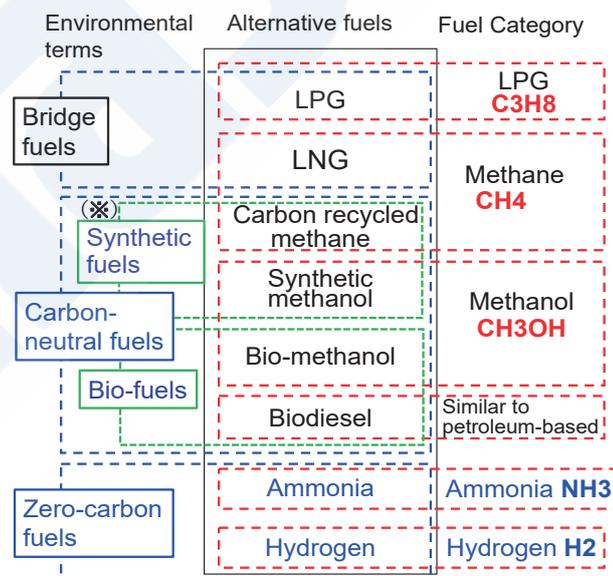
1. INTRODUCTION

The development of marine engines that burn zero-carbon fuels such as hydrogen and ammonia is urgently needed to achieve the IMO target of significantly reducing greenhouse gas (GHG) emissions from international shipping. Methane and methanol, if synthesized in a carbon-neutral way, could also be considered net zero-carbon in the same sense as biofuels¹⁾. This paper describes the combustion of these five alternative fuels in engines.

Fig. 1 shows the classification of these fuels. It should be noted that LPG is not discussed in this paper. As the diagram shows, the molecules of methane and methanol contain carbon C, and combustion of these fuels produce CO₂. However, as they are considered “bridge fuels” to zero-carbon fuels, the amount of CO₂ produced (per calorific value) compared to marine gas oil (MGO) or heavy fuel oil (HFO) is reduced by about -25 % for methane and -10 % for methanol.

To achieve further CO₂ reductions from LNG- and methanol-fueled vessels, the carbon-neutral methane and methanol mentioned above need to be mixed with those fuels. Fig. 2 shows an example of the carbon-neutral methane production route¹⁾, where synthetic methane is made from green hydrogen and CO₂ captured at power plants, steel mills, etc. If this means that CO₂ has been emitted on the land side, the methane synthesized by recycling the captured CO₂ would be defined as carbon neutral. Green methanol can also be made from this methane.

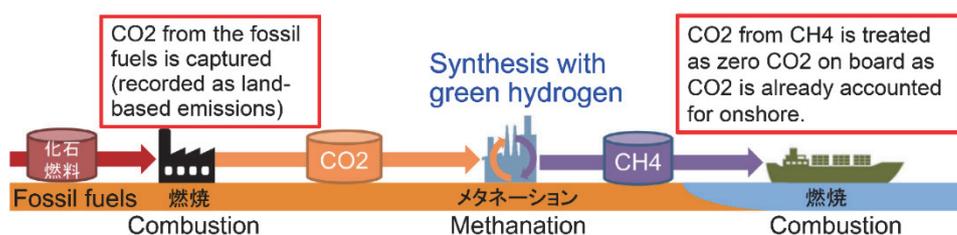
On the other hand, ammonia and hydrogen do not contain C and therefore do not produce CO₂, but marine engines that use them are still under development. This paper also introduces the development status of ammonia and hydrogen engines funded by the Green Innovation (GI) Fund of Japan’s New Energy and Industrial Technology Development Organization (NEDO).



(*) The term ‘Synthetic’ refers to that recycled CO₂ and H₂ derived from renewable energy sources are utilized.

Fig. 1 Classification of alternative fuels
(Source: The Japan Association of Marine Safety)

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Fig. 2 Example of carbon-neutral methane production route¹⁾Table 1 Properties of zero-emission fuels for onboard liquid storage (extracted from MLIT website¹⁾)

	Hydrogen H ₂ (LH ₂)	Ammonia NH ₃	Carbon recycled (CR) synthetic methane CH ₄	CR synthetic methanol CH ₃ OH	Biodiesel (FAME)
Lower Calorific Value (GJ/t)	120.0	18.8	50.0	19.9	37.1
Liquid density (t/m ³)	0.0708	0.7	0.422	0.79	0.885
Volume ratio per calorific value (VLSFO ratio @ liquefied)	4.42	2.86	1.78	2.39	1.14
Boiling point (°C) at P atm.	-253	-33	-161	65	345~354
Storage method on board (liquid state)	Vacuum heat shielded tank	Type C (low temp. or pressurized) Independent square tank / Membrane	Type C (low temp. or pressurized) Independent square tank / Membrane	Tank with hull, normal temp. and press.	Tank with hull, normal temp. and press.
Properties stored on board (liquid state)	abt.-250 °C, 0.5 MPa	-30~-10 °C, 0.07~0.5 MPa	-160~-140 °C, 0.07~0.5 MPa	Normal temp. and press.	Normal temp. and press.

Table 2 Properties of alternative fuels (ClassNK)

	State at fueling to engine						
	Liq. or Gas (3) NH ₃	Gas (4) CH ₄	Liq. (Standard)	Liq. (2) CH ₃ OH	(Liq. (LPG)) (C ₃ H ₈)	Gas (5) H ₂	
	Ammonia	Methane	HFO	Methanol	Propane	Hydrogen	
Gas specific gravity kg/m ³ @ boiling point	0.876	1.820		1.206	2.385	1.340	
Gas specific gravity kg/m ³ @ 20°C	0.707	0.659		---	1.840	0.083	
Liquid gravity kg/m ³ @ 4°C	633.1	---	989 @15°C	805.9	523.2	---	
Liquid gravity kg/m ³ @ boiling point	682.3	422.5		748.7	580.8	70.8	
Boiling point °C @ atmospheric pressure	-33	-161	---	65	-42	-253	
Saturated vapor pressure barA @ 45 °C	17.8	---	---	---	15.3	---	
Self-ignition temperature °C	630	537	250	385	450	585	
Flash point °C	---	-175	>60	12	-105	---	
Lower flammable limit (fuel vol.%)	15	5.3	1	6	1.7	4	
Upper flammable limit (fuel vol.%)	30	17	7	36.5	10.9	75	
Minimum ignition energy mJ	45	0.274	0.24 (ガソリン)	0.174	0.240	0.017	
Combustion speed cm/s	7	37	30 (ガソリン)	48	47	270	
Lower calorific value MJ/kg	18.8	48.0	40.2	19.9	46.3	119.9	

The properties of the five fuels are shown in Table 1, which is cited from the website of the GHG Zero Emissions Project¹⁾ of the Ministry of Land, Infrastructure, Transport and Tourism (MLIT). This is a selection of items relating specifically to liquid storage on board (tank capacity and type). Each tank capacity is determined by the calorific value per volume of liquid. The

current tank type and storage conditions are set as shown in the table according to the boiling point under atmospheric pressure.

The alternative fuel properties table published by ClassNK is shown as Table 2. This table is used as a basis for this paper. Explanations will be given in the following order: (1) biofuels, (2) methanol, (3) ammonia, (4) methane, (5) hydrogen. The paper refers to ignition and combustion characteristics of these fuels in marine engines, and discusses the harmful exhaust components from (3) ammonia.

(1) Biofuels, (2) methanol and (3) ammonia can maintain a liquid phase in the line from the tank to the engine, enabling diesel injection into the cylinder. (3) Ammonia becomes a gas at room temperature if not pressurized, and can also be supplied to the intake pipe of the four-stroke cycle engine that realizes Otto cycle premixed combustion.

On the other hand, (4) methane and (5) hydrogen are liquefied at very low temperatures in the tank, but are supplied as a gas phase to the engine. Diesel cycle or Otto cycle type engine can be applied with these two fuels. The characteristics of the two types of engines in combustion of natural gas will be reviewed later. Both types are also applicable for hydrogen combustion and are being developed with support from the GI Fund mentioned above.

2. COMBUSTION OF BIOFUEL (FAME)

Types of biofuels include (1) crude biofuels such as palm oil and rapeseed oil, (2) fatty acid methyl esters (FAME), which are converted from crude biofuels to reduce viscosity to the level of marine diesel oil (MDO), (3) HVO (Hydrotreated Vegetable Oil), paraffinic hydrocarbons that are further hydrotreated so that their characteristics are no different from those of mineral oils and (4) bio-methanol and bio-ethanol.

Since HVO is a high-grade fuel that is also used for aircraft and is not expected to be diverted to ships, this section focuses on FAME. In general, FAME is not inferior to MDO in density and viscosity, or in self-ignition and combustion characteristics.

The calorific value of FAME is lower than that of heavy fuel oil (HFO) due to the presence of about 10 % oxygen in the fuel molecule. As shown in Table 1, the calorific value of FAME is around 37 (GJ/t) compared to that of HFO, which is normally 40 to 42 (GJ/t). However, this is hardly a problem when FAME is mixed with HFO (for example, B30 (30 % FAME + 70 % HFO)).

FAME has one problem, in that NO_x increases by 10 to 20 % compared to MDO. However, a clear decision on this has already been made in MEPC 78 and this means that the increase in NO_x due to biofuel mixing is no longer subject to regulation. This makes FAME a true “drop-in” fuel that can be used in marine diesel engines without adjustment.

For this reason, there is likely to be greater demand from shippers, but production volume is recognized as a challenge. There is global resistance to using food as fuel, and although FAME is now made from waste cooking oil and other raw materials, the amount is limited, and there are also concerns about competition with the aviation industry.

In terms of the handling of crude biofuels and FAME, some points such as the development of microbials require attention and long-term storage is prohibited. The Machinery Department of ClassNK has provided explanations on these points. (https://www.classnk.or.jp/hp/ja/info_service/bio/). The Maritime Bureau of MLIT also published Guidelines for the Handling of Biofuels on Ships in March 2023, and a member of the Research Institute of ClassNK is contributing to this effort (<https://www.mlit.go.jp/report/press/content/001597437.pdf>).

3. METHANOL COMBUSTION

The author conducted a visualization analysis of methanol spray combustion prior to the development of MAN's low-speed two-stroke methanol engine (2015)²⁾. The properties of methanol (CH₃OH) and heavy fuel oil (HFO) are compared in Table 2.

Methanol has a boiling point of 65 °C at atmospheric pressure and is a liquid at room temperature, which means that high-pressure liquid injection as in conventional diesel engines is possible. However, half of its molecular weight consists of oxygen, and its calorific value per mass is less than half that of HFO. Therefore, when using methanol, about 2.4 times the volume, equal to twice the mass of HFO, must be injected to obtain the same power output.

This paper demonstrates that methanol shows good combustion characteristics despite its lower calorific value. As the self-ignition temperature is higher than that of HFO (Table 2), ignition of methanol spray requires pilot injection of diesel fuel. However, once ignited, it exhibits excellent combustion characteristics, as described below. The same point, i.e., it is necessary to distinguish between self-ignitability and combustibility, also applies to methane and hydrogen.

Fig. 3 shows an apparatus that can visualize the combustion of a single spray in high-pressure, high-temperature air like that in a diesel engine²⁾. The spray flames of gas oil and methanol were photographed using this apparatus. The injection pressure patterns of both fuels are also shown in the figure. The color photograph at the top right is a direct photographic image, showing that the gas oil spray is burning emitting a luminous color. In the case of methanol, only the pilot gas oil at the tip of the spray has a luminous flame, and the methanol flame itself, which follows the pilot flame, is non-luminous and invisible by the direct photographic technique. The left shows an image of the same flame taken by shadowgraph, in which the methanol non-luminous flame is captured in black.

A luminous flame of gas oil gives the impression of good combustion, but in fact the opposite is true: The luminous flame is the emission from particles of soot as it is formed in the flame. In other words, the non-luminous flame of methanol indicates good combustion with less soot formation. No black carbon is emitted from actual methanol engines. It is also clear from the comparison of the heat release rates in the figure that methanol has faster combustion after the end of fuel injection, as the after-burning of methanol is shorter.

Data from the prototype engine (500 mm bore: 7S50ME-B9.3-LGI) tested at Mitsui Engineering & Shipbuilding in 2015³⁾ has shown similar or slightly better thermal efficiency than that by MDO and a reduction of about -30 % in NO_x. A major advantage of using methanol is that engines of this type have already been developed and are in service. However, the challenge is the availability of carbon-neutral (green or bio-) methanol. Maersk, the largest container shipping company, which has sparked the development of methanol-fueled ships, is also reportedly making efforts to procure such methanol⁴⁾.

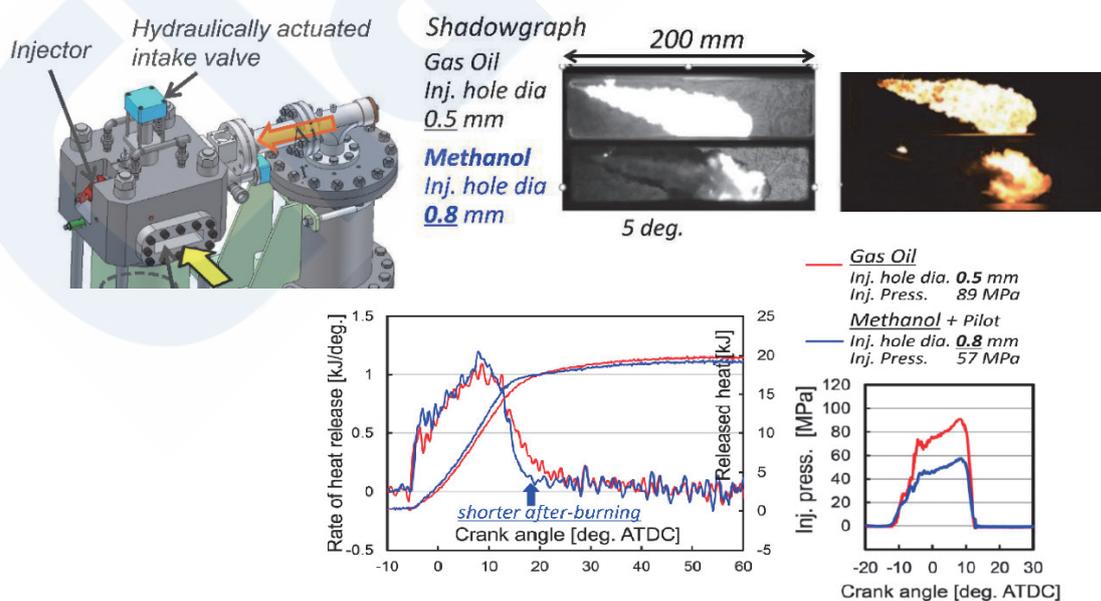


Fig. 3 Results of methanol spray combustion analysis (top left: combustion visualization apparatus (RCM), top right: spray flame of gas oil and methanol, bottom: heat release rates of two fuels).

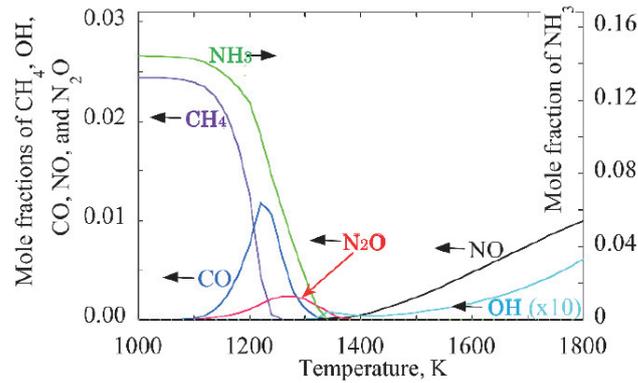


Fig. 5 Temperature range for formation of toxic exhaust components, including N₂O⁵⁾

Fig. 5 shows the result of a study by Prof. Kobayashi et al. at Tohoku University on the formation temperatures of toxic exhaust components, including N₂O⁵⁾. The figure shows that the temperature range at which N₂O is formed in the flame (about 1 300 K) is considerably lower than the normal range of the flame temperature where NO is formed. Unburnt ammonia also increases significantly at such lower temperatures.

To suppress N₂O formation, it seems important to avoid making conditions where combustion of the ammonia spray becomes inactive and the flame temperature drops. The following introduces the technology of stratified injection of diesel fuel oil and ammonia, which is being researched as a countermeasure jointly by the National Maritime Research Institute, Japan (NMRI) and Japan Engine Corporation.

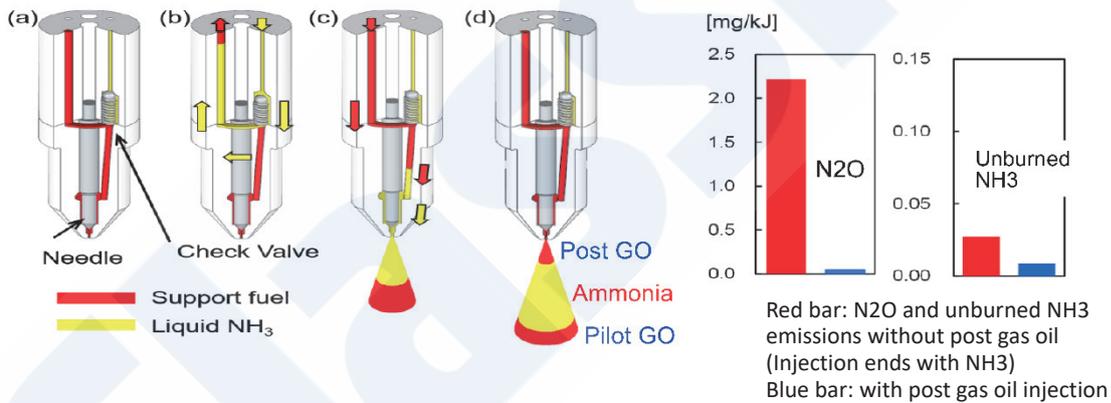


Fig. 6 Mechanism of stratified gas oil (GO) & ammonia injection system (left) and emission data from fundamental study by NMRI⁶⁾ (right)

As shown in (d) on the left in Fig. 6, a small amount of gas oil is injected before and after ammonia injection. The first layer of gas oil acts as a pilot flame to ignite the ammonia, while the third (last) layer of gas oil acts as a post-fuel to activate ammonia spray combustion at the end of the combustion phase, keeping the flame hot and reducing N₂O⁶⁾.

NMRI has clarified the effect of post-injection on exhaust components by experiments using a combustion chamber simulating the inside of a diesel cylinder. The right side of Fig. 6 shows an example of the experimental results, where the N₂O and unburnt NH₃ emissions shown in red indicate the case without post-injection, which ends with ammonia combustion, and the emissions in blue indicate the case with post-injection. Post gas oil injection shows a dramatic effect in reducing N₂O, and unburnt NH₃ is also drastically reduced by post-injection. This system will be applied to a single-cylinder test engine of Japan Engine Corp. this year.

5. REVIEW OF NATURAL GAS (METHANE) COMBUSTION FOR HYDROGEN STUDY

Similar to natural gas engines, diesel cycle and Otto cycle combustion are also possible with hydrogen engines, which will be discussed below. Both types of combustion are reviewed in this section with natural gas. Currently, orders for LNG-fueled ships are increasing, and MAN's low-speed two-stroke diesel cycle engine is used as the main engine of K-Line's first car carrier, while WinGD's Otto cycle type is used as one of NYK's first vessel.

Fig. 7 shows the differences between the operation and combustion patterns of these two types of natural gas engines. The diesel cycle type shown as (A) in the figure is similar to a diesel engine, in which the piston compresses only air and then a pilot fuel and high-pressure (30 MPa) natural gas are injected. This is also known as the high-pressure type. For the Otto cycle type shown as (B) in the figure, natural gas with a pressure of about 1 MPa is supplied to the cylinder before compression by the piston starts, forming a mixture with air. The mixture is ignited by the pilot fuel after being compressed by the piston, and the flame spreads through the mixture (flame propagation). This is also called the low-pressure type because the supply gas pressure is much lower than in the former.

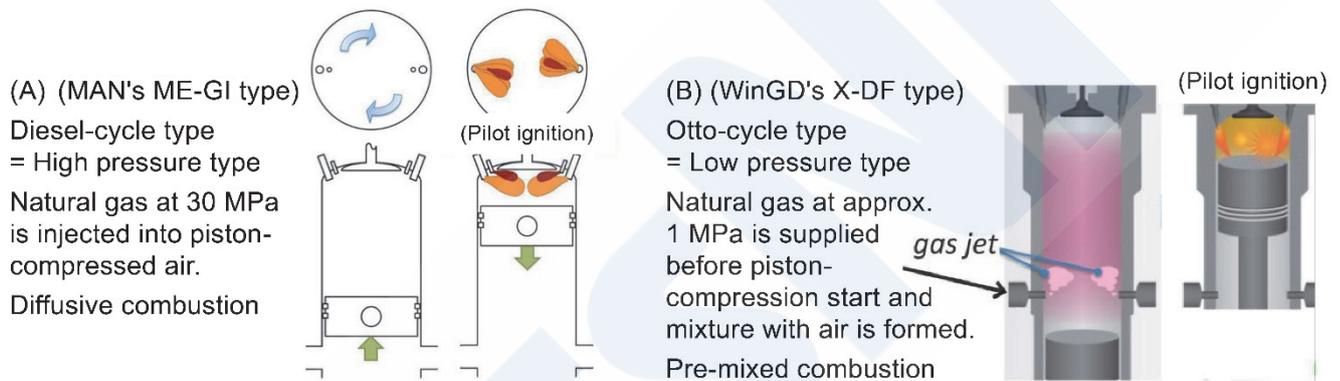


Fig. 7 Two operating patterns for low-speed two-stroke natural gas engines

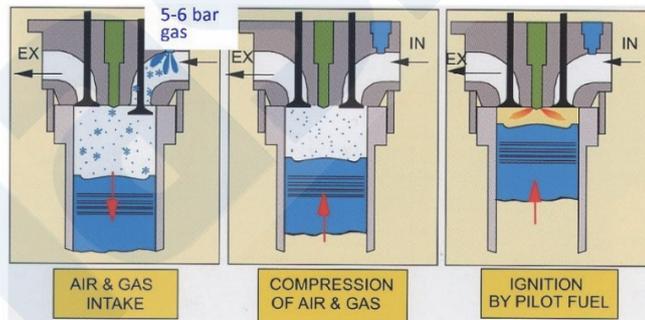


Fig. 8 Formation of air-gas mixture in medium- and high-speed 4-stroke natural gas engines (Otto cycle type)
(In 4-stroke hydrogen engines, hydrogen is supplied at the same position as above.)

So far, all medium- and high-speed four-stroke natural gas engines are of the Otto cycle type. As shown in Fig. 8, natural gas is supplied to the intake pipe to form a mixture with air. The hydrogen-fueled four-stroke engines described below are similar, with a hydrogen supply nozzle at the same position in the intake pipe. In practice, because the hydrogen engines are being developed on the base of natural gas engines, both hydrogen and natural gas nozzles are fitted, and an approach in which the amount of hydrogen is increased while that of natural gas is decreased is adopted.

Knocking and pre-ignition are concerns in Otto cycle type combustion. These problems are caused by the activity of the mixture. Pre-ignition is a phenomenon where, for example, the cylinder lubricating oil ignites the mixture during the compression stroke, as shown in Fig. 9. If pre-ignition occurs, the cycle fluctuations in cylinder pressure become extreme. The aforementioned X-DF solves this problem by applying EGR (Exhaust Gas Recirculation) to reduce the activity of the mixture.

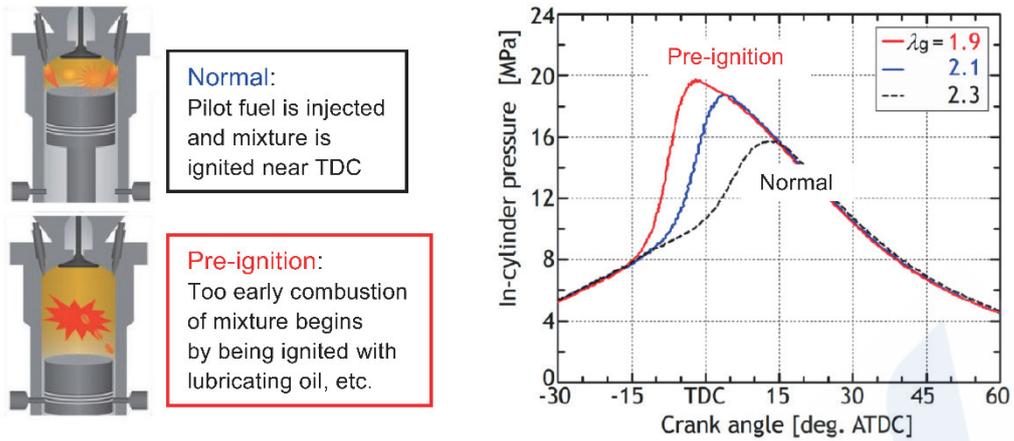


Fig. 9 Mechanism of pre-ignition (left) and cylinder pressure rise by pre-ignition of natural gas mixture (right) (In actual engines, random occurrence of pre-ignition leads to excessive cycle fluctuations.)

Hydrogen mixtures are even more active than methane (natural gas) mixtures. This means that the low minimum ignition energy and wide upper and lower flammable limits (fuel vol.% of the flammable range) of hydrogen in Table 2 should be noted. Even before the mixture is fully formed, the possibility of pre-ignition by lubricating oil particles or residual gases in the cylinder is increased.

Fig. 10 provides an overview of the aforementioned Green Innovation Fund project to develop marine hydrogen engines. In the development of medium- to high-speed four-stroke Otto cycle type hydrogen engines by KHI and YANMAR Co., Ltd. in the project, pre-ignition and knocking are suppressed applying not only EGR but also a leaner mixture than in the case of natural gas.

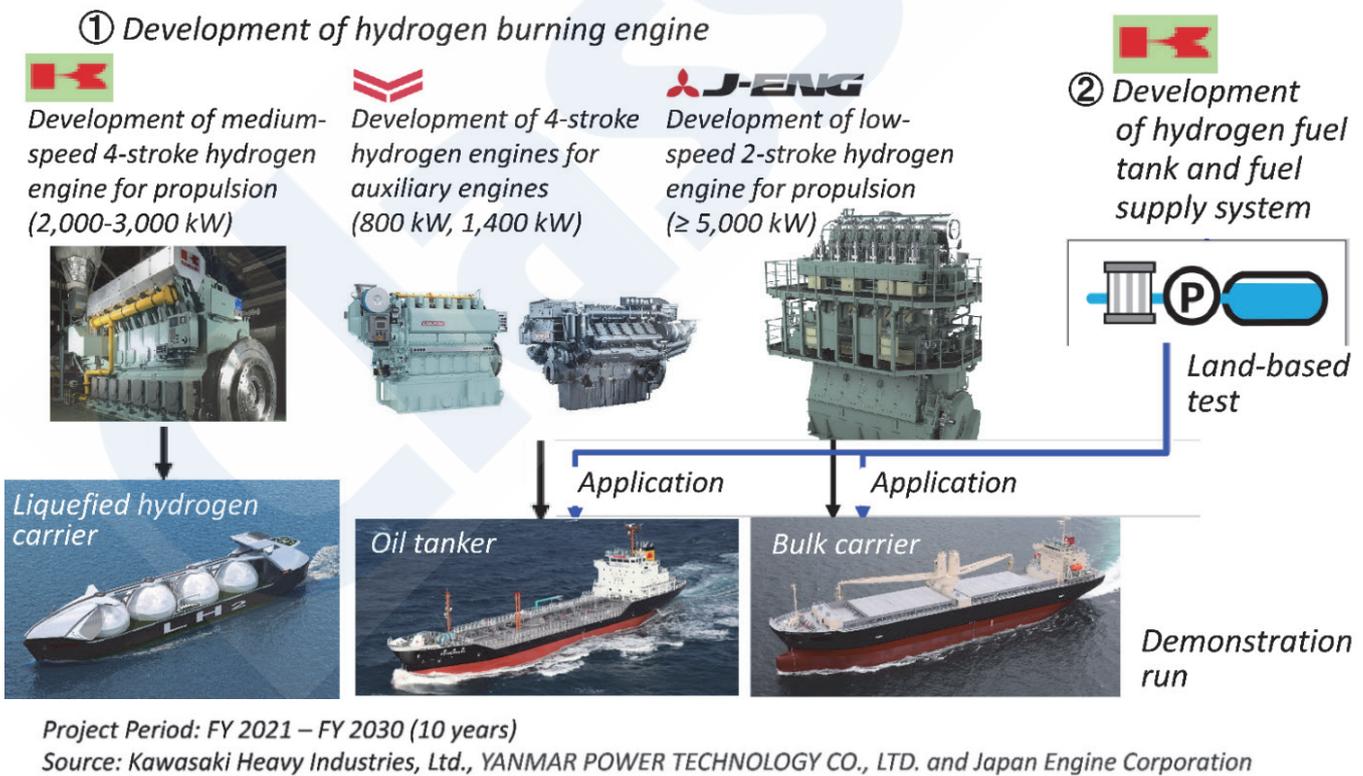


Fig. 10 Green Innovation Fund project, Development of marine hydrogen engines and MHFS (Marine Hydrogen Fuel System) (MLIT website: <https://www.mlit.go.jp/maritime/content/001484436.pdf>)

6. COMBUSTION IN DIESEL CYCLE HYDROGEN ENGINE

In the project to develop marine hydrogen engines (Fig. 10), the diesel cycle was adopted in Japan Engine Corp.'s low-speed, two-stroke engine. This section presents the author's previous research on a diesel cycle type hydrogen engine, which has not been studied as much as the Otto cycle type. Based on the ratio of the molecular weights of hydrogen and methane (2 :16), the density of hydrogen is 1/8 that of methane. Table 2 shows that the calorific value per mass of hydrogen is 2.5 times that of methane, but when considered per volume of gas, a volume about three times larger than that of methane must be injected to obtain the same heat. However, in high-pressure injection, where the initial speed of injection is the sonic velocity, a sufficient volume of hydrogen can be injected at the same gas pressure without extremely enlarging the injection hole because the sonic velocity of hydrogen is about three times faster than that of methane.

The combustion of a hydrogen jet injected at high pressure was visualized by shadowgraphs using the apparatus shown in Fig. 3. As the self-ignition temperature of hydrogen is high, as shown in Table 2, it is ignited with pilot gas oil (5 % heat) in the first stage. The ignition image is shown in Fig. 11(a). The white flame is produced by the pilot gas oil, while the ignited hydrogen flame appears black as a non-luminous flame.

On the other hand, Fig. 11(b) shows the result of an attempt to self-ignite the hydrogen jet by raising the air temperature to higher than normal (estimated to be around 700 °C, although this has not been measured). From this photograph, it appears that the hydrogen jet self-ignites in the second frame (5.5°), after which the flame front penetrates in proportion to the square root of the elapsed time based on the momentum theory, like a normal diesel spray flame.

Fig. 11(c) compares the heat release rates of high-pressure jets of hydrogen and methane. Both are ignited by pilot gas oil. Both fuels are injected at the same pressure (30 MPa) and at the approximately the same timing, and both show an almost constant heat release rate in line with the injection rate. However, it can be seen that the hydrogen burns up earlier after the end of injection. In principle, the diesel cycle type does not suffer from pre-ignition and knocking like that in the Otto cycle type. Furthermore, the combustion rate can be controlled primarily by the fuel injection rate, which is an advantage over the Otto cycle type.

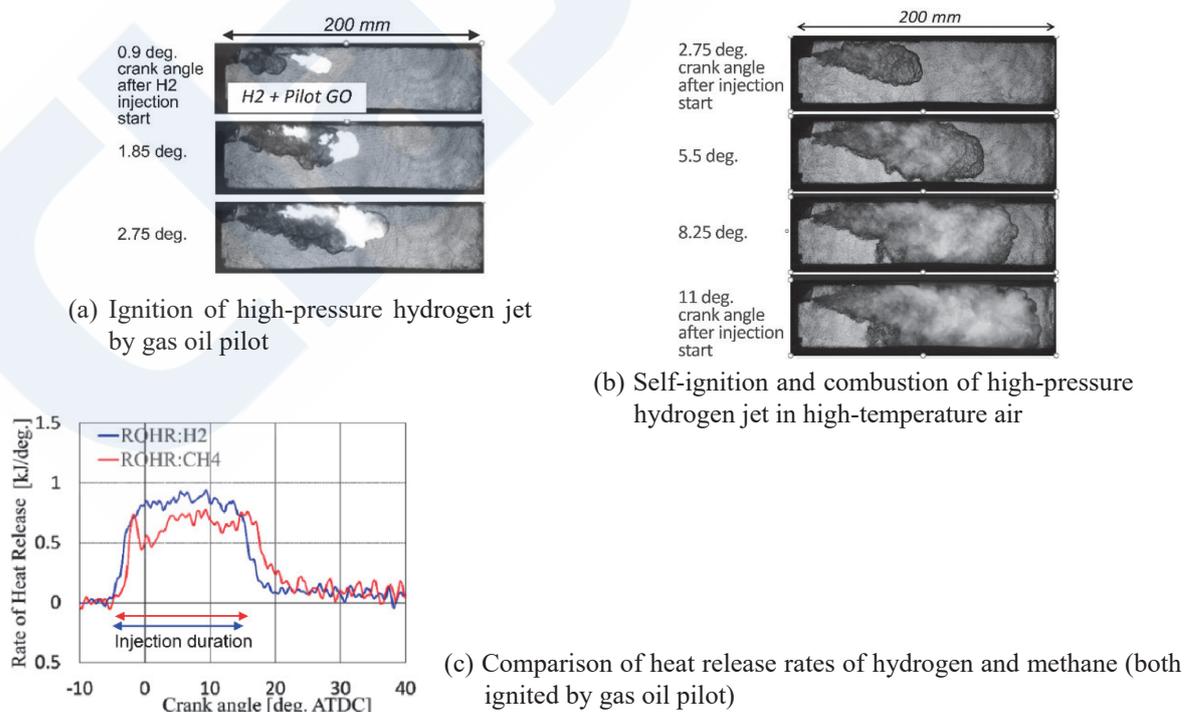


Fig. 11 Combustion analysis of high-pressure hydrogen jet (30 MPa hydrogen jet into 8 MPa air)

7. CONCLUSION

Which of the fuels introduced above is the most realistic future marine fuel? At this moment, they are expected to coexist in the world based on the following advantages and disadvantages.

- Biofuels are “drop-in” fuels and have no combustion problems, but the quantity of raw materials is the main issue.
- The same applies to carbon-neutral methanol, which requires a pilot fuel for ignition but has good combustion characteristics. The development of methanol engines has already been completed. However, as far as building a global supply chain for carbon-neutral methanol which would only be used as a marine fuel, one challenge is how much supply and demand will emerge compared to hydrogen and ammonia, which are also used on land.
- N₂O-related challenges are anticipated in the case of ammonia combustion, but the results of the forthcoming engine running tests are waited for further research and development.
- The development of hydrogen engines is progressing well, supported by the existing technology of natural gas engines.

As the above-mentioned zero-carbon or carbon-neutral fuels will be several times more expensive than heavy fuel oil, subsidies and other measures will be needed in order to achieve widespread use. In this regard, Japan has proposed a “Feebate” mechanism to the IMO MEPC as an economic approach.

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