Standardization of dimethyl ether (DME) fuel specifications

Mitsuharu OGUMA

[Translation from *Synthesiology*, Vol.10, No.1, p.11–23 (2017)]

Legislation and standardization are necessary and important for fuel quality control to ensure safety, security, and stability with regard to the commercialization and trading of new fuels. The author began R&D of dimethyl ether (DME) fuel utilization technology in 2001. This work involved basic research on fuel spray and combustion, applied research on the development of test vehicles, and field tests of these applications. In addition, work on standardizing DME fuel specifications commenced in 2007. In 2015, five ISO standards were published. In this paper, the standardization of DME fuel is presented, which includes a way to define limits on impurities, and the results of round-robin-tests for deterioration by impurities from the users' viewpoint.

Keywords : Dimethyl ether, DME, fuel specification, standardization, impurity

1 Introduction

Internal combustion engines are to remain the powertrain of trucks and buses for a while, as it is impossible under the present circumstances to convert them to electric vehicles. Although the rise in oil prices has stabilized, energy security is an urgent issue, and we must continue to pursue resource diversification including unused resources while keeping in mind the effect of greenhouse gas emissions.

Dimethyl ether (DME, chemical equation CH_3-O-CH_3) is a clean fuel that emits almost no particulate matter (PM) during combustion since it contains oxygen without a carbon-carbon bond. Similar to liquefied petroleum gas (LPG), this gas becomes liquid at pressurization of about 6.1 kgf/cm^2, and the cetane number is equal or higher than that of diesel fuel. When used as fuel for diesel engines, it requires no PM countermeasures, and therefore, the nitrogen oxide (NOx) reduction measure can be applied effectively by reducing the combustion temperature. Hence, it can clear the strict emission regulations without employing the advanced emission reducing catalyst system. If the synthetic gas (CO, H_2) can be obtained, it will not be necessary to rely on specific raw materials, and it can be manufactured using various raw materials including coal, oil sand, natural gas, shale gas, biomass, and others. Other than as fuel for diesel engines, it is usable as a hydrogen carrier in addition to household uses in boilers and gas turbines as alternative to LPG and city gas. The main catch copy for DME is that it is a multi-source and multi-use fuel. Currently, DME is manufactured using coal and natural gas as raw materials, but if the technology is established for manufacturing the fuel via synthetic gas from woody biomass using lumber from thinning and black liquor from paper mills and if such technology becomes economically feasible, the potential for greenhouse gas reduction in well-to-tank (from the excavation of primary energy to the filling of fuel tanks) is large, and its expectation is high as the next-generation biodiesel fuel.

In introducing the new fuel to the market, standardization of fuel quality is mandatory. As the international distribution of DME fuel including household use became highly conceivable, from 2007, DME became a subject in SC4 and SC5 of the ISO/TC28 (the technical committees for LNG and LPG). For the SC5 that discusses the sampling and measurement methods for international distribution, Japan was the secretariat (secretary: Nippon Kaiji Kentei Kyokai). For the SC4 in charge of DME quality, the secretariat was France (secretary TOTAL). Under the French secretariat, the DME quality standard was organized jointly with Japan, which was the only country in 2007 that had already defined the DME quality as industrial and power generation fuel (TS K0011, published November 2005). Japan actively dispatched experts to the ISO/TC28/SC4/WG13 [Classification and specifications of commercial dimethyl ether (DME)], WG14 [Joint project with TC28 on "Test methods for dimethyl ether (DME)"], SC5/WG3 (Procedures for measurement and calculation of refrigerated fluids), and WG4 (Sampling of refrigerated fluids). The author participated as an expert in these working groups. In July 2011, the author was appointed as convener of SC4/WG13 following the retirement of the French convener.

The discussion of DME fuel quality at the WG13 started with at which point the quality should be defined. Figure 1 shows the image of manufacturing, distribution, and use in various machines for the DME fuel. Finally, it was determined at the WG13 that the fuel quality should be defined for the base

Research Institute for Energy Conservation, AIST Tsukuba East, 1-2-1 Namiki, Tsukuba 305-8564, Japan
E-mail: mitsu.oguma@aist.go.jp

Original manuscript received November 12, 2016, Revisions received December 8, 2016, Accepted December 16, 2016

fuel immediately before shipment to the end user as fuel for household, industrial, and automobile use, after being shipped from the manufacturing plant and transported by tankers to primary and secondary stations. It is necessary to add lubricity improvers (LI) to automobile fuel, and in some countries, the addition of an odorant is required to enable detection of fuel gas leakage in household use. Since there are variations in country policies concerning additives, it was excluded from the definition of DME fuel quality in the WG13.

In this paper, we present the effects of impurities, the definition of contamination limit, the round-robin result of impurity analysis method, and the verification test data, that were studied from the standpoint of the fuel utilization system in the standardization of DME fuel quality.

2 Investigation of impurity contamination limit in DME fuel quality

The definition of fuel quality depends largely on compromises, including economic feasibility, of how the manufacturing side can make fuel of certain quality and what the user side demands in fuel quality for use in its system. Although DME is a multi-use fuel, when considering how much inclusion of contamination in the fuel can be tolerated from the standpoint of the utilization systems, it is necessary to correspond to the most sensitive utilization system in which the fuel will be used. Therefore, upon participating in the discussion of impurity contamination limit for DME fuel in the WG13 as an expert, the author started the experimental evaluation of the effect of impurity contamination when DME was used as fuel for diesel engines.

Figure 2 shows the points that were investigated when defining the DME fuel quality used as fuel for automobile

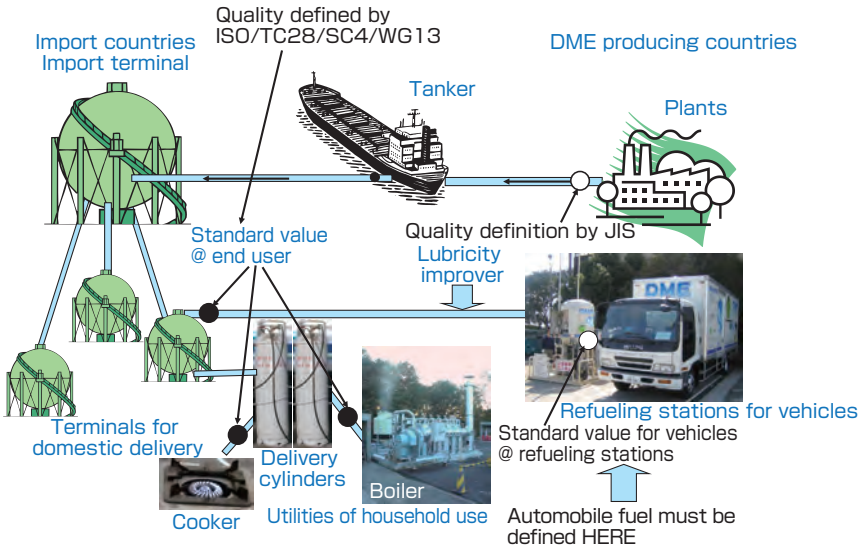

Fig. 1 The point at which DME fuel quality is defined

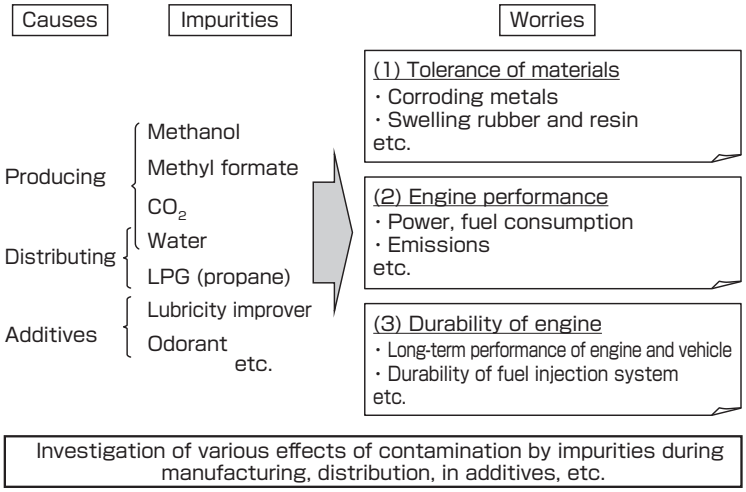

Fig. 2 Substances that may become contaminants in automobile DME fuel standardization and the concerns caused by such substances

Table 1. Test pieces for immersion test

Test materials		Test piece size	Parts*
Rubber	Modified HNBR	- Dumbbells #3 (JIS K 6251) - O-ring (P-12)	IP FT
	FFKM	- Dumbbells #3 (JIS K 6251) - O-ring (P-6)	
Metals	SG steel plate	15x15x3.2 mm with ϕ3.5 hole	FT
	Copper (C1100)	15x15x2.0 mm with ϕ3.5 hole	IP
	Brass (C3604)	15x15x2.0 mm with ϕ3.5 hole	IP
	Injector nozzle needle	-	EG
	Injector nozzle body	-	EG

*IP: Injection pump, FT: Fuel tank, EG: Engine

diesel engines. The effects that were investigated for the additives and others that could be used in automobiles and the impurities that might be introduced in the fuel manufacturing or distribution processes include the following: (1) tolerance of materials, (2) engine performance, and (3) durability of the engine systems. The verification test conducted for each points and the outline of results will be explained by presenting some data.

2.1 Effects of impurities and additives on the tolerance of materials [1]

The evaluation of effects of the impurities on the tolerance of device materials was conducted by immersion tests, where the actual materials were immersed in the DME fuel and then evaluated. The rubber and metal materials used as subjects were selected from the ones actually used in DME vehicles (Table 1).

The immersion conditions are shown in Table 2. The test pieces were immersed in pressure-tight containers, left for 1,000 h in a 80 ºC condition, and the conditions of test pieces were checked. To observe the progression, conditions at 72 h, 250 h, and 500 h were also checked. The base test fuel was DME (purity 99.9 % or higher) that is commercially distributed as a chemical product (for propellant use), and this was mixed with impurities discussed in ISO at certain mass ratio and considered as fuel DME. To obtain lubricity essential for automobile fuel, in one sample, 100 ppm of commercially available fatty acid based lubricity improver (LI) for low-sulfur diesel fuel was added, and in another sample, an excessive amount was added to raise the acid number to 0.13 mgKOH/g for the whole fuel, or until the quality standard of diesel oil mixed with 5 % biodiesel fuel (diesel fuel defined by laws concerning quality control of gasoline and other oils) was surpassed. By comparing these two, the effects of impurities and fatty acid based additives

Table 2. Test condition

Temperature [ºC]	80
Tset duration [hr.]	70, 250, 500, 1000
Test fuels	- Pure DME - Fuel DME* - Fuel DME with LI** 100 ppm - Fuel DME with LI 700 ppm

*Fuel DME: pure DME
+500 ppm of methanol
+100 ppm of water
+1.0 % of propane
+500 ppm of formic acid
+around 2 ppm of sulfur
**LI: Fatty acid based lubricity improver

Table 3. Evaluation items

Test materials	Evaluation items
Rubber	- Changing ration of tensile strength, elongation, hardness, volume and weight - Figure - Compression set (for O-ring only)
Metals	Weight changing ratio, figure

were checked. After immersion at certain time intervals, measurements and observations were done for the points shown in Table 3.

(1) Effect on rubber materials

Tetrafluoroetylene-Perfluoroalkylvinylether fluoro-rubber (FFKM) and improved hydrogenated nitrile rubber (HNBR) are rubber materials used in fuel tanks and injection pumps. According to the immersion test using these materials, there were hardly any differences between pure DME and fuel DME (no Fig.). The effect of DME that swelled the rubber material was strong, and it is thought that the impurities would have almost no effect on the rubber material with anti-DME property. Also, the effect of LI was not seen. In comparison of FFKM and improved HNBR, while there were differences in mechanical properties between the two, this was the difference of rubber material properties against DME, and it was confirmed that there was no effect by impurities or LI.

(2) Effect on metal materials

From the results of the immersion tests for metal materials used in fuel tanks, there was no conspicuous change in appearance in any condition for SG steel plates, injector nozzle needles, and the body. All parts maintained good conditions (no Fig.).

On the other hand, discoloration due to oxidation reaction was seen (Figs. 3 and 4) for copper (C1100) and brass (C3604) that are parts for the injection pump. In copper C1100, the test piece lost luster and became slightly discolored in pure DME, and nearly black discoloration occurred in fuel DME. With the addition of LI, the black discoloration was clear, indicating transformation of the surface. In brass C3604, although not as apparent as C1100, a similar tendency was seen. Since the fatty acid LI was added, it is thought that the acid number of the fuel increased and discoloration occurred by oxidation reaction. There is a possibility of fuel leakage if the corrosion by oxidation progresses in copper that is

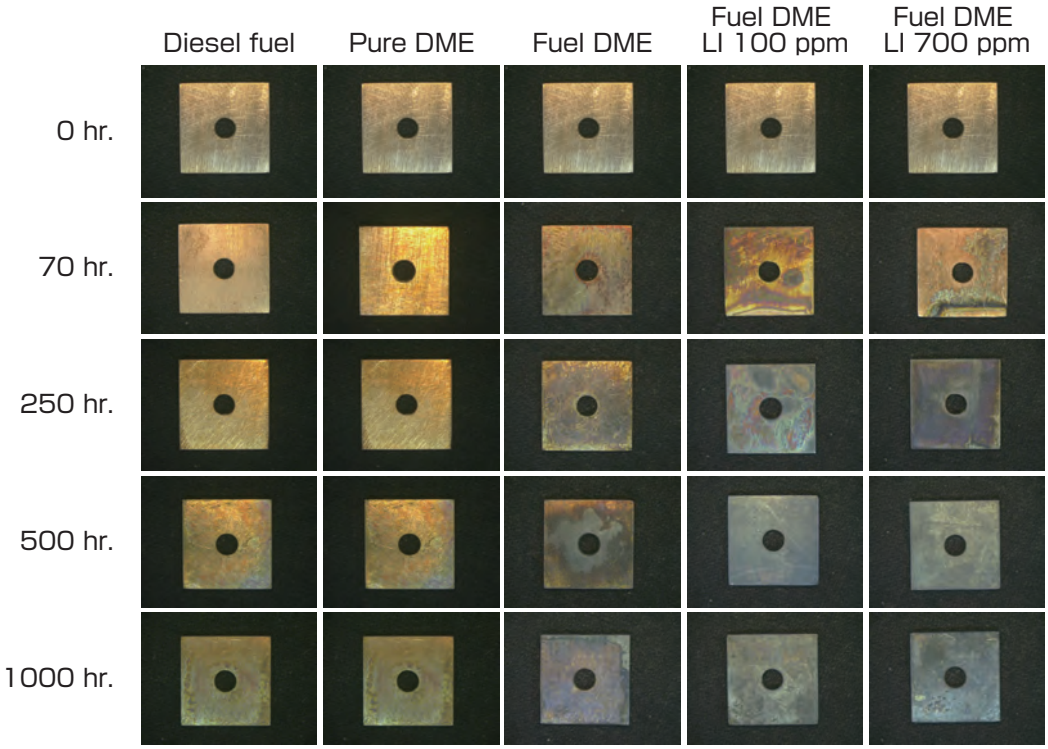

Fig. 3 Appearance of test piece after immersion test (Copper C1100)[1]

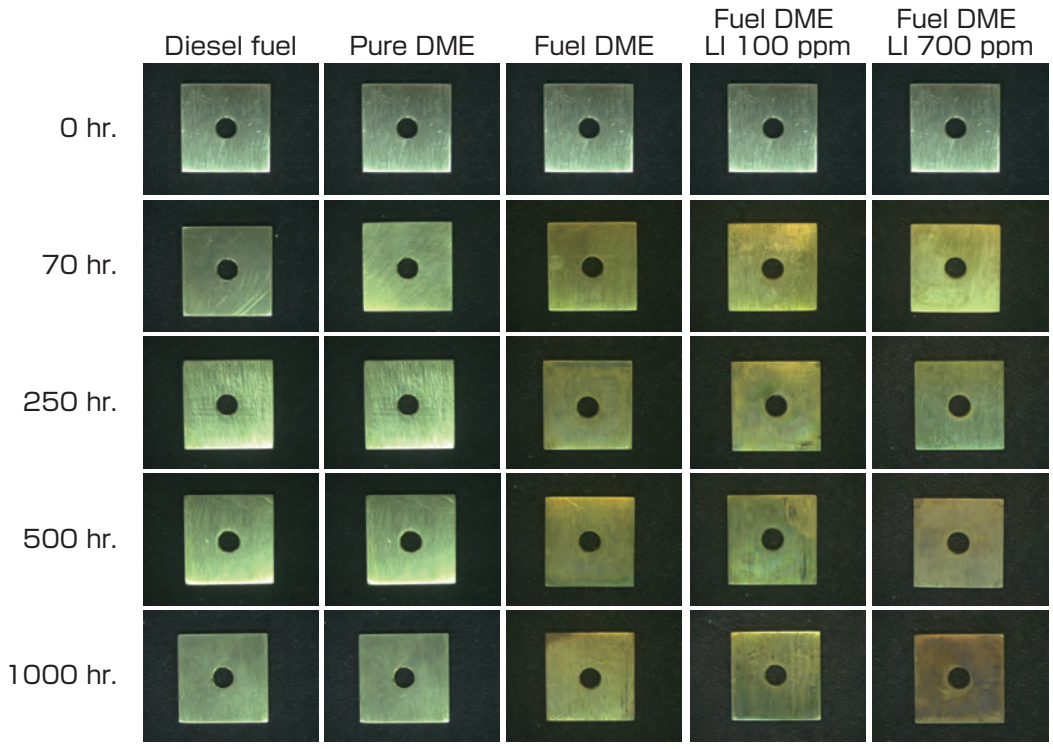

Fig. 4 Appearance of test piece after immersion test (brass C3604)[1]

Table 4. Test fuel (Effect of impurities)

Fuel name	Impurities	Lubricity improver (LI)
Reference DME	–	Fatty acid type 100 ppm
Methanol 5%	Methanol 5 %	Fatty acid type 100 ppm
Propane 5%	Non-odorant propane 5 %	Fatty acid type 100 ppm
FAME 5%	FAME 5 %	–
Water 5%	Water 5 %	Fatty acid type 100 ppm

Table 5. Test fuel (Effect of additives)

Fuel name	Impurities	Additives
Reference DME	–	LI (Fatty acid type 100 ppm)
LI 500	–	LI (Fatty acid type 500 ppm)
Pure fatty acid	–	LI (High concentration fatty acid type 100 ppm)
Odorant	–	Odorant 40 ppm (include sulfur content) LI (Fatty acid type 100 ppm)

used as a sealant for the fuel system, and care must be taken for the excessive addition of fatty acid LI. Also, fuel DME contains water of 100 ppm concentration and methyl formate of 500 ppm concentration, and it is indicated that there is a possibility that formic acid is produced from hydrolysis and increases the fuel acid number. This is thought to be one of the reasons that discoloration was seen only in fuel DME with LI additives. These test results did not show loss of weight in test pieces after the immersion test, but attention must be paid.

2.2 Effects of impurities and additives on engine performance[2][3]

Evaluations were conducted by partial load performance tests using engine dynamometer and JE05 mode tests.

The test fuel for the evaluation of impurity effect is shown in Table 4, and the test fuel for the evaluation of additive effect is shown in Table 5. For both tests, the main fuel was DME (purity of 99.9 % or higher) that is currently commercially distributed as a chemical product (for propellant use). The mixture of DME with about 100 ppm of commercially available fatty acid based LI for low-sulfur diesel fuel was used as the reference DME. The concentration of each impurity is the mass ratio of the total amount.

To investigate the effect of impurities, 5 % of the following impurities were added to the test fuel with 100 ppm of LI: methanol that may remain as residue in the DME manufacture process made by methanol dehydration; deodorized propane (no odorant additive) that may be introduced since LPG facilities may be used until the dedicated DME distribution network becomes available; water that may contaminate or be present as residue in the manufacturing and distribution processes; and fatty acid methylester (FAME, also widely called biodiesel fuel) that is reported to have functions as LI.[4] However, for FAME 5%, since there was data that lubricity becomes equivalent to diesel fuel by adding 3,000 ppm of FAME to DME,[5] no LI was added to FAME. Also, for FAME, commercially available mixed methyester was used as the model FAME. The possibility of water contamination in the market is most likely to occur as contamination by absorbed moisture in the connecting hose when the fuel is transferred between containers. Also, moisture adhesion may occur due to humidity in the filling port of vehicles and at the filling stations. DME fuel samples were taken from installed fuel tanks of medium duty DME trucks belonging to AIST and others, with which the field tests were conducted from 2004 to 2007. Moisture was measured in the fuel samples, and there were cases in which 177 ppm of water contamination was found.

To investigate the effect of additives, the following samples were evaluated: fuel with 500 ppm additive concentration of fatty acid based LI (Fuel name: LI500) used in reference DME (Fuel name: Reference DME); fuel that uses only the main ingredient fatty acid as LI (Fuel name: Pure fatty acid); and assuming that odorants are introduced as in LPG and city gas when it is used widely as fuel, fuel with 40 ppm of an LPG odorant (Fuel name: Odorant). The same LI as the Reference DME was also added to the fuel with an odorant additive.

The effects of the impurities in DME fuel and the additives to DME fuel on the engine performance and emission property were evaluated by engine tests. The tendencies are summarized in Fig. 5. The items shown in yellow and pink in the table indicate caution levels, and pink shows a higher degree of caution than yellow. The results showed that

caution was required for methanol during no-load operation where the active temperature of oxidizing catalysts had not been reached, for emissions from DME containing 5 % propane or water, and for PM number concentration by DME containing 5 % propane and 5 % FAME.

However, although the tendency was as shown in Fig. 5, it was confirmed that "the effect on the emission gas performance test results by mode operation was not that large even if DME containing 5 % impurities was accidentally used." That is, as factors that can define the purity and impurity contamination limit of DME as a fuel quality standard, rather than the effect on emission performance, there was greater effect on tolerance of engine part materials that came in contact with the DME fuel, such as fuel supply systems and fuel injection systems, as well as on the durability of the engine system and the vehicle system. Therefore, the contamination limit of impurities should be determined based on these factors.

2.3 Effects of impurities and additives on lubricity

The evaluation of the effect of impurities and additives in fuel on the durability of engine systems was substituted by the evaluation of fuel lubricity. For the lubricity evaluation of DME, multi-pressure/temperature high-frequency reciprocating rig (MPT-HFRR) adapted to liquefied gas was used.[6] This device achieved the same testing principle as the conventional HFRR device in a hermetically sealed container (Fig. 6). Table 6 shows the comparison of specs with the conventional HFRR device. The testing conditions were the same as the conditions for diesel fuel set by the Japan Petroleum Institute (JPI) standard,[7] and vapor pressure of DME at test temperature (60 ºC) was applied only to atmospheric pressure. The data management method used was that of the author *et al.*[8] in which the additional number of data was determined by the deviation from four measurements.

Please refer to a published report[8] for the relationship of the wear scar diameter (WS1.4) and the additive concentration of LI for DME with poor self-lubricity, the effect of water contamination on the wear scar diameter, and the effect of methanol contamination on the scar diameter. From these results, the following was confirmed: by adding about 100 ppm of commercially available fatty acid based LI for low-sulfur diesel fuel, the same wear scar diameter was obtained as when the commercially available diesel fuel was evaluated with the same device (that is, lubricity equal to diesel fuel was obtained); when the amount of ratio of water was increased with fixed 100 ppm concentration of the same LI, the wear scar diameter started to increase at water concentration of 300 ppm, and the scar diameter of diesel fuel was surpassed at about water concentration of 1,000 ppm (that is, lubricity equal to diesel fuel could not be achieved); and the contamination of methanol had no effect on the wear scar diameter (that is, lubricity).[8] In this paper, we add the evaluation result of the effect of coexisting methanol and water and fuel DME lubricity, and the effect of impurities on fuel lubricity is explained.

Warning index: □ << □

Impurities	Partial load constant mode test						JE05 mode test with oxidation catalyst
	Engine out			Catalyst out			
	Low → <Load> → High High → <λ> → Low			No Low → <Load> → High High → <λ> → Low			
Methanol	Formaldehyde, methanol: slight increase	THC, CO: slight increase		Formaldehyde, methanol: slight increase			
Propane	Formaldehyde: slight increase	THC: slight increase		Formaldehyde: slight increase			PM number concentration: increase
FAME		CO: increase HC: increase					CO, THC: slight increase PM number concentration: increase
Water	Ignition timing: delay THC, CO: increase Formaldehyde, Formic acid: increase			Ignition timing: delay THC, CO: increase Formaldehyde, Formic acid: increase			

Additives	Partial load constant mode test						JE05 mode test with oxidation catalyst
	Engine out			Catalyst out			
	Low → <Load> → High High → <λ> → Low			Low → <Load> → High High → <λ> → Low			
LI 500		THC (CH_4) increase			CH_4 slight increase		
Pure fatty acid							
Odorant			CO, THC increase				

Fig. 5 Summary of engine test for studying the effect of fuel property[1]

Table 6. Specification of MPT-HFRR compared to standard HFRR

	Unit	STD (JPI)	Standard HFRR*	MPT-HFRR
Fuel volume	cm^3	2±0.20	←	500
Stroke	μm	1000±30	20–2000	1000–5000
Frequency	Hz	50	10–200	10–50
Load	N	1.96 ±9.81×10^{-3}	0.98–9.8	←
Surface area of fuel bath	cm^2	6±1	←	113
Fuel temperature	˚C	60±2	ambient–150	max. 100
Pressure	MPa	ambient	←	max. 10
Test duration	min	75±0.1	←	←

*Manufactured by PCS Instruments

Figure 7 shows the change in the wear scar diameter when methanol of 500 ppm concentration is mixed in pure DME and then water of 5,000 ppm concentration is gradually added. The LI remained constant at 100 ppm for the whole fuel. Figure 8 is the enlargement of the 0–1000 ppm water mixing ratio of Fig. 7. As in the water-only case in the published report, the wear scar diameter started to increase around water of 300 ppm concentration, and the scar diameter surpassed that of diesel fuel at water of 1,000 ppm concentration or higher. From this result, it can be said that when methanol and water coexist, methanol does not enhance or inhibit the effect of increasing scar diameter caused by water contamination, and the decrease of lubricity is determined only by the mixing ratio of water. The mechanism of the decreased lubricity by water is because water has some kind of effect on the breakage of boundary lubricating film that is chemically absorbed to the metal surface. The assumed cause was that the melting point decreased as the boundary lubricating film that metallic soap returned to fatty acid and reached the transformation temperature, or water might have affected the decrease of the transformation temperature.

The white dots in Fig. 7 and 8 are wear scar diameters by fuel DME that was also used in the immersion test. There are two dots in concentration of 100 ppm and 300 ppm, and along with the sample adjusted to 300 ppm by adding water to fuel DME, there are two plots for each water inclusion ratio. While the wear scar diameter increase was not significantly changed by the contamination by other impurities, the effect of impurities was not small compared to others when the water mixture fraction was small.

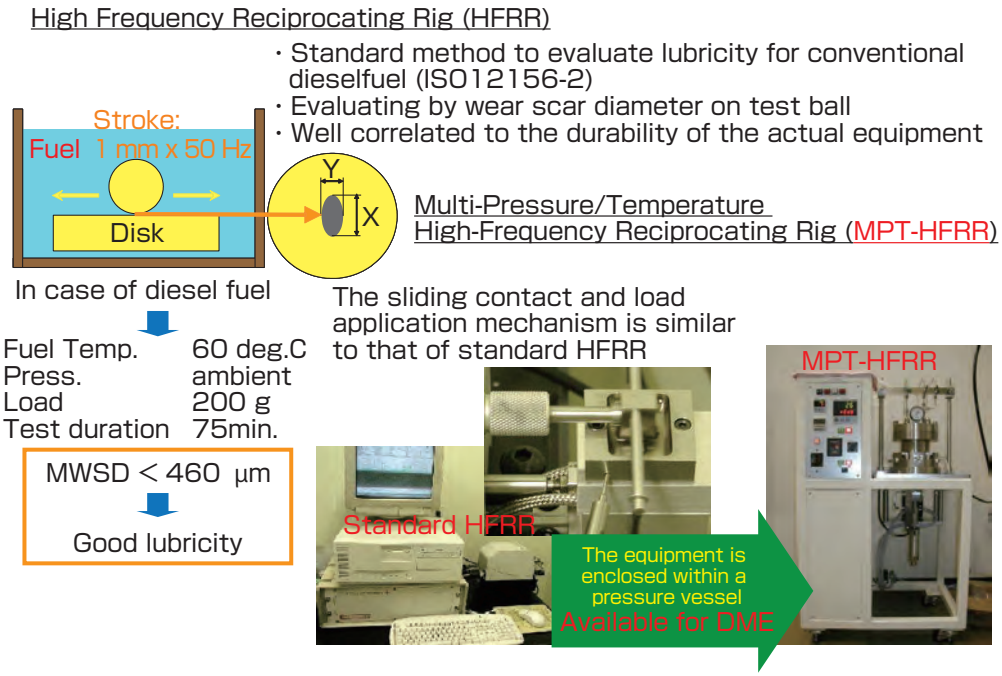

Fig. 6 Lubricity evaluation device and evaluation method

Table 7. Specification of ISO16861: 2015 (DME fuel quality) compared to ASTM D7901-14 (DME fuel quality)

Characteristic	Unit	Limit	ISO16861: 2015	ASTM D7901-14
Purity	mass %	min.	98.5	←
Methanol	mass %	max.	0.050	←
Water	mass %	max.	0.030	←
Hydrocarbons (up to C_4)	mass %	max.	1.00*	–
CO_2	mass %	max.	0.10	–
CO	mass %	max.	0.010	–
Methyl formate	mass %	max.	0.050	report
Ethyl methyl ether	mass %	max.	0.20	–
Residue after evaporation	mass %	max.	0.0070	0.05 (ml/100 ml)
Sulfur	mg/kg	max.	3.0	←
Vapor pressure @ 37.8 °C	kPa	max.	–	758
Corrosion, copper strip @ 37.8 °C		max.	–	No. 1

*In case infrastructure for LPG is diverted or converted in the DME distribution process

2.4 Definition of DME fuel quality

Table 7 shows the comparison of the specifications of ISO16861: 2015 (DME fuel quality) that was published in May 2015 after about seven years of discussion, with ASTMD7901-14 (DME fuel quality) that was published in 2014 before ISO although it was a follower to ISO. For water, 300 ppm was set as the contamination limit value considering the request from manufacturers, based on the data of the aforementioned lubricity evaluation data. For hydrocarbon (C_4 or lower), 1 % contamination was tolerated to enable diversion and conversion of LPG infrastructure at the early stages of the introduction of DME fuel to the market. For this decision, the data used as reference showed that the effect on emission gas performance was small even with 5 % contamination of LPG (represented by propane) according to the engine test. For sulfur component, it should be as close to zero as possible from the standpoint of the utilization systems such as the engine system. However, 3.0 ppm was set as the tolerance value considering the facts that sulfuric acid dehydration was still used in the manufacturing process of some DME manufacturing plants, and the low-sulfur diesel fuel that was the conventional fuel of diesel engines contained slightly less than 5 ppm of sulfur even in advanced nations. For evaporation residue, while there was extremely small possibility that high boiling point ingredients might remain in the DME manufacturing process, for the purpose of capturing contamination, the value of 70 ppm or less was employed. For other impurities, the values that took into consideration the economy of manufacturers were employed, since the effects were extremely small from the standpoint of utilization systems.

ASTM conducted exchange of information several times with the ISO/TC28/SC4/WG13 and WG14, and defined the

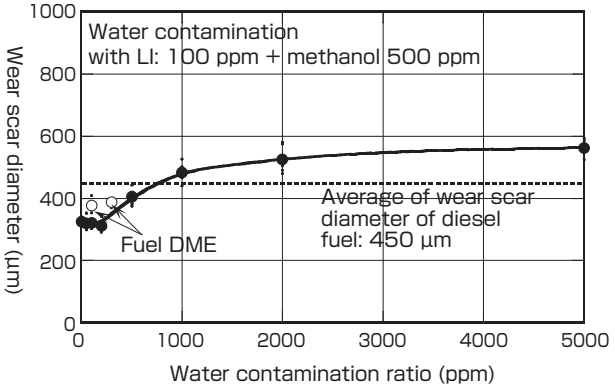

Fig. 7 Effect of water contamination on abrasion scar diameter[1]* (water 0–5,000 ppm, methanol 500 ppm)
*Data added to ref. [1]

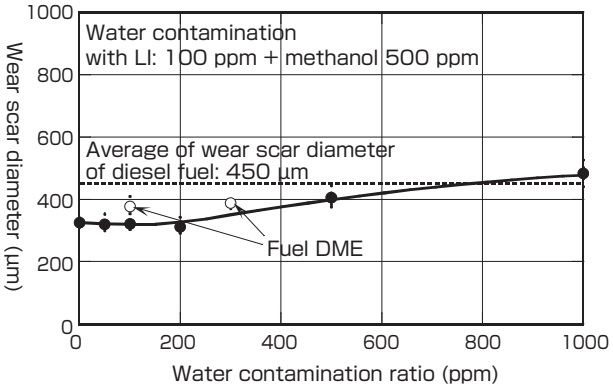

Fig. 8 Effect of water contamination on abrasion scar diameter[1]* (water 0–1,000 ppm, methanol 500 ppm)
*Data added to ref. [1]

respective items based on the discussions at ISO. Although vapor pressure and copper plate corrosion were not defined at ISO, it is thought that ASTM referred to the LPG standards.

3 Investigation of the DME fuel quality analysis method

The analysis method to determine whether the quality was satisfied was necessary when defining and standardizing the DME fuel quality in ISO16861: 2015. Since DME is a liquefied gas fuel, based on the analysis methods of mostly LPG (liquefied petroleum gas) and LNG (liquefied natural gas), the following four analysis methods were drafted, the round-robin tests were conducted, several discussions were held, and the standard methods were issued.

ISO17198: 2014, Dimethyl ether (DME) for fuels–Determination of total sulfur, ultraviolet fluorescence method (2014.11.15)
ISO17786: 2015, Dimethyl ether (DME) for fuels–Determination of evaporation residues–Mass analysis method (2015.5.1)
ISO17197: 2014, Dimethyl ether (DME) for fuels–Determination of water content–Karl Fischer titration method (2014.11.15)
ISO17196: 2014, Dimethyl ether (DME) for fuels–Determination of impurities–Gas chromatographic method (2014.11.15)

For the round-robin tests, in the case of this DME, it was necessary to consider the measurement standard of the analysis subject, that is, it was necessary to conduct precision analysis by preparing several standards for types and concentrations of impurities in the DME within the range of analysis application. However, due to the limitation of samples and time, it was conducted for one measurement standard only. For the round-robin tests, in addition to the seven laboratories in Japan, there was participation by two labs in Korea, and one lab each from Sweden, Canada, and Belgium. Eight labs participated in all analysis items although they differed in capacities to conduct certain analysis items.

The test samples were made by the author's research group by mixing the impurities in pure DME by a gravimetric method, and the labs were asked to conduct analysis with no information given about the values. In this paper, we present the results of the round-robin tests of impurity concentration by gas chromatography through which the issues became most visible.

First, Fig. 9 and Fig. 10 show the analysis results of hydrocarbon (HC) of C_4 or less and methanol, respectively, and most labs showed relatively similar analysis results for the impurity concentration mixed by a gravimetric method. The scatterings of the measurement values within the labs are shown by error bars. The precision analysis of the round-robin tests was conducted by Cochran's tests and Grubb's tests as designated by ISO5725-2, and the repeatability standard deviation and the reproducibility standard deviation were calculated. As a result, for HC of C_4 or less, the repeatability standard deviation was Sr = 0.0134 and the reproducibility standard deviation was SR = 0.0393. However, this accuracy was obtained by a 0.0952 wt.% standard test with the participation of six labs. In this experiment, one 1 % outlier each was found for Cochran and Grubb tests, but these were kept and included in the calculation. The concentration of HC of C_4 or less in the sample made by a gravimetric method was 0.100 wt.%, and this was relatively close to the general average value of 0.0952 wt.% obtained from the analysis result of the round-robin test.

For methanol, the repeatability standard deviation was Sr = 0.0025 and the reproducibility standard deviation was SR = 0.0072. This accuracy was obtained by a 0.0160 wt.% standard test with the participation of six labs. In this experiment, one 5 % outlier each was found for a Cochran's test, but these were kept and included in the calculation.

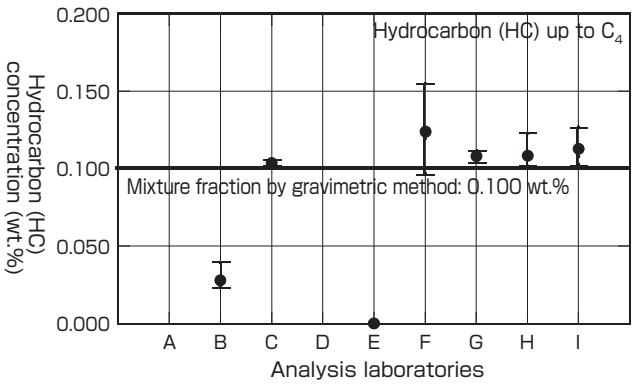

Fig. 9 Analysis result of hydrocarbon (HC) of C_4 or less in the round-robin test[9]*
*Graph based on data of ref. [9]

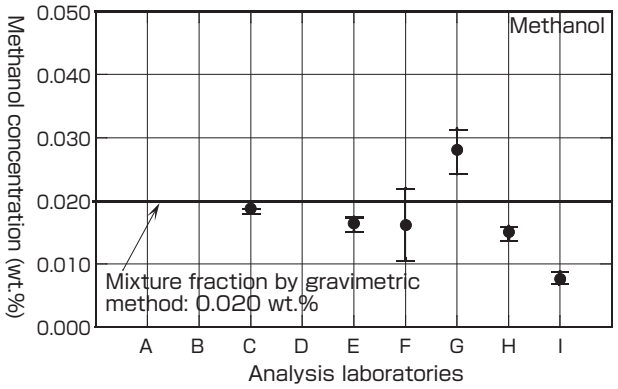

Fig. 10 Analysis result of methanol in the round-robin test[9]*
*Graph based on data of ref. [9]

The concentration of methanol in the sample made by a gravimetric method was 0.020 wt.%, and this was relatively close to the general average value of 0.016 wt.% obtained from the analysis result of the round-robin test. For the HC of C_4 or less and methanol, it is thought that the accuracy will improve through increased skill of the laboratories.

On the other hand, Fig. 11 and Fig. 12 show the analysis results of carbon monoxide (CO) and carbon dioxide (CO_2), and several labs showed highly differing analysis results compared to the impurity concentration mixed by a gravimetric method. Similarly, the scatterings of measurement values within the labs are shown by error bars, the accuracy analysis was conducted by Cochran's tests and Grubb's tests as designated by ISO5725-2, and the repeatability standard deviation and the reproducibility standard deviation were calculated. As a result, for CO, the repeatability standard deviation was Sr = 0.0006 and the reproducibility standard deviation was SR = 0.009. This accuracy was obtained by a 0.0013 wt.% standard test with the participation of five labs. In this experiment, one 1 % outlier each was found for a Cochran's test, but these were kept and included in the calculation. The concentration of CO in the sample made by a gravimetric method was 0.010 wt.%, and this was vastly disparate from the general average value of 0.0013 wt.% obtained from the analysis result of the round-robin test. However, the repeatability standard deviation and the reproducibility standard deviation were relatively small, the reproducibility was good within the lab and among the labs, and the analysis result was about one-tenth the CO concentration made by the gravimetric method.

The CO_2 showed a similar trend as CO, and the repeatability standard deviation was Sr = 0.0018 and the reproducibility standard deviation was SR = 0.0018. This accuracy was obtained by a 0.0064 wt.% standard test with the participation of six labs. In this experiment, one 1 % outlier each was found in the Cochran's test, but these were kept and included in the calculation. The concentration of CO_2 in the sample made by the gravimetric method was 0.010 wt.%, and this was vastly disparate from the general average value of 0.0064 wt.% obtained from the analysis result of the round-robin test, as in CO. However, the repeatability standard deviation and the reproducibility standard deviation were relatively small, and the reproducibility of the analysis result was good within the lab and among the labs.

The analysis of impurities by gas chromatography created so far could not be applied to CO and CO_2. Therefore, to analyze the disparity factors of the analysis results, the solubility of CO and CO_2 in DME was measured. The CO was supplied at various pressures in the container holding pure DME, the containers were shuffled to promote the mixture of DME and CO, the sample was removed from the liquid phase, and the analysis by gas chromatography was conducted. Samples were made similarly for CO_2, and the analysis was conducted. Figure 13 shows the CO solubility in DME for CO partial pressure, and Figure 14 shows the CO_2 solubility in DME regarding CO_2 partial pressure. From these data, it was confirmed that the solubility in DME of CO and CO_2 was determined by partial pressure. It became clear that, in order to accurately analyze the concentration in the samples, CO = 0.010 wt.% and CO_2 = 0.10 wt.%, made by gravimetric methods in this round-robin test by secondary polynomial approximation, it was necessary to apply backpressure of 0.0194 MPa and 0.0825 MPa or higher, respectively, during sample extraction.

As a result, since there is low possibility that CO and CO_2 are introduced in the manufacturing or distribution processes of DME, although there were issues unsolved in the analysis method, we attained issuance of ISO by describing the information of solubility in the appendix.

4 Discussion and issues

After about seven years of discussion, we were able to issue the DME fuel quality and the four types of analysis methods

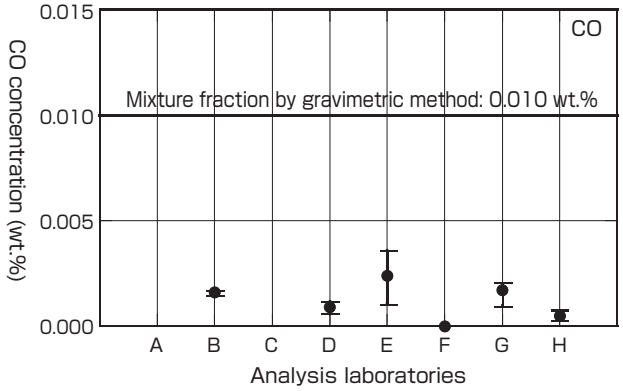

Fig. 11 Analysis result of carbon monoxide (CO) in the round-robin test[9]*

*Graph based on data of ref. [9]

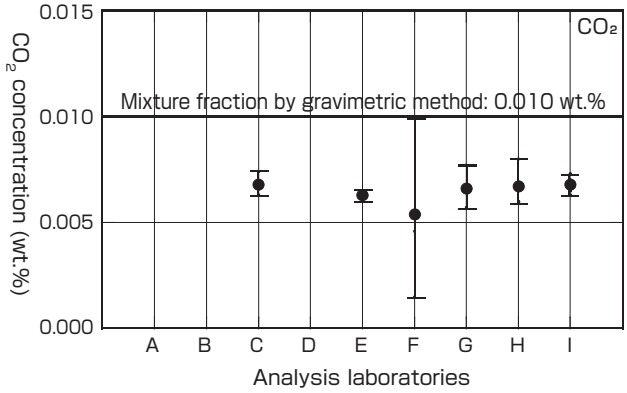

Fig. 12 Analysis result of carbon dioxide (CO_2) in the round-robin test[9]*

*Graph based on data of ref. [9]

as ISO. Here, the points encountered by the author toward the establishment of ISO will be described

(1) Efficacy of measurement data for the determination of water contamination tolerance limit

As mentioned earlier, the determination of impurity contamination limit in the DME fuel quality was made through compromise between the standpoint of manufacturers (please tolerate this much impurities) and the standpoint of users (if this much impurities are present failures may occur in the utilization systems such as engines). Since this argument was evident particularly over the determination of water contamination tolerance limit, we shall present the case here.

For the DME diesel engine that was a utilization system expected to demand the severest fuel quality, the Japanese experts including the author were aware based on the experimental data that the water contamination tended to decrease the fuel lubricity that greatly affected durability, and therefore stated that the water contamination tolerance limit should be up to 100 wt. ppm. On the other hand, the experts of a country that had several operating DME manufacturing plants demanded the tolerance of 300 wt. ppm for the manufacturing technology. This was the demand from a country with the top share in the world DME fuel market, and it was determined that it would not be positive to totally deny the demand considering the formation and expansion of the DME fuel market. Therefore, as there was some room to the level where the lubricity seriously decreased based on the experimental data, ultimately, the water contamination tolerance limit of 300 wt. ppm was accepted.

At the time, there were only three institutions, including the one to which the author belongs, that were able to evaluate the lubricity of DME fuel that was liquefied gas. The three institutions once evaluated the same sample, and from that result, the author had confidence in his and his colleagues' measurement accuracy, and was able to make decisions instantly during the working group meetings based on abundant backup data.

(2) Accumulation of experience in conducting the round-robin tests

The author and his colleagues are researchers and technicians of mechanical engineering. Although we were not planning to participate in the round-robin tests to check the accuracy of the analysis method, we started from the introduction of analysis devices as we were requested to join to secure the necessary number of participating laboratories. For manufacturing the samples by gravimetric methods, we had experience in making fuel for engine tests, and we were able to gain lots of experience along with chemical analyses. This accumulated experience became very valuable in the case where we clarified that the solubility of CO and CO_2 was affecting the analysis accuracy.

(3) Discussion and negotiation

In the discussions in international meetings, it is said that lobbying activities such as consultations and consensus building outside the meeting room are extremely important. While there are pros and cons for such activities, it is true that we witnessed such actions. On the other hand, the persuasiveness of scientific experimental data is tremendous. At the place of discussion of ISO standardization for DME fuel quality and test methods, the intentions of corporations, mainly of Europe, that were aiming to commercialize this fuel were trying to take lead of discussions. They were engaging in negotiations (consensus building led by profit and interest) based on assumptions and hypotheses, as there was lack of data on the effect of impurities on the utilization systems and impurities analysis results. There was concern that the Japanese national interest and Japanese DME industries would be affected, including the chemical manufacturers that manufactured good quality DME fuel as well as automobile manufacturers that manufactured high-performance DME automobiles. I remember that we gradually gained the lead by shifting from "negotiation" to

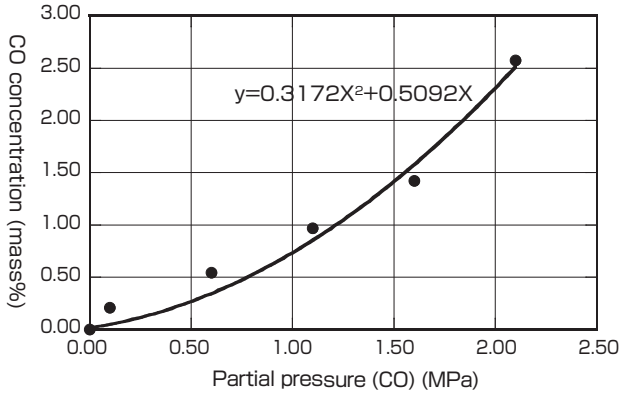

Fig. 13 Effect of CO partial pressure on CO solubility in DME[9]

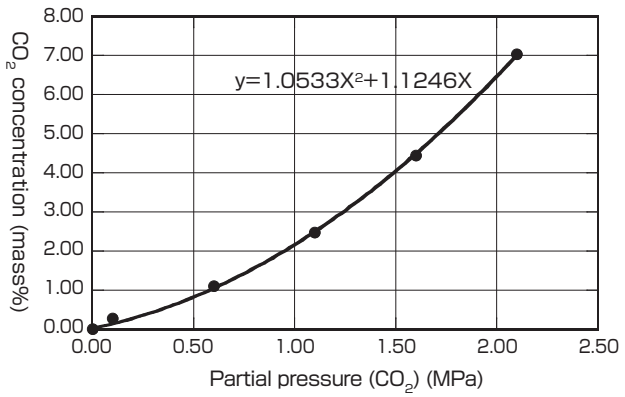

Fig. 14 Effect of CO_2 partial pressure on CO_2 solubility in DME[9]

"discussion" (technological arguments based on data) based on the abundant experimental data and analysis results.

5 Conclusion

For the standardization of DME fuel quality, we summarized the evaluation of the effect of impurities, the definition of the contamination limit, the round-robin result of the impurity analysis method, along with the investigated experimental data that were studied from the standpoint of the fuel utilization systems. The author was given a precious opportunity and was able to gain valuable experience by participating in the stage of international discussion of ISO standardization. In this process, I experienced a tense atmosphere where the national interest might be compromised unless one raised one's voice, and learned that technological argument based on data was convincing even with incomplete English. There, I experienced firsthand the importance of data. The joy in participating in international standardization activities is building networks and interacting with engineers around the world. I would like to spend effort on increasing my skills as a researcher and helping train younger researchers.

Acknowledgements

The MPT-HFRR test device was developed jointly with the Iwatani Corporation. This research includes the results of the following: the "International Standard Joint R&D Project: Standardization for Dimethyl Ether (DME) Fuel," FY 2009 Standardization R&D Commission Fund, Ministry of Economy, Trade and Industry; and the "Standardization R&D: Dimethyl Ether (DME) Fuel Standardization," FY 2010 Strategic International Standardization Promotion Project, New Energy and Industrial Technology Development Organization (NEDO). Guidance for research and standardization activity was provided by Shinichi Goto, Emeritus Researcher, Research Institute for Energy Conservation, Department of Energy and Environment, AIST. Takuro Watanabe, Senior Researcher, Research Institute for Material and Chemical Measurement Gas and Humidity Standards Group, helped us with the DME quality analysis. This standardization was accomplished through the cooperation of members of several groups, such as assistance in experiments by Kazuaki Higurashi, Technical Staff, Engine Combustion and Emission Control Group, Research Institute for Energy Conservation, AIST, and round-robin test analysis by Akiko Ohmuta, former Technical Staff, Combustion and Engine Research Team, (former) Research Center for New Fuels and Vehicle Technology, AIST. I express my gratitude to all people involved.

References

[1] M. Oguma, T. Yanai and S. Goto: Investigation of Fuel Impurities Effect on DME Powered Diesel Engine System (Total Evaluation for JASO Standardization), *Proc. 21st Internal Combustion Engine Symposium*, 593–598 (2010) (in Japanese).

[2] M. Oguma, S. Goto, T. Nishimura and Y. Mikita: Investigation of fuel impurities effect on DME powered diesel engine performances, *Trans. Society of Automotive Engineers of Japan*, 40 (4), 1003–1009 (2009) (in Japanese).

[3] M. Oguma, S. Goto, T. Nishimura and Y. Mikita: Effect impurities on DME powered diesel engine performances —Emission characteristics on transient conditions, *Proc. Society of Automotive Engineers of Japan*, 12-09, 21–24 (2009) (in Japanese).

[4] T. Nakasato, T. Okamoto and M. Konno: Combustion characteristics and fuel properties of a DI diesel engine fueled with palm oil methyl ester/DME composite fuel, *Proc. Society of Automotive Engineers of Japan*, 80-04, 15–20 (2004) (in Japanese).

[5] M. Oguma, T. Tsujimura, S. Goto and N. Suzuki: Analysis of particulate matter (PM) emitted from DME powered DI diesel engine—Evaluation of SOF characteristics by chemical analysis, *Trans. Society of Automotive Engineers of Japan*, 36 (6), 91–97 (2005) (in Japanese).

[6] K. Sugiyama, M. Kajiwara, M. Fukumoto, M. Mori, S. Goto and T. Watanabe: Lubricity of liquefied gas assessment of multi-pressure/temperature high-frequency reciprocating rig (MPT-HFRR)-DME fuel for diesel, *SAE Paper*, 2004-01-1865 (2004).

[7] Japan Petroleum Institute: Keiyu–Junkatsu-sei shiken hoho (Light diesel oil–Lubricity test method), JPI-5S-50-98 (1998) (in Japanese).

[8] M. Oguma, S. Goto, T. Yanai and Y. Mikita: Evaluation of DME fuel lubricity by HFRR test method, *Trans. Society of Automotive Engineers of Japan*, 41 (6), 1353–1358 (2010) (in Japanese).

[9] ISO 17196: 2014, Dimethyl ether (DME) for fuels—Determination of impurities—Gas chromatographic method.

Author

Mitsuharu OGUMA

Completed the doctoral course at the Department of Industrial Science, Graduate School of Science and Engineering, Ibaragi University in 2001. Doctor (Engineering). After two and a half years of post-doctorate period, joined AIST in 2003. Senior Researcher, Combustion and Engine Research Team, Research Center for New Fuels and Vehicle Technology in 2009; Team Leader, Combustion and Engine Research Team in 2010; and Director, Collaborative Engine Research Laboratory for Next Generation Vehicles and Group Leader, Engine Combustion and Emission Control Group, Research Institute for Energy Conservation in 2015. Engages in R&D for new fuel systems and standardization and R&D for low-pollution high-efficiency engines. Convener for ISO/TC28/SC4/WG13 from 2011. Received the 56th Asahara Science Award, Society of Automotive Engineers of Japan in 2006; the 62nd Outstanding Technical Paper Award, Society

of Automotive Engineers of Japan in 2012; and the Award for Contribution to International Standardization Division (Award of the Director-General of the Industrial Science and Technology Policy and Environment Bureau), Industrial Standardization Project Awards in FY 2016.

Discussions with Reviewers

1 Overall

Comment (Haruhiko Obara, AIST)

This paper is a concise summary of the research in which the author engaged for the standardization of DME fuel quality. Particularly, the author received this year's Industrial Standardization Project Awards of the Ministry of Economy, Trade and Industry, and his standardization activities are highly acclaimed both in and outside Japan. This paper also describes the international standardization activities such as the round-robin measurements, and it emphasizes the importance of international standardization activities. I believe it will be relevant to the readers outside of the field.

Comment (Hiroki Yotsumoto, AIST)

I think this paper clearly illustrates the requirements of the DME fuel as well as the efforts and hardships of international standardization.

2 Future of DME

Comment (Hiroki Yotsumoto)

In the introduction, you mention that "if the technology is established for manufacturing the fuel via synthetic gas from woody biomass using lumber from thinning and black liquor from paper mills…." How is this assumption likely to be realized? If you mention synthetic gas, all carbon resources become possible candidate raw materials, don't they? I am asking this question because I feel that the discussion may be lost on how high the feasibility of using black liquor and lumber from thinning is compared to other carbon sources.

Answer (Mitsuharu Oguma)

While the technology of manufacturing synthetic gas (CO, H_2) from black liquor or woody biomass is not that difficult, it is inferior in terms of economy compared to coal and natural gas.

I shall change the expression to the following: "if the technology is established for manufacturing the fuel via synthetic gas from woody biomass using lumber from thinning and black liquor from paper mills and if such technology becomes economically feasible…."

3 Effects of impurities and additives on metal material

Comment (Hiroki Yotsumoto)

In Fig. 3, there is discoloration in copper C1100. What kind of reaction is happening to copper? Also, how about adding the harm there may be to the material?

Answer (Mitsuharu Oguma)

The discoloration is due to oxidation reaction. Copper is used as sealant for fuel systems, and fuel leakage may occur if the corrosion by oxidation progresses. I shall add this to the paper.

4 Effects of impurities and additives on engine performance

Comment (Hiroki Yotsumoto)

It is unclear what you mean by "total emission performance," and I think you should provide an explanation. If it means the amount of environmental pollutants in the emission, I think you need to better explain the relationship with "Caution" in the explanation of Fig. 5. What do you think?

Answer (Mitsuharu Oguma)

I shall correct the applicable text to the following: "The effects of the impurities in DME fuel and the additives to DME fuel on the engine performance and emission property were evaluated by engine tests. The tendencies are summarized in Fig. 5. The items shown in yellow and pink in the table indicate the caution levels, and pink shows a higher degree of caution than yellow." Change is also made to the following: "However, although the tendency was as shown in Fig. 5, it was confirmed that 'the effect on the emission gas performance test results by mode operation was not that large even if DME containing 5 % impurities was accidentally used.'"

5 Discussions and issues in the international standardization process

Comment (Hiroki Yotsumoto)

Don't you think you should explain the specific difference between "negotiation" and "discussion" in the meetings for international standardization?

Answer (Mitsuharu Oguma)

Thank you very much for pointing this out. I shall explain as follows. Negotiation is consensus building led by profit and interest. Discussion is technological argument based on data.