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AMENDMENTS TO THE IGF CODE AND DEVELOPMENT OF GUIDELINES FOR ALTERNATIVE FUELS AND RELATED TECHNOLOGIES

Technical characterization of the differences between ethanol and methanol as marine fuel

Submitted by Brazil, IBIA and CEA

SUMMARY

Executive summary:	This document characterizes, on technical grounds and with reference to international standards and norms, the differences between ethanol and methanol relevant to the safety of ships using them as fuel, and examines their implications for the sizing of the detection, ventilation, protection and segregation measures. The analysis indicates that requirements calibrated to the profile of one substance do not constitute a technically transferable parameter to the other, and that a risk-based approach, specific to the hazard of each fuel, of each installation and to the vessel's certification envelope, is the most appropriate way forward, ensuring the required level of safety.
Strategic direction, if applicable:	2
Output:	2.3
Action to be taken:	Paragraph 22
Related documents:	MSC-MEPC.2/Circ.17; MSC.1/Circ.1621, MEPC.1/Circ.761/Rev.1, MEPC.1/Circ.917 and CCC 12/3/6

Introduction

1 The *Interim guidelines for the safety of ships using methyl/ethyl alcohol as fuel* (MSC.1/Circ.1621) apply broadly common risk-mitigation requirements to methanol and ethanol, although the two substances present measurable technical differences in toxicity, fire behaviour, flame visibility and combustion behaviour, with direct consequences for the sizing of safety measures. This document brings together these parameters and examines their consequences for a proportionate, risk-based application under paragraph 4.2 of MSC.1/Circ.1621.

Toxicity and occupational exposure

2 Under the criteria of the Globally Harmonized System of Classification and Labelling of Chemicals (GHS), of the United Nations, based on median lethal dose (LD_{50}) and median lethal concentration (LC_{50}) values, methanol is classified as acutely toxic by the oral, dermal and inhalation routes (category 3), owing to its metabolization into formaldehyde and formic acid, with cumulative effects on the central nervous system and vision. Under the same criteria, ethanol falls within a lower acute toxicity category (category 4 or higher, depending on the route), with effects generally reversible following accidental exposure. The relevant parameters are set out in table 1.

Parameter	Methanol (CH_3OH)	Ethanol (C_2H_5OH)
GHS classification (acute toxicity)	Category 3	Category 4 or higher
Occupational exposure limit (OEL, 8-h TWA)	200 ppm (ACGIH)	1,000 ppm (OSHA/NIOSH)
Short-term exposure limit (STEL, 15 min)	250 ppm (ACGIH)	1,000 ppm (ACGIH)
Immediately dangerous to life and health (IDLH)	6,000 ppm (health-based, NIOSH)	3,300 ppm – flammability-based (10% LEL), not a toxicity value (see paragraph 10)
Skin notation	Yes	No

Table 1 – Toxicological and occupational-exposure parameters (GHS/UN criteria; exposure limits from the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) and from the Occupational Safety and Health Administration (OSHA) / National Institute for Occupational Safety and Health (NIOSH) Permissible Exposure Limit (PEL) and Recommended Exposure Limit (REL); Immediately Dangerous to Life and Health (IDLH) from NIOSH)

3 The ACGIH (TLV-TWA) and NIOSH occupational exposure limits reflect this contrast. The time-weighted-average limit (TWA), representing the mean concentration over an 8-hour working day, and the short-term exposure limit (STEL), representing a 15-minute peak, are distinct exposure criteria and should not be compared directly. For methanol, the TWA is 200 ppm (STEL 250 ppm, skin notation, IDLH 6,000 ppm), whereas for ethanol the TWA is 1,000 ppm, a difference of approximately one order of magnitude. The ethanol IDLH, by contrast, is fixed by flammability rather than toxicity and is addressed in the flammability section below. These values condition the sizing of detection alarm thresholds, air-change rates and personal protective equipment. Thresholds calibrated to the more restrictive methanol limit are not technically necessary for ethanol, whose limit is five times higher. The skin notation of methanol imposes specific dermal protection, which is not required for ethanol. Such measures are pertinent only to spaces where crew presence is possible.

Ventilation criteria and air changes

4 The ventilation capacity of spaces in which leakage may occur is associated with the exposure profile and the vapour behaviour of each substance, and its effectiveness must be assessed by control of the dispersion and persistence of an explosive atmosphere, in accordance with the ventilation-effectiveness concept of IEC 60079-10-1. It follows directly from the exposure limits examined in the preceding section that the sizing of ventilation follows the toxicity profile of the fuel in use.

5 MSC.1/Circ.1621 prescribes 30 air changes per hour under a continuous regime. A lower normal ventilation rate allows a leak to be detected before it accumulates, whereas very high continuous ventilation disperses it and delays the alarm. For methanol, with its higher toxicity and wider flammability range, a configuration of 10 air changes per hour under the normal regime and 20 additional under emergency is appropriate. Ethanol, although of narrower flammability range, forms a flammable atmosphere at lower concentration, so early detection is equally important; for ethanol, 15 air changes per hour under normal regime and 15 additional under emergency are appropriate. Both configurations achieve 30 air changes under emergency, fully preserving exhaust capacity. Only the normal regime differs, calibrated to each fuel.*

6 Ventilation requirements should not be fully prescriptive but should admit differentiation according to the properties of the fuel, supported by gas-dispersion and detection-capacity assessments, ensuring an equivalent level of safety rather than a single set of values for both substances.

Operational experience and mitigation technologies

7 MSC-MEPC.2/Circ.17 classifies, by volumetric composition, the regime applicable to blends of biofuels with MARPOL Annex I cargoes. Blends containing up to 25% biofuel, including ethanol, are carried under the Annex I regime, a threshold subsequently raised to 30% by MEPC.1/Circ.917 (MEPC 83, April 2025), illustrating the gradual maturation of this composition-based approach. Current requirements include chapter II-2 of SOLAS (alcohol-resistant foam (AR-AFFF) for blends above 5% ethanol), without the detection and containment provisions of the International Bulk Chemical (IBC) Code.

8 By analogy with that composition-based classification for carriage as cargo, ethanol used as fuel in low concentrations (up to 25%, not stored in the machinery space and mixed only at the point of combustion) presents an effective risk profile distinct from that of pure or high-content ethanol. The governing hazard remains that of the most hazardous admissible component, but is assessed on the actual composition of the mixture. Within this range, a calibrated regime equivalent to that of the base fuel is proposed, while the Administration and the classification society retain the discretion to establish additional measures; above that concentration, measures follow from a specific risk assessment. This 25% figure is a deliberately conservative starting point, mirroring the progression already followed for carriage as cargo, and does not extend to hazards independent of dilution, such as the acute toxicity and skin notation of methanol, which remain governed by the component that presents them.

* The air-change configurations proposed in this paragraph are indicative and are intended to be confirmed, for the installation concerned, by gas-dispersion (e.g. CFD) analysis demonstrating control of the formation and persistence of an explosive atmosphere, consistent with the ventilation-effectiveness concept of IEC 60079-10-1 and the risk assessment of paragraph 4.2 of MSC.1/Circ.1621, subject to approval by the classification society.

Physicochemical properties and fire behaviour

9 The physicochemical properties of the two substances are set out in table 2. The flashpoint, determined by the Abel closed-cup method (ISO 13736), suitable for low-flashpoint liquids, places both substances in the class of flammable liquids.

Property	Methanol (CH_3OH)	Ethanol (C_2H_5OH)
Molecular mass	32.04 g/mol	46.07 g/mol
Flashpoint, closed cup (ISO 13736)	~11 °C	~13 °C
Autoignition temperature	~464 °C	~363 °C
Lower explosive limit (LEL)	~6.0% v/v	3.3% v/v
Upper explosive limit (UEL)	36% v/v	19% v/v
Cetane number (approx.)	0	0 to 8
Water miscibility	Complete	Complete

Table 2 – Physicochemical and fire-behaviour properties (flashpoint per ISO 13736)

10 The flammability range of the two substances differs in two respects that point in opposite directions and do not warrant ordering them on a single scale of hazard. Ethanol's lower flammability limit (LEL) of 3.3% v/v is below methanol's (~6.0% v/v), so a lower concentration of ethanol vapour already forms a flammable atmosphere; methanol, in turn, presents a wider range (about 6.0 to 36% v/v, against 3.3 to 19% v/v for ethanol), so that a wider range of concentrations is flammable. Each parameter shifts the sizing of detection and ventilation in its own direction, and neither, in isolation, renders one fuel more hazardous than the other. A one-dimensional comparison is therefore technically invalid: under the hazardous-area classification criterion of IEC 60079-10-1, founded on the probability and extent of formation of an explosive atmosphere, both parameters must be considered jointly in the definition of hazardous zones. It is in this flammability domain, and not in toxicity, that the ethanol IDLH of 3,300 ppm belongs. Under the NIOSH criteria for determining IDLH values, where the health-based concentration for a flammable vapour would exceed 10% of the lower explosive limit, the IDLH is capped at that 10%, as a conservative safety ceiling, the toxicological data indicating that irreversible health effects arise only at higher concentrations. The ethanol value (10% of a 3.3% v/v LEL) is set on that basis and is therefore an explosivity ceiling, not a toxicity figure. The methanol IDLH of 6,000 ppm, by contrast, is health-based, governed by acute toxicity. The two figures therefore measure different hazards, and a lower numerical value for ethanol does not denote greater toxicity than methanol.

Flame visibility and selection of detection systems

11 Both substances burn with low-luminosity flames and produce less soot than diesel, and in both cases flame visibility may be limited by lighting conditions. The methanol flame is of particularly low luminosity, and alternative detection methods are recommended, such as thermal cameras (Computer-Aided Management of Emergency Operations (CAMEO) of the National Oceanic and Atmospheric Administration (NOAA); Emergency Response Guidebook (ERG) Guide 131). The ethanol flame, owing to its higher molecular carbon content, tends to exhibit greater luminosity than methanol, although its visualization remains dependent on environmental conditions. The technically relevant question is therefore not to contrast a 'visible' flame with an 'invisible' one, but to recognize that the detectability of both is conditioned and variable. The visibility of the ethanol flame varies, moreover, according to its composition. Pure ethanol burns with a blue flame that is difficult to see, whereas denatured formulations and the presence of water alter the optical characteristics of the flame (OSHA Technical Manual, Section IV, Chapter 5). Ignition improvers employed in ethanol formulations for

diesel-cycle engines have the purpose of reducing ignition delay, and the literature does not establish, in general terms, that their presence implies flames of lower visibility. This variability confirms that visual detectability is not uniform across ethanol compositions, making the prescription of a single detection solution technically inadequate, whether through the mandatory use of infrared detection or its general waiver.

12 Other measures of proven effectiveness remain required, such as intrinsically safe electrical equipment, designed to limit the available electrical and thermal energy to levels incapable of causing ignition by spark or heating, in accordance with the type of protection "i" (IEC 60079-11).

Combustion behaviour in diesel-cycle engines

13 Both ethanol and methanol present a cetane number close to zero, resulting in high resistance to compression ignition. In diesel-cycle engines, neither sustains combustion on its own, both operate in a dual-fuel configuration with an ignition pilot of higher flashpoint, typically diesel oil, or with an ignition-improving additive. The proportions and formulations employed vary according to the engine technology and remain under development.

14 The dual-fuel arrangement is therefore common to both substances and does not, in itself, differentiate the level of safety. The pilot fuel does not govern the sizing of the safety measures. The measures applicable to each fuel remain determined by the main fuel in use, as best established through an installation-specific risk assessment under paragraph 4.2 of MSC.1/Circ.1621.

Segregation and function of the cofferdam

15 The cofferdam functions as a dedicated segregation space, protecting against the passage of fire and toxic or flammable vapours between the fuel tank and the other spaces of the ship. Void spaces, ballast tanks and sandwich structural arrangements, which serve distinct structural and operational purposes, are not automatically equivalent to a cofferdam.

16 Acceptance of an equivalent arrangement should be conditional on demonstrating an equivalent level of safety through a specific design and risk assessment under paragraph 4.2 of MSC.1/Circ.1621, analogous to the secondary enclosures provided for in the IGF Code, and subject to approval by the Administration and the classification society. This preserves the protective barrier without precluding technically justified alternatives.

Matrix calibrating the safety measures to the governing hazard

17 Table 3 associates each safety measure with the hazard that effectively governs it, with the parameter that triggers the more severe regime, and with the layer at which that parameter applies. Structural measures, determined at the construction stage, are calibrated to the envelope of fuels for which the vessel is certified; operational measures are calibrated to the composition of the fuel in use, within the limits of that envelope.

Safety measure	Governing hazard	Trigger of the more severe regime	Layer
Gas-detection alarm threshold	Acute toxicity and OEL of the fuel in use	Composition with the more restrictive OEL	Operational
Personal protective equipment (dermal protection)	Skin notation and route of absorption of the fuel in use	Presence of a fuel with skin notation in a space with crew	Operational
Air-change rate (ventilation)	Exposure profile and vapour behaviour; control of explosive atmosphere	Composition in use of higher toxicity and in which early detection is critical	Operational
Selection of the type of flame detection	Flame visibility according to the effective composition	Composition whose flame requires a specific method, by installation-specific risk assessment	Operational
Hazardous-area classification and definition of zones	Flammability limits (LEL/UEL) of the admissible fuel	LEL and UEL considered jointly, not by one-dimensional comparison	Operational
Segregation by cofferdam	Dedicated barrier against fire and toxic and flammable vapours of the certified worst case	Certification envelope admitting the most hazardous fuel	Structural
Piping and containment material and arrangement	Compatibility and hazard of the fuel admissible within the envelope	Vessel certification envelope	Structural
Leak detection in equivalent arrangement	Barrier equivalence demonstrated by specific design	Certification envelope; pressure or temperature monitoring where gas detection is not suitable	Structural

Table 3 – Calibration of safety measures to the governing hazard, to the trigger of the more severe regime and to the layer of application

18 The structural layer is designed for the worst case within the certification envelope, while the operational layer adjusts to the fuel in use; certification for a less hazardous fuel constitutes a technical boundary that bars operation with a more hazardous fuel without approval of a redesign.

Synthesis and scope of application

19 The parameters presented, grounded in international standards, indicate that ethanol and methanol have distinct profiles of toxicity, fire behaviour, flame visibility and combustion behaviour. Measures for detection, ventilation, protection and segregation dimensioned for one of the substances are not technically transferable to the other. Where a requirement follows from a substance-specific hazard (for example, the acute toxicity and skin notation of methanol), it applies only to that substance. At the vessel level, the safety regime follows the envelope of fuels for which the ship is certified: a vessel certified for ethanol, even if fitted with a multi-fuel engine, is technically barred from operating with methanol without redesign

approval, the burden of expanding the certification envelope falling on the party seeking to expand it.

20 Finally, a systemic consideration: The safety framework for alternative fuels is being built fuel by fuel and will guide the sector's energy transition. The aim is not to relax safety but to calibrate it to the actual risk. Excessive prescription, transferred by analogy without assessing the effective risk, imposes cost without corresponding benefit, and raises a barrier to decarbonization that serves no party's interest, without ensuring any proportionate safety gain. Calibrating measures to the governing hazard of each fuel and installation offers a consistent criterion for the incorporation of future fuels, while fully preserving the level of safety.

21 The concrete amendments giving effect to the proportional, risk-based approach set out in this document, are proposed in document CCC 12/3/6 (Brazil), to which the present document provides the technical basis.

Action requested of the Sub-Committee

22 The Sub-Committee is invited to note the information presented in this document when considering the proposal contained in document CCC 12/3/6.

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