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PREVENTION OF AIR POLLUTION FROM SHIPS

Considerations of CO_2 conversion factors for vessels using liquefied gases as fuel

Submitted by the Society of International Gas Tanker & Terminal Operators (SIGTTO)

SUMMARY

Executive summary:	This document proposes revision of the CO_2 conversion factors contained in MEPC/Circ.471. The combustion scientific background to the proposed changes is included.
Strategic direction:	7.3
High-level action:	7.3.1
Planned output:	7.3.1.3
Action to be taken:	Paragraph 26
Related document:	MEPC/Circ.471

Introduction

1 Table 1 below is reproduced from MEPC/Circ.471, "Interim Guidelines for voluntary ship CO_2 emission indexing for use in trials". This document addresses issues used in the values in the table assigned to "Liquid Petroleum Gas (LPG)" and for "Natural Gas". Attempts to validate the values in the table have been frustrated. The source is ascribed to IPCC, but the compositions used and methodology has not been discovered. Others are addressing issues related to the values for the other fuels. The table is copied in full below:

Table 1 – *MEPC/Circ.471*

Type of Fuel	ISO specification	Carbon content m/m	C_{Carbon} [gCO_2/t Fuel]
1 Diesel/Gasoil	ISO 8217 Grades DMX through DMC	0.875	3,206,000
2 Light Fuel Oil (LFO)	ISO 8217 Grades RMA through RMD	0.86	3,151,040

Table 1 – *MEPC/Circ.471* (continued)

3 Heavy Fuel Oil (HFO)	ISO 8217 Grades RME through RMK	0.85	3,114,400
4 Liquid Petroleum Gas (LPG)		0.81	2,967,840
5 Natural Gas		0.80	2,931,200

2 With reference to the nomenclature in the table, the following should be noted:

2.1 "Liquid Petroleum Gas (LPG)". The normal descriptor for this product is "Liquefied Petroleum Gas (LPG)". There are commonly two grades of LPG, – one being predominantly Propane and one being predominantly Butane. These are generally carried as separate grades, but may occasionally be transported as a mixture.

2.2 "Natural Gas". Natural Gas is a very broad description of gas whose main component is methane. Carriage of natural gas at sea, either as cargo, or, more rarely, as a propulsion fuel, is in the form of "Liquefied Natural Gas (LNG)". The natural gas is converted to LNG by means of cooling to about – 160°C. The demands of this process result in a product with a very limited range of compositions. In particular, CO_2, which may be present in natural gas, has to be removed since it would form a solid in the liquefaction process. The following explanation arises, in part, from this limited range of compositions.

3 To simplify the explanation, the above table has been re-composed showing the key figures that of CO_2/tonne of fuel burnt expressed in tonnes/tonne. The explanation of the issues is clearer if consistent units are used.

Table 2 – *CO_2 Conversion Factors t/t of fuel*

Diesel	3.206
Gasoil	3.206
LFO	3.151
HFO	3.114
LPG	2.968
LNG	2.931

4 The main difference between the conventional liquid fuels and the gas fuels (LPG and LNG) is that the gas fuels are characterised in each case by having a single dominant component with a simple chemical formula whereas the liquid fuels are complex mixtures of hydrocarbon compounds. The section below titled 'Derivation of Conversion Factors' expands on this point.

5 The following points should be noted.

5.1 The conversion factor for LNG, or more specifically, boil-off gas (BOG) used as fuel, the figure should be 2.75, not 2.931. This is derived from the chemical formula and laws of combustion. (Note: this assumes BOG is 100 % methane, typically it contains a few percent nitrogen which would have the effect of reducing the value.) For LNG, as opposed to BOG, (this would arise if LNG is force-vaporized to provide supplementary fuel) the value will rise slightly, this is further discussed in paragraph 14.

5.2 LPG: for propane the value is 3.0 and butane 3.03. Commercial grade LPGs may have traces of heavier hydrocarbons which would slightly increase the figure. Non-hyrdrocarbons/inerts would slightly decrease the figure.

6 From the perspective of the operators of LNG vessels, it is important to rectify the figure as per paragraph 5.1 above. The use of boil-off gas as fuel significantly decreases the CO_2 emitted for a given power production compared to that if heavy fuel oil were used. It is important that the full and correct credit be given for these fuels if the desire to reduce CO_2 emissions to the environment is to be realised. For LPG, the issue may be theoretical since, at the time of writing, there are no LPG-fuelled seagoing vessels and current codes do not permit the use of LPG as fuel in ships' engine rooms. Nevertheless, the figure should be corrected since the future is not foreseeable and the use of LPG as propulsion fuel could occur.

Derivation of Conversion Factors[1]

7 As noted above, the boil-off gas from an LNG cargo is primarily methane. The scientific explanation of this can be found in paragraphs below. The start point for the derivation of the CO_2 conversion factor for LNG is therefore to consider methane.

8 Fundamentals:

Atomic weight of	Carbon (C)	12
	Hydrogen (H)	1
	Oxygen (O)	16

9 Methane – CH_4
Combustion equation:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (1)$$

On both sides of the equation there are:

Carbon	1 atom
Hydrogen	4 atoms
Oxygen	4 atoms

Therefore the equation balances.

Putting in the atomic weights:

$$(12 + 4) + (64) \rightarrow (12 + 32) + (4 + 32) \qquad (2)$$

10 From the point of view of determining the CO_2 conversion factor, the only interest is the fuel (CH_4) and the CO_2, i.e. the ratio of (12 + 4) to (12 + 32) or 16:44 or 2.75. (Note that the effects of excess air typically present in industrial/marine burning systems have no impact on the mass ratio of CO_2 emitted to mass of fuel burnt.)

1 "Combustion Engineering and Gas Utilization", 3rd Edition.

11 An identical process gives the following CO_2 conversion factors for:

Table 3 – *Conversion Factors*

Methane	CH_4	2.75
Ethane*	C_2H_6	2.93
Propane	C_3H_8	3.0
Butane	C_4H_{10}	3.03

* Note: Ethane is not generally carried as a bulk liquid cargo.

Sensitivities

12 **Effects of Nitrogen in LNG**

As noted above, LNG vessels typically utilize boil-off gas from the cargo as fuel. An examination of Raoult's law:

$$Y_1 = \frac{X_1 P_1}{\sum_1^n X P} \qquad (3)$$

Where: Y_1 is the molar fraction of component "1" in the vapour phase
X_1 is the molar fraction of component "1" in the liquid phase
P_1 is the vapour pressure of component "1" at the prevailing liquid temperature,

quickly leads to the position that the impact of the ethane, propane, butane and C_{5+} in mixture that is LNG is negligible since their vapour pressure at a typical LNG temperature of -160°C is less than 5 mb in a container where the vapour pressure is of the order of 1100 mb absolute.

13 In assessing the composition of the boil-off gas, this only leaves the methane and nitrogen content of the LNG as contributors. Typical nitrogen contents of LNG are of the order of 0.1 to 0.35% at the point of export, see annex 1. Applying Raoult's Law, this gives a nitrogen content in the vapour space (mass base) in the range of 6.5% to 20%. This will decline exponentially as the voyage progresses and the nitrogen boils off preferentially. Nevertheless, the effect of nitrogen in LNG will be to reduce the theoretical CO_2 conversion factor suggested above from 2.75, if the calculation is based on total cargo mass loss over the voyage.

14 **Effects of 'Forced Boil-off' on LNG ships**

The contribution to the total fuel demand by boil-off gas varies depending on type of ship (e.g., membrane or Moss) and on whether the vessel is laden or in ballast. The range is wide and can vary from 40% to 95% of the total. Traditionally, the fuel used to supplement the shortfall of that available from boil-off gas has been heavy fuel oil, but there has been a trend towards use of LNG from the cargo to supplement the fuel demand. The implication is that, up to 60% of the fuel gas consumed may be of LNG composition rather than boil-off gas. Annex 1 contains compositional details of a range of commercial LNG as transported by sea. The average CO_2 conversion factor for LNG form the compositions listed is 2.759 in a range of 2.730 to 2.774 and calculating out the CO_2 conversion factor assuming a mixture of 40% boil-off gas and 60% LNG delivers a factor of 2.755.

Sources of Inaccuracy and Uncertainty for LNG

15 **Mass Measurement of Boil-off Gas**

The most accurate method of determining the mass of boil-off gas consumed over a voyage is by reference to the Custody Transfer System records. Accurate readings are taken before and at completion of cargo transfer in any port. From these it is possible to determine the mass loss from the cargo over the voyage. The process is described in reference[2], which also determines that the overall accuracy of the measurement of the total mass of LNG (plus vapour) on board is of the order of 0.49%.

16 **Ideal Gas**

The application of Raoult's law assumes an ideal gas. Real mixtures do not behave in this manner and there is some very small deviation from the ideal due to compressibility factors "Z". This only tends to become significant in calculations for gases over 20 bar and hence, at the pressures considered here, is a second order effect. Given the other uncertainties, it has been ignored for simplicity.

17 **Atomic Weights**

The atomic weight figures used in equation (2) have been rounded and are widely used. Reference[3] gives more accurate figures, but there are disputes in scientific circles over the exact figures. Reference (3) gives:

Hydrogen	1.00794
Carbon	12.0107
Oxygen	15.9994

18 Using these in the equation (2) above yields a CO_2 conversion figure of 2.743.

19 **Nitrogen in LNG**

The effect of the nitrogen component of LNG is described above. In determining a default figure for CO_2 conversion factor, this probably represents the biggest area of uncertainty and, in extreme cases could lead to a 20% overestimation of environmental emission of CO_2. The effect of nitrogen is specific to each cargo and voyage length and it is therefore not possible to arrive at a practical mean figure for use in a default calculation.

20 For LNG cargoes with nitrogen contents in the liquid phase of greater than 0.1%, the mass of boil-off gas determined from CTS readings should be reduced by the change in mass of the nitrogen content, derived from the compositional analysis performed as per ref (2).

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2 "LNG Custody Transfer Handbook" 2nd Edition. GIIGNL.

3 Periodic Table published by International Union of Pure and Applied Chemistry 2006.

Sources of inaccuracy and uncertainty for LPG

21 **Composition as transported**

The figures given in Table 3 are for pure components. In practice, "commercial" grades of propane and butane contain some other components. From the data sheets attached, this leads to a range of CO_2 conversion factors shown in Table 4 below. From this, it is concluded that the use of the conversion factor for the pure product as a default value is acceptable.

Table 4 – *CO_2 Conversion Factors for LPG*

Propane	Pure	3.0
	Representative	2.9995
	Extreme	3.017
Butane	Pure	3.03
	Representative	3.0291
	Extreme	3.0297

22 **Use of LPG a fuel**

As noted above, LPG is not currently used as a fuel for propulsion of ships. Assuming that industrial practice is followed, the LPG will be supplied as liquid to a vaporizing system which vaporizes all components before being fed to the combustion process, then in consideration of environmental emissions of CO_2, the composition as loaded should be used, rather than the composition in the cargo tank vapour space as for LNG ships.

23 **Determination of mass**

There are uncertainties around the measurement of mass, the accuracy is not expected to be better than that for LNG above.

Conclusions and recommendations

24 The table below gives recommended default values for the CO_2 conversion factors. Note that, for LNG, the nitrogen content may need special consideration.

Table 5 – *Recommended Conversion Factors*

	C_{Carbon} [t CO_2/t Fuel	C_{Carbon}[gCO_2 / t Fuel]
LNG	2.75	2,750,000
LPG - Propane	3.0	3,000,000
LPG - Butane	3.03	3,030,000

25 The values in the table are given to three significant figures. The various uncertainties and inaccuracies described above would render calculation to a greater number of significant figures meaningless and may give a spurious sense of accuracy. Taking these values and reworking into Table 1, and including the comments on nomenclature, the following table results:

Table 6 – *MEPC/Circ.471 (amended)*

Type of Fuel	ISO specification	Carbon content m/m	C_{Carbon} [gCO_2/t Fuel]
1 Diesel/Gasoil	ISO 8217 Grades DMX through DMC	0.875	3,206,000
2 Light Fuel Oil (LFO)	ISO 8217 Grades RMA through RMD	0.86	3,151,040
3 Heavy Fuel Oil (HFO)	ISO 8217 Grades RME through RMK	0.85	3,114,400
4 Liquefied Petroleum Gas (LPG)	Propane Butane	0.819 0.827	3,000,000 3,030.000
5 Liquefied Natural Gas (LNG)		0.75	2,750,000

Action requested of the Committee

26 The Committee is invited to consider the information contained in this document and take action as appropriate.

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ANNEX 1

LNG COMPOSITION

From SIGTTO's internal records, the composition of LNG at the export point from 19 major exporters has been examined. Plants excluded from the analysis are Skikda – currently undergoing a major refurbishment and Marsa el Brega, whose LNG production composition is atypical. Marsa el Brega production represents about 2% of world capacity. The last column shows the calculated figure for Nitrogen content of the boil-off gas for the compositions of LNG shown. It has been included here to show the large scatter in the result.

Methane mol %	Ethane mol %	Propane mol %	Butane mol %	Nitrogen mol %	Pentane + mol %	Nitrogen in BOG mol %
87.4	8.6	2.4	0.05	0.35	0.02	21.788
91.23	4.3	2.95	1.4	0.12	0	8.383
90.4	5.2	2.8	1.5	0.07	0.02	5.111
97.7	1.8	0.22	0.2	0.08	0	5.389
84.83	13.39	1.34	0.28	0.17	0	12.235
93.4	6.5	0.1	0	0	0	0.000
97.2	2.3	0.3	0.2	0	0	0.000
91.09	5.51	2.48	0.88	0.03	0	2.240
89.33	7.14	2.22	1.17	0.08	0.01	5.865
99.8	0.1	0	0.1	0.1	0	6.516
89.4	6.3	2.8	1.3	0.05	0.05	3.745
91.8	5.7	1.3	0.4	0.8	0	37.743
87.9	7.3	2.9	1.6	0.4	0	24.045
90.1	6.2	2.3	1	0.4	0	23.596
96.2	3.26	0.42	0.07	0.008	0.01	0.575
90.1	6.47	2.27	0.6	0.25	0.03	16.179
89.02	7.33	2.56	1.03	0.06	0	4.479

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ANNEX 2

LPG COMPOSITION

The compositions of commercial grades of Propane and Butane as transported by sea are variable since differing compositional standards exist around the world The table below shows three compositions for each of Propane and Butane. One is the pure product, one is called representative and is derived from a review of actual cargo certificates held by a major international LPG ship operator and the third, labelled ‘extreme’, is derived from limit conditions from various MSDS to give a high value for the CO_2 conversion factor.

	Ethane	Propane	Propylene	Butane	Pentane
	mol %	mol %	mol %	mol %	mol %
Propane, pure		100			
Representative	2	95		3	
Extreme	5	85	5	5	
Butane, pure				100	
Representative		4		95	1
Extreme		3		95	2

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