Economic Commission for Europe

Inland Transport Committee

6 January 2022

Working Party on the Transport of Dangerous Goods

Joint Meeting of Experts on the Regulations annexed to the European Agreement concerning the International Carriage of Dangerous Goods by Inland Waterways (ADN) (ADN Safety Committee)

English

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Item 4 (c) of the provisional agenda
Implementation of the European Agreement concerning the International Carriage of Dangerous Goods by Inland Waterways (ADN): interpretation of the Regulations annexed to ADN

Additional information of transport of Carbon dioxide (CO_2); (addendum to working document ECE/TRANS/WP.15/AC.2/2022/15)

Transmitted by EBU/ESO

Introduction

1. In working document ECE/TRANS/WP.15/AC.2/2022/15, EBU/ESO provides information about the transport of CO_2 in tank barges, type G and asked the ADN Safety Committee to reconsider the adding of remark "42" in Table C; to be able to carry this product under the same conditions as i.e. Ethylene (UN 1038) and Methane ("LNG"; UN 1972). This means transport without a required refrigeration system.

2. During further investigation of the transport conditions and transport provisions, EBU/ESO gathered recent and more extensive information which EBU/ESO would like to add this information to the discussion of document 2022/15.

I. Product information, provisions en prospected transport volumes

A. Product information

3. EBU/ESO was informed about a potential risk, which is specific for Carbon Dioxide. The triple point of CO_2 is relatively high (-56,57 ° C), compared to other refrigerated liquids. Below this temperature of -56,57° C, CO_2 can sublimate; transfer directly from the gaseous phase directly to the solid form ("cold ice"). This will cause problems in cargo tanks and pipe line systems and should be avoided in any case. (Relevant comparable product information refrigerated liquids under IV)

4. The distinction line between the solid and gas phase is always a combination of temperature and pressure. A pressure of 5 bar and lower is therefore associated with a temperature of -56 and lower (see graphics on page 3). These are circumstances that are outside the transport conditions.

5. To avoid the possibility of sublimation, the transport temperature should be allowed only above -41°C (a safety marge of 15° is taken into account, which is usual in the ADN

provisions). During the transport temperature and pressure cannot not decrease further. With this transport condition provision, the risk to sublimation would be eliminated.

6. This restriction could be added in a special remark 42, or a new remark 46 could be considered, to make a more specific provision.

B. Transport volumes

7. To give a view on the industries' wishes to transport CO_2, due to the climate protection plans; the following figures will give a realistic idea of the volumes to be transported:

Transport request by type G-barges for 2025

500.000 Tons/year within the NL

500.000 Tons/year Rhine-river destination-ARA

500.000 Tons ARA traffics.

The transport of 1-1,5 MTO CO_2 is foreseen from 2025, which will increase until at least 4,5 MTO in 2035.

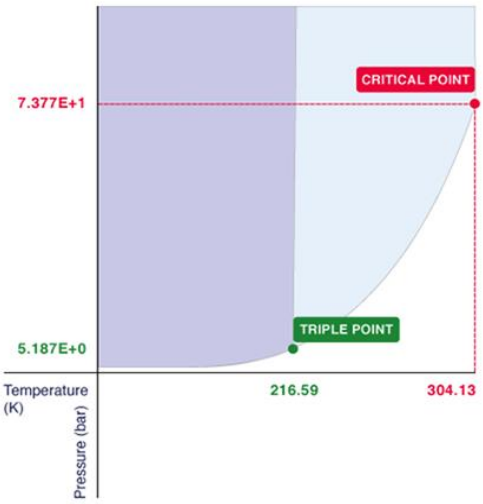
II. Question & Proposal

8. EBU/ESO asks the Safety Committee to discuss this additional information, as addendum of working document 2022/15.

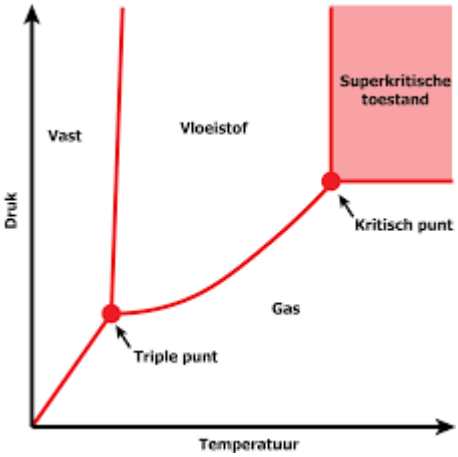
III. Information of triple point of gases, transported in the form of refrigerated liquids

	Triple point gasses		*Boiling point*		*Critical point*		
	Temperature (°C)	*Pressure (bar)*	*Temperature (°C)*	*Pressure (bar)*	*Temperature (°C)*	*Druk (bar)*	*Transport mode*
Methane	-182,47	0,117	-161,52	1	-82,62	45,96	Refrigerated
Ethane	-183,27	0,000011	-88,68	1	32,27	48,84	Refrigerated
Propane	-187,68	3,3E-09	-42,045	1	96,67	42,5	Refrigerated and pressurised
Butane	-138,86	0,000004	-0,5	1	152,03	37,96	Refrigerated and pressurised
Ethylene	-169,18	0,0012	-103,72	1	9,5	50,76	Refrigerated
Propylene	-185,4	3,6E-09	-47,72	1	91,6	46,1	Refrigerated and pressurised
Butadiene	-108,92	0,00069	-4,5	1	152	43,22	Refrigerated and pressurised
CO_2*	**-56,57**	5,185	-78,5	1	31,06	73,825	Refrigerated

* boiling point is sublimation point for CO_2



Purple = Solid phase
Blue = Liquid phase
White = Gas phase



Triple point:

9. At the Triple point all phases are present at the same moment. It's a combination between pressure and temperature

Boiling point:

10. Temperature of the substance at which the pressure generated by the substance is 1 bar.

Critical point:

11. A point on a phase diagram at which both the liquid and gas phase have the same density, and are therefore indistinguishable. It's the end point of the pressure–temperature curve that designates conditions under which a liquid and its vapor can coexist. At higher temperatures, the gas cannot be liquefied by pressure alone.

Background

12. When conditions drop under the triple point the substance can change from gas to solid in one step. So no vapour phase will occur. As solids can't be pumped this creates problems with discharging a cargo tank.

Refrigerated or pressurised

13. As stated above the critical point should be under ambient temperatures (0-30 °C) to be able to liquify by pressurising only. Therefore, for example can methane as a liquid only be transported under refrigerated conditions. Which is the same for Ethylene.

14. Ethane and CO_2 could be liquefied by pressure alone as long as the temperature stays under 31-32 degrees, but the pressure needed (50-73 bar) will be that high that the weight of the required cargo tanks will be to large and transport is not viable.

Transport conditions CO_2

15. To attain manageable pressures and temperatures and to stay away from the triple point CO_2 will therefore be transported at approx. -30 °C and a pressure of approx. 14 bar. See table below for the pressure at a certain temperature for CO_2.

Temperature (°C)	*Pressure (Bar)*
-57	5
-50	7
-40	10

Temperature (°C)	*Pressure (Bar)*
-30	14
-20	19
-10	27
0	35

Holding time, cooling installation vs sublimation:

16. Triple point of CO_2 is nearer to the transport conditions than the other gasses. The triple point of the other gasses has a much lower temperature and even lower pressures than their normal transport conditions:

> As stated above the normal transport conditions of CO_2 will be around -30 degrees and 14 bar. This is for the normal transport sufficiently away from the triple point and the danger of sublimation

17. When transport is based on isolated tanks only (So on holding time of the tank) due to energy influx from the environment into the product the temperature will rise and the pressure will rise as result:

> Over time the temperature and pressure will rise and the conditions will thus move further away from the triple point. The possible danger of sublimation will further decrease.

18. When transport is based on cooling installation the conditions will remain the same as during loading and will thus remain away from the triple point.