ALBERO – Transport of alternatively powered vehicles on ro-ro-ferries

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WP 1.2: Behaviour of alternative fuels in hazardous situations

Report

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I. Introduction

This report summarizes the chemicals used in alternative propulsion systems and their relevant physicochemical properties.

I.1 Fuels for gas-powered vehicles

The fuels used in gas-powered vehicles are LPG (liquified petroleum gas), CNG (*compressed natural gas*), LNG (*liquified natural gas*) and CGH2 (*compressed hydrogen gas*). Whereas conventional drives, gas drives and electric drives using fuel cells are primarily subject to hazards due to leaks, the following hazards can also occur in the case of gas-powered vehicles. (1), (2), (3), (4), (5), (6)

The fuels listed below have no particular toxic properties. LPG, CNG and LNG are small hydrocarbon molecules which do not differ fundamentally from conventional fuels in their reactivity to other chemicals and extinguishing agents. In particular, strong oxidizing agents should be avoided. The substances are not self-igniting, but can form explosive air mixtures under ambient conditions. Hydrogen/air mixtures are explosive over a particularly wide range.

In the event of fire, the gaseous hydrocarbons - comparable to conventional fuels - give rise to carbon monoxide and carbon dioxide, as well as water vapor. Foam is unsuitable for fire fighting. (7)

I.1.1 LPG (liquified petroleum gas)

LPG stands for liquefied natural gas that is a by-product of natural gas and crude oil production and refining.

Table 1: Relevant physicochemical properties of LPG

composition (8)	Summer: 60 % Butane, 40 % Propane (class E) Winter: 40 % Butane, 60 % Propane (Klasse B) geringe Mengen an Propen, Butenen und Pentanen/Pentenen bis 2 g/kg Methanol als Gefrierschutz
density liq. **density 1 bar**	0,58 - 0,60 g/cm^3 2,0 - 2,1 kg/m^3 > air (7)
tank pressure [bar]	5 - 15
temperature	ambient temperature
explosion limit	2 – 10 Vol-%

I.1.2 CNG (compressed natural gas)

CNG stands for compressed, gaseous natural gas.

Table 2: Relevant physicochemical properties of CNG

composition gas group 2H (9)	87 - 93 mol-% Methane up to 13 mol-% Propane/Butane
density 1 bar	0,7 - 1,0 kg/m^3 < air (7)
tank pressure [bar]	200 - 250
temperature	ambient temperature
explosion limit	4 – 17 Vol-%

I.1.3 LNG (liquified natural gas)

LNG stands for liquefied natural gas.

Table 3: Relevant physicochemical properties of LNG

composition gas group 2H (9)	87 - 93 mol-% Methane up to 13 mol-% Propane/Butane
density liq. **density 1 bar**	0,4 - 0,5 g/cm^3 0,70 - 1,0 kg/m^3 < air (7)
tank pressure [bar]	8
temperature	-170 .. -120 °C
explosion limit	4 – 17 Vol-%

I.1.4 CGH2 (compressed hydrogen gas)

CGH_2 is compressed gaseous hydrogen (H_2).

Table 4: Relevant physicochemical properties of Hydgrogen

composition [EN 17124] (10)	**>** 99,97 mol-% Hydrogen (H_2)
density 1 bar	0,09 kg/m^3 < Luft (7)
tank pressure [bar]	250 - 700
temperature	ambient temperature
Explosion limit	4 - 77 Vol-%

I.2 Battery-powered vehicles

At battery-powered electric vehicles, hazards also occur when charging the battery.

Currently, lithium-ion secondary batteries (accumulators) are primarily used for battery-powered vehicles. A large number of different variants of these exist, e.g. LiPo/LiPoly, lithium cobalt dioxide, lithium manganese dioxide, lithium vanadium, lithium nickel cobalt aluminum, lithium iron phosphate. The negative electrode is often made of garphite or amorphous carbon compounds, while the positive electrode is usually made of metal (mixed) oxides. (11)
The electrolyte solution consists of hydrous organic solvents e.g. propylene carbonate, ethylene carbonate, gamma-butyrolactone. The solvent may contain e.g. additives of 1,2-dimethoxyethane, dimethyl carbonate or diethyl carbonate. (11) (12) (13)
Conducting salts containing lithium (e.g. lithium tetrafluoroborate, lithium hexafluorophosphate, lithium bis(oxalate)borate, lithium trifluoromethanesulfonimide, lithium bis(fluorosulfonyl)imide) are dissolved in the electrolyte. (14) (12) (13)
Polyethylene or polypropylene foils are used as separators in the cell. Plastic-coated aluminum foil (bag cells, pouch-cells) and aluminum or steel sheet are used as primary wrapping. (15)

It is known that the use of lithium anodes poses a safety risk, as lithium tends to form dendrites which can lead to a short circuit (16), (17), (18). Short circuits can cause the battery to heat up, which can result in fires and even explosions in extreme cases. (19). In a guideline on the use of lithium batteries, the Natural Environment Research Council listed some examples of accidents when the batteries were used incorrectly. For example, fires and sometimes explosions occurred when charging times were too long.

The electrolytes used and the salts they contain represent a further safety risk. If the battery is damaged (also by excessive temperatures, for example by overheating after short circuits), the electrolyte liquid can leak out (20), (21), (22). If they are toxic, reactive to water or highly flammable, a high safety risk will be the result.

Overall, considerable research and development activities continue to take place in the field of Li-ion batteries. It is therefore to be expected that there may be changes in the materials used in the further future.The exact composition of the batteries are generally subject to trade secrecy and are not published.

Table 5: List of typical chemical substances in li-ion secondary batteries, the list does not claim to be complete

	li-ion secondary batteries
electrodes	- lithium and lithium intercalate compounds - graphite and amorphous carbon compounds - manganese oxides (e.g. manganese dioxide) - cobalt oxides - nickel oxides - iron phosphate connector: - polyvinylidene fluoride (23) (24)
electrolyte solution	- propylene carbonate - ethylene carbonate - gamma-butyrolactone additives from: - 1,2-dimethoxyethane - dimethyl carbonate - diethyl carbonate - ethyl acetate (24)
conducting salts	- lithium tetrafluoroborate - lithium hexafluorophosphate - lithium bis(oxalate) borate - lithium bistrifluoromethanesulfonimide - lithium bis(fluorosulfonyl)imide)
separator film	- polyethylene - polypropylene
housing	- aluminum sheet - steel sheet - plastic coated aluminum foil

In the following (from Table 7) some properties of the components listed in Table 5 are listed in the same order in separate tables. Further explanations on polyethylene, polypropylene, aluminum sheet, steel sheet and coated plastic foil are omitted. No unusual emissions or special reactions are to be expected with the plastics and metals mentioned.

Table 6: Relevant physicochemical properties of lithium-ion secondary batteries from product data sheets (23) (24)

	li-ion secondary batteries
hazards	- risk of fatal electric shock - chemical hazards for humans and the environment due to escaping ingredients and decomposition products - combustible - explosive
violent reaction at	- damage - heating >120 °C and fire possible - contact of the electrode material with moisture/water

Table 7: Relevant physicochemical properties of lithium, also representative for lithium intercalation compounds as safety data sheets were found here (7)

	lithium
properties	- solid - insoluble in water - melting point: 180 °C
hazards	- spontaneously combustible in contact with water or air - contact with water liberates flammable gases - causes severe skin burns and eye damage
dangerous chemical reactions	when in contact with: - water - oxidizing agents (e.g. air, oxygen, halogens) - alcohols - halogens - oxidizing acids (e.g. sulfuric acid, nitric acid) - hallogenated hydrocarbons (e.g. iodomethane, chloroform), for further details see data sheet
reaction products in case of fire and contact with water	- lithium oxide (corrosive) - lithium hydroxide (corrosive) - hydrogen (highly flammable)

Table 8: Relevant physicochemical properties of graphite, also representative for amorphous carbon compounds as safety data sheets were found here (7)

	graphite
properties	- solid - flame retardant - insoluble in water - no melting point under normal pressure; sublimates at 4.500 °C
hazards	--
dangerous chemical reactions	when in contact with: - fluorine - chlorine trifluoride
reaction products in case of fire	- carbon monoxide - carbon dioxide

Table 9: Relevant physicochemical properties of manganese dioxide (7)

	manganese dioxide
properties	- solid - non flammable - insoluble in water - no melting point under normal pressure; decomposition temperature 535 °C
hazards	- harmful when inhaled and if swallowed
dangerous chemical reactions	when in contact with: - oxidierbaren Stoffen - Säuren (weitere Angaben siehe Datenblatt)
reaction products in case of fire	no details

Table 10: Relevant physicochemical properties of cobalt oxides (7)

	cobalt oxides
properties	- solid - non combustible - poorly soluble in water
hazards	- toxic if swallowed - danger to life when inhaled - sensitizing - suspected of being carcinogenic - highly hazardous to water
dangerous chemical reactions	when in contact with: - cobalt(II/III) and cobalt (III) with hydrogen peroxide
reaction products in case of fire	metal oxide smoke

Table 11: Relevant physicochemical properties of nickel oxide (7)

	nickel oxide
properties	- solid - non combustible - poorly soluble in water
hazards	- sensitizing - may cause cancer when inhaled - hazardous to water
dangerous chemical reactions	when in contact with: - peroxides such as hydrogen peroxide (for further details see data sheet)
reaction products in case of fire	metal oxide smoke

Table 12: Relevant physicochemical properties of iron (III) phosphate (7)

	iron (III) phosphate
properties	- solid - non combustible - poorly soluble in water
hazards	- slightly hazardous to water
dangerous chemical reactions	when in contact with: no details
reaction products in case of fire	no details

Table 13: Relevant physicochemical properties of polyvinylidene fluoride (25)

	polyvinylidene fluoride
properties	- solid - flammable - insoluble in water - melting range 155-170 °C - thermal decomposition from approx. 300 °C
hazards	no details
dangerous chemical reactions	when in contact with: no details
reaction products in case of fire	- carbon monoxide - hydrofluoric acid - other low molecular weight fluorinated compounds

Table 14: Relevant physicochemical properties of propylene carbonate (7)

	propylene carbonate
properties	- liquid - flammable - water soluble - melting point: -49 °C - vapor pressure at 20 °C: 4 Pa - thermal decomposition from approx. 300 °C
hazards	- causes eye irritation - slightly hazardous to water
dangerous chemical reactions	when in contact with: no details
reaction products in case of fire	no details

Table 15: Relevant physicochemical properties of ethylene carbonate (7)

	ethylene carbonate
properties	- solid - flammable - water soluble - melting point: 36 °C
hazards	- causes severe eye irritation - slightly hazardous to water
dangerous chemical reactions	when in contact with: no details
reaction products in case of fire	no details

Table 16: Relevant physicochemical properties of gamma-butyrolactone. The substance has a neurotropic effect, which also leads to its misuse as an intoxicant. (7)

	gamma-butyrolactone
properties	- liquid - flammable - water soluble - aqueous solution reacts acidic - melting point: -44 °C - vapor pressure at 20 °C: 34.4 Pa - UEG: 1.4 % by volume - OEG: 16 % by volume
hazards	- harmful if swallowed - causes serious eye damage - may cause drowsiness and dizziness - slightly hazardous to water
dangerous chemical reactions	when in contact with: no details
reaction products in case of fire	no details

Table 17: Relevant physicochemical properties of 1,2-dimethoxyethane (7)

	1,2-dimethoxyethane
properties	- liquid - highly flammable - water soluble - melting point: -58 °C - vapor pressure at 20 °C: 7780 Pa - UEG: 1,4 % by volume - OEG: 10.6 % by volume - vapors heavier than air
hazards	- highly flammable liquid and vapor - harmful by inhalation - may affect fertility, may affect the unborn child - may form explosive peroxides - slightly hazardous to water
dangerous chemical reactions	when in contact with: - oxidizing agent - formation of peroxides in air
reaction products in case of fire	no details

Table 18: Relevant physicochemical properties of dimethyl carbonate (7)

	dimethyl carbonate
properties	- liquid - highly flammable - water soluble - melting point: 5 °C - vapor pressure at 20 °C: 5300 Pa - UEG: 3.26 % by volume - OEG: 12.87% by volume - vapors heavier than air
hazards	- highly flammable liquid and vapor - slightly hazardous to water
dangerous chemical reactions	when in contact with: - oxidizing agents - reducing agents - potassium tert-butoxide
reaction products in case of fire	no details

Table 19: Relevant physicochemical properties of diethyl carbonate (7)

	diethyl carbonate
properties	- liquid - flammable - water soluble - melting point: - 43 °C - vapor pressure at 20 °C: 1100 Pa - UEG: 1,4 % by volume - OEG: 11.7% by volume - vapors slightly heavier than air
hazards	- flammable liquid and vapor - slightly hazardous to water
dangerous chemical reactions	when in contact with: no details
reaction products in case of fire	- carbon monoxide - carbon dioxide

Table 20: Relevant physicochemical properties of ethyl acetate (7)

	ethyl acetate
properties	- liquid - highly flammable - water soluble - melting point:- 83 °C - vapor pressure at 20 °C: 9840 Pa - UEG: 2.0% by volume - OEG: 12.8% by volume - vapors heavier than air
hazards	- highly flammable liquid and vapor - causes severe eye irritation - may cause drowsiness and dizziness - slightly hazardous to water
dangerous chemical reactions	when in contact with: - alkali/eralkali metals - oleum - strong oxidizing agents - fluorine - strong acids - strong bases - potassium tert-butoxide
reaction products in case of fire	- carbon monoxide - carbon dioxide

Table 21: Relevant physicochemical properties of lithium tetrafluoroborate (26)

	lithium tetrafluoroborate
properties	- solid - water soluble - melting point: -283-300 °C
hazards	- harmful if swallowed and inhaled - causes severe skin burns and eye damage
dangerous chemical reactions	when in contact with: - acids - water - bases - oxidizing agents
hazardous decomposition products	- hydrogen fluoride - boron oxide - lithium oxide

Table 22: Relevant physicochemical properties of lithium hexafluorophosphate (7)

	lithium hexafluorophosphate
properties	- solid - water soluble - decomposition temperature: -200 °C
hazards	- toxic if swallowed by ingestion and when inhaled - causes severe skin burns and eye damage - causes damage to organs through prolonged or repeated exposure - significantly hazardous to water
dangerous chemical reactions	when in contact with: no details
hazardous decomposition products	- hydrogen fluoride - phosphorus oxides - metal oxide smoke

Table 23: Relevant physicochemical properties of lithium bis(oxalato)borate (27)

	lithium bis(oxalato)borate
properties	- solid - melting point >300 °C
hazards	- causes skin irritation - causes severe eye irritation - may cause respiratory irritation
dangerous chemical reactions	when in contact with: no details
hazardous decomposition products	no details

Table 24: Relevant physicochemical properties of lithium trifluorosulfonimide (27)

	lithium trifluorosulfonimide
properties	- solid - non combustible - soluble in water - melting point: 234-238 °C - alkaline
hazards	- toxic if swallowed or in contact with skin - causes severe skin burns and eye damage - highly hazardous to water
dangerous chemical reactions	when in contact with: - water/moisture - strong oxidizing agents
hazardous decomposition products	- carbon oxides - nitrogen oxides - sulfur oxides - hydrogen fluoride - lithium oxide

Table 25: Relevant physicochemical properties of lithium bis(fluorosulfonyl)imide (28)

	lithium bis(fluorosulfonyl)imide
properties	- solid - non combustible - soluble in water - melting point: 234-238 °C - alkaline
hazards	- toxic if swallowed or in contact with skin - causes severe skin burns and eye damage - highly hazardous to water
dangerous chemical reactions	when in contact with: - water/moisture - strong oxidizing agents
hazardous decomposition products	- carbon oxides - nitrogen oxides - sulfur oxides - hydrogen fluoride - lithium oxide

In the course of various tests, it was found that CO_2 and H_2 are formed as oxidation products of the electrolyte on the surface of the electrode. Small amounts of CH_4, C_2H_4, C_2H_6, C_3H_8 etc. are also formed. In cell components containing fluorine, organic fluorine compounds are formed (29).

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