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Natural Refrigerant on Board Marine Vessels

Abstract

The paper deals with the topic of refrigerants, their historical evolution, applied legislation and trends in maritime affairs. Regarding the Environmental care paper considers the impact of refrigerants of refrigeration systems, both on stationary plants on land and on plants on board. New regulations of the European Union, and IMO maritime organization, require the reduction and complete abolition of harmful synthetic refrigerants and the introduction of new refrigerants that will have a significant economic and environmental impact. The trend is the introduction of natural refrigerants as a replacement for existing environmentally unacceptable ones. On-board refrigeration systems introduce natural refrigerants such as ammonia and carbon dioxide into applications that require lower refrigeration temperatures. Absorption cooling plants are introduced into air conditioning applications on board the ship. They work with water/lithium bromide ($H_2O/LiBr$) mixtures, thus increasing the efficiency of the plant and reducing the impact on the environment.

Keywords: Refrigerants, Natural refrigerants, Synthetic refrigerant, Ozone Depletion Substances (ODS), Ozone Depletion Potential (ODP), Global Warming Potential (GWP), Total Equivalent Warming Impact (TEWI)

1. Introduction

Modern refrigeration techniques characterized by the use of the first generation of refrigerants so-called natural refrigerants have been used since the early 19th century. Water and air were the first refrigerants used in refrigeration equipment (Figure 1). In 1844 John Gorrie developed a refrigeration cycle with a reciprocating refrigeration unit in which he used compressed air as a natural refrigerant. This cooling cycle was later used by Brayton in 1873. In 1834, Perkins proposed ethyl ether ($C_4H_{10}O$) as a refrigerant in his patent for a closed-loop vapor-compression refrigeration system. It is a good refrigerant, but it is toxic and flammable. Also, the entire ethyl ether cooling system operated below atmospheric pressure, making it difficult to prevent air from entering the system.

The danger and complexity of ethyl ether refrigeration devices led other inventors to look for alternative refrigeration technologies, which ultimately led to the rapid development of refrigeration cycles between 1860 and 1890. French inventor Charles Tellier introduced dimethylether (CH_3Cl) as a substitute for ethyl ether in 1863. Although methyl was also toxic and flammable, it allowed the entire cooling system to operate above atmospheric pressure, eliminating problems caused by air penetration into the system, [1]. In 1876, Linde designed the first machine to work with ammonia (CH_4), and in 1862, Lowe developed a carbon dioxide (CO_2) cooling system. Carbon dioxide, requires high pressure in devices and was impractical to use due to the low critical temperature (31.6 °C). In order to improve the technical characteristics of refrigeration devices which will be safe to use in terms of flammability and toxicity, a generation of synthetic refrigerants, chlorofluorocarbon (CFC) is emerging (Figure 1).

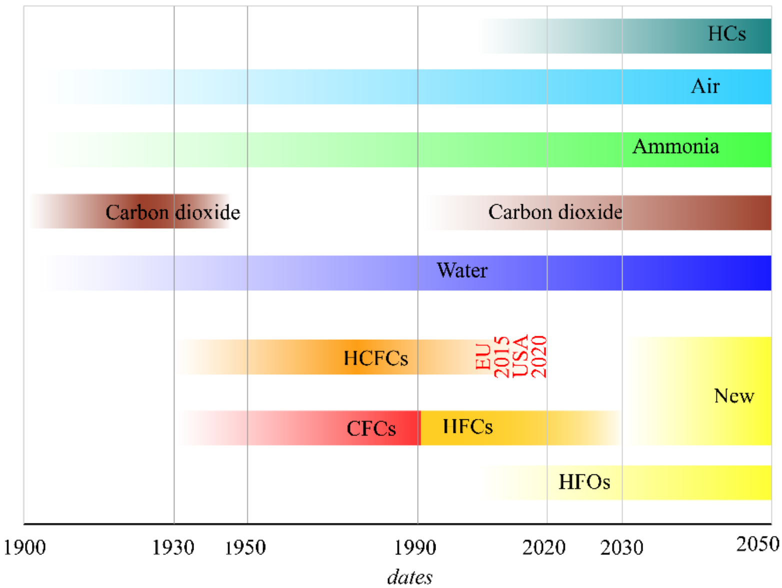

Figure 1. Histogram of synthetic and natural refrigerant [3,4].

The first such refrigerant was developed in 1928 under the designation R12 (Table 1), in 1931 commercial production began, then in 1932 R11 was developed and finally R13 was developed in 1945 for the use in devices for achieving lower temperatures. Since 1950, hydrochlorofluorocarbons (HCFCs) represented by R22 and R502, and hydrofluorocarbons (HFCs) represented by R-134A, R404A, R410A and R32 have appeared. In 1974, researchers Roland and Molina predicted that CFC emissions could damage the Earth's atmosphere by destroying ozone. The hypothesis was proven by 1985 measurements that showed a destruction of the ozone layer across Antarctica. In 1987, the Montreal Protocol restricted the production and consumption of CFCs. Between 1990 and present emissions of Ozone Depleting Substances (ODS) have decreased significantly as a result of the Montreal Protocol and its subsequent entry into force of the amendment, [2].

Table 1. List of synthetic and natural refrigerant [2,5].

Refrigerant	Mark	Chemical formula	Safety group	Type	ODP	GWP_{100}
Freon 12	R12	CCl_2F_2	A1	CFC	1	8500
Freon 22	R22	$CHClF_2$	A1	HCFC	0.055	1700
Freon 404A	R404A	R143A/ R125/ R134A (52/44/4)	A1	HFC	0	3700
Puron	R410A	R32/R125 (50/50)	A1	HFC	0	2100
Freon 134a	R134A	CF_3CH_2F	A1	HFC	0	1370
Water	R718	H_2O	A1	Natural	0	0
Ammonia	R717	NH_3	B2	Natural	0	0
Nitrogen	R728	$_N2$	A1	Natural	0	0
Carbon dioxide	R744	CO_2	A1	Natural	0	1
Isobutane	R600a	C_4H_{10}	A3	Natural	0	3
Propane	R290	C_3H_8	A3	Natural	0	3
Ethylene	R1150	C_2H_4	A3	Natural	0	20
Propylene	R1270	C_3H_6	A3	Natural	0	6

The ban on the use of CFCs (2006) and HCFCs (2015) brings us to the current state of use of HFCs, their mixtures and the reintroduction of natural refrigerants, thus closing the cycle of using natural refrigerants, Figure 2. In EU countries, the phasing out of HCFCs has accelerated and they are no longer used. Today's refrigerants must not contain chlorine, they must have a good effect and little impact on global warming.

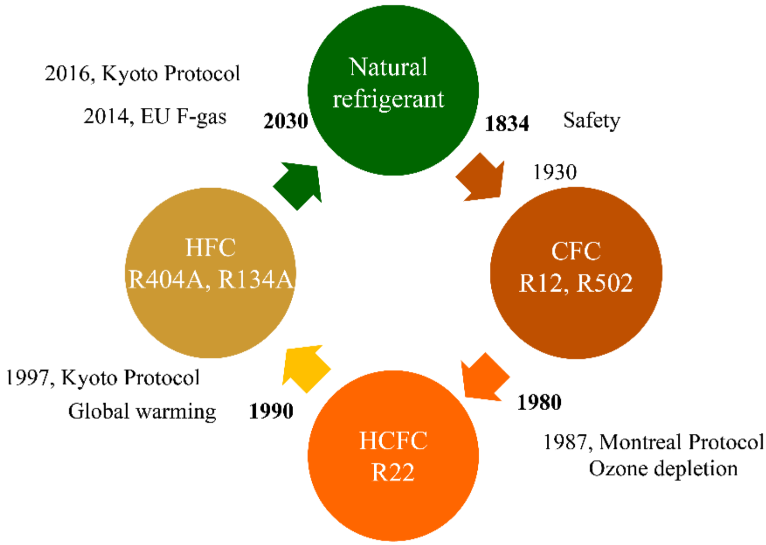

Figure 2. Closed loop natural and synthetic refrigerants.

2. Refrigerant on board

According to the International Maritime Organization (IMO, 2014), the total use of HCFCs/HFCs as a refrigerant in the world merchant fleet is estimated at 70% for R22, 26% for R134a and 4% for R404A. The release of refrigerants from global transport (excluding refrigerated containers) is estimated at 8,400 tons, which corresponds to CO_2 equivalent emissions of about 15 million tons, which is 2% of CO_2 emissions from shipping, [6].

The average annual loss of refrigerants from the global fleet, based on the latest statistics, indicates that air conditioning equipment is responsible for about 69.8% of the total loss of refrigerants; however, 30.2% of this loss is cooling equipment based. Figure. 3 shows the contribution of each ship type based on the loss in refrigerants due to air conditioning. It noticed that general cargo and cruise ships contribute considerable amounts of loss of refrigerants rather than the other various ship types (IMO, 2014), [7].

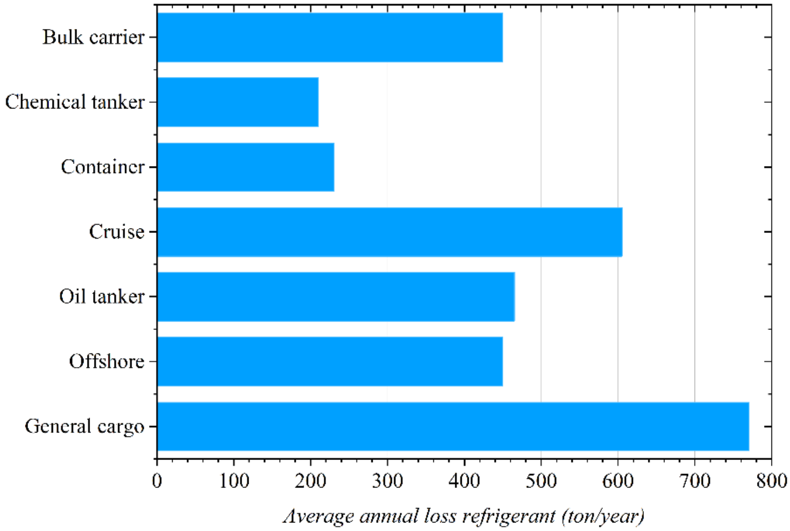

Figure 3. Average annual refrigerant losses by direct emission depending on the type of vessel, [7].

The high level of direct greenhouse gas emissions from marine vessels compared to the ashore systems can be explained by the constant exposure of the entire system to stress and vibration, a small number of crew members trained to work with refrigeration when a ship is at sea for several weeks. Leaks are usually not repaired, in order to provide cooling in these cases, refrigeration devices are simply replenished with refrigerant. It is widely believed that the primary duties of the ship's crew must be focused on the ship's propulsion, so maintenance and troubleshooting of refrigeration plants is given low priority. Problems that occur could be reduced by replacing worn-out equipment. In the design phase, more attention should be paid to the simplification of the plant, i.e. it is necessary to take into account the length of the pipeline, which should be kept to a minimum and thus prevent potential leaks. It is also necessary to take into account the procurement of quality equipment when designing or replacing the system. It is mandatory to keep records of the amount of installed and refilled refrigerant. Stricter controls and heavier penalties are also needed for non-compliant shipping companies.

3. Total greenhouse gas emissions on board

The total greenhouse gas emissions that occur on ships consists of direct and indirect greenhouse gas emissions. Total emission is expressed in terms of TEWI (Total Equivalent Warming Impact).

By applying this parameter, it is possible to determine the total amount of greenhouse gas emissions associated with the use of refrigerant through the calculation of direct emissions (leakage) and indirect greenhouse gas emissions, which are emissions from electricity production consumed by the cooling system - parameter related to cooling system efficiency.

The value of indirect greenhouse gas emissions (registered during the life of the refrigerant) represents the largest share of greenhouse gas emissions associated with the use of refrigerant. Therefore, the TEWI index depends on how electricity is generated so replacing a high GWP refrigerant with a lower GWP one based only on direct GHG emissions is not the best solution, as we can increase indirect emissions. For example, if the replaced refrigerant has lower thermodynamic properties, replacement will result in reduced cooling COP. In this case, refrigeration systems will consume more electricity to achieve equal COP. Therefore, refrigerant replacement needs to be properly planned or will lead to increased system costs and increased greenhouse gas emissions.

The value of this parameter is obtained by applying the following equation [5,10]:

$$TEWI = Direct\ GHG\ emissions + Indirect\ GHG\ emissions \quad (1)$$

$$TEWI = GWP\{L \cdot n + m(1 - C)\} + GWP\{n \cdot E \cdot \beta\} \quad (2)$$

Where L is annual amount of the refrigerant emissions (leakage) [kg]; n is lifetime of the refrigeration system [years]; m is refrigerant charge [kg]; C is recovery factor/refrigerant recycling, between 0 and 1; E is annual energy consumption of the refrigeration system [kWh]; β is the amount of CO_2 emissions for 1 kWh energy generation [kgCO_2 /kWh].

4. Regulations for refrigerant on marine vessels

In order to reduce greenhouse gas emissions, a number of regulations have been passed. The first one was adopted in 1978 by the U.S. The Environmental Protection Agency (EPA), it prohibits the use of CFCs in all nonessential aerosol cans. Then in 1980 the European Community limited CFC production and use in aerosols. 1987. The Montreal Protocol was signed by 43 nations to reduce overall production of CFCs by 50% by 1999. In 1992, the signers of the Montreal Protocol agreed to a phase-out schedule for all HCFCs (including R-123) by the year 2030, [1].

The main regulatory institutions for marine installations are the International Maritime Organization (IMO) and maritime registries. IMO International Convention MARPOL (International Convention for the Prevention of Maritime Pollution) is the main international convention covering the prevention of marine pollution by ships from operational or accidental causes (IMO, 2017a). MARPOL, Annex VI (Regulations for the Prevention of Air Pollution from Ships. Regulation 12 – the use of ozone depletion substances (ODS) in marine applications). New installations containing CFC or Halon are not permitted on ships constructed on or after 19 May 2005, while new installations of HCFC equipment are prohibited after 1 January 2020, both on new and existing ships. Furthermore, it is prohibited to deliberately discharge ODS to the atmosphere; these refrigerants should be collected in a controlled way and be either reused on board or sent to an appropriate facility (IMO, 2017b).

First European Regulation, EU no. 842/2006 on fluorinated greenhouse gases (F-gases) was adopted in 2006 with the aim of reducing fluorinated greenhouse gas emissions through, for example, periodic leak tests, record keeping, proper recovery and certification. However, this regulation only applies to stationary equipment, i.e. not to seagoing vessels. The new EU Regulation on F-gases, no. 517/2014, which applies from 1st January 2015 was introduced in 2014. The regulations restrict the use of gases in production, i.e. taking care of gas leakage by periodic testing for leakage into the environment through, keeping records of correct use and certification. It should be noted that these regulations do not apply to ships. There is only a general regulation on the avoidance of intentional discharges of HFCs that applies to all types of installations. However, there is a ban on services for existing high GWP systems that applies to ships. This means that it is forbidden to refuel equipment on an EU-flagged ship using HFCs with a GWP > 2500 and a quantity corresponding to 40 tons of CO_2 equivalent with a new refrigerant after January 1st 2020 and recycled refrigerant after January 1st 2030. As mentioned above, an EU F-gas regulation requires mandatory leak checks for stationary equipment but not for on-board equipment.

Some maritime registries suggest introducing class remittances for low-impact refrigeration systems. Most Nordic-flagged ships are classified according to DNV-GL. This register offers two environmental class labels: “Clean” and “Clean Design”. The label “Clean” means: The refrigerant can be HFC or natural refrigerants such as NH_3 and CO_2. The annual leakage must not exceed 10% of the total refrigerant charge for each system. The leak must be documented. The term “Clean Design” means: The refrigerants used must be either natural refrigerant or HFC with a GWP of not more than 2000, [6].

5. Natural refrigerants

Natural refrigerants are back in use with a tendency to replace harmful synthetic refrigerants (Table 1). It should be emphasized that natural refrigerants are not derived from nature, they are produced industrially like any other synthetic refrigerants. We call them “natural refrigerants” because they are substances that occur directly in nature. Their advantage is that they are cheap to manufacture, long-lasting, they enable reliable and efficient operation of the system, and have the lowest total cost of plant life, which includes installation, maintenance and disposal. The best known natural refrigerants are water, ammonia, carbon dioxide, hydrocarbons and binary mixtures with natural refrigerants water and ammonia.

5.1. Water, R718

Water (R718) is one of the oldest refrigerants used for applications in refrigeration technology. Compared to conventional synthetic refrigerants, it requires much higher volume flows and higher pressure ratios for the same applications. Therefore, water is often used as an indirect cooling circuit coolant. Water mixed with antifreeze solutions (propylene or ethylene glycol), can be used below the freezing point of water, applied in the form of an ice slurry (binary ice). Water is easily available and has excellent thermodynamic and chemical properties. Nowadays, it is used in binary mixture for operation with absorption refrigeration devices for HVAC and refrigeration. However, due to their high specific volume at low pressures, absorption refrigerants take on larger dimensions, which may be a disadvantage on some ships.

5.2. Ammonia, R717

Natural refrigerant, R-717 (ammonia, NH_3, GWP = 0) is used since the 19th century in vapor-compression and absorption refrigerants. Ammonia was first used in the compression process by David Boyle in 1872 in the United States. Carl von Linde used ammonia in his vapor-refrigeration units for a brewery in Trieste in 1876, which he had chosen after he tried to use ether that exploded in a laboratory, [8]. Since then, ammonia has been the dominant refrigerant for industrial applications. This is due to its unique, thermodynamic quality and the fact that ammonia-based cooling systems are also efficient and cost-effective. The advantage of the R717 is a wide operating temperature range due to its high critical point and high latent heat of vaporization. Cooling capacity per unit mass flow is the highest of all refrigerants used in traditional vapor-compression systems. The disadvantages of this refrigerant R-717 are: it is very toxic, flammable and has a very unpleasant smell. Smell is actually an advantage because the smallest leaks are easily detected and then corrected. Ammonia is easily soluble in water, when it contains water, it is corrosive to copper and most copper alloys. Therefore, it is unsuitable for use with hermetic compressors because it can destroy the copper windings of electric motors. It is flammable and toxic, so it is classified in safety group B2L and requires additional safety measures. Ammonia systems designed over the last 20-30 years in accordance with the law on pressure vessels are of very high quality, with excellent safety standards, [6]. The future of ammonia is positive because it has superior properties as a refrigerant. Ammonia has always been a refrigerant used in large, industrial plants. Political pressure on HFCs will increase and this will result in new technical solutions with natural refrigerants, such as ammonia. If used properly, ammonia not only has a good level of safety but also has good economic viability. If used properly, this refrigerant gives the best efficiency of most refrigerants.

5.3. Carbon dioxide, R744

Carbon dioxide, R744 (CO_2, GWP = 1, ODP = 0) is relatively inexpensive natural refrigerant. It's a natural substance so it does not cause the ozone depletion (ODP), it's global warming potential (GWP) is 1 and it is not a threat to the environment. From a safety and environmental point of view it is almost ideal for applications where relatively large amounts of refrigerant are required. Despite the high pressures associated with its use, carbon dioxide has been used as a refrigerant since the 19th century. It is odorless, non-toxic, non-flammable, non-explosive and non-corrosive. Carbon dioxide continued to be used in marine cooling as a non-toxic alternative to ammonia and methyl chloride. Introduction of synthetic refrigerants in the 1930s led to the abandonment of much less efficient carbon dioxide, which finally fell out of use in the 1950s. The reason for the poor efficiency obtained by using carbon dioxide as a refrigerant is that it has a low critical temperature. As a result of modern methods and developments, carbon dioxide is returning to use as a refrigerant in systems that have at least as much efficiency as systems with ammonia and synthetic refrigerants. There is a wide range of applications in which R744 is the preferred working fluid (application for freezing, commercial refrigeration, hot water heat pumps, mobile AC, etc.). The American Society of Heating, Refrigeration and Air Conditioning Engineers (ASHRAE) has declared CO_2 as a non-flammable and non-toxic (safety class A1) refrigerant. It is recognized as the most promising refrigerant in shipbuilding in places where ammonia cannot be used. It does not subject to F-gas regulations. It can be an ideal refrigerant if applied properly. The problem of CO_2 systems is the high pressure in the system at rest. If the plant has been shut down due to maintenance, power outage or anything else for other reasons, then the refrigerant inside the plant will begin to receive heat from the environment and the pressure inside the plant will consequently increase. Which can result in different system components that are typically designed for a maximum pressure of 40 bar. The most common and simplest protection technique is to release part of the CO_2 charge from the plant when the pressure reaches a certain preset value, consequently, the pressure and temperature of CO_2 in the plant will decrease. The plant must then be recharged to make up for lost CO_2, [8].

5.4. Hydrocarbons

Hydrocarbons (HC) are made of hydrogen and carbon found in high concentrations in crude oil. Used as a modern refrigerant, they are non-toxic and environmentally friendly alternative to CFC/HCFC/HFC. Methane (R50), ethane (R170), propane (R290), butane (R600), isobutane (R600a) are some of the compounds belonging to the HC family. Butane and isobutane also have high critical temperatures, which makes them very efficient in operation, they are most commonly used in household refrigeration devices. Propane (R-290) and Propylene (R1270) are used as refrigerants in heat pumps, air conditioners, refrigerators and freezers. They are a good replacement for existing environmentally friendly refrigerants due to compatibility with mineral oils and components found in many existing systems, [3]. They are cheap and offer great energy efficiency. R1270 is a propane-like refrigerant but much more expensive and therefore unlikely to be widely used. This type of compound has the following characteristics: highly flammable and explosive; low toxicity; and environmentally friendly because it is not involved in the ozone depletion process and has a very little impact on the greenhouse effect. Because they are highly flammable and explosive, it is necessary to reduce the refrigerant charge in the systems to minimize the risks of its use. There are no problems with the compatibility between these compounds and materials traditionally used in refrigeration systems.

5.5. Binary mixtures

The binary mixture of lithium bromide and water (H_2O/LiBr) is the most commonly used working medium in absorption refrigeration devices for HVAC (Heating, Ventilation, Air Conditioning) on board and on land. Due to its non-toxicity and environmental friendliness, this working medium is an excellent replacement for synthetic refrigerants that deplete the ozone layer and which, due to various regulations, must be almost completely phased out. Some other advantages of the H_2O/LiBr mixture as a working medium are low cost and availability of water as a component of the binary mixture, as well as high absorption capacity and low viscosity of the mixture. In an absorption refrigeration device, water is used as a refrigerant and lithium bromide is used as an absorbent. The binary ammonia-water mixture, NH_3/H_2O is not used in low temperature systems and is therefore suitable on ships for the transport of frozen products.

6. Natural refrigerants in maritime applications

Direct emissions of greenhouse gases on board, which are achieved by leakage of refrigerant from the plant, make up about 2% of the total greenhouse gas emissions, [6]. The largest part of greenhouse gas emissions comes indirectly through the transformation of fuel energy into electricity and thus affects the increase in TEWI. In addition to the propulsion system on board, the largest energy consumers are HVAC, [9]. Conventional refrigeration systems for achieving low temperatures on ships are based on vapor-compression systems that use electricity generated indirectly through diesel engines or gas turbines that emit greenhouse gases into the environment and thus contribute to the overall greenhouse gas emissions on board indirectly. Which means that if we want to reduce indirect greenhouse gas emissions we need to increase the energy efficiency of the onboard system.

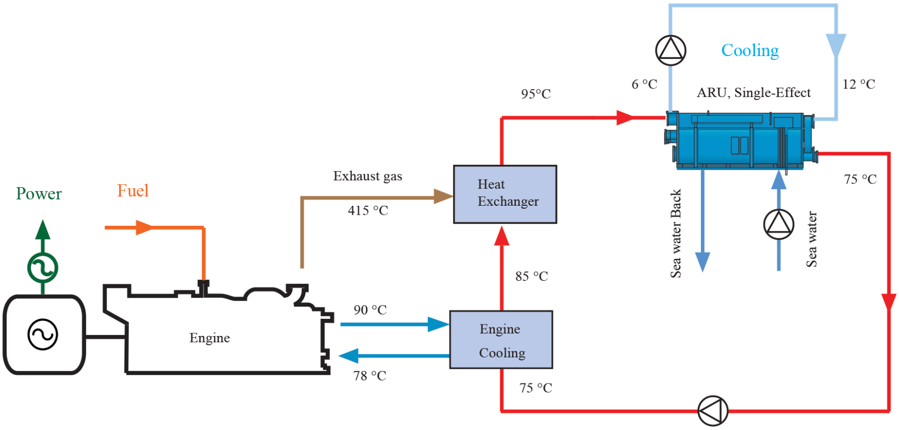

Figure 4. Single–Effect ARU Water/LiBr on board.

Energy efficiency on board could be increased by utilization of the waste heat on board for the needs of HVAC system by using absorption refrigeration devices, ARU. These devices work with environmentally friendly refrigerants and thus, in addition to reducing indirect greenhouse gas emissions, they further reduce the potential risk of direct emissions caused by leakage of refrigerants into the environment. Absorption refrigeration units that work with the H_2O/LiBr mixture are used in air conditioning on land and on board. Absorption cooling is a technique that has been used in onshore installations for many years, [11-14]. Absorption cooling devices use heat to start the cooling cycle consequently producing cooled water in the HVAC system. Electricity consumption is very low, and when waste heat is used as a heat source the energy efficiency becomes very high. And thus contributes to the overall efficiency of the marine system. Waste heat sources are available on board which can be used to power the absorption refrigeration unit, steam/hot water produced by the exhaust gases of the main engine or "hot" cooling water from the main engine, Figure 4. An absorption cooling device was installed on the AIDAmar 2012 cruiser. The heat source is waste heat from the cooling water of the diesel engine (about 80-90 °C), and the cooling capacity is 1200 kW. An absorption chiller is also connected to a desalination plant for drinking water production (Fisher group, 2012), [6].

Average efficiency of COP compression refrigeration units (CRUs) ranges from 3-6, while the efficiency of absorption refrigeration units depends on the effect of absorption (single, double) and ranges from 0.5-1.5. Seemingly the efficiency of the ARU system is small but these efficiencies should not be directly compared, we must take into account the thermal efficiency of the system that produces electricity. The degree of efficiency of the compression refrigeration device that can be compared with the absorption refrigeration device is: , thus we come to the realization that ARU is a superior refrigeration unit compared to CRU in terms of environmental, economic and energy efficiency. In terms of ecology because of direct and indirect greenhouse gas emissions and in terms of energy because such systems ultimately increase the overall efficiency of the plant resulting in reduced fuel consumption and increase the economic viability of the entire system, [11,12].

Of the natural refrigerants that have found their application on board are on-board gas liquefaction systems. These systems are used to achieve low temperatures (-161°C) on LNG (Liquefied Natural Gas) ships. Refrigeration systems for re-liquefaction of gases are based in most cases on the Brayton cycle that works with the natural refrigerant nitrogen, N_2 (R728), [15,16]. Newer solutions based on cascading refrigeration cycles using propylene/ethylene refrigerants (R1270/R1150) are also proposed, [17]. Regarding the application of R744 on ships, Johnson Controls predicts that within few years, much of the new HVAC and refrigeration plant installations on cruise ships will be indirect cooling systems with R744 primary working fluid and glycol as the secondary refrigerant fluid, [6].

7. Conclusion

Environmental care is carried out in the field of application and impact of refrigerant refrigerants on board ships. New regulations of the European Union, and the IMO maritime organizations, require the reduction and complete abolition of synthetic refrigerants and the introduction of new refrigerants that result in a significant impact on the economic and environmental impact of individual plants. Since natural refrigerants are cheap to manufacture, they are imposed as replacement refrigerants in the shipping industry. A big deal of energy consumption is attributed to the HVAC and refrigeration system. In their work, these systems use electricity that is used to drive refrigeration devices, and thus the indirect efficiency of the plant depends on the indirect emission of greenhouse gases. Therefore, it is necessary to maximize the efficiency that can be achieved with the use of absorption refrigeration devices that work with environmentally friendly refrigerants. In this way, increase the overall level of efficiency and reduce indirect greenhouse gas emissions. Direct emissions (by refrigerant leakage) can be reduced by training and certifying staff, by investing in quality equipment. It is necessary to work on raising the awareness of the shipping company to apply the most modern, optimal solutions in new construction, based on devices that work with natural working substances.

8. Nomenclature

Abbreviation

ARU	Absorption Refrigeration Units
BOG	Boil of Gas
CFC	ChloroFluoroCarbons
COP	Coefficient of Performance
CRU	Compression refrigeration Units
EPA	Environmental Protection Agency
EU	European Union
GWP	Global Warming Potential
HCFC	HydroChloroFluoroCarbons
HFC	HydroFluoroCarbons
HFO	HydroFluoroOlefin
HVAC	Heating, Ventilation, Air conditioning
IMO	International Maritime Organization
LNG	Liquefied Natural Gas
MARPOL	International Convention for the Prevention of Maritime Pollution
ODP	Ozone Depletion Potential
ODS	Ozone Depletion Substances
R	Refrigerant
TEWI	Total Equivalent Warming Impact

Symbols

B	Carbon dioxide emissions	kg/kWh
C	Recovery factor/refrigerant recycling, between 0 and 1	-
E	Annual energy consumption of the refrigeration system	kWh
L	Annual amount of the refrigerant emissions (leakage)	kg
m	Refrigerant charge	kg
n	Lifetime of the refrigeration system	year
η	Efficiency	-

Index

CRU	Compression refrigeration nits
t	Thermal

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