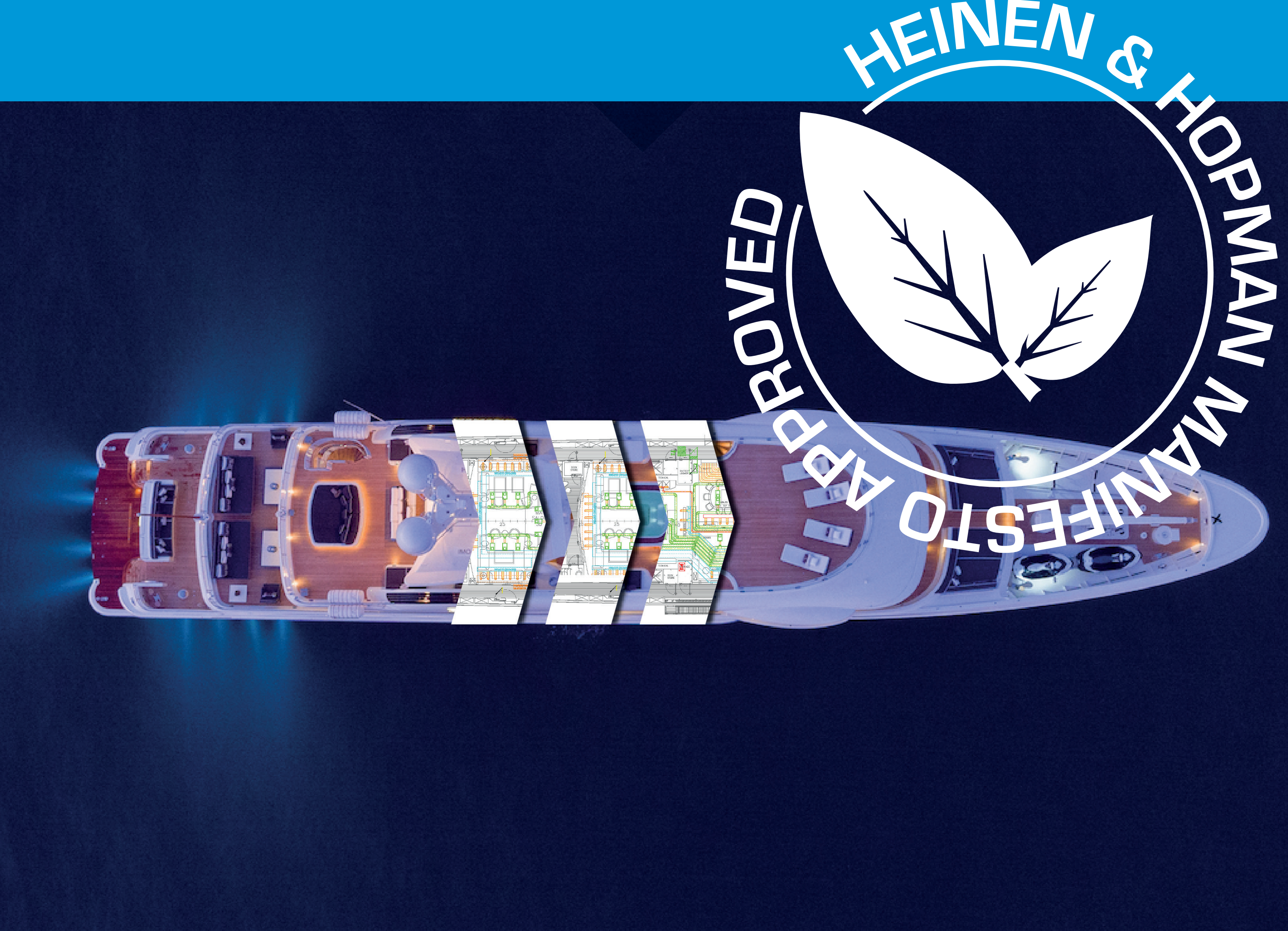
# NATURAL REFRIGERANTS

A GOOD ALTERNATIVE TO HIGH-GWP REFRIGERANTS?



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**Selecting the right natural refrigerant is not an easy task as each type has its own pros and cons.**

# INTRO

**Natural refrigerants are a hot topic. More and more onshore utility-based installations are switching to natural gas. What's the situation in the maritime industry? Selecting the right refrigerant is no easy task as each type has its own pros and cons. In this whitepaper we will explore the most common natural refrigerants so you can understand which one best suits your specific application.**

The ability to design an installation that contributes to a cleaner environment is always welcome and natural refrigerants have a part to play. At the same time, we need to be aware of the multiple factors involved in choosing the right refrigerant for your specific application.

Please note that the values and calculations given in this whitepaper have been simplified in order to give you a general overview of the pros and cons of every refrigerant. More specific information is needed for a detailed calculation and we strongly recommend contacting one of our engineers if you are considering the use of natural refrigerants.

> **More and more onshore utility-based installations are switching to natural gas**

# CHAPTERS

PART 1
# INTRODUCTION

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# INTRODUCTION

## WHAT ARE NATURAL REFRIGERANTS?

**The main advantage of natural refrigerants is their low global warming potential (GWP) – the equivalent $CO_2$ impact on the environment. Natural refrigerants have GWPs ranging from 0 to 3, while the majority of synthetic refrigerants are extreme greenhouse gases with GWPs up to 4000 – yes, that's 4000 times the equivalent of $CO_2$. It is a common error to presume that natural refrigerants are automatically more energy efficient which, as we shall see, is not always the case. The reason why natural refrigerants are more sustainable is on a whole other level.**

## HOW TO COMPARE NATURAL REFRIGERANTS?

Before we dive in let's establish the rules of the game. In this whitepaper we'll compare five different refrigerants on a fixed set of properties. Three of them are natural refrigerants, namely, R744 ($CO_2$), R717 ($NH_3$), and R290 (Propane). Then we have R1234ze (HFO), one of the newer synthetic refrigerants with a low GWP. Lastly, we take one of the most used synthetic refrigerants R134a (HFK) as a benchmark.

All starting points are the same for every refrigerant. We compare them on the following temperatures:

**Evaporation temperature**: -10°C
**Condensation temperature**: 25°C
**Overheating:** 20K
**Subcooling:** 5K

To give you an honest review and a better understanding, we compare every refrigerant on a fixed set of properties. These are:

| Thermodynamic properties | Safety | Sustainability |
|---|---|---|
| Temperatures | Flammability | GWP |
| Pressures | Toxicity | Ozone depletion |
| Latent heat capacity | Pressure | Energy efficiency |
| | Corrosive | |

Why are these properties important? Read on...

## THERMODYNAMIC PROPERTIES

The concept of cooling depends on **evaporation** and **condensation**. Each refrigerant has its own specific boiling point and operating zone. The preferred refrigerant for your specific application (air-conditioning, provision cooling, etc.) should fit within the operating zone of this refrigerant.

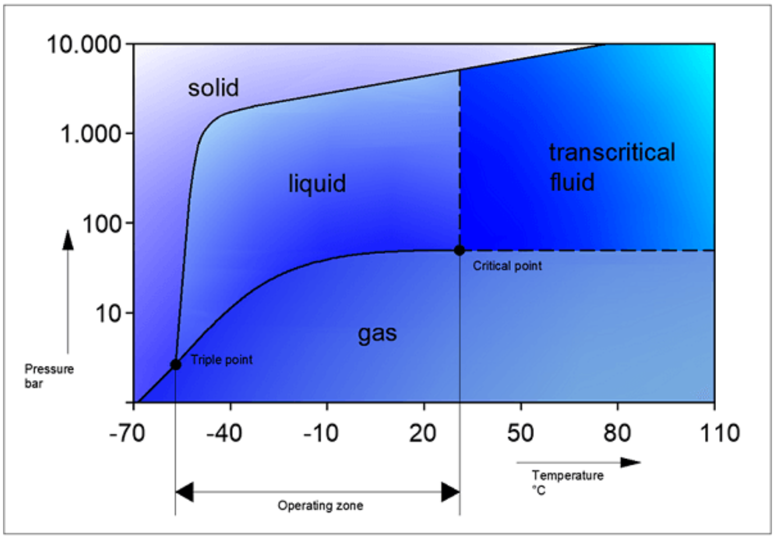



Image 1: Phase diagram $CO_2$

Another key factor is the amount of **latent energy** the refrigerant can absorb before evaporating. This is the energy a refrigerant can absorb or release while the phase changes (liquid to gas/gas to liquid) at a constant temperature and pressure. Fully turned into gas or liquid, the temperature will change with the pressure remaining constant while adding/releasing heat – a process called superheating/sub-cooling.

## SAFETY

Unlike stationary systems on land installations, the cooling plant on a vessel has a far higher leaking ratio. The constant presence of movements (waves) and vibrations (surrounding machinery) make the refrigerant leaks more frequent, with annual refrigerant losses of 20 to 40% reported.

As you know, it's annoying enough when faced with leakage of synthetic refrigerants, which causes emissions and affects the operation of the chiller. But the damage is even worse with most natural refrigerants as they are **asphyxiating, toxic** and **extremely flammable.** This has obvious consequences for the space in which the cooling installation is installed.

Here we review the refrigerant according to the EN378 safety classification, which consists of two sections: A or B followed by 1, 2L, 2 of 3.

- A or B states the toxicity
  - Class A has the lowest toxicity
  - Class B has the highest toxicity

- 1, 2L, 2 or 3 states the flammability
  - 1, non-flammable
  - 2L, low flammability
  - 2, flammable
  - 3, highly flammable

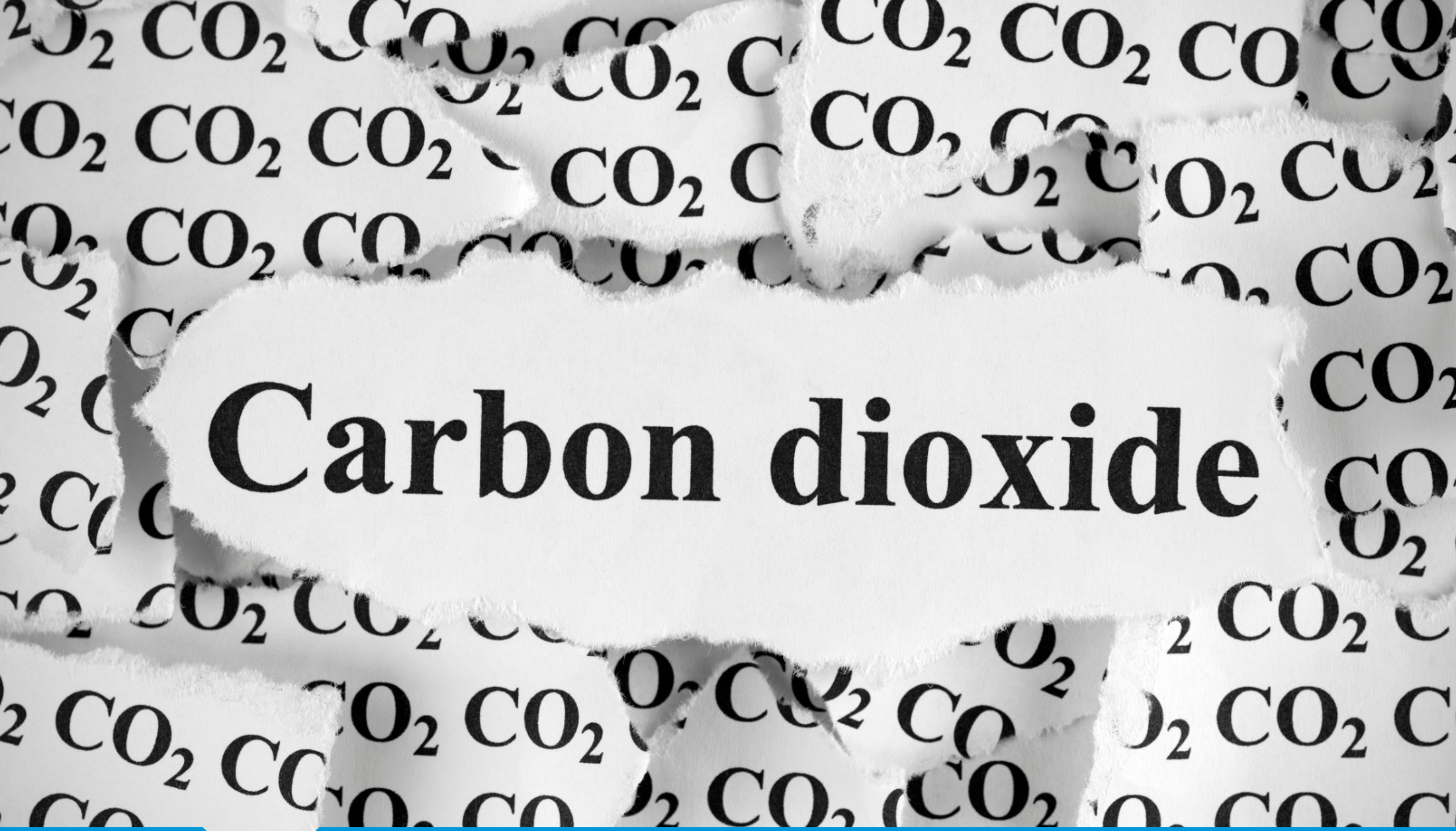
## SUSTAINABILITY

This is the main reason why natural refrigerants are now on the agenda as people strive to reduce emissions and stop global warming due to the greenhouse effect. The high leakage ratios in the maritime sector make the switch to natural refrigerants worth considering.

There are, however, other factors to take into account such as the energy efficiency of the installation. An installation that is more energy efficient obviously consumes less power. A lower load balance reduces $CO_2$ emissions from the fuel burning generator. In addition to the **GWP** of a refrigerant, therefore, the **energy efficiency** of a system is a point of interest when it comes to sustainability.

## CONCLUSION

The ability to design an installation that contributes to a cleaner environment is always welcome and natural refrigerants have a part to play. At the same time, we need to be aware of the multiple factors involved in choosing the right refrigerant for your specific application.




PART 2

# R744: $CO_2$

# PART 2
# R744: $CO_2$

**Let's take a closer look at R744 or $CO_2$. This refrigerant has been in use since the early days of refrigeration in the 19th century and is nothing more than the natural gas carbon dioxide. Naturally present in the earth's atmosphere and crucial for life on earth, $CO_2$ consists of one carbon atom and two oxygen atoms.**

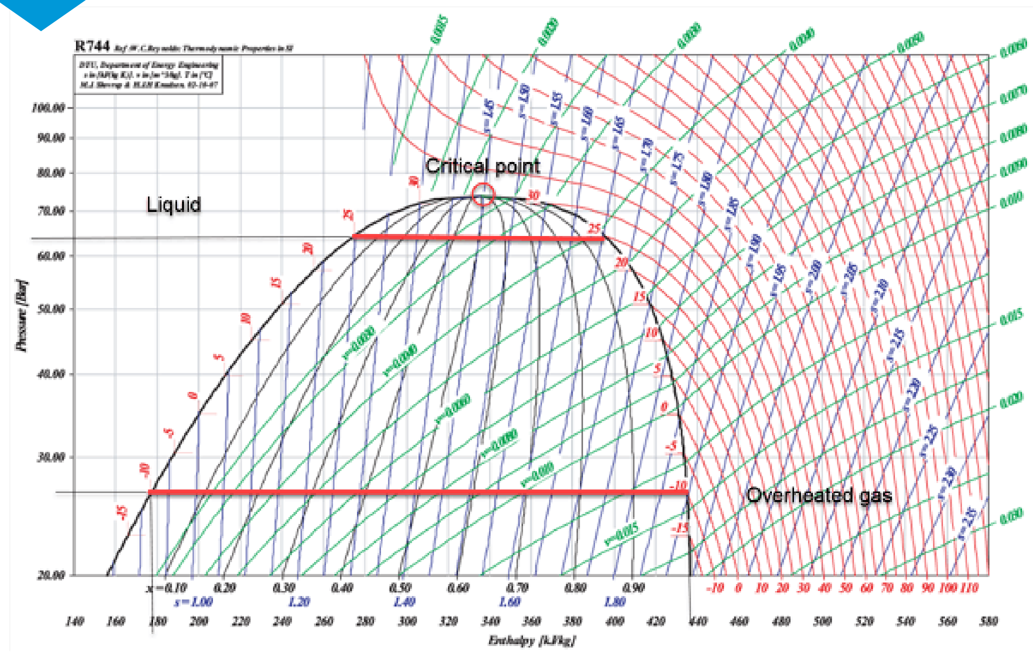



Image 2: H-log/P diagram R744 ($CO_2$)

## THERMODYNAMIC PROPERTIES

The first thing you will notice with R744 is the low critical temperature and high pressures. The critical point is found at the top of the curve (see image 2). Above this temperature and pressure a condenser cannot condense the refrigerant and a gas cooler is needed.

### Evaporation and condensation temperature

R744 has a temperature range with its critical point at 31.1°C so the refrigerant can be subcritically applied for lower temperature applications. In regions with higher ambient or (sea)water temperature the system needs to be designed for transcritical application.

### Evaporation and condensation pressure

Another thing you will notice are the high pressures, especially compared to conventional refrigerants. At -10°C the pressure is already around 25 bar, reaching 65 bar at 25°C.

**Latent heat capacity**

R744 has a good latent heat capacity, especially compared with R22 and R404a. Follow the -10°C line in figure 1 and you see an enthalpy difference of 258 kJ/kg.

## SAFETY

Looking at the safety classification, R744 has favourable properties compared to other natural refrigerants. It is classified as A1: non-flammable.

| Safety group | Lower toxicity | Higher toxicity |
|---|---|---|
| High flammability | A3 | B3 |
| Flammable | A2 | B2 |
| Lower flammability | A2L | B2L |
| No flame propagation | A1 | B1 |

**Flammability**

Non-flammable.

**Toxicity**

Non-toxic. Like every other refrigerant, $CO_2$ can cause suffocation.

**Pressure**

Systems running on R744 operate at pressures varying from 30 to 90 bar (even higher when transcritical).

**Corrosion**

Non-corrosive

## SUSTAINABILITY

$CO_2$ scores high on the sustainability ranking. With low GWP and ozone depletion values, leakages have hardly any effect on the environment.

**GWP & ozone depletion**

The global warming potential of $CO_2$ is 1. It makes a negligible contribution to the greenhouse effect compared to other refrigerants. The ozone depletion capacity is equal to 0 so emissions have no effect on the ozone layer.

**Energy efficiency**

The energy efficiency depends on the design at specific temperatures. For an accurate comparison we use the same temperature value for each refrigerant as specified above. Based on these conditions the EER is 3.2, which is an last in the row. This can offcourse be improved with smart system design.

## CONCLUSION

$CO_2$ is somewhat tricky to compare to other refrigerants. When used with the low seawater temperatures found in the North Atlantic, North and Baltic seas, the system is comparable to conventional refrigerants. At higher seawater temperatures, however, the installation needs to be designed for transcritical applications. This requires a completely different and far more advanced machine. $CO_2$ is not flammable or toxic and has little to no impact on the environment.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PART 3

# R717: AMMONIA

PART 3
# R717: AMMONIA

**Ammonia is one of the oldest refrigerants there is, used from the days of the first cooling machines. A common gas in nature, ammonia ($NH_3$) consists of one nitrogen and three hydrogen atoms.**

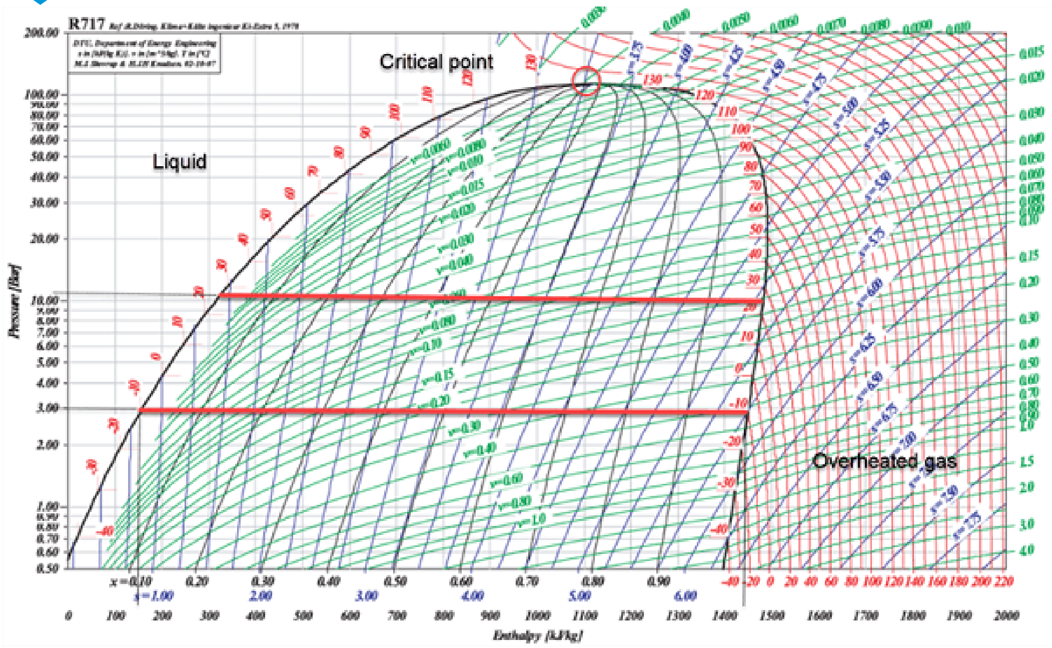


Image 3: H-log/P diagram R717 ($NH_3$)

## THERMODYNAMIC PROPERTIES

Ammonia has one of the best thermodynamic properties of all refrigerants. With a broad temperature spectrum, relatively low working pressures and a massive latent heat capacity, it is a great gas to use as a refrigerant.

**Evaporation and condensation temperature**
R717 has a high temperature range and with a critical point above 132°C can easily be used with seawater condensers. The triple point lies at -78°C, making it suitable for both chilled water and provision cooling purposes.

**Evaporation and condensation pressure**
While having a higher pressure than R134a, the difference is slight. At an evaporating temperature of -10°C the absolute pressure is around 3 bar; at a condensation temperature of 25°C the absolute pressure is around 11 bar.

- **Latent heat capacity**
  Latent heat values are very high with ammonia which can absorb large amounts of thermal energy before being changed in phase. The enthalpy at the -10°C line will be around 1,250 kJ/kg.

## SAFETY

Looking at the safety classification, R717's specs are less favourable than other natural refrigerants. It is classified as B2L.

| Safety group | Lower toxicity | Higher toxicity |
|---|---|---|
| High flammability | A3 | B3 |
| Flammable | A2 | B2 |
| Lower flammability | A2L | B2L |
| No flame propagation | A1 | B1 |

- **Flammability**
  Low flammability so can ignite when exposed in certain concentrations.
- **Toxicity**
  Exposure to high concentrations causes immediate burning of the nose, throat and airways, which can result in respiratory distress or failure. Inhalation of lower concentrations may cause coughing and irritation of the nose and throat. Although the pungent smell of R717 fortunately provides early warning of its presence, exposure also causes loss of smell. Consciousness is reduced with prolonged exposure at low concentrations. Exposure to low concentrations can quickly lead to skin or eye irritation. Exposure to higher concentrations can lead to serious injuries and burns. Contact with liquid ammonia can lead to frostbite, although that is the case with all refrigerants.
- **Pressure**
  R717 has no pressure issues.
- **Corrosion**
  The corrosiveness of ammonia makes it unsuitable for installations with copper pipes and the electric wiring inside the compressor must be separated from moving parts.

## SUSTAINABILITY

Although toxic to humans, R717 is a substance that occurs naturally on earth. With low GWP and ozone depletion values, leakages have hardly any effect on the environment. The high efficiency contributes to fewer $CO_2$ emissions from generators.

- **GWP & ozone depletion**
  As the global warming potential of ammonia is 0 it makes no contribution to the greenhouse effect. With the ozone depletion capacity equal to 0, emissions have no effect on the ozone layer.
- **Energy efficiency**
  At the given conditions the maximum energy efficient ratio will be 4.5. The combination with R717's high latent heat capacity has an especially beneficial effect. Far less refrigerant and compressor power is required for a large cooling capacity. The high efficiency means less generator power is needed and the $CO_2$ emissions caused by generator use are further reduced.

## CONCLUSION

R717 is a wonderful refrigerant with excellent thermodynamic properties, a high efficiency and a low environmental impact. The downside is the high degree of toxicity, which means that many safety measures are required.


# PART 4
# R290: PROPANE

# PART 4
# R290: PROPANE

**Propane is a well-known gas that is used as a fuel for patio heaters, gas barbecues and even vehicles. In a more purified form where it has been stripped of moisture, unsaturated hydrocarbons and other contaminants, it is an excellent refrigerant.**

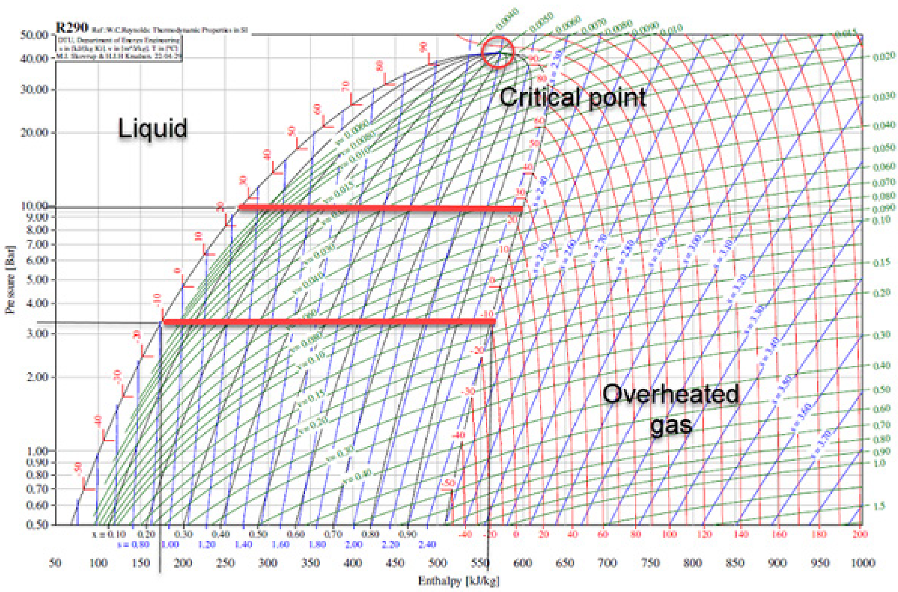


Image 4: H-log/P diagram R290

## THERMODYNAMIC PROPERTIES

Propane has very good thermodynamic properties similar to that of R22, which has been phased out for a while. It is perfectly suitable for use in chilled water systems.

### Evaporation and condensation temperature

R290 has a high temperature range and with a critical point above 96°C can easily be used with seawater condensers. The triple point lies at -188°C, making it suitable for both chilled water and provision cooling purposes.

### Evaporation and condensation pressure

The pressure range is comparable with that of ammonia. At an evaporating temperature of -10°C the absolute pressure is around 3,4 bar; at a condensation temperature of 25°C the absolute pressure is around 10 bar.

### Latent heat capacity

Latent heat values are quite decent.
The enthalpy at the -10°C line will be around 380 kJ/kg.

## SAFETY

Propane is highly flammable! It is classified as A3.

| Safety group | Lower toxicity | Higher toxicity |
|---|---|---|
| High flammability | A3 | B3 |
| Flammable | A2 | B2 |
| Lower flammability | A2L | B2L |
| No flame propagation | A1 | B1 |

- **Flammability**
  Propane is the third most common vehicle fuel after gasoline and diesel. So yes, it is highly flammable and explosive. The installation needs to be equipped with sensors that detect leakage.
- **Toxicity**
  R290 is not toxic, however it does displace oxygen in a confined space. Measures such as proper ventilation must be applied to avoid asphyxiation.
- **Pressure**
  R290 has no pressure issues.
- **Corrosion**
  Inhalation, eye and skin contact needs to be avoided, R290 is not corrosive for the installation's materials.

## SUSTAINABILITY

Propane has low GWP and ozone depletion values. Leakages have hardly any effect on the environment. The high efficiency contributes to fewer CO2 emissions from generators.

- **GWP & ozone depletion**
  As the global warming potential of propane is 3 it makes almost no contribution to the greenhouse effect. With the ozone depletion capacity equal to 0, emissions have no effect on the ozone layer.
- **Energy efficiency**
  The energy efficiency depends on the design at specific temperatures. For an accurate comparison we used the same temperatures value for each refrigerant as specified above. Based on these conditions the EER is 4.3. This can be improved with smart system design.

## CONCLUSION

Propane is a multi-functional substance that is used for many different applications, like fuel and it also is an excellent refrigerant. With thermodynamic properties that are comparable to that of synthetics like R-22 and R134a. The only downside is its very high flammability.

PART 5

# R1234ZE: TETRAFLUOROPROPENE

# PART 5
# R1234ZE: TETRAFLUOROPROPENE

**In the previous parts we discussed pure natural refrigerants, but there are also synthetics that meet the latest environmental requirements. R-1234ze is specially designed as a replacement of R-134a but with a global warming potential around seven. This synthetic refrigerant of the fourth generation is a HFO (Hydro Fluor Olefine) and is mainly used in chillers but can also in heat pumps.**

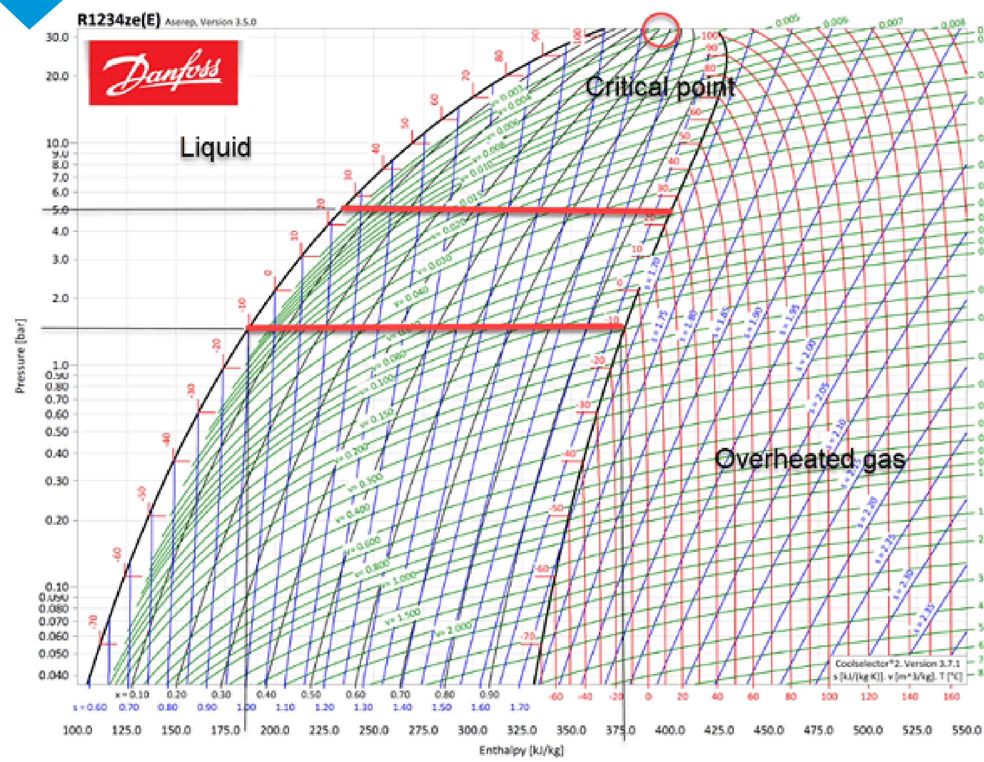


Image 5: H-log/P diagram R1234ze

## THERMODYNAMIC PROPERTIES

While evaporation/ condensation pressure and temperatures are not out of the ordinary, the latent heat capacity of R1234ze is lower than its natural counterparts.

### Evaporation and condensation temperature

R1234ze has a high temperature range and with a critical point above 109°C can easily be used with seawater condensers. The triple point lies at -104°C, making it suitable for both chilled water purposes.

**Evaporation and condensation pressure**

The pressure range is pretty low. At an evaporating temperature of -10°C the absolute pressure is around 1,5 bar; at a condensation temperature of 25°C the absolute pressure is around 5 bar.

**Latent heat capacity**

Latent heat values are below average. The enthalpy at the -10°C line will be around 190 kJ/kg.

## SAFETY

R1234ze is classified as a mildly flammable refrigerant. It is labelled as A2L.

| Safety group | Lower toxicity | Higher toxicity |
|---|---|---|
| High flammability | A3 | B3 |
| Flammable | A2 | B2 |
| Lower flammability | A2L | B2L |
| No flame propagation | A1 | B1 |

**Flammability**

Classified as mildly flammable R1234ze can ignite under certain conditions. However, when stored at temperatures under 30°C it does not produce any flammable mixtures with air.

**Toxicity**

R1234ze is not toxic, however it does displace oxygen in a confined space. Measures such as proper ventilation must be applied to avoid asphyxiation.

**Pressure**

R1234ze has no pressure issues.

**Corrosion**

Inhalation, eye and skin contact needs to be avoided, R1234ze is not corrosive for the installation's materials.

## SUSTAINABILITY

R1234ze has low GWP and ozone depletion values. Leakages have hardly any effect on the environment.

**GWP & ozone depletion**

As the global warming potential of R1234ze is 7 it makes almost no contribution to the greenhouse effect. With the ozone depletion capacity equal to 0, emissions have no effect on the ozone layer.

**Energy efficiency**

The energy efficiency depends on the design at specific temperatures. For an accurate comparison we used the same temperatures value for each refrigerant as specified above. Based on these conditions the EER is 4.1. This can be improved with smart system design.

## CONCLUSION

The synthetic refrigerant R1234ze is designed as a replacement for R134a but has a higher specific volume. Therefore, a compressor with more displacement is needed to achieve the same capacity. This means the chiller itself must be bigger/ more expensive.

PART 6

# R134A: TETRAFLUOROETHANE

PART 6

# R134A: TETRAFLUOROETHANE

**We finalize this whitepaper about natural refrigerants with the HFC R134a. This way we can compare all the natural refrigerants with one of the mostly used synthetic refrigerant in the world. R134a was designed in the early nineties as a replacement of the much more harmful R-12. Although you wouldn't say it now, it was really a big improvement back then with insignificant ozone depletion and an GWP that is almost a factor ten lower. R134a is mainly used in chillers.**

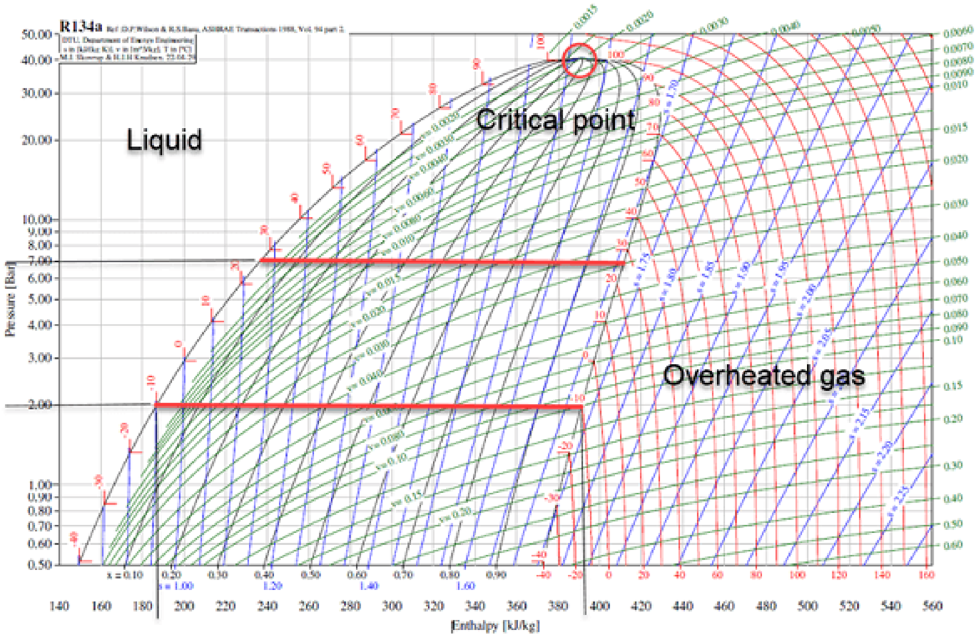


Image 6: H-log/P diagram R134a

## THERMODYNAMIC PROPERTIES

R134a has pretty decent thermodynamic properties. With a broad temperature spectrum, relatively low working pressures and a good latent heat capacity, it is a great gas to use as a refrigerant for chilled water purposes.

- **Evaporation and condensation temperature**
  R134a has a high temperature range and with a critical point above 101°C can easily be used with seawater condensers. The triple point lies at -104°C.

### Evaporation and condensation pressure

The pressure rangers are low with an evaporating temperature of -10°C the absolute pressure is around 2 bar; at a condensation temperature of 25°C the absolute pressure is around 7 bar.

### Evaporation and condensation pressure

Latent heat values are below average. The enthalpy at the -10°C line will be around 210 kJ/kg.

## SAFETY

R134a is a very safe refrigerant with an ASHRAE safety classification of A1. It is not flammable and has very low toxicity levels.

| Safety group | Lower toxicity | Higher toxicity |
|---|---|---|
| High flammability | A3 | B3 |
| Flammable | A2 | B2 |
| Lower flammability | A2L | B2L |
| No flame propagation | A1 | B1 |

### Flammability

Classified as A1, R134a has no flammability issues or whatsoever.

### Toxicity

R134a is not toxic, however like all refrigerants it does displace oxygen in a confined space. Measures such as proper ventilation must be applied to avoid asphyxiation.

### Pressure

R134a has no pressure issues.

### Corrosion

Inhalation, eye and skin contact needs to be avoided, R134a is not corrosive for the installation's materials.

## SUSTAINABILITY

In the nineties R134a became the replacement of the much more harmful refrigerant R12. While it has much lower GWP-values it still is sky high compared to modern synthetic and natural refrigerants.

### GWP & ozone depletion

With a global warming potential of 1430, the refrigerant R134a has a significant contribution to the greenhouse effect. R134a is an HFC, that means it has no chlorine molecule and therefore doesn't deplete the ozone layer.

### Energy efficiency

The energy efficiency depends on the design at specific temperatures. For an accurate comparison we used the same temperatures value for each refrigerant as specified above. Based on these conditions the EER is 4.4. This can be improved with smart system design.

## CONCLUSION

The synthetic refrigerant R134a is used in chilled water systems, medium and high temperature refrigeration, as well as domestic refrigeration and transport refrigeration. Eventually it will be replaced by refrigerants with a lower GWP, which is more sustainable. However, R134a has not been banned yet, it is still used in many refrigeration systems.

PART 7
# CONCLUSION

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# CONCLUSION

**As we expect most high-GWP refrigerants will be phased out over the years, we have been looking over the options to implement low-GWP refrigerants like R1234yf, R1234ze, R449a and natural refrigerants ammonia, carbon dioxide, propane and water in our HVAC and refrigeration systems.**

We have already used R449a in our systems. R1234yf and R1234ze can be used as well, but only when taking into account additional safety requirements during installation on board ships as these are flammable refrigerants. We can also use some natural refrigerants – including carbon dioxide ($CO_2$), propane (R290) and ammonia ($NH_3$) – but additional safety measures are required as well.

## SUBSTITUTES

When refrigerants cannot be replaced anymore, or it is very expensive to replace it, there are other options available. In diagram 2 we give options to substitute your current refrigerant. Warning: not all substitutes are drop-in replacement refrigerants.

| Refrigerant | Type | GWP | Substitutes |
|---|---|---|---|
| R22 | HCFC | 1760 | R422D (GWP2470) / R417A (GWP2130) / R407C (GWP1260) |
| R404A | HFC | 3940 | R407F (GWP1670) / R449A (GWP1280) |
| R410A | HFC | 1920 | No suitable replacement [R32 (GWP667) is flammable] |
| R407C | HFC | 1620 | No suitable replacement [R444B (GWP295) is flammable] |
| R134a | HFC | 1300 | R513A (GWP573) [R1234yf (GWP<1) / R1234ze (GWP<1) are flammable] |

Please note that the values and calculation given in this whitepaper have been simplified in order to give you a general overview of the pros and cons of every refrigerant. More specific information is needed for a detailed calculation and we strongly recommend contacting one of our engineers if you are considering the use of natural refrigerants.

HEINEN & HOPMAN

Heinen & Hopman encourages a more sustainable world. By providing eco-friendly solutions and services we offer our clients the option of reducing energy consumption and thus $CO_2$ emissions.

HEINEN & HOPMAN MANIFESTO APPROVED

"Do you require more information about natural refrigerants? I am keen to help you further!"


Eric Stoffelsen
- Sales Manager
sales@heinenhopman.com


| OUTSIDE | HUMIDITY |
|---|---|
| 35°C | 90% |
| 45°C | 40% |

22°C Inside

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