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# Performance and Stability of E-1233zd in Energy Recovery Applications

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## ABSTRACT

Developed and identified as a refrigerant for low pressure chillers, trans-1-chloro-3,3,3-trifluoropropene (E-1233zd) an unsaturated molecule, with a GWP of 1, has also shown a high potential as a working fluid for energy recovery applications, such as Organic Rankine Cycle or high temperature heat pumps. As a refrigerant for low pressure chillers, E-1233zd has shown positive attributes of high performance and low environmental impact, while maintaining the safety benefits of refrigerants commonly used today, by being non-flammable and having a low toxicity. However, when significant heat is applied, E-1233zd was found to undergo geometric isomerization, which could limit its performance in energy recovery applications where the system could be subjected to sustained temperatures higher than 150°C. This paper will present the work done to understand the parameters impacting the kinetic of isomerization of E-1233zd and introduce the approaches that were taken to stabilize the molecule. The performance of E-1233zd in energy recovery applications will also be discussed.

## 1. INTRODUCTION

Being responsible for nearly 40% of energy consumption in a typical office (Australian Government, Department of the Environment and Energy, 2013), HVAC equipment manufacturers are continuously being challenged to improve efficiencies to meet stringent energy regulations. At the same time, the HVAC industry is undergoing a transition as some of the conventional refrigerants are being phased out due to their high global warming potential (GWP). While new technologies can help increase efficiency of the equipment, recovering and utilizing available heat can significantly lower the electricity consumption thus increasing the overall system efficiency.

High temperature heat pump and Organic Rankine Cycle (ORC) are promising technologies for energy recovery, electrical power production or efficiency improvement. These two technologies are in line with the global effort toward sustainable energy production.

ORC or ORC like cycles can be classified based on the source temperature level. Generally, in these cycles, the temperature ranges from low level heat around 80°C to medium level around 350°C (Saitoh *et al*., 2007, Bonalumi *et al*., 2017). For geothermal sources, temperatures are about 100°C or somewhat higher. For solar sources, in standard collectors such as flat plate types, the heat source temperatures are between 90°C and 200°C (Saitoh *et al*., 2007), which the application is promising where access to the grid is very limited while solar energy is largely available. Peak temperatures of 220°C or higher can be reached in summer time with special collector technologies. Biomass and heat recovery are also two important applications for ORCs. In 2017, the largest ORC market is the geothermal market followed by biomass and heat recovery (Thomas *et al.*, 2017). ORC can also be used to increase the efficiency of energy storage technologies such as compressed air technology (Meng *et al.*, 2018).

In ORC installation, all heat sources are usually connected to a heat storage system (brine or phase change material) in order to reduce temperature and energy unsteadiness. Thermal energy storage is also used to establish equilibrium between the thermal energy production and electrical power demand on the grid. The ORC combined with storage systems allow the conversion of green thermal energy to electrical power depending on the demand.

## 2. R-1233zd(E) FLUID PROPERTIES

The selection of working fluid for ORC mainly depends on the available heat source temperature. For standard subcritical cycles, the evaporating temperature should be lower than the critical temperature and the heat source temperature. R-1233zd(E) with a critical temperature of about 167°C, Table 1, can be used for geothermal, solar or heat recovery applications. Recent papers show the advantage of using R-1233zd(E) in ORC versus R-245fa or n-pentane (Giuffrida and Pezzuto, 2017, Bonalumi *et al.*, 2017, Huck, 2013).

In addition to being used in ORCs, R-1233zd(E) can also be used as a fluid for high temperature heat pumps where industrial waste heat is available such as food, chemistry or paper industry where cooling water, effluent, condensate, moisture are produced as part of the major processes. These waste heat can be recovered and the resulting energy can be recycled and used in the process. High temperature heat pumps are needed when the temperature of the process is higher than the temperature of the different waste streams.

The full chemical name of R-1233zd(E) is trans-1-chloro-3,3,3-trifluoroprop-1-ene. There are two isomers for 1-chloro-3,3,3-prop-1-ene: E (trans) and Z (cis) isomers. The fluid of interest for high temperature heat pumps and ORCs is the E isomer with the following properties.

**Table 1:** R-1233zd(E) basic properties

| CAS N° | Molecular weight | GWP (AR5) | ASHRAE 34 classification | Normal boiling temperature (°C) | Critical temperature (°C) |
|---|---|---|---|---|---|
| 2730-43-0 | 130 | 1 | A1 | 18.3 | 167.3 |

R-1233zd(E) is already being used today in air conditioning for large chiller applications with centrifugal compressors. It is also used as a blowing agent for thermoset foams. R-1233zd(E) has shown good thermal stabilities for the two aforementioned applications where conversion to Z-1233zd was not detected when the refrigerant was continuously aged for 1 year at 75°C (Kim *et al.*, 2017).

For high temperature heat pump and ORC, the fluid can be heated up to temperatures close or higher than 150°C. At high operating temperature conditions (T>150°C), a small portion of E-1233zd can isomerize to Z-1233zd. Kontomaris (2014) observed less than 9 wt% of E-1233zd to Z-1233zd isomerization at 175 and 200°C with metal coupons for 14 days. Because of the thermodynamic property difference between the E and Z isomer, the isomerization will change the properties of the fluid. These changes can impact the equipment performance.

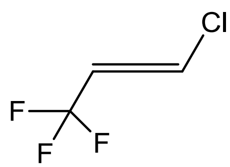
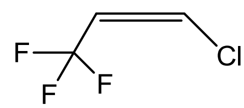
In the first part of this paper, material compatibility and options to suppress the isomerization of E-1233zd to Z-1233zd for usage of R-1233zd(E) in high temperature system applications will be demonstrated. The second part of the paper will discuss the performance of R-1233zd(E) in these applications.

## 3. EXPERIMENTAL RESULTS AND DISCUSSION

### 3.1 Thermal Stability of R-1233zd(E)

As discussed earlier, 1-chloro-3,3,3-prop-1-ene can exist either in E or Z isomer form, Table 2. Although the chemical formula of the isomers are exactly the same, they will exhibit different thermodynamic properties due to the difference in chemical structure. In chemistry, the C=C double bond, which is a flat connection, prevents rotation of the molecule. The presence of isomers induces the fact that a molecular rearrangement has taken place following the separation of H or Cl from the molecule. The best guess we can make at this stage is that the C=C double bond is broken by the presence or formation of free radicals and/or acids. Then, a new C=C double bond is created after the molecular rearrangement. These radicals and acids could be potentially generated by a combination of factors such as high temperature, presence of halogenated atoms or oxygen. This isomerization phenomenon can be applied to any olefins with isomers.

**Table 2:** 1233zd isomer

| E-1233zd isomer | Z-1233zd isomer |
|---|---|
|   |   |

In this work, the thermal stability evaluation of R-1233zd(E) was assessed as described in ASHRAE Standard 97-2007, Sealed Glass Tube Method to Test the Chemical Stability of Materials for Use Within Refrigerant Systems. Upon completion of aging, the sealed tubes were broken and fluids were analyzed. Special gas chromatography methods are used to measure composition changes. The thermal stability test of pure E-1233zd at 180°C and 220°C shows isomerization reactions that leads to Z-1233zd isomer formation, Figure 1.(a) and (b). At 180°C, the percentage of isomerization is fairly low, less than 1.6% after 14 days. For 14 days of aging at 220°C, the isomerization is significantly higher with about 9% of E-1233zd conversion to Z-1233zd.

To increase the R-1233zd(E) stability at high temperatures, additives that will inhibit or strongly limit the isomerization phenomenon were evaluated. Large number of molecules with different molecular structures and functional groups were assessed and few were selected based on their efficiency to inhibit the isomerization reaction as well as other key criteria such as compatibility, stability or solubility. This paper presents the results of one of the selected additives.

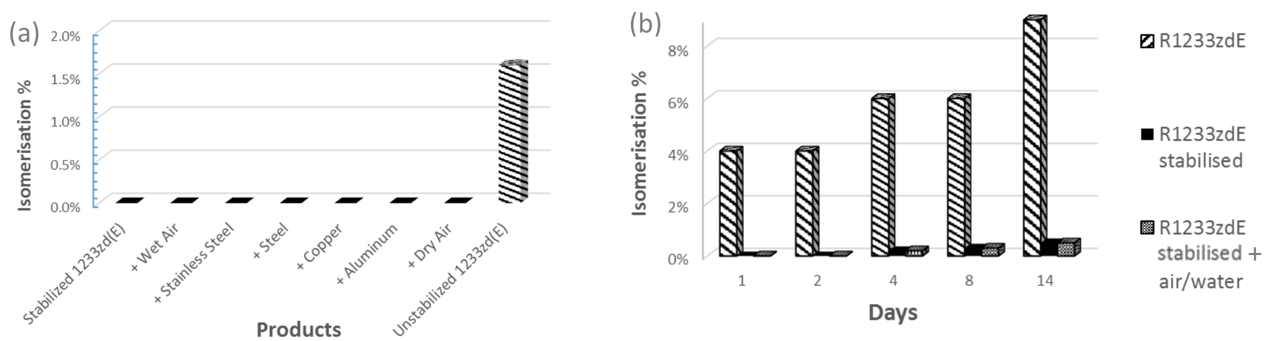



**Figure 1:** (a) Isomerization % after 14 days with various materials at 180°C and (b) isomerization % after aging at 220°C for different time durations

Figure 1(a) shows the aging test results of stabilized R-1233zd(E) in combination with air, moisture and metals versus pure (unstabilized) R-1233zd(E). In all these various test cases, there was no Z-1233zd formed when the stabilizer was used. In other words, the use of stabilizer inhibits the isomerization reaction during 14 days of aging at 180°C.

To confirm the efficiency of the stabilizer, additional tests were conducted at 220°C and the results are shown in Figure 1(b). At this higher temperature, the isomerization reaction is strongly suppressed with the use of stabilizer. The isomerization percentage dropped from 9 to less than 0.5% after 14 days of aging with the help of the stabilizer. For less than 4 days of aging time at 220°C, the analysis didn't show any isomerization. Interestingly, at 220°C, the isomerization percentage of the stabilized R-1233zd(E) is at the same level with or without the addition of air and water (as illustrated in Figure 1(b)).

### 3.2 Thermal Stability Tests with POE Oils

Stabilized R-1233zd(E) was also tested with different POE oils and dry air at 180°C for 14 days. For tests with oils, the acidity and the color of oil were measured in addition to gas phase composition. The test results didn't show any evidence of isomerization reaction, Table 3. The total acid number (TAN) is low and the coloration according to garden scale is yellow. Only POE oil 5 shows slightly higher coloration level (dark yellow).

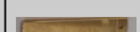
**Table 3:** Stabilized R-1233zd(E) thermal stability test results at 180°C for 14 days with dry air and oil

| oil | POE oil 1 | POE oil 2 | POE oil 3 | POE oil 4 | POE oil 5 | POE oil 6 |
|---|---|---|---|---|---|---|
| Z-1233zd (%) | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Oil color (garden) | Yellow | Yellow | Yellow | Yellow | Dark Yellow | Yellow |
| TAN (mg KOH/g) | Low | Low | Low | Low | Low | Low |
| |  |  |  |  |  |  |

### 3.3 Materials Compatibility

Material compatibility of R-1233zd(E) was also tested by immersing various materials in a 95% R-1233zd(E) and 5% lubricant mixture at 20°C for 100 hours, Table 4. No weight or visual changes were noticed with stainless steel, Iron, Aluminum, and Brass. PTFE and Neoprene had minor weight increase while HNBR showed significant weight increase in wet state, but any visual changes such as cracks were not noticed. Depending on the location within the system, the tested materials may be exposed to higher temperatures and therefore additional compatibility testing will be needed accordingly.

**Table 4:** Compatibility of R-1233zd(E) with common materials of construction

| | PTFE | Neoprene | HNBR | Stainless steel | Iron | Aluminum | Brass |
|---|---|---|---|---|---|---|---|
| t=0 |  |  |  |  |  |  |  |
| t=100hr |  |  |  |  |  |  |  |
| Weight Change | Slight increase in wet state | Slight increase in wet state | 60% increase in wet state | x | x | x | x |
| Visual change | x | x | x | x | x | x | x |

# 4. THERMODYNAMIC CYCLE CALCULATION

The purpose of this thermodynamic cycle study is to show the potential of R-1233zd(E) usage in ORC and high temperature heat pump applications. REFPROP software was used with Microsoft® Excel®/Visual Basic where computational codes were developed for thermodynamic cycle calculations.

## 4.1 Basic Organic Rankine Cycle Calculation

For ORC, the performance is a function of large number of parameters. The operating conditions, equipment technologies, and the type of ORC will all have an impact on the system performance. The cycle type selection is related to the temperature source level and profile. At the same time, the ORC type selection, equipment size and electrical power output may depend on the choice of refrigerant for a given heat source capacity and temperature profile. It should be noted that each application requires careful evaluation from a total system point of view to determine the most cost effective system (Abbin, 1976). Comparison between different types of ORCs is outside the scope of this paper.

For the purpose of this work, we are only interested in the highest fluid temperature that can occur in an ORC and the potential impact on the R-1233zd(E) stability. Therefore, certain operating conditions were considered in this work: (i) the maximum heat source temperature is higher than the critical temperature, (ii) the evaporation temperature is lower than the critical temperature, (iii) any available energy between the evaporating temperature and maximum temperature will produce superheat, and (iv) turbine efficiency was assumed to be 100% (isentropic work). The condensing and evaporating temperature were set at 40°C and 150°C, respectively.

A simple typical sub critical cycle calculation can show the impact of the superheat on the cycle efficiency and volumetric power (Figure 2). At a set condensing and evaporating temperature, increasing the superheat can increase the efficiency, but at the same time this will increase the specific volume ($m^3$/kg) and decrease the volumetric power (kJ/$m^3$) generated by the turbine. Consequently, the optimum highest superheat is not only a question of fluid selection, but also about system design.

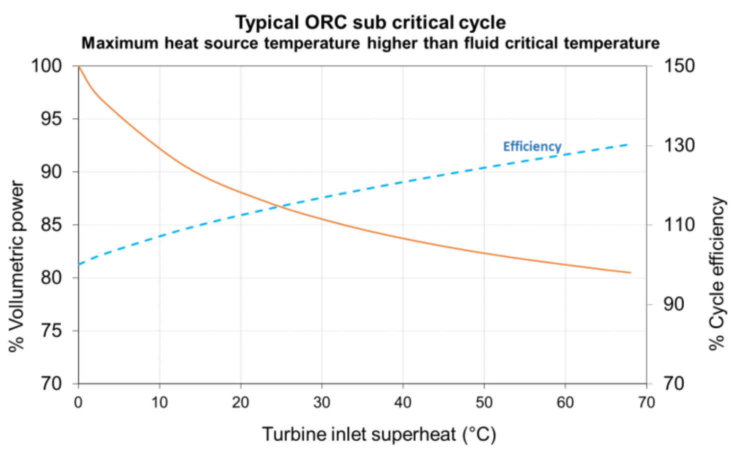



**Figure 2**: R-1233zd(E) performance versus superheat

This analysis shows that the maximum temperature should be defined after an overall study of the application from a technical and economical point of view. The fluid should be a part of this study as well.

## 4.2 Thermal Stability in ORCs

The worst thermal stability constraint in ORC occurs after the fluid phase change in the evaporator. When the maximum secondary fluid temperature is around 175°C, the working fluid will be at lower temperatures. At these conditions, the stabilized R-1233zd(E) shows good thermal stability. Additional materials and test conditions with the working fluid could be evaluated to closely resemble a real system.

For higher temperature heat source applications, the thermal stability is more critical and special consideration should be taken into account. As previously shown in Figure 1(b), stabilized R-1233zd(E) didn't show any isomerization at 220°C when aging time was less than 4 days and after 14 days, the isomerization level was still very low (<0.5%). Consequently, for high temperature level applications, additional investigation will be required to understand the exact conditions in order to evaluate the stability of the refrigerant.

### 4.3 Basic High Temperature Heat Pump Cycle Calculations

Similar to ORC, the technology used in the high temperature heat pump system will impact the fluid selection and system performance. In this work, R-1233zd(E) performance using basic cycle calculations has been evaluated. The selected cycle is a basic compression cycle with 5 °C superheat, 80% efficiency with an internal heat exchanger (IHE). The heat source is 45°C ($dT_{sat}$ = 45°C) lower than the heat sink. In Figure 3, the discharge temperature is plotted versus the condensing temperature. The discharge temperature remains very close to the condensing temperature at the given operating conditions. The cycle coefficient of performance (COP) is also shown in Figure 3 for temperatures up to 160°C, which are conditions where stabilized R-1233zd(E) has shown good thermal stability in this work. At the aforementioned conditions, the COP curve shows a maximum around 110°C and a steep decline when condensing temperature is higher than 140°C.

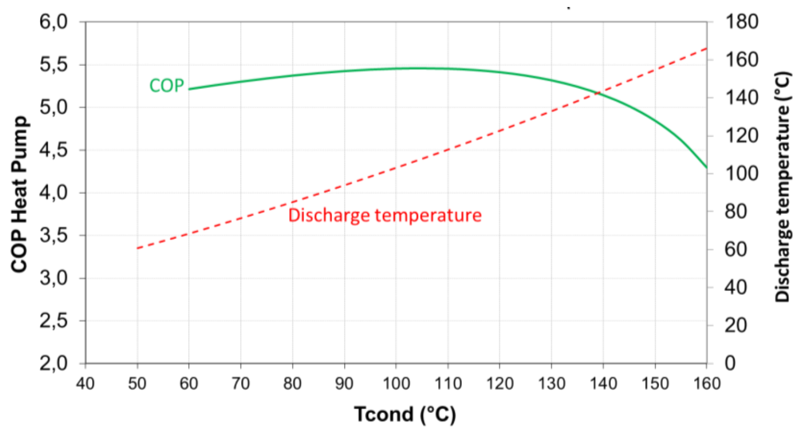



**Figure 3:** R-1233zd(E) performance at different condensing temperatures

## 5. CONCLUSIONS

The use of a stabilizer with R-1233zd(E) was demonstrated to significantly reduce the formation of the Z isomer at high temperatures. The stabilized product showed great stability at 180°C after 14 days of aging with metals, air and oil. At 220°C and 14 days of continuous aging, a very low isomerization level (<0.5%) was detected. Therefore, high temperature applications such as high temperature heat pump and ORC can benefit from the performance of R-1233zd(E) for wide range of temperature conditions.

The operating conditions of high temperature systems may be of potential concern due to isomerization reaction of E-1233zd. At optimum operating conditions of high temperature heat pumps, the thermal stability is not a concern because the discharge superheat is relatively low. For ORC systems, superheat should not be increased to a level that is detrimental to the evaporating temperature, pressure and system performance. When maximum heat source temperature is much higher than the critical temperature of the fluid, special analysis should be done to be sure that this will not impact the stability or performance of the system.

## NOMENCLATURE

| | |
|---|---|
| CAS | Chemical Abstracts Service |
| GWP | global warming potential |
| IHE | Internal heat exchanger |

| | |
|---|---|
| ORC | Organic Rankine Cycle |
| POE | polyol ester oil |
| TAN | total acid number |
| wt | weight |

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