

PvT properties of next generation refrigerants
at low temperatures: development of apparatus,
measurement and data analysis.

コロンバタンティリゲ, ウトゥパラ, アモダ, ペレラ

<https://hdl.handle.net/2324/5068258>

出版情報 : Kyushu University, 2022, 博士 (学術), 課程博士
バージョン :
権利関係 :



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Name

論文名 : *PvT* properties of next generation refrigerants at low temperatures: development of apparatus, measurement and data analysis. (低温域における次世代冷媒の *PvT* 性質; 測定装置の開発、測定及びデータ解析)

Title

区 分 : 甲

Category

論文内容の要旨

Thesis Summary

This thesis presents two new isochoric apparatus developed for measuring *PvT* (Pressure-Specific Volume-Temperature) properties of next generation refrigerants within the temperature range of 240 K to 410 K and provides the measured *PvT* properties and correlations of several next generation refrigerants in their pure form and as mixtures.

Next generation refrigerants have a vital role to play in reducing the climate and environmental impact of the heating, ventilation, air conditioning and refrigerant (HVAC&R) industry so as to meet many local and international policies such as the Kigali Amendment. The measurement of thermodynamic properties including the *PvT* properties of these refrigerants are essential for selecting suitable refrigerants and for implementing them in HVAC&R systems.

Based on the literature review a gap in the applicable temperature range for *PvT* measurement at NEXT-RP laboratory, Kyushu University was identified and two isochoric apparatus were developed to fill this gap. The objectives of these apparatus were, to achieve property measurement capacity for temperatures below 300 K reaching 240 K and to measure properties using a single apparatus across the ‘complete’ temperature range from 240 K to 420 K. These two main objectives were satisfied with the construction of the isochoric apparatus-**LRT** (Lower than Room Temperature) and the isochoric apparatus-**WRT** (Wide Range of Temperatures). The apparatus were calibrated and verified using refrigerants with high accuracy equations of state (EoSs) and utilized for measuring the thermodynamic properties of several pure and mixed next generation refrigerants.

Since the group of refrigerants, hydrofluoroolefins (HFOs) have been identified as suitable candidates for next generation refrigerants, the refrigerants studied within this thesis are ether HFOs, mixtures containing HFOs or additional refrigerants required to provide suitable characteristics for mixtures containing HFOs. The refrigerant R-13I1 is initially studied as a non-flammable component for mixtures containing HFOs, which suffer from flammability

issues. Even though R-131I has been studied previously in the late 1990s, the renewed interest in this refrigerant was sufficient to prompt the re-measuring of its PvT properties, critical parameters, saturated densities along the coexistence curve and for formulating correlations for these properties. Next, the novel pure HFO refrigerant R-1132(E) was studied since no data on this refrigerant were available in the literature. It is potentially considered as a highly suitable refrigerant to replace R-32 in mixtures. The afore mentioned thermodynamic properties were measured and correlations were established. Lastly, an isomer of R-1132(E), R-1132a was studied due to the renewed interest in it for the purposes of potentially replacing R-23 in low temperature (LT) and ultra-low temperature (ULT) refrigeration systems for storing vaccines such as those for COVID-19. The thermodynamic properties mentioned before were also measured and the correlations are presented.

As for the refrigerant mixtures, three primary candidates were studied. These include R-32+R-1234ze(E) for heat pump applications for replacing R-410A and R-134a, R-1132(E)+R-1234yf a HFO based mixture to be potentially used in mobile air conditioners (MACs) to replace either pure R-134a or R-1234yf and R-473A as a lower GWP alternative to pure R-23 for LT and ULT applications. Both the two phase and single phase PvT properties in the vapor and liquid regions have been studied for several isochores (constant volume lines) of different densities. The vapor liquid equilibrium (VLE) was derived for the R-32+R1234ze(E) pair using the Peng-Robinson (PR) EoS together with the ‘Flash Method’ and the binary interaction parameters (k_{ij}) were optimized for the VLE and single phase properties. The single phase properties were correlated for the remaining two refrigerant mixtures R-1132(E)+R-1234yf and R-473A and their k_{ij} values were optimized for both the PR EoS and virial EoS. The measured properties are presented in the form of data tables within the appendices and are a valuable source of property data for both the formulation and improvement of equations of state for these next generation refrigerants and for their application in real world scenarios.