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Theoretical analysis of low GWP mixture R600a/R1234ze as a possible alternative to R600a in domestic refrigerators

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ABSTRACT

In this study, a thermodynamic analysis of R600a and R600a/R1234ze mixture at three compositions of 0%, 20% and 50% R1234ze is measured in a domestic refrigerator. The main purpose of this study is to theoretically verify the possibility of applying the mixture R600a/R1234ze in large capacity refrigerator. The performance has been assessed for different condensing temperatures between 30°C and 50°C with constant -20°C evaporating temperature. The performance of the refrigerator was compared in terms of volumetric cooling capacity, COP (coefficient of performance), compression ratio and compressor discharge temperature. The results show that the volumetric cooling capacity, COP, compressor power consumption and compressor discharge temperature of R600a/R1234ze mixture are similar to those of pure R600a, so that R600a compressor can be used for R600a/R1234ze mixture without any modifications. The amount charge of the mixture R600a/R1234ze is slight lower than that of R600a in the same equipment. Flammability decreases in R600a/R1234ze mixtures with increasing fractions of R1234ze. This is one of desirable characteristic that can reduce risk of flammability and explosion in large capacity refrigerator system.

1. INTRODUCTION

Domestic refrigerators are identified as major energy consuming domestic appliances in every household (R. Radermacher & Kim, 1996). Over the past decades, conventional refrigerants such as HCFCs and HFCs have been used extensively in domestic refrigerators fields owing to their well chemical and thermodynamic properties. However, the increasing attention to environmental problems such as global warming, ozone depletion and atmospheric pollution has led to a large number of studies related to the selection of environmentally friendly refrigerants as working fluids for domestic refrigerators in recent years. R134a is considered as an environmentally safe refrigerant and is essentially non-toxic (Dietrich, 1993), but its GWP (global warming potential) effect is very high. The Kyoto Protocol of the United Nations Framework Convention on Climate Change (UNFCCC) asked for reduction in emission of six categories of greenhouse gases, including R134a, used as refrigerant in domestic refrigerators (Tasi, 2005). Therefore, according to Kyoto protocol (protocol, 1997), the consumption of R134a must be seriously reduced. From the environmental, ecological and health points of view, it is urgent to find some better substitutes for HFC (hydro fluorocarbon) refrigerants (Johnson, 1998).

Recently, Mohanraj et al. (M. Mohanraj, C. Muraleedharan, & Jayaraj, 2011) have reviewed the developments of new refrigerant mixtures for vapor compression based refrigeration systems. They stated that hydrocarbon refrigerants are identified as long-term alternatives to phase out the existing halogenated refrigerants in the vapor compression based systems. Regarding the performance, hydrocarbon mixtures are found to be better substitutes for R12 and R134a in domestic refrigerators (M. Mohanraj, S. Jayaraj, & Muraleedharan, 2009). A survey conducted by Jose et al. (M.C. Jose, S. Jacobo, C. Daniel, & Jose, 2008) proved that certain hydrocarbons have excellent characteristics as refrigerants from a thermodynamic point of view. Furthermore, hydrocarbon as a refrigerant may be used in small systems like refrigerators and small freezers (with hydrocarbon charge lower than 150 g) provided that they incorporate a few special safety measures.

Even though R600a and its blends are widely used in domestic sector in Europe, their use in North America is not extensive yet (Bansal P., Vineyard E., & O., 2011). The reason is manufacturers' fear of flammability and explosion hazards in domestic refrigerators (J.M., 2008). Nevertheless, R600a is the most frequently used hydrocarbon refrigerant with more than 95% of market share in many countries (RTOC, 2006). In 2004, 33% of global domestic refrigerator production used pure isobutane or its blends. It should be noted that normal use of R600a in refrigerators

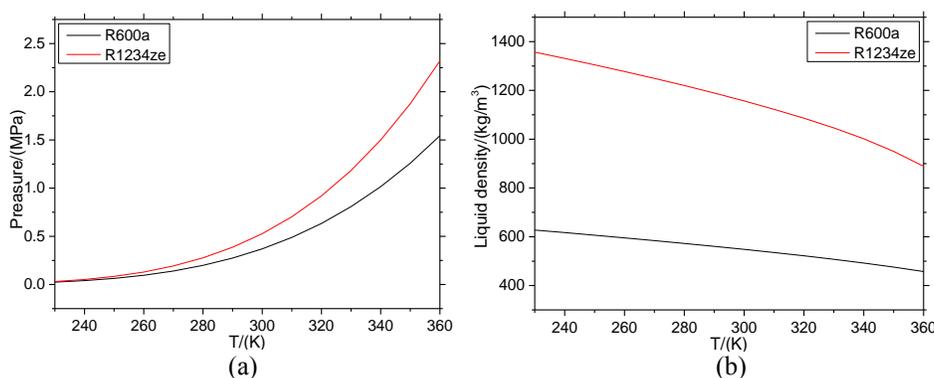
has not resulted in any accidents (P. Wennerstrom, 2006). In contrast, some accidents have been reported during manufacturing or in the retrofitted equipment using hydrocarbons (Colbourne D., Suen K., & T., 2003). R600a has a higher density than air, and in case of leakage it spreads close to the floor; thus, the risk of flammability increases (Clodic D. & W., 1996). On the other hand, lower refrigerant charge reduces explosion risk. Some solutions to overcome the flammability of hydrocarbon refrigerants were presented (A. Giegel, 2004). Mixture refrigerants can have each advantages of individual. So, R600a mixing with synthetic refrigerants, such as R1234ze, can reduce the risk of flammability and explosion. Focus on R1234ze, this refrigerant has a GWP of 4 (Nielsen, O.J., & al., 2007). According to the investigation by Osafune K. (2012) and Koyama S. (2013), R1234ze is expected to be categorized as ASHRAE safety classification A2L, and most metals, plastics, and elastomers are stable in this refrigerant.

As the global environment is progressively concerned, greenhouse warming has also become very important these days besides the ozone depletion issue. One of the ways to alleviate greenhouse warming is to adopt the mixtures with low GWP and develop high efficiency refrigeration devices. From this point of view, the hydrocarbons and new synthetic refrigerant R1234ze with zero ODP and lower GWP could be possible alternative working fluid that can meet this need. The intention of this study is to show the possibility of applying the chosen refrigerant mixture in relatively large amount of charge refrigerator. Through this study, we hope that it could provide some useful data for the promising development of such domestic refrigerators in the future.

2. CHARACTERISTICS OF R600a AND R1234ze

The properties of R600a and R1234ze (such as vapor pressure, liquid density, latent heat, and suction specific volume) for wide range of temperatures (between 230 and 360K) are compared in Figs. 1. Fig. 1(a) depicts the variation of vapor pressure of R600a and R1234ze against temperature. It was observed that both have approximately the same vapor pressure at lower temperatures. However, the vapor pressure of R1234ze was found to be a little higher than that of R600a at higher temperatures from 330K to 360K. The liquid densities of R1234ze and R600a are compared in Fig. 1(b). The liquid density of R1234ze was found to be twice as much than that of R600a in the study range temperature, which will significantly reduce the refrigerant charge requirement. The variation of latent heat of two investigated refrigerants is shown in Fig. 1(c). It was observed that R1234ze is almost the half compared to R600a. From this point of view, R1234ze is slightly disadvantageous compared with R600a. But, this disadvantage could be compensated by the lower suction specific volume of R1234ze. Fig. 1(d) shows the variation of compressor suction specific volume of the refrigerants under study. The lower suction specific volume of R1234ze than that of R600a indicates the need for a smaller compressor size for the same mass flow rate, and this property would compensate the lower enthalpy of vaporization of R1234ze than that of R600a discussed earlier in Fig. 1(c).

The other properties such as critical temperature, critical pressure, boiling point, molecular weight, ODP and GWP of R1234ze and R600a are compared in Table 1. R1234ze has zero ODP with low GWP of 4. The critical temperature and critical pressure of R1234ze were found to be lower than those of R600a. Computational analysis of the above said thermophysical properties have been done using REFPROP software version 9.0.



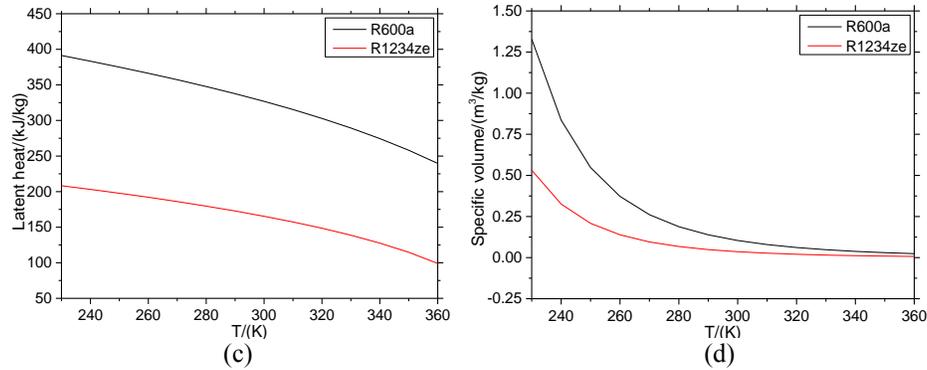


Fig. 1: Thermodynamic properties of R134a and R1234yf: (a) Variation of vapor pressure with temperature, (b) Variation of liquid density with temperature, (c) Variation of latent heat with temperature, (d) Variation of specific volume with temperature

Table 1: Properties of R600a and R1234ze

Refrigerant	Boiling point (°C)	Molecular weight (kg/kmol)	Critical temperature (°C)	Critical pressure (MPa)	Ozone depletion potential	Global warming potential
R600a	-11.73	58.12	135	3.650	0	0
R1234ze	-18.8	114.04	109.5	3.636	0	4

3. CYCLE PERFORMANCE ANALYSIS

Fig. 2(a) shows a schematic diagram of a simple refrigerator cycle composed of an evaporator, condenser, compressor, capillary tube expansion device. As shown in Fig. 2(b), this refrigerator cycle consists of a non-isentropic compression process, an isobaric heat rejection process, an adiabatic expansion process, and an isobaric evaporation process. In the pressure–enthalpy diagram, the process path 1-2-3'-3-4-1'-1. In order to obtain meaningful results from the refrigerator, the thermodynamic performances of the cycle are evaluated based on thermodynamic cycle analysis method. Steady flow energy equation and mass balance equation have been employed in each individual process of the cycle. Also the following assumptions have been made to simplify the analysis:

1. Heat transfer with the ambient is negligible.
2. Compression process is adiabatic but non-isentropic.
3. Evaporation and condensation processes are non-isobaric but pressure drops are constant.
4. Throttling process is adiabatic.
5. Vapor is at saturated or superheated condition at the exit to the evaporator.

The detailed characteristics of the cycle can be found as follows:

Refrigerating capacity of evaporator per unit of mass:

$$q_e = h_1 - h_4 \quad (1)$$

Volumetric heating capacity per unit of swept volume at the inlet of the compressor:

$$q_{hv} = q_e / v_1 \quad (2)$$

Specific work of compressor:

$$w = (h_{2s} - h_1) / \eta_s \quad (3)$$

The isentropic efficiency of the compressor is defined as:

$$\eta_s = (h_{2s} - h_1) / (h_2 - h_1) \quad (4)$$

The coefficient of performance of heat pump (COP):

$$COP = q_e / w \quad (5)$$

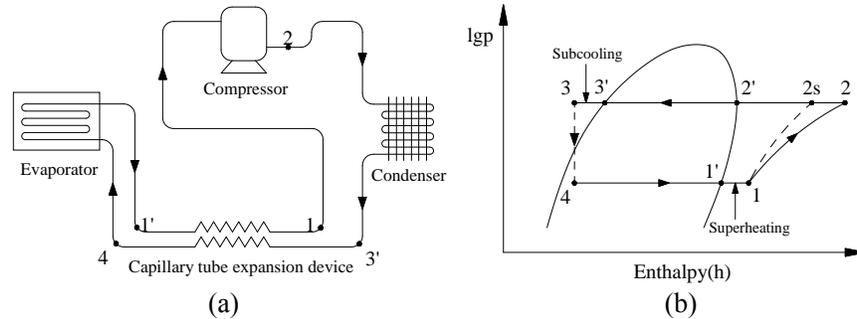


Fig. 2: (a) A Schematic diagram of refrigerator cycle, (b) Pressure-enthalpy diagram of refrigerator cycle.

Where h_1 is the enthalpy of the compressor inlet; h_{2s} is the enthalpy of the compressor outlet at the isentropic compression processes; h_2 is the enthalpy of the compressor outlet at the actual compression processes. In the following analysis, these calculations are accomplished by using REFPROP software version 9.0. (Lemmon, Huber, & McLinden, 2010).

4. RESULTS AND DISCUSSIONS

The effects of the two parameters on the cycle performance are analytically investigated over a range of values. The performance has been assessed for different condensing temperatures between 30 and 50°C with constant -20°C evaporating temperature. In addition, the compressor is assumed to have an isentropic efficiency $\eta_s = 0.85$, which is constant and does not vary with the compression ratio in all cases.

3.1 Variation of Coefficient of performance (COP)

The COP is compared in Fig. 3(a). The COP of mixtures was found to be close to R600a for a wide range of condensing temperatures. The deviations for pure R600a and mixtures are 0.3% and 0.6% at 40°C condensing

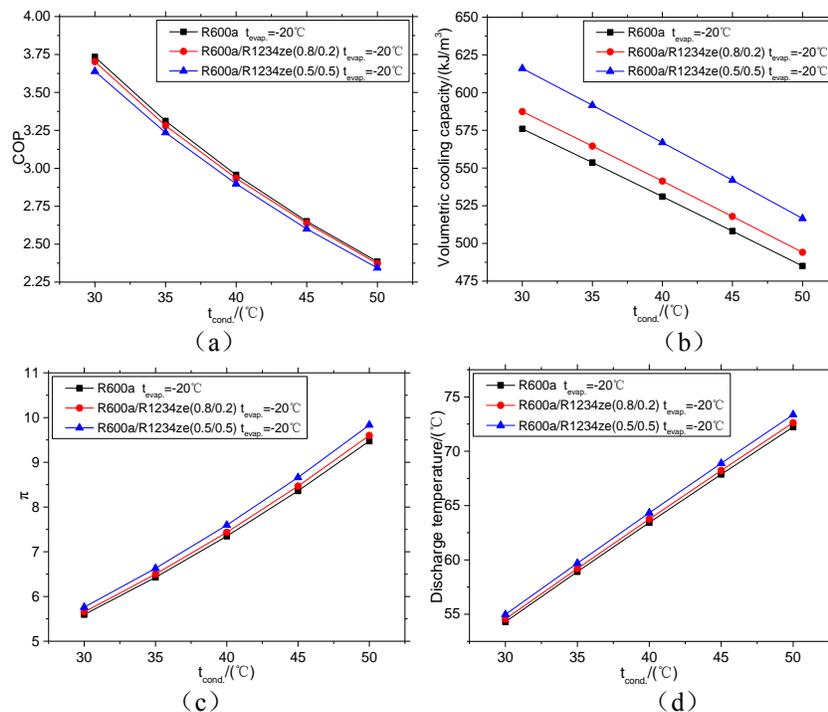


Fig. 3: (a) Variation of pressure ratio with evaporator temperature, (b) Variation of volumetric cooling capacity with evaporator temperature, (c) Variation of COP with evaporator temperature, (d) Variation of compressor discharge temperature with evaporator temperature.

temperature, respectively. And the deviations are found to be small with condensing temperature decreases. The COP for both R600a and mixtures decrease by about 35.1%, 34.7% and 33.9% with an increase in condensing temperature from 30°C to 50°C, respectively.

3.2 Variation of volumetric cooling capacity (VCC)

VCC is the major factor considered for choosing the alternative, which influences the size of the compressors. The variation of VCC at different operating temperatures is illustrated in Fig. 3(b). VCC of mixtures were found to be slightly large than that of R134a for a wide range of condensing temperatures. The maximum deviations in VCC are found to be 2.3% and 7.1%, respectively. Hence, the mixtures can be used as drop-in substitute without major modification in the existing R600a systems. So, from this point of view, the size of the compressors can be smaller for using these mixtures.

3.3 Variation of pressure ratio

For any refrigerants to be a suitable alternative for R600a in a conventional refrigeration system, it must meet certain criteria. One of these criteria is the compression ratio. The pressure ratio of the refrigerant influences the volumetric efficiency of the compressor. Fig. 3(c) shows the pressure ratios as a function of condensing temperature. The pressure ratio of mixtures were observed to be slightly higher than that of R600a by about 1.9% and 5.3% at 40°C condensing temperature, respectively. Hence, the mixtures can be used as drop-in substitute without major modification in the existing R600a systems.

3.4 Compressor discharge temperature

The compressor discharge temperature is the major factor influencing the life of the refrigerant compressors. The higher compressor discharge temperature will affect the properties of lubricants. The comparison of compressor discharge temperature of R600a and mixtures is depicted in Fig. 3(d). The compressor discharge temperatures of mixtures were found to be slightly higher than that of R600a for a wide range of condensing temperatures. The compressor discharge temperature increases with condensing temperature rises for both R600a and mixtures. And, the maximum of the temperature is within the safe level.

3.5 Degree of superheat

Analyzing the influence of the superheat degree on the COP, Fig. 4(a), it can be observed that the value of the COP obtained using R600a and mixtures both increases with the superheat degree rises. Fig. 11, it can be seen that the COP obtained increases 5.6~5.9% with the average superheat degree rises 10°C for both R600a and mixtures. And the COP obtained using mixtures are more sensitive than that of R600a with the superheat degree rises. So, from this point of view, the COP is improved more for mixtures than that of R600a with the superheat degree rises. But, the compressor discharge temperature increases with the superheat degree rises for both R600a and mixtures depicted in Fig. 4(b), which is due to the higher compressor suction temperature with the superheat degree rises. This fact influences the life of the refrigerant compressors and affects the properties of lubricants. But, the maximums are all within the safe value.

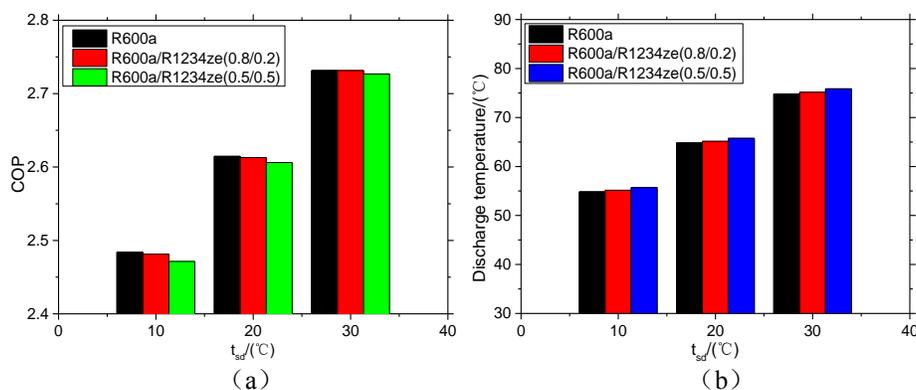


Fig. 4: (a) Variation of COP with degree of superheat ($t_{\text{vap.}}=-25^{\circ}\text{C}$; $t_{\text{cond.}}=40^{\circ}\text{C}$),
(b) Variation of Compressor discharge temperature with degree of superheat ($t_{\text{vap.}}=-25^{\circ}\text{C}$; $t_{\text{cond.}}=40^{\circ}\text{C}$).

5. CONCLUSIONS

Thermodynamic performance assessment has been made for a domestic refrigerator working with pure R600a and mixture of R600a and R1234ze, and the following conclusions were made.

- VCC of the mixtures was found to be closer with R600a. Hence, the mixtures can be used in R600a domestic refrigerator without major modifications.
- The COP of the domestic refrigerator working with mixtures were found to be slightly lower than that of R600a by 0.3% and 0.6% at 40°C condensing temperature, respectively. And, the deviations are found to be smaller with the condensing temperature decreases.
- The flammability and explosion of the mixture R600a/R1234ze decrease greatly compares with pure R600a. So, the mixture R600a/R1234ze can be charged to the large system at the same risk of flammability and explosion.

NOMENCLATURE

The nomenclature should be located at the end of the text using the following format:

COP	coefficient of performance
P	pressure (kPa)
H	specific enthalpy ($\text{kJ}\cdot\text{kg}^{-1}$)
η_s	isentropic efficiency
w	specific work of compressor($\text{kJ}\cdot\text{kg}^{-1}$)
π	pressure ratio
q_e	refrigerating capacity per unit of mass ($\text{kJ}\cdot\text{kg}^{-1}$)
q_h	heating capacity per unit of mass ($\text{kJ}\cdot\text{kg}^{-1}$)
q_{hv}	heating capacity per unit of swept volume ($\text{kJ}\cdot\text{m}^{-3}$)
t	temperature ($^{\circ}\text{C}$)
v	specific volume ($\text{m}^3\cdot\text{kg}^{-1}$)

Subscripts

d	compressor discharge
e	evaporator
c	condenser
sd	superheat degree
evap.	evaporating
cond.	condensing
1-4	state points of refrigerant

REFERENCES

- A. Giegel. (2004). Safety testing of domestic refrigerators using flammable refrigerants. *Int. J. Refrigeration*, 27, 621-628.
- Bansal P., Vineyard E., & O., Abdelaziz. (2011). Advances in household appliances- A review. *Appl. Therm. Eng.*, 31, 3748-3760.
- Clodic D., & W., Cai. (1996). *Tests and simulations of diffusion of various hydrocarbons in rooms from air conditioners and refrigerators*. Paper presented at the In: IIF/IIR Conf. Applications for Natural Refrigerants, Aarhus, Denmark.
- Colbourne D., Suen K., & T., Ritter. (2003). A risk assessment model for hydrocarbon refrigerants. *Proc. Inst. Refrigeration*, 1-14.
- Dietrich, W. (1993). A positive outlook for the future. *ASHRAE J.*, 35, 64-65.
- J.M., Calm. (2008). The next generation of refrigerants e historical review, considerations, and outlook. *Int. J. Refrigeration*, 31, 1123-1133.
- Johnson, E. (1998). Global warming from HFC. *Environ. Impact Assess. Rev.*, 18, 485-492.

- Koyama S., Higashi T., Miyara A., & R., Akasaka. (2013). Research and development of low-GWP refrigerants suitable for heat pump systems *In: JSRAE Risk Assessment of Mildly Flammable Refrigerants-2012 Progress Report* (pp. 29-34).
- Lemmon, Eric W., Huber, Marcia L., & McLinden, Mark O. (2010). NIST Reference Fluid Thermodynamic and Transport Properties(REFPROP) (Version 9.0).
- M. Mohanraj, C. Muraleedharan, & Jayaraj, S. (2011). A review on recent developments in new refrigerant mixtures for vapor compression-based refrigeration, air-conditioning and heat pump units. *Int. J. Energy Res.*, 35(8), 647-669.
- M. Mohanraj, S. Jayaraj, & Muraleedharan, C. (2009). Environment friendly alternatives to halogenated refrigerantsda review. *Int. Journal Greenhouse Gas Control*, 3, 108-119.
- M.C. Jose, S. Jacobo, C. Daniel, & Jose, G. (2008). Review of standards for the use of hydrocarbon refrigerants in A/C, heat pump and refrigeration equipment. *Int. J. Refrig.*, 31(4), 748-756.
- Nielsen, O.J., & al., et. (2007). Atmospheric chemistry of CF₃CFCH₂: Kinetics and mechanisms of gas-phase reactions with Cl atoms, OH radicals, and O₃. *Chemical Physics Letters*, 439(1-3), 18-22.
- Osafune K., Nishiguchi Y., Okamoto S., Sakyu F., & S., Koyama. (2012). *Development of low GWP refrigerants suitable for heat pump systems*. Paper presented at the Int. Symp. New Refrigerants and Environmental Technology 2012, Kobe, Japan.
- P. Wennerstrom. (2006). *HC in Domestic Refrigeration, Natural Refrigerant Heat Pumps*. Paper presented at the Royal Inst. of Technol. (KTH), Energy Technol. Dept, Stockholm, Sweden.
- protocol, Kyoto. (1997). *United Nations Framework Convention on Climate Change*. Paper presented at the United Nations, New York, USA.
- R. Radermacher, & Kim, K. (1996). Domestic refrigerators: recent developments. *Int. J.Refrig.*, 19, 61-69.
- RTOC. (2006). UNEP Report of the Refrigeration Air Conditioning and Heat Pumps Technical Options Committee.
- Tasi, W.T. (2005). An overview of environmental hazards and exposure and explosive risk of hydrofluorocarbon HFCs. *Chemosphere*, 61, 1539-1547.

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