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Development of Alternative Binary Mixtures to Replace HFC 134a in Domestic Refrigerator

Parashurama Siddegowda[a,*],Govindegowda Mundur Sannappagowda[b], Ramesha D Kempegowda[c]

[a] Mechanical Engineering Department, VTU, Belagavi,590018, India
[b] Vivekananda college of Engineering and Technology, Puttur, D.K, India
[c] Mechanical Engineering Department, UVCE,Bengaluru,India
parashurams@rediffmail.com

Thermodynamic and volumetric properties of alternate Refrigerant mixtures to replace R134a have been predicted using SRK EOS and modified PSRK mixing rule using UNIFAC method. The performance of alternate refrigerant mixtures has been comparatively assessed using standard refrigeration parameters such as COP, compressor work input, condenser heat rejection, compressor discharge temperature, refrigeration effect. In this paper an attempt is made to find new alternatives for R134a by considering flammability, azeotropic behavior, thermodynamic properties and performance parameters of domestic refrigerator. According to our results, R134a (75)/R290 (25), R134a (50)/R270 (50), R1270 (32)/R600a (68), R1270 (32)/R600 (68) R290(30)/R600a(70), R290(35)/R600(65) and R134a (65)/R1270 (35) are proposed as alternatives for R134a.An attempt has been made to quench the flammability and increase the miscibility of HFCs with lubricating oil of the mixture

1. Introduction

The CFC hazard to atmosphere and regulations of these substances according to Montreal and Kyoto protocols one has to think of using eco-friendly alternatives. Refrigerants like R134a, R152a and R419 are recommended to replace R134a.But these Refrigerants are either having lower performance than R134a or higher GWP than R134a. The number of pure (single component) refrigerants HFCs (Hydro fluorocarbons) and HCs (Hydrocarbons) available for use is fairly limited due to limitations such as ODP, GWP, toxicity, flammability, miscibility with lubricant oil etc. for use in the Refrigeration systems. As number of pure refrigerants available is fairly less, one has to go for mixtures of refrigerants. The only disadvantage of Hydrocarbons is flammability. The reduction in flammability can be achieved by mixing HCs and HFCs together and in turn cost also reduces. Hence there is a need to develop new alternative refrigerant mixtures.
Many researchers have studied the performance of HFC/ HC mixtures experimentally as substitutes of R12 and R134a. Jung et al., (2000) performed computer simulation of domestic refrigerator charged with many pure and mixtures as possible alternatives of R12 and studied experimentally R290/ R600a (60/40) and obtained 2.45% increase in energy efficiency compared to R12. There is uncertainty in the reliability of derived results as NBP and structural details are the only input parameters. Somchai et al., (2005) have determined the performance of vapour compression system with Propane, HC, HFC mixtures and recommended R290/R600a/R14a (40/30/30) as alternative from energy point of view. Tashtoush et al., (2002) investigated experimentally ternary mixture of butane/ propane/R134a (43.91/33.31/22.78) and the obtained performance was higher than that of R12. Sekhar et al., (2005) suggested R134a/R600a/R290 as a retrofit mixture for R12 systems and obtained 4.1-7.6 % energy savings compared to R12.
HFCs like R134a are not miscible with conventional mineral oil. They are compatible with Polyester oil which is synthetic and costly. Miscibility of different refrigerants with mineral oil is analyzed theoretically using Gibbs energy principle. The activity coefficients of mixture are calculated by UNIFAC (StanleyWalas 1985) method and the Gibbs energy are obtained. The binary mixture is considered as a mixture of refrigerant and oil at different compositions. The graphs of Gibbs energy and composition are plotted for different temperatures.

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From these graphs one can conclude about the miscibility behavior of refrigerant with oil. If the Gibbs energy decreases with composition then the refrigerant and oil are miscible with each other; otherwise immiscible.
Flammability behavior of mixtures is assessed by calculating a recently introduced index RF Number which characterizes the threshold between flammable and nonflammable blend formulations. RF-Numbers for pure components and mixtures are calculated using the procedure as given in references (Shigio et al., 2002) and categorized as indicated in Table 2. Junghung et al., (2018) gave an overview of Hydrocarbon refrigerants in HVAC systems. Genco et al., (2017) discussed about the energy efficiency of HVAC systems.
Determination of azeotropic behavior of refrigerant mixture is more essential because once it is found that mixture is azeotropic there is no necessity of mixture theory for property generation; instead one can straight away use single component theory. Aslam et al., (2004) has given method of computing all the azeotropes in refrigerant mixtures through equations of state. This method uses the fugacity concept for determining the azeotropes, calculations are much more involved and iterative. In our work, Group contribution method is used to study azeotropic behaviour of refrigerant mixtures which is simple and probably accurate than the previous method. From the previous studies it is observed that by using hydrocarbons as components in the mixture improves the performance and miscibility of HFCs with mineral oil. In this direction an attempt is made to find new alternate refrigerant mixtures from the view point of increasing the performance, miscibility with lubricant oil and also for quenching the flammability in an unmodified domestic refrigerator.

2. Development of thermodynamic properties of pure components

Some basic properties of the pure refrigerants considered as components of the mixtures along with environmental factors like ODP, GWP are listed in Table 1. Thermodynamic properties are estimated by using SRK equation of state. The vapour specific volume has been calculated using SRK EOS. The liquid specific volume is estimated by using HBT technique. The roots of the cubic equation are obtained using Cardon's method. Thermodynamic properties such as liquid enthalpy, vapour enthalpy, liquid entropy, vapour entropy have been calculated over a range of temperatures and pressures using enthalpy and entropy departure functions. The reference state is chosen to be having a saturated liquid enthalpy and a saturated liquid entropy of 200 kJ/kg and 1kJ/kgK at 0°C, respectively. A C-program was developed to obtain thermodynamic properties at any temperature T and pressure P.

Table 1: General properties of the components of refrigerant mixtures

Refrigerant	Molecular Weight (Kg/Kg mol)	Normal Boiling Point (°C)	Critical Temperature (°C)	Critical Pressure (bar)	ODP	GWP	Accentric Factor ω	Source of VP	Source of C_P^0
R 12	120.91	-27.95	385	41.4	0.82	8100	0.204	11	11
R 290	44.10	-42.1	96.7	42.5	0.00	20	0.153	11	11
R 1270	42.08	-47.7	92.4	46.7	0.00	20	0.144	11	11
R 270	42.08	-33.5	125.2	55.8	0.00	20	0.130	11	11
R152a	66.05	-24	113.3	45.2	0.00	140	0.256	11	11
R600a	58.12	-11.6	134.7	36.4	0.00	20	0.183	11	11
R600	58.12	-0.5	152	38.0	0.00	20	0.199	11	11
R134a	102.03	-26.1	101.1	40.6	0.00	1300	0.327	26	27
R32	52.02	-51.7	78.2	58	0.00	550	0.271	11	11

3. Development of thermodynamic properties of multi-component mixtures

The steps involved in the development of Thermodynamic Properties are:
Calculation of Critical Properties and Molecular Weight.
Calculation of Liquid activity coefficient.
Vapor pressure calculation (Bubble point & Dew point)
Specific volume calculation
Calculation of Latent heat
Calculation of Enthalpy and Entropy departure functions
Calculation of Saturated and Superheated properties
For the development of properties SRK equation of state is used along with modified PSRK mixing rule. The (Reid 1987; Yang et al., 2000; Yang et al., 2004; Kay 1936; Prausnitz et al., 1958) The activity coefficients are calculated by UNIFAC method. (Joffe 1971; Wark 1995; Redlich Otto et al., 1949; Holderbaum 1991) In this

work modified PSRK mixing rule **(**Soave 1972) is used in order to obtain better the prediction results in particular for asymmetric mixtures containing Refrigerants [for calculating SRK EOS parameters a and b]
C- programs are written using the procedure as mentioned in section 3 to obtain Thermodynamic properties at any temperature T. and for Thermodynnamic analysis.The vapour specific volume is calculated by using Secant method. The input to the programs are M, NBP,T_c,P_c, ω, activity coefficients, interaction parameters ,Wagner constants and zero pressure specific heat. The saturated and super-heated properties are displayed in separate output files. The estimated properties are then used in the thermodynamic analysis of vapour compression cycle. A C program is also written for optimizing the mixture (to find mass fractions) for the same displacement, for same or maximum COP as that of R134a and to reduce flammability.

4. Theoretical Thermodynamic analysis of domestic refrigerator

Thermodynamic analysis of Domestic Refrigerator is done based on ten state point vapour compression cycle. Thermodynamic cycle considered for analysis is as shown in figure 1. The results of thermodynamic analysis are tabulated in table 2The performance of alternative refrigerants are compared with that of R134a by various parameters such as Pressure ratio, Discharge Temperature, COP, Refrigeration effect and Compressor work input. °C Figure 1 shows standard ten state points vapour compression cycle according to the data supplied by the manufacturer is employed here for thermodynamic analysis. The ten state points shown on the p-h diagram in Figure 1 corresponding to the conditions as obtained from Voltas manufacturer's catalouge are specified as follows. (Arora 1990)

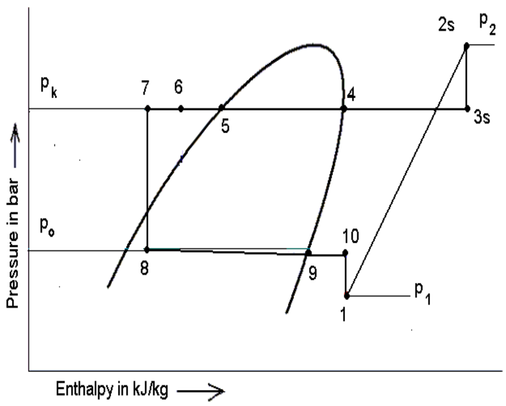

Figure 1: Ten-point cycle used for theoretical thermodynamic analysis

(10) State at inlet to the shell of hermetic compressor (1) Refrigerant state in the cylinder before compression begins (2) Refrigerant state in the cylinder after compression ends. (2s isentropic compression (3) Compressor shell outlet/ condenser inlet condition. (3s isentropic condition) (4) Saturated vapor state in the condenser at 55°C (5) Saturated liquid state in the condenser at 55°C(6) Sub cooled liquid state leaving condenser at 43°C (7) Capillary inlet condition at 32°C (8) Capillary outlet/evaporator inlet condition at -25°C (9) Saturated vapor refrigerant state leaving evaporator
(1) Pressure drops at inlet and outlet valves of compressor are assumed as follows: (Ashok Babu 1997)
For proposed mixtures ΔPi = 0.1 and ΔPo = 0.4 bar. For R12, ΔP_i = 0.1 and ΔP_e = 0.25 bar.
(2) Pressure drop in evaporator is ΔP_e = 0.1 bar for all refrigerants.
(3) Pressure drop in evaporator is ΔPe = 0.1 bar for all refrigerants.
Performance parameters such as pressure ratio, volumetric efficiency, displacement volume, starting torque discharge temperature, refrigerating effect, coefficient of performance, rating of motor, condenser heat rejection rate with different refrigerants to obtain same refrigerating capacity of 89 Was with R134a are given by equation 1 to 10. When a compressor designed for R134a refrigerant is used with alternate refrigerant mixtures the volumetric efficiency is going to be affected and hence the performance of the system changes. It is very essential to have an expression which predicts the volumetric efficiency of the compressor matching with experimental performance. A modified expression adopted in this work, has been taken from [25] (vide equation (1) below) to estimate the volumetric efficiency of the alternate refrigerants especially the HCs whose specific heats are much higher when compared to CFCs and HFCs.

Table 2: Performance parameters of Domestic Refrigerator at T_e=-25^{0}C and T_k=55^{0}C

Refrigerant	Composition	ODP	GWP	Azeotrope/ Zeotrope	RF No	ASHRAE Flammability Category	Mass flow Rate ×10^3 (Kg/s)	Pres-sure Ratio
R12	R12	0.82	8100	-	-	-	0.722	10.99
Mix 1	R134a(75) /R290(25)	0	980	Z	3.701	2	0.458	12.9
Mix 2	R32(44) /R134a(56)	0	1000	Z	0.384	2	0.447	15.59
Mix 3	R134a(31) /R270(69)	0	660	Z	19.15	2	0.339	12.22
Mix 4	R1270(21) /R600a(79)	0	20	Z	54.83	3	0.312	12.57
Mix 5	R1270(32) /R600(68)	0	20	Z	58.98	3	0.311	12.57
Mix 6	R270(95) /R600a(05)	0	20	A	53.64	3	0.238	14.28
Mix 7	R152a(30) /R290(70)	0	50	Z	36.52	2	0.335	10.65
Mix 8	R290(30) /R600a(70)	0	20	Z	21.49	2	0.317	12.6
Mix 9	R290(35) /R600(65)	0	20	Z	56.5	3	0.305	12.93
Mix 10	R218(28) /R290(72)	0	2422.4	Z	-	-	0.369	11.27
Mix 11	R134a(65) /R1270(35)	0	852	Z	3.937	2	0.401	12.13
R134a		0	1300	-	-	-	0.597	17.64

Table 3: Performance parameters of Domestic Refrigerator at T_e=25^{0}C and T_k=55^{0}C (continued)

Refrigerant	Discharge temperature (°C)	Work input (W)	COP	Compressor size (cc)	Isentropic Index	Volumetric Efficiency (%)	Condenser capacity (W)
R12	139.1	43.94	2.026	4.6	1.137	0.756	136.23
Mix 1	126.5	42.53	2.09	5.6	1.12	0.42	153.78
Mix 2	166.52	48.97	1.82	5.22	1.15	0.35	155.34
Mix 3	140.42	40.75	2.18	5.15	1.14	0.466	146.20
Mix 4	120.97	44.16	2.08	5.6	1.11	0.435	253.72
Mix 5	121.63	41.15	2.163	5.346	1.113	0.436	141.83
Mix 6	149.84	41.96	2.117	6.475	1.140	0.429	156.66
Mix 7	108.39	39.88	2.234	3.084	1.104	0.519	158.63
Mix 8	116.99	40.72	2.19	5.61	1.11	0.4302	240.64
Mix 9	118.92	40.20	2.216	5.34	1.109	0.416	141.04
Mix 10	131.56	44.20	2.011	3.278	1.132	0.511	143.93
Mix 11	134	43.11	2.06	5.283	1.131	0.471	152.73
R134a	125	45.58	1.91	5.3	1.102	0.608	151.9

$$\eta_v = K\left[1-(C\left(\frac{P_2}{P_1}\right)^{1/n}-1)\right] \quad (1)$$

Pressure ratio

$$P = \frac{P_2}{P_1} \quad (2)$$

Refrigerating effect,$q_0 = (h_9 - h_8) = h_9 - h_7$ (3)

$$\dot{m} = \frac{\dot{Q}_0}{q_0} \quad (4)$$

$$V_p = \frac{\dot{m}v_1}{\eta_v} \quad (5)$$

$$\dot{Q}_0 = \dot{m}q_0 = \dot{m}(h_9 - h_8) \quad (6)$$

$$Q_k = \dot{m}(h_{3s} - h_6) \quad (7)$$

$$W_{is} = \dot{m}(h_{2s} - h_1) \quad (8)$$

Theoretical COP is calculated from

$$COP = \frac{Q_0}{W_{is}} \quad (9)$$

5. Results and discussion

Several Binary mixtures were considered as substitutes for R134a.The basic component of the mixture was one of the most promising HFCs R32, R152a and R134a and a HC. The values of vapour pressure, liquid specific volume, vapour specific volume, liquid enthalpy, vapour enthalpy, liquid enropy, vapour entropy have been estimated over the temperature range from -25°C to +55 °C. To confirm the reliability of SRK equation of state, volumetric and thermodynamic properties of R134a have been estimated and these are found to be in good agreement with experimental data.To confirm the reliability of SRK equation of state volumetric and thermodynamic properties of R134a have been calculated and validated with experimental data from ASHRAE (Ashrae 1995). The estimated values are within 10% maximum error for liquid specific volume, 1% for vapour specific volume, for enthalpies within 10% and 8% for entropies. Thermodynamic analysis of Refrigerator is done for the candidate mixtures and different parameters are calculated along with R134a using equation (1) to (10) and tabulated in Table 2 and 3. The use of Hydrocarbons facilitates the miscibility of mineral oil and improves the performance of the Refrigerator. The Condenser duty for most of the mixtures was found to be closer to R134a except for Mix 1, Mix 2, Mix 3, Mix 6, Mix 7, Mix 9, Mix 9, Mix 11 for which it is slightly higher as can be seen from Table 2. However, this is not a problem as this can be overcome by slightly tuning capillary. The Compressor discharge Temperature for almost all mixtures was found to be lower than that of R134a except for Mix 2, Mix 3 and Mix 6. This is important factor because the compressor runs smooth and the life of compressor will increase. The Flammability of the mixtures is quenched in some of the cases and remaining are weakly flammable as can be seen from Table 2. But the Flammability nature can be ignored because the amount of charge required is considerably negligible. Except for Mix 6 all mixtures are Zeotropes as seen from Table 2. The Refrigeration effect of all mixtures is higher than that of R134a which is indeed desirable. The volumetric efficiency values for all the mixture are lower and isentropic index values are slightly higher than that of R134a. From Table 2 it is observed that the mass flow rate and pressure ratios are lower than that of R134a.The compressor power requirement is lower than R134a for all mixtures except for R32/R134a. COP for all mixtures is higher than that of R134a except for R32/R134a as seen from Table 2. Mixture R270/600a requires slightly higher displacement compressor when compared to R134a.On the other hand R152a/R290, R218/R290 require lower displacement compressor. The performance of all refrigerant mixtures is better than R134a except R32(44)/R134a (56).

6. Conclusions

In this study we did a broad examination of refrigerant mixtures suggested as replacements for HFC 134a. The present investigation has resulted in the development of ozone friendly, energy efficient, safe and cost-effective alternatives for R134a in domestic Refrigerator. As per our results, mixtures R270 (95)/R600a (5) is recommended with slightly higher displacement compressor and R152a(30)/R290(70) with lower displacement. Finally, R134a (75)/R290 (25), R134a (50)/R270 (50), R1270 (32)/R600a (68), R1270 (32)/R600 (68) R290(30)/R600a (70), R290(35)/R600(65) and R134a (65)/R1270 (35) are appropriate and proposed as drop in substitutes without any modification in the existing system. Flammability is quenched in some of the cases and others are weakly flammable

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