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Development of Zero ODP, Low TEWI, Binary, Ternary and Quaternary Mixtures to Replace HCFC-22 in Window Air-Conditioner

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ABSTRACT

Due to ecological problems like ozone depletion and global warming certain refrigerants like R22 have to be replaced. Alternative refrigerants like R407C, R410A and R417 are having high TEWI values compared to R22. Pure HFCs are having some disadvantages like flammability, miscibility etc. In this paper an attempt is made to find new alternatives for R22 by considering flammability, azeotropic behaviour, miscibility with lubricant oil, thermodynamic properties, and performance parameters of window air-conditioner. By comparing the performance parameters like discharge temperature, COP, TEWI, displacement volume etc. it is recommended to use the binary mixture R32/R134a with POE oil & ASHRAE flammability category 1 or ternary mixture R32/R134a/R290 with mineral oil & ASHRAE flammability category 2 as drop in substitute for R22 in window air-conditioner with modification only in capillary.

1. INTRODUCTION

Refrigerant mixtures like R407C, R410A and R417A are recommended to replace R22. But these mixtures are either having lower COP than R22 or higher GWP than R22. The number of pure (single component) refrigerants HFCs (Hydrofluorocarbons) 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 air conditioning systems. As number of pure refrigerants available is fairly less, one has to go for mixtures of refrigerants. Also no pure substance can replace R22. Hence there is a need to develop new alternative refrigerant mixtures.

The fractionation behavior of a multicomponent blend can greatly change the nominal formulation and cause the blend to shift to flammable formulation due to a new concentration balance of its components. Today, tools are readily available to evaluate the fractionation (by depletion test or computer simulation) and the combustion (per flammability tests standards) behaviors of a blend formulation. The RF number has been introduced in the industry and characterizes the threshold between flammable and nonflammable blend formulations [1]. Determination azeotropic behaviour of refrigerant mixture is more essential because once it is found that mixture is azeotropic we need not go for mixture theory for property generation, thermodynamic analysis etc. instead we straightaway use single component theory. Hence it is very important consideration when we are in search of alternative refrigerant mixtures. Group contribution method is used to study azeotropic behaviour of refrigerant mixtures. It is necessary to know the miscibility of the new refrigerant mixtures developed with mineral oil. Theoretical analysis is done using Gibbs energy principle to find the miscibility of the newly developed mixtures with mineral oil. The accuracy of properties of these mixtures greatly affects the performance results. Hence it is necessary to validate the accuracy of thermodynamic properties developed. Thermodynamic analysis of window air conditioner is done for the new mixtures and the performance parameters are compared with that of R22.

1.1. RF-Number Analysis

The flammability study is crucial for the developers and users of alternative refrigerants. There is no question that the flammability limit is a most widely used index for representing the flammability characteristics of gases and vapors. There is a large volume of flammability limits data available. However, it is not necessarily easy to understand the true flammability characteristics of individual gases solely from the data of flammability limits.

Considering this situation, recently introduced an index called RF-number to represent the flammability characteristics of a given gas in terms of one unique number [1]. RF-Numbers for pure components and mixtures are calculated using the procedure as given in references [1, 2, 3, 4, 5] and categorized as indicated in Table 1.

1.2. Azeotropic behaviour of refrigerant mixtures

Group contribution method is used to study azeotropic behaviour of refrigerant mixtures. This method includes following steps:

1) Finding activity coefficients using UNIFAC method for a fixed composition of mixture say x1 and x2.
2) Using modified Raoults laws [6] determination of the dew point pressure and bubble point pressure.
3) If the dew point pressure is equal to bubble point pressure then the mixture is an azeotrope at that temperature and composition.

After determination of activity coefficients the bubble and dew point pressures are determined using following formulae [6]:

$$p_b = \sum x_i \gamma_i P_i^{sat} \qquad \textbf{(1)} \qquad\qquad p_d = \frac{1}{\sum \frac{x_i}{\gamma_i p_i}} \qquad \textbf{(2)}$$

1.3. Miscibility criteria of refrigerant mixtures

Miscibility of different refrigerants with mineral oil is analyzed theoretically using Gibbs energy principle [7]. Activity coefficients are calculated by UNIFAC method [6]. Gibbs energy is given by

$$G = \sum x_i G_i = RT \sum x_i \ln(\gamma_i) \qquad (3)$$

Here the binary mixture taken is mixture of refrigerant and oil at different compositions. The graphs of Gibbs energy and composition are plotted at different compositions at different temperatures. From these graphs we can conclude the miscibility of refrigerant with oil either miscible or immiscible depending on Gibbs energy decreases or increases with composition change. If the Gibbs energy decreases with composition then the refrigerant and oil are miscible with each other and if Gibbs energy increases with composition then the refrigerant and oil are immiscible [7]. In case of binary refrigerant mixture with lubricant oil there are three compositions and are not represented on the two dimensional graph. Hence the composition of one component is kept constant and by varying the compositions of other component Gibbs energy is found. And this data is plotted. Similar procedure is followed for another component of the refrigerant and second graph is drawn. If in the two graphs one component shows miscibility with lubricant oil then the mixture is miscible with that lubricant oil. The same procedure is followed for ternary and quaternary mixtures. The results of miscibility of various mixtures are tabulated in Table number 1.

1.4. TEWI Value calculation

The TEWI values are calculated as per reference [19, 20]. The following assumptions are made for the calculation of TEWI value:
Amount of Refrigerant mixture considred in the equipment = 1.5 kg, Leakage rate per year = 5%, Service life of refrigerant Equipment = 10 years, Working time of window air conditioner = 8 hrs/day.

The ratio of TEWI values of mixtures and R22 are calculated and tabulated in Table 1 in increasing order for comparison

Table 1: General properties of refrigerant mixtures

Refrigerant	ODP	GWP	Azeotrope or Zeotrope	ASHRAE Flammability Category	Miscibility with Mineral oil	ASHRAE Toxicity Category	CO_2 Produced Yearly	TEWI Value
R134a/R290 (54/46)	0	0.41824	Z	2	YES	A	1.0378	0.55829
R134a/R290 (75/25)	0	0.57647	Z	2	YES	A	1.03966	0.68117
R32/R134a/R1270 (20/70/10)	0	0.60118	Z	2	YES	A	1.04096	0.70059
R32/R134a/R290 (20/70/10)	0	0.60118	Z	2	YES	A	1.04613	0.70176
R32/R134a (35/65)	0	0.61	Z	1	NO	A	1.03278	0.70557
R32/R134a/R1270 (25/70/5)	0	0.61647	Z	2	YES	A	1.03817	0.7118
R32/R134a (30/70)	0	0.63235	Z	1	NO	A	1.03018	0.72228
R32/R134a/R600 (25/70/5)	0	0.63059	Z	2	YES	A	1.03669	0.72239
R32/R134a/R290 (20/75/5)	0	0.63882	Z	2	YES	A	1.03636	0.72869
R32/R134a (26/74)	0	0.65	Z	1	NO	A	1.02657	0.73512
R134a/R1270 (85/15)	0	0.65176	Z	2	YES	A	1.03111	0.73751
R125/R134a/R290 (50/45/5)	0	0.75647	Z	1	YES	A	1.06885	0.82708
R125/R134a/R600 (50/45/5)	0	0.77059	Z	1	YES	A	1.06134	0.83631
R32/R125/R134a/R600 (15/20/60/5)	0	0.86294	Z	1	YES	A	1.03615	0.90209
R32/R125/R134a/R600a (15/15/66/4)	0	0.86529	Z	1	YES	A	1.04274	0.90541
R32/R125/R134a/R600a (15/20/60/5)	0	0.86353	Z	1	YES	A	1.04942	0.90555
R32/R125/R134a/R1270 (10/15/70/5)	0	0.86824	Z	1	YES	A	1.0412	0.90733
R32/R125/R134a/R600 (15/15/67/3)	0	0.86941	Z	1	YES	A	1.03891	0.90773
R32/R125/R134a/R290 (20/25/50/5)	0	0.94765	Z	1	YES	A	1.05322	0.97151
R22	0.05	1	-	1	NO	A	1	1

2. DEVELOPMENT OF THERMODYNAMIC PROPERTIES OF MULTI-COMPONENT MIXTURES

For the development of thermodynamic properties SRK EOS is used with modified PSRK mixing rule [8, 9, 10]. The PSRK mixing rule [18] is given by

$$\frac{a}{bRT}=\sum x_i \frac{a_{ii}}{b_i RT}+\frac{1}{A}\left(\frac{G_0^E}{RT}+\sum x_i \ln\left(\frac{b}{b_i}\right)\right) \tag{4}$$

Modification of PSRK mixing rules for the EOS parameter ‘b’ [21. In this work the following nonlinear combination rule for b is used:

$$b_{ij}^{3/4}=\frac{1}{2}\left(b_i^{3/4}+b_j^{3/4}\right) \tag{5}$$

in which the exponent 3/4 has the same value as that used in the combinatorial part of Modified UNIFAC (Dortmund), which shows good results for systems with components which are very different in size.
 The activity coefficients are calculated by UNIFAC method [11, 12, 13]. In this work, modifications of the PSRK mixing rules [14, 15, 16] are used in order to further improve the prediction results in particular for asymmetric mixtures containing Refrigerants.
After finding the constants of EOS thermodynamic properties are determined by using same procedure as that of pure substance. The thermodynamic properties of seven pure refrigerants which form the mixture of binary, ternary and quaternary mixtures are developed. Thermodynamic properties of six binary, nine ternary and seven quaternary are developed. Among these mixtures, the properties of R410A, R407C and R417A properties were available in literature and hence the properties of these mixtures are compared with ASHRAE, Dupont, Altofina and found that the errors are well within 2-4% in operating range of temperature and pressure. It is confirmed that procedure used to develop these properties are confident. The properties of remaining alternate mixtures are developed whose properties are not available in literature and hence are not compared.

3. THEORETICAL THERMODYNAMIC ANALYSIS OF WINDOW AIR-CONDITIONER

Thermodynamic analysis of window air conditioner is done based on ten state point vapour compression cycle. In this analysis pressure drops at suction, discharge valves of compressor, at evaporator an at condenser are considered. Thermodynamic cycle considered for analysis is as shown in figure 1. The performance parameters calculated by thermodynamic analysis for R 22 and alternative mixtures. The ratios of the performance parameters of alternative mixtures and performance parameters of R 22 are tabulated in tables 2, 3 and 4.

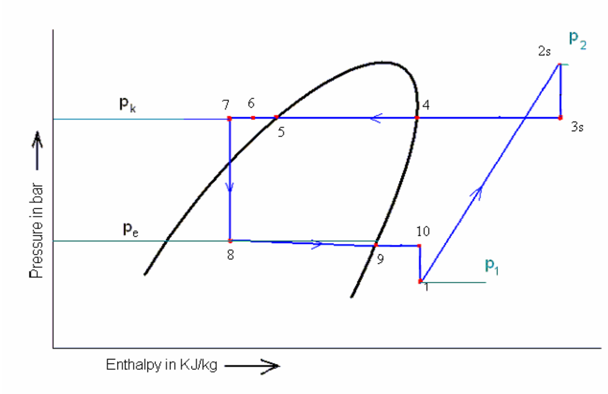

Figure 1: Thermodynamic analysis of window air-conditioner

State points:

10-1	Pressure drop in suction valve,	1-2s	Polytropic compression,
2s-3s	Pressure drop in discharge valve,	3s-4	Superheat horn region, 4-5Condensation at Pressure p2,
5-6	Sub-cooling in condenser,	6-7	Sub-cooling in regenerator, 7-8 Expansion in expansion valve,
8-9	Pressure drop in evaporator,	9-10	Superheating in regenerator.

Following manufacturer data are used for thermodynamic analysis of window air conditioner:Pressure drop in the suction valve is 0.2 bar.

- Pressure drop in discharge valve is 0.4 bar.
- Pressure drop in the evaporator is 0.1 bar.
- Pressure drop in the suction line is 0.1 bar.
- Pressure drop discharge line is 0.1 bar.
- Evaporator temperature is 7.2^{0}C.
- Condenser temperature is 55^{0}C.
- Speed of compressor is 2900 rpm.
- Slip=0.04%
- Refrigeration capacity 0.75 ton.

4. RESULTS AND DISCUSSIONS

The Ecological properties (ODP, GWP, TEWI), physical properties (Azeotrope or non-azeotrope, Miscibility with mineral oil) are calculated for the mixtures and tabulated in the Table 1.

Thermodynamic properties like discharge temperature, Volumetric efficiency of compressor, work input, refrigeration effect, COP, mass flow rate, condenser duty and compressor size are calculated for all the mixtures without regenerator and tabulated in Tables 2 in increasing order of compressor size. The same thermodynamic parameters are calculated for a degree of superheat 5^0C, 10^0C are tabulated in Tables 3 and 4 respectively. Here the values of R22 are set to unity and correspondingly the values of other refrigerants are calculated so that it becomes very easy to compare the results of new refrigerants with that of R22.

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5. CONCLUSIONS

After comparing all the results of new refrigerant mixtures with that of R22 it is concluded that there are many alternative mixtures made of R32, R134a, R125, R290, R1270, R600 and R600a which are having lower TEWI value than R22 with marginal lower COP than R22. Some alternatives like R134a/R1270, R134a/R290, R125/R134a/R600a, R125/R134a/R290 etc. require modification in both compressor and capillary size in existing set up of R22. the selection of the mixture is done considering the factors TEWI, mineral oil miscibility, flammability category, and compressor size. Alternatives like R32/R134a (26/74) with POE oil, R32/R134a/R1270 and R32/R134a/R290 require modification only in capillary length without any change in existing compressor size. Hence these refrigerants are selected and recommended as drop in substitute for the replacement of R22.

NOMENCLATURE

a , b constants G Gibbs energy P Pressure R gas constant T temperature K

TEWI total equivalent warming impact x mole fraction γ activity coefficient

Subscripts

b bubble point d dew point i component

Superscripts

sat – saturation state

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Table 2: Relative performance parameters of window air conditioner without regenerator.

Refrigerant	Discharge temperature	Volumetric Efficiency	Work input	Refrigeration Effect	COP	Mass flow Rate	Condenser capacity	Compressor size
R410A	1.02026	1.02061	1.08825	1.04787	0.96307	0.95424	1.05473	0.65598
R32/R134a (35/65)	0.96824	0.99726	1.12636	1.0907	0.96858	0.91692	1.09674	0.92041
R32/R125/R134a/R290 (20/25/50/5)	0.88553	1.00429	0.94155	0.894	0.94977	1.1186	0.90439	0.93475
R407C	0.88814	1.00071	0.94699	0.9067	0.95761	1.10295	0.91475	0.97085
R32/R134a/R1270 (25/70/5)	0.92392	0.99845	1.07106	1.03181	0.96346	0.9693	1.03945	0.9723
R32/R134a (30/70)	0.94537	0.99261	1.09198	1.0604	0.97131	0.94341	1.06597	0.97359
R32/R134a/R1270 (20/70/10)	0.90497	1.00095	1.06533	1.02349	0.9608	0.97712	1.03221	0.9877
R22	1	1	1	1	1	1	1	1
R32/R134a/R290 (20/70/10)	0.8956	1.00012	1.04613	0.99994	0.95592	1	1.01	1.00397
R32/R134a (26/74)	0.92641	0.98832	1.06504	1.0376	0.97443	0.96388	1.04258	1.02163
R32/R134a/R290 (20/75/5)	0.89406	0.99345	1.02464	0.98891	0.96527	1.01144	0.99656	1.03837
R32/R134a/R600 (25/70/5)	0.91101	0.98725	1.07622	1.03811	0.9648	0.96328	1.0456	1.06781
R32/R125/R134a/R290 (10/25/60/5)	0.83861	0.99452	0.88711	0.84374	0.95117	1.18543	0.85381	1.08006
R32/R125/R134a/R600a (15/20/60/5)	0.85496	0.98689	0.94527	0.9008	0.95322	1.11017	0.91049	1.12122
R32/R125/R134a/R1270 (10/15/70/5)	0.84666	0.98975	0.93181	0.89507	0.96058	1.1174	0.90321	1.12431
R32/R125/R134a/R600a (15/15/61/4)	0.86242	0.98534	0.96275	0.92341	0.95935	1.08308	0.93183	1.12554
R32/R125/R134a/R600 (15/20/60/5)	0.82782	0.98415	0.94355	0.91056	0.96505	1.09813	0.91844	1.13417
R125/R134a/R290 (50/45/5)	0.77817	0.99535	0.75387	0.70542	0.93574	1.41782	0.71752	1.14111
R32/R125/R134a/R600 (15/15/67/3)	0.86088	0.98236	0.96189	0.92593	0.96269	1.08007	0.93357	1.15131
R417A	0.75329	0.99345	0.73209	0.71446	0.97608	1.39976	0.72054	1.19475
R125/R134a/R600a (60/35/5)	0.76739	0.98951	0.73152	0.67872	0.928	1.47321	0.69151	1.19598
R134a/R290 (54/46)	0.80401	0.99285	1.27593	1.22996	0.96421	0.81337	1.24098	1.26746
R125/R134a/600a (50/45/5)	0.76656	0.98236	0.76877	0.72281	0.94018	1.3835	0.73398	1.27184
R125/R134a/R600 (50/45/5)	0.76526	0.98022	0.77421	0.72955	0.94245	1.37086	0.74039	1.29108
R134a/R1270 (85/15)	0.81716	0.98046	1.01461	0.98419	0.97023	1.01626	0.99123	1.32105
R134a/R290 (75/25)	0.80401	0.98284	1.08883	1.04705	0.96175	0.95485	1.05704	1.33883

Table 3: Relative performance parameters of window air conditioner with degree of superheat 5° C

Refrigerant	Discharge Temperature	Volumetric Efficiency	Work input	Refrigeration Effect	COP	Mass flow Rate	Condenser Capacity	Compressor Size
R410A	1.02026	1.02061	1.08825	1.04187	0.95755	0.95983	1.05473	0.65983
R32/R134a (35/65)	0.96824	0.99726	1.12636	1.09083	0.96858	0.91667	1.09674	0.92071
R32/R125/R134a/R290 (20/25/50/5)	0.88553	1.00429	0.94155	0.89336	0.94902	1.1199	0.90439	0.93593
R407C	0.88814	1.00071	0.94699	0.91682	0.96828	1.09113	0.9147	0.96003
R32/R134a/R1270 (25/70/5)	0.92392	0.99845	1.07106	1.03144	0.96313	0.96942	1.03945	0.9731
R32/R134a (30/70)	0.94537	0.99261	1.09198	1.06028	0.97117	0.94305	1.06597	0.97415
R32/R134a/R1270 (20/70/10)	0.90497	1.00095	1.06533	1.02296	0.96024	0.97782	1.03221	0.98867
R22	1	1	1	1	1	1	1	1
R32/R134a/R290 (20/70/10)	0.8956	1.00012	1.04613	0.99918	0.95518	1.0012	1.01	1.00517
R32/R134a (26/74)	0.92641	0.98832	1.06504	1.03719	0.97406	0.96403	1.04258	1.02242
R32/R134a/R290 (20/75/5)	0.89406	0.99345	1.02464	0.98817	0.9645	1.01199	0.99656	1.03962
R32/R134a/R600 (25/70/5)	0.91101	0.98725	1.07622	1.03744	0.96415	0.96403	1.0456	1.06901
R32/R125/R134a/R290 (10/25/60/5)	0.83861	0.99452	0.88711	0.84244	0.94964	1.18705	0.85381	1.08225
R32/R125/R134a/R600a (15/20/60/5)	0.85496	0.98689	0.94527	0.89962	0.95189	1.11211	0.91049	1.12332
R32/R125/R134a/R1270 (10/15/70/5)	0.84666	0.98975	0.93181	0.8938	0.9592	1.1193	0.90321	1.1264
R32/R125/R134a/R600a (15/15/61/4)	0.86242	0.98534	0.96275	0.92226	0.9581	1.08453	0.93183	1.12756
R32/R125/R134a/R600 (15/20/60/5)	0.82782	0.98415	0.94355	0.90424	0.95827	1.10612	0.91844	1.14267
R125/R134a/R290 (50/45/5)	0.77817	0.99535	0.75387	0.70354	0.93324	1.42146	0.71752	1.14464
R32/R125/R134a/R600 (15/15/67/3)	0.86088	0.98236	0.96189	0.92473	0.96143	1.08153	0.93357	1.15335
R417A	0.75329	0.99345	0.73209	0.71543	0.97735	1.39808	0.72054	1.19355
R125/R134a/R600a (60/35/5)	0.76739	0.98951	0.73152	0.67666	0.92511	1.47782	0.69151	1.20023
R134a/R290 (54/46)	0.80401	0.99285	1.27593	1.2277	0.96238	0.81475	1.24098	1.2704
R125/R134a/600a (50/45/5)	0.76656	0.98236	0.76877	0.72062	0.93732	1.38789	0.73398	1.27627
R125/R134a/R600 (50/45/5)	0.76526	0.98022	0.77421	0.72732	0.93955	1.3753	0.74039	1.29561
R134a/R1270 (85/15)	0.81716	0.98046	1.01461	0.98229	0.96839	1.01799	0.99123	1.32414
R134a/R290 (75/25)	0.80401	0.98284	1.08883	1.04485	0.95969	0.95923	1.05704	1.34232

Table 4: Relative performance parameters of window air conditioner with degree of superheat 10° C.

Refrigerant	Discharge Temperature	Volumetric Efficiency	Work input	Refrigeration Effect	COP	Mass flow Rate	Condenser Capacity	Compressor Size
R410A	1.01152	1.02039	1.09048	1.04482	0.95789	0.95719	1.05788	0.65926
R32/R134a (35/65)	0.96532	0.99714	1.12678	1.09242	0.96928	0.9156	1.09842	0.91864
R32/R125/R134a/R290 (20/25/50/5)	0.88577	1.00417	0.9475	0.89989	0.94957	1.11131	0.91161	0.92978
R407C	0.89036	1.00072	0.95113	0.92158	0.96873	1.08502	0.92027	0.95461
R32/R134a/R1270 (25/70/5)	0.92336	0.99821	1.07428	1.03509	0.96351	0.96636	1.04355	0.96911
R32/R134a (30/70)	0.94417	0.99249	1.09327	1.0623	0.97166	0.94128	1.06825	0.97124
R32/R134a/R1270 (20/70/10)	0.90535	1.00083	1.07009	1.02771	0.96043	0.97309	1.03758	0.98377
R32/R134a/R290 (20/70/10)	0.89584	1	1.05138	1.0049	0.95556	0.99511	1.01634	0.99942
R22	1	1	1	1	1	1	1	1
R32/R134a (26/74)	0.92661	0.9882	1.06674	1.03967	0.97456	0.96208	1.0453	1.01871
R32/R134a/R290 (20/75/5)	0.8955	0.99332	1.02904	0.99281	0.96462	1.00734	1.00175	1.03407
R32/R134a/R600 (25/70/5)	0.91161	0.98712	1.07931	1.04104	0.96453	0.96086	1.04961	1.06421
R32/R125/R134a/R290 (10/25/60/5)	0.83766	0.99416	0.8883	0.84968	0.95647	1.17737	0.86054	1.07299
R32/R125/R134a/R600a (15/20/60/5)	0.85534	0.98665	0.94666	0.90565	0.95647	1.10459	0.91632	1.11508
R32/R125/R134a/R1270 (10/15/70/5)	0.84762	0.98951	0.9327	0.89983	0.96473	1.11131	0.90885	1.11803
R32/R125/R134a/R600a (15/15/61/4)	0.8635	0.98522	0.96454	0.92772	0.96173	1.07829	0.93721	1.11988
R125/R134a/R290 (50/45/5)	0.78161	0.99511	0.75789	0.7133	0.94094	1.40245	0.72705	1.1294
R32/R125/R134a/R600 (15/20/60/5)	0.82871	0.9839	0.94443	0.91136	0.96491	1.09725	0.92498	1.13287
R32/R125/R134a/R600 (15/15/67/3)	0.86261	0.98212	0.96342	0.92983	0.96509	1.07584	0.93856	1.14563
R417A	0.7599	0.9932	0.73611	0.72446	0.984	1.38043	0.72966	1.17831
R125/R134a/R600a (60/35/5)	0.77154	0.98927	0.73583	0.68677	0.93308	1.45627	0.70149	1.18282
R125/R134a/600a (50/45/5)	0.77221	0.98212	0.77241	0.72979	0.94467	1.37064	0.74298	1.25933
R134a/R290 (54/46)	0.80801	0.99261	1.27562	1.23649	0.9691	0.80856	1.2491	1.25938
R125/R134a/R600 (50/45/5)	0.7712	0.97997	0.77744	0.7363	0.94693	1.35841	0.74925	1.27873
R134a/R1270 (85/15)	0.82144	0.98033	1.0134	0.98828	0.97503	1.01162	0.99659	1.31355
R134a/R290 (75/25)	0.80835	0.98259	1.0888	1.05244	0.96653	0.94985	1.06404	1.33029