

Available online at www.sciencedirect.com



REVUE INTERNATIONAL JOURNAL OF refrigeration

International Journal of Refrigeration 30 (2007) 3-10

www.elsevier.com/locate/ijrefrig

# Natural refrigerant-based subcritical and transcritical cycles for high temperature heating

J. Sarkar, Souvik Bhattacharyya\*, M. Ram Gopal

Department of Mechanical Engineering, Indian Institute of Technology, Kharagpur 721302, India

Received 11 April 2005; received in revised form 31 January 2006; accepted 13 March 2006 Available online 5 June 2006

#### Abstract

Theoretical analyses of subcritical/transcritical heat pumps using four natural refrigerants, carbon dioxide, ammonia, propane and isobutane have been carried out for high temperature heating applications at different heating outlet temperatures and heat sources using computer models. The compressor discharge pressures have been optimized for transcritical and subcritical (with near critical operation of condenser) cycles. Results show that for subcritical heat pumps, use of subcooling is efficient for heating applications with a gliding temperature. Results also show that although propane yields better coefficient of performance (COP) in low temperature heating applications, ammonia performs the best in high temperature heating applications. Finally, design aspects of major components of all the four heat pumps for high temperature heating have been discussed, particularly with reference to suitability of available lubricants to the newly evolved operating conditions. © 2006 Elsevier Ltd and IIR. All rights reserved.

Keywords: Heat pump; Carbon dioxide; Ammonia; Propane; Isobutane; Research; Thermodynamic cycle; Transcritical cycle; Performance; COP

## Cycles souscritiques et transcritiques utilisant des frigorigènes naturels dans les applications à température élevée

*Mots clés* : Pompe à chaleur ; Dioxyde de carbone ; Ammoniac ; Propane ; Isobutane ; Recherche ; Cycle thermodynamique ; Cycle transcritique ; Performance ; COP

### 1. Introduction

In the last few decades, several studies have been carried out to find suitable refrigerants for heat pumps applicable to high temperature heating. Previously, R115 was used for high temperature process heat applications, but due to its

E-mail address: souvik@mech.iitkgp.ernet.in (S. Bhattacharyya).

negative impact on the environment, researchers have proposed various alternative synthetic refrigerants of zero ODP such as R143, R152, E143 and E245 [1]. However, these refrigerants have higher GWP. Hence, environmentally benign natural refrigerants such as carbon dioxide, ammonia, propane, butane, isobutane and propylene [2] appear to be better alternatives for heat pump applications. Ammonia is a very old refrigerant, which is generally used up to a temperature of about 70 °C. Carbon dioxide has been revived as a potential refrigerant for heat pump applications,

<sup>\*</sup> Corresponding author. Tel.: +91 3222 282904; fax: +91 3222 255303.

<sup>0140-7007/\$35.00</sup> @ 2006 Elsevier Ltd and IIR. All rights reserved. doi:10.1016/j.ijrefrig.2006.03.008

Nomenclature							
AT	temperature approach (K)	Subscri	<i>ipts</i>				
COP	coefficient of performance	1-6	state points of refrigerant				
f	friction factor	с	refrigerant outlet in condenser/gas cooler				
h	specific enthalpy $(kJ kg^{-1})$	ci	fluid inlet to condenser/gas cooler				
$Nu_0$	Nusselt number at bulk property	со	fluid outlet from condenser/gas cooler				
Р	pressure (MPa)	crit	critical property				
Pr	Prandtl number	dis	compressor discharge				
$R_{\rm c}$	compressor pressure ratio	e	evaporator				
Re	Reynolds number	opt	optimum				
t	temperature (°C)	SV	saturated vapour				
$V_{\rm c}$	volumetric capacity (MJ/m <sup>3</sup> )						

which can be used up to 120 °C [3]. Although most of the common process heat applications in pulp, paper, chemical, plastics, agricultural, textile, plaster and food industries require heating up to 140 °C [1], some food drying and petrochemical processes require temperatures above 200 °C. Because no such heat pump system is available for these high temperature heating applications, electrical heater or heat transformer is used in these applications (e.g. in milk powder production, air is heated up to 70-80 °C by a heat pump and then by an electrical heater up to the required temperature), which yields a COP less than or equal to 1.0. In this study subcritical and transcritical heat pumps using four natural refrigerants, ammonia, carbon dioxide, propane and isobutane have been proposed for high temperature heating applications. Barring a few individual deficiencies, such as toxicity and flammability of ammonia, flammability of hydrocarbons, and high pressure and low theoretical COP of CO2, these natural refrigerants offer various advantages when compared to synthetic refrigerants. Even though the theoretical COP of a simple CO<sub>2</sub> cycle is relatively low, the COP of an actual CO<sub>2</sub> system could be considerably higher due to high compressor efficiency and excellent transport properties of CO2. During the last few years there have been many studies, which show that the COP of a real  $CO_2$  cycle is higher than that of cycles using conventional working fluids. This indicates that actual system's COP depends very much on component and system design. However, this aspect cannot be revealed in a relatively simple theoretical study such as the one presented in this paper.

In the present study, the compressor discharge pressure of transcritical cycles have been optimized and then performance analyses of heat pumps based on four natural refrigerants (carbon dioxide, ammonia, propane and isobutane) have been carried out for heating applications at different heating outlet temperatures. Two heat sources: a low temperature source (e.g. ambient air or ground water) and a high temperature source (e.g. power plant condenser) have been considered for the analyses. Finally, design related issues of the major components of all the four refrigerants based heat pumps for high temperature heating have been discussed with a special reference to whether currently available lubricants would be suitable for use in the new systems having difficult operating conditions.

#### 2. Optimum discharge pressures

Performance analyses of a carbon dioxide based transcritical cycle showed that there exists an optimum compressor discharge pressure, where the cycle yields the maximum COP. The optimum pressure depends on evaporation temperature, cooler exit temperature, internal heat exchanger effectiveness and compressor isentropic efficiency. However, the effect of the last two parameters is found to be negligible compared to others [4]. Similar behaviour can be observed for other refrigerant-based transcritical cycles also. It is very interesting to note that subcritical cycles also yield optimum discharge pressure when the condenser is operated near the critical point (Table 1). For the subcritical cycles, if the temperature of the refrigerant at condenser exit is in subcooled region, an optimum condensation pressure is found to exist, which yields maximum COP. Fig. 1 shows the P-h diagram with several constant temperature lines. Due to the curvy nature of the isotherms in the super-critical region, such cycles tend to have an optimum gas cooler pressure [4]. If we lower the gas cooler exit temperature in subcooled region, this nature of the isotherms may continue up to some extent and the existence of optimum condensation pressure is observed; however, eventually the isotherms become vertical and there is no optimum point in the subcooled region. In that case, the saturated liquid point becomes the optimum. Thus, to

Table 1				
Critical	properties of	natural	refrigerants	studied

Refrigerant	Carbon dioxide	Ammonia	Propane	Isobutane
t <sub>crit</sub> (°C)	31.06	132.25	96.70	134.70
P <sub>crit</sub> (MPa)	7.377	11.33	4.248	3.640



Fig. 1. *P*-*h* diagram of isobutane.

summarize, the central concept is that for subcritical cycles, with near critical operation of condenser, an optimum refrigerant outlet condition in the condenser exists in subcooled region near critical point, and with far critical operation, the optimum point shifts to saturated liquid line for a given refrigerant outlet temperature.

Employing the latest available literature on the thermophysical properties of carbon dioxide [5], a comprehensive property code 'CO2PROP' has been developed [4]. Based on the seminal works of Haar and Gallagher [6], and Younglove and Ely. [7], additional property codes have been developed to estimate thermodynamic properties of ammonia, propane and isobutane in both subcritical and super-critical region. Since all other properties are based on temperature and density, efficient iterative procedures have been employed to predict assorted state properties. A systematic comparison with the published property tables [6,7] calculated from the equation of state yields a maximum of 0.1% error.

In the present study, following simplifying assumptions have been made for the theoretical analysis of the heat pumps based on the aforementioned four natural refrigerants:

- 1. Refrigerant at the evaporator outlet is saturated vapour.
- Evaporation and condensation/gas cooling processes are isobaric.
- 3. Heat transfer with the ambient is negligibly small.
- 4. Compression process is adiabatic but non-isentropic with an isentropic efficiency of 70%.
- 5. Effectiveness of the internal heat exchanger is 60%.

The optimum pressure in the subcooled region depends on the refrigerant properties and operating parameters. Isobutane yields considerable improvement in COP over the saturated condenser exit and over a wider range compared to propane and ammonia as shown in Fig. 2. Lower evaporation temperature leads to higher optimum discharge pressure



Fig. 2. COP improvement through discharge pressure optimization.

with higher increment of COP value due to the divergent nature of compression line in superheated region. So, for most of the refrigerants, this behaviour may be observed significantly till about 5 K below the critical temperature.

A detailed thermodynamic analysis has yielded optimum discharge pressures for carbon dioxide, ammonia, propane and isobutane based transcritical cycles. Computer codes for cycle simulations have been developed incorporating, in turn, property code for each refrigerant. The discharge pressure has been optimized numerically. It is observed that variation of the optimum compressor discharge pressure with cooler exit temperature and evaporation temperature of the transcritical ammonia cycle shows similar behaviour as that of carbon dioxide [4] as shown in Fig. 3. The optimum compressor discharge pressures for propane and isobutane based subcritical/transcritical cycles also show similar behaviour with the condenser/gas cooler exit temperature for different evaporation temperature as shown in Figs. 4 and 5, respectively.



Fig. 3. Variation of optimum discharge pressure for a transcritical ammonia cycle.



Fig. 4. Variation of optimum discharge pressure for a transcritical propane cycle.

Lower evaporator temperature yields higher optimum pressure due to divergent nature of the constant entropy lines. Higher refrigerant exit temperature in gas cooler results in higher optimum pressure due to flattening of isotherms with increase in temperature. Based on the regression analysis of the numerical results for optimum pressures, the following general correlation with coefficients given in Table 2 can be established for the optimum discharge pressure (in bar) for all the four natural refrigerant-based cycles:

$$P_{\rm dis,opt} = \frac{t_{\rm c} - A}{B + Ct_{\rm e}} + \frac{D}{t_{\rm c}} \tag{1}$$

where the range of application is as follows.

Evaporation temperature  $t_e$ : -10 to 20 °C and cooler exit temperature  $t_c$ : 30 to 90 °C for carbon dioxide;  $t_e$ : 0 to 60 °C



Fig. 5. Variation of optimum discharge pressure for a transcritical isobutane cycle.

Table 2Coefficients of Eq. (1)

Refrigerant	Α	В	С	D
Carbon dioxide	16.730	0.32453	0.0011366	1044.30
Ammonia	122.03	0.22068	0.0007258	10614.0
Propane	87.439	0.42794	0.0029186	2755.30
Isobutane	120.92	0.32447	0.0037894	2064.30

and  $t_c$ : 125 to 150 °C for ammonia;  $t_c$ : 0 to 60 °C and  $t_c$ : 90 to 130 °C for propane;  $t_c$ : 0 to 60 °C,  $t_c$ : 130 to 150 °C for isobutane. Similar to carbon dioxide based cycle, the gas cooler exit temperature has greater effect than evaporation temperature on optimum pressure for ammonia, propane and isobutane. However, for the ammonia cycle, effect of evaporator temperature is lower than that for others (Figs. 3–5). With a decrease in  $t_c$ , the effect of  $t_e$  becomes negligible and to some extent the corresponding saturation pressure becomes the optimum pressure.

#### 3. Performance comparison

A comparative performance evaluation has been carried out for four natural refrigerant-based heat pump systems for different heating applications. Two evaporator temperatures have been considered: 20 °C for low temperature heat source such as ambient air, ground water, etc., and 60 °C for high temperature heat source. The various heating applications considered in this study, are (i) heating of water or air from 30 to 100 °C, (ii) heating of air from 30 to 150 °C, (iii) heating of air from 30 to 200 °C, (iv) heating of steam/air from 100 to 200 °C. Of course, these systems can also be used for sensible heating of media other than air and water.

It is well known that refrigeration and heat pump systems operating near the critical point have a very low COP due to the large throttling loss. Use of a subcooler with substantial subcooling of the condensate can improve the COP of these systems. However, the improvement in COP with subcooling is much less in case of ammonia compared to propane and isobutane due to much lower specific heat and higher enthalpy of vaporization of ammonia. Fig. 6 represents T-s diagram of the subcritical cycle with and without subcooling and the transcritical cycle. The temperature variation of secondary fluid in counter flow condenser or gas cooler is also shown on the T-s plane. Incorporating the property subroutines mentioned earlier, a computer code has been developed for the numerical analyses. Although the temperature approach (AT) for condenser/gas cooler depends on the heat exchanger design and heat transfer properties of the refrigerant, in the present study a temperature approach (AT) of 5 K has been assumed for all four refrigerants to simplify the analysis. For saturated (without subcooling) subcritical cycles, the pinch point can occur at inlet to condenser or at saturated vapour state of the refrigerant and hence for



Fig. 6. T-s diagram of subcritical and transcritical heat pump cycles.

numerical calculations, the following condition should be met [4]:

$$\min\left[(t_2 - t_{co}), t_{sv} - \left(t_{ci} + \frac{h_{sv} - h_3}{h_2 - h_3}(t_{co} - t_{ci})\right)\right] = AT \qquad (2)$$

for subcritical cycles with subcooling, the following condition should be satisfied [4] to avoid pinch in the heat exchangers:

$$\min\left[(t_3 - t_{\rm ci}), (t_2 - t_{\rm co}), t_{\rm sv} - \left(t_{\rm ci} + \frac{h_{\rm sv} - h_3}{h_2 - h_3}(t_{\rm co} - t_{\rm ci})\right)\right]$$
  
= AT. (3)

For the transcritical cycle, to confirm the condition of temperature approach, the entire temperature range in the gas cooler is divided into 50 divisions; thus at any point within these 50 elements, the temperature difference between refrigerant and secondary fluid must be more than or equal to AT. Thus Eqs. (2) and (3) are used to solve the conditional statement incorporated in the numerical analysis code. Employing an effective iteration procedure  $t_3$  has been found to satisfy AT. Although for the saturated cycle, condenser pressure is the saturated pressure at  $t_3$ , for transcritical and subcritical cycles with subcooling, the discharge pressure is changeable.

Saturated subcritical cycle is used for normal refrigeration or heat pump systems. Normally in these systems the refrigerant in condenser rejects heat to external fluids having negligible temperature glide; hence, it is advantageous to keep the refrigerant temperature constant during heat rejection as far as possible to minimize overall temperature difference between refrigerant and the external fluid. Conversely, for gliding temperature heating (variable temperature of secondary fluid) applications, it is possible to employ the subcooling cycle to increase the performance of heat pump, and as discussed before, there exists some optimum condensing pressure for which the COP is maximum. The reason behind the existence of an optimum condensing pressure may be elucidated through Fig. 7 (P-h diagram of isobutane heat pump). At an evaporator temperature of 20 °C, and inlet and outlet temperatures of secondary fluid of 30 °C and 100 °C, respectively, the cycle 1-2-3-4-5-6-1 is the saturation cycle, which satisfies condition of pinch point (Eq. (2)). So  $P_2$  (1.54 MPa) is the minimum possible condensing pressure for this application, yielding a heating COP of 3.20. If we increase the condensing pressure, the outlet state of the refrigerant in the condenser (point 3) shifts to the subcooled region and to satisfy the pinch condition (Eq. (3)), outlet temperature of refrigerant in the condenser decreases and the heating COP will increase in the resulting subcooling cycle. When the refrigerant outlet temperature reaches point 3', where AT is just 5 °C, the condensing pressure is 2 MPa and heating COP increases from 3.20 to 3.92 (about 23% rise) as shown in Fig. 8. With further increase in pressure,  $\Delta h_{3'} \rightarrow 0$ , and hence COP will decrease as shown in Fig. 8; this can be explained as follows. As COP =  $(h_{2'} - h_{3'} + \Delta h_{2'} + \Delta h_{3'})/(h_{2'} - h_{1'} + \Delta h_{2'}) > 1$ ,  $\Delta h_{3'} \rightarrow 0$ ,  $\Delta h_{2'}$  increases, COP decreases, where,  $\Delta h_{2'}$  and  $\Delta h_{3'}$  are the increment of enthalpies over states 2' and 3', respectively, with certain increment of condensing pressure. Thus for these operating conditions, 2 MPa is the optimum pressure yielding the maximum COP for isobutane based heat pumps. Ammonia and propane based subcritical heat pumps also exhibit similar trends and an optimum condensing pressure exists for the subcritical cycle with subcooling. So, the performance is evaluated both for saturated (without subcooling) and subcooling cycle corresponding to the optimum condensing pressure.

For a transcritical heat pump, performance is evaluated based on the optimum gas cooler pressure and assuming



Fig. 7. P-h diagram of an isobutane heat pump cycle.



Fig. 8. Variation of heating COP with condensing pressure in isobutane heat pumps.

that the available compressors are capable to deliver up to 20 MPa. Table 3 shows the performance of a CO<sub>2</sub> based transcritical heat pump for optimum pressure based on the correlation stated already (Eq. (1)). For heating output at 200 °C, the optimum pressure exceeds 20 MPa; however, for this study an upper limit of 20 MPa is considered. It is clear that for high temperature applications (such as at 200 °C), CO<sub>2</sub> heat pumps are not suitable. Due to the low critical temperature (31.2 °C), the CO<sub>2</sub> heat pump is not suitable when it employs high temperature heat sources. The ammonia based subcritical heat pumps both without (saturated) and with subcooling are more effective choices and their performance data are shown in Table 4. The improvement in system performance by using subcooling is significant, although the improvement is more for higher temperature glide of secondary fluid (the heating COP increases by about 15% as the secondary fluid temperature increases from 30 to 100 °C or 100 to 200 °C, whereas the increase is about 20% as the secondary temperature increases from 30 to 200 °C). Use of subcooling is also very effective in isobutane and propane based heat pumps. For 100 °C heating application, the isobutane based heat pump vields a 22.6% rise in heating COP whereas a propane based heat pump offers more (25%) through the use of subcooling

Table 3 Calculated performance of a transcritical carbon dioxide heat pump

t <sub>e</sub> (°C)	$t_{ci}$ (°C)	t <sub>co</sub> (°C)	$R_{\rm c}$	P <sub>dis</sub> (MPa)	t <sub>dis</sub> (°C)	Heating COP	V <sub>c</sub> (MJ/m <sup>3</sup> )
20	30	100	2.10	11.9	109	3.25	29.88
20	30	150	2.70	16.0	155	2.32	34.21
20	30	200	3.50	20.0	205	1.67	34.72
20	100	200	3.50	20.0	213	1.52	32.59
60	100	200		]	Not app	licable	

Table 4 Calculated performance of a subcritical ammonia heat pump

t <sub>e</sub> (°C)	$t_{ci}$ (°C)	t <sub>co</sub> (°C)	Cycle	R <sub>c</sub>	P <sub>dis</sub> (MPa)	t <sub>dis</sub> (°C)	Heating COP	$\frac{V_{\rm c}}{({\rm MJ/m^3})}$
20	30	100	Subcritical <sup>a</sup>	4.78	4.1	235	3.47	7.87
20	30	100	Subcritical <sup>b</sup>	5.42	4.7	199	3.93	9.79
20	30	150	Subcritical <sup>a</sup>	6.88	5.9	298	2.70	7.87
20	30	150	Subcritical <sup>b</sup>	8.81	7.6	270	3.16	10.67
20	30	200	Subcritical <sup>a</sup>	8.59	7.4	338	2.36	7.86
20	30	200	Subcritical <sup>b</sup>	11.75	10.1	307	2.84	11.23
20	100	200	Subcritical <sup>a</sup>	12.13	10.4	401	1.91	7.60
20	100	200	Subcritical <sup>b</sup>	13.14	11.3	392	2.14	8.91
60	100	200	Subcritical <sup>a</sup>	4.14	10.8	276	2.71	16.71
60	100	200	Subcritical <sup>b</sup>	4.31	11.3	260	3.34	18.78

<sup>a</sup> Without subcooling (saturated).

<sup>b</sup> With subcooling.

(Tables 5 and 6). Hence it is observed that performance improvement through incorporation of subcooling in the process cycle is relatively larger in case of hydrocarbon based heat pumps compared to ammonia based heat pumps.

For low temperature heating applications, a propane based heat pump yields the highest heating COP whereas an ammonia system performs best in high temperature applications (heating COP is 40% higher than that of CO<sub>2</sub>) as shown in Fig. 9. Although in a low temperature heating applications, a CO<sub>2</sub> heat pump exhibits lower heating COP (about 28% lower than that of propane), it has several advantages such as lower compressor pressure ratio, lower discharge temperature, higher volumetric capacity, non-toxicity and non-flammability compared to ammonia, propane and isobutane based systems. Although the heating COP and the discharge temperature are comparable for both the hydrocarbon based heat pumps, propane systems are better with respect to compressor pressure ratio (30% less) and volumetric capacity (more than doubles) whereas an isobutane system is superior with respect to discharge pressures (about 40% lower) as shown in Tables 5 and 6. It is noteworthy that in heating applications up to 200 °C, it is not necessary to employ the transcritical cycle for ammonia. Ammonia systems operate at higher volumetric capacity than that of hydrocarbon systems (about 40% more) whereas it is less

Table 5					
Calculated 1	performance	of a	propane	heat r	oump

t <sub>e</sub> (°C)	$t_{ci}$ (°C)	$t_{co}$ (°C)	Cycle	R <sub>c</sub>	P <sub>dis</sub> (MPa)	t <sub>dis</sub> (°C)	COP	$V_{\rm c}$ (kJ/m <sup>3</sup> )
20	30	100	Subcritical <sup>a</sup>	3.55	3.0	123	3.33	5.06
20	30	100	Subcritical <sup>b</sup>	4.45	3.7	113	4.17	7.23
20	30	150	Transcritical	8.48	7.1	155	3.29	7.89
20	30	200	Transcritical	20.84	17.4	205	2.59	8.83
20	100	200	Transcritical	11.80	9.8	212	1.95	5.69
60	100	200	Transcritical	6.68	14.1	205	2.51	13.55

<sup>a</sup> Without subcooling (saturated).

<sup>b</sup> With subcooling.

Table 6 Calculated performance of an isobutane heat pump

t <sub>e</sub> (°C)	$t_{ci}$ (°C)	$t_{co}$ (°C)	Cycle	R <sub>c</sub>	P <sub>dis</sub> (MPa)	$t_{\rm dis}$ (°C)	Heating COP	$V_{\rm c}$ (kJ/m <sup>3</sup> )
20	30	100	Subcritical <sup>a</sup>	5.09	1.5	121	3.20	2.27
20	30	100	Subcritical <sup>b</sup>	6.64	2.0	110	3.92	3.19
20	30	150	Subcritical <sup>a</sup>	8.09	2.3	155	2.37	2.14
20	30	150	Transcritical	14.25	4.3	155	3.21	3.44
20	30	200	Transcritical	43.20	13.0	205	2.65	3.72
20	100	200	Transcritical	20.36	6.1	206	2.02	2.57
60	100	200	Transcritical	9.81	8.5	205	2.71	6.73

<sup>a</sup> Without subcooling (saturated).

<sup>b</sup> With subcooling.

than that of a  $CO_2$  system (about 40% less). The results show that an ammonia heat pump is most effective for high temperature applications; with the high discharge temperature appearing to be the only major drawback.

#### 4. Design issues

Design of compressors for high pressure and temperature, and stability of compressor lubricants at high temperature are the major issues for heat pumps employed in high temperature heating. High discharge pressure is a serious handicap for CO<sub>2</sub> based heat pumps. Currently available CO<sub>2</sub> compressors [8] can be used up to a discharge pressure of 15 MPa. Hence in systems operating at temperatures higher than 140 °C, it is desirable to set a lower discharge pressure than the optimum value, however, with a risk of vielding a low COP. The maximum pressure limits of currently available hydrocarbon and ammonia compressors are much lower (a maximum of 4 MPa). A high pressure CO<sub>2</sub> compressor is not suitable for other refrigerants due to its low pressure ratio, but it appears possible to use CO<sub>2</sub> compressor design concepts to develop high pressure compressors for ammonia, propane and isobutane. Discharge temperature in case of propane, isobutane and CO<sub>2</sub> systems



Fig. 9. Heating COP of natural refrigerant-based heat pumps.

does not pose any serious problem. Several lubricants are available for use up to a maximum temperature range of about 250 °C [9-11]. The synthetic lubricants for CO2 compressors, PAG (Polyalkylene glycol), POE (Polyolester), PVE (Polyvinyl ether) and PC (Polycarbonate) have been tested for a maximum temperature of 220 °C [12]. Since the discharge temperatures of CO2 and hydrocarbon systems are within 215 °C, the available lubricants can still be used. The problem of high discharge temperature is very serious for an ammonia compressor, both for cooling and lubrication. Adequate cooling is required to increase compressor life. Adhvaryu and Erhan [13] proposed epoxidized soybean oil as a potential high temperature lubricant. Products such as Christo-Lube lubricants (operating range up to 287 °C) [14] and Krytox fluorinated lubricants (operating range up to 426 °C) [15], although have not been used for refrigerant compressors, may be employed in such applications. Solid lubricants such as calcium sulfate [16] and zinc thiomolybdenate [17] are reliable for temperatures up to 500 °C, and cerium dithiomolybdate [18] for temperatures up to 600 °C. Finally, it is noted that the ammonia based high temperature heat pump requires special types of cooling and lubrication systems that are cost effective.

A favourable heat transfer characteristic at high temperature and pressure is another important feature for high temperature heat pumps, which will decide the dimensions and weight of the heat exchangers for a given capacity. For a mass velocity of 800 kg/m<sup>2</sup> K and an inner tube diameter of 5 mm, the heat transfer coefficient of the refrigerants is shown in Figs. 10 and 11, based on the Gnielinski correlation given by:

$$Nu_{0} = \frac{(f/8)(Re - 1000)Pr}{1.07 + 12.7(f/8)^{1/2}(Pr^{2/3} - 1)},$$

$$f = [0.79\ln(Re) - 1.64]^{-2}.$$
(4)



Fig. 10. Single-phase heat transfer coefficients of the four refrigerants at  $t_{ci} = 30$  °C and  $t_{co} = 100$  °C.



Fig. 11. Single-phase heat transfer coefficients of the four refrigerants at  $t_{ci} = 100$  °C and  $t_{co} = 200$  °C.

Although, the heat transfer coefficients of CO<sub>2</sub>, propane and isobutane are comparable in an application having  $t_{ci} = 30$  °C,  $t_{co} = 100$  °C (Fig. 10), the heat transfer properties of the hydrocarbons are superior to carbon dioxide for an application with  $t_{ci} = 100$  °C and  $t_{co} = 200$  °C (Fig. 11). Ammonia exhibits higher heat transfer coefficients in both cases. The discontinuity in the plots for ammonia (Figs. 10 and 11) indicates the transition of saturated liquid to vapour (saturation zone). The liquid phase heat transfer coefficient of ammonia is higher than that of vapour phase, whereas, both are comparable in case of hydrocarbons due to the operation near critical pressure. It may be noted that the heat transfer coefficient of ammonia shows (Fig. 11) unusually high value within the range of 130–140 °C because of the proximity to critical point.

#### 5. Conclusion

Comparative performance characteristics of four natural refrigerants, carbon dioxide, ammonia, propane and isobutane have been performed for high temperature heat pump applications. The compressor discharge pressures have been optimized for subcritical cycles with near critical operation and transcritical cycles for all four refrigerants. In the subcritical heat pumps, for gliding temperature heating applications, use of subcooling yields significant increase in COP compared to the saturated condenser outlet condition, although the discharge pressure will also be higher in this case. Results indicate that propane is more effective in low temperature applications, although CO<sub>2</sub> can be employed as well due to its lower pressure ratio and higher volumetric capacity. For high temperature applications, ammonia is more effective in spite of drawbacks such as toxicity, flammability and very high discharge temperature. Hydrocarbon based systems offer slightly lower COP but have no other demerits barring flammability, whereas CO<sub>2</sub> is unsuitable due to its poor COP and high discharge pressure, although its volumetric capacity is higher. With respect to heat transfer characteristics, ammonia is the best refrigerant;  $CO_2$  exhibits comparable heat transfer properties for low temperature applications, then it deteriorates sharply in high temperature applications. However, it should be noted that in the present paper, relatively simple theoretical analysis is presented. For real heat pumps, the systems will be designed to utilize the properties of refrigerant and this may change the COP and operating conditions considerably.

#### References

- J. Sarkar, S. Bhattacharyya, M. Ram Gopal, Transcritical carbon dioxide based heat pumps: process heat applications, in: Proceedings of 10th International Refrigeration and Air Conditioning Conference at Purdue University, USA, July 12–15, 2004.
- [2] S.F. Pearson, Natural refrigerants for heat pumps, IEA Heat Pump Center Newsl. 20 (1) (2004) 13–16.
- [3] S.D. White, M.G. Yarrall, D.J. Cleland, R.A. Hedley, Modelling the performance of a transcritical CO<sub>2</sub> heat pump for high temperature heating, Int. J. Refrigeration 25 (4) (2002) 479–487.
- [4] J. Sarkar, S. Bhattacharyya, M. Ram Gopal, Optimization of a transcritical CO<sub>2</sub> heat pump cycle for simultaneous cooling and heating applications, Int. J. Refrigeration 27 (8) (2004) 830–838.
- [5] R. Span, W. Wagner, A new equations of state for Carbon dioxide covering the fluid region from triple point temperature to 1100 K at pressure up to 800 MPa, J. Phys. Chem. Ref. Data 25 (1996) 1509–1596.
- [6] L. Haar, J.S. Gallagher, Thermodynamic properties of ammonia, J. Phys. Chem. Ref. Data 7 (1978) 635–792.
- B.A. Younglove, J.F. Ely, Thermophysical properties of fluids.
   II. Methane, ethane, propane, isobutane and normal butane,
   J. Phys. Chem. Ref. Data 16 (1987) 577–798.
- [8] Casini, Dorin. CO<sub>2</sub> compressors and equipment, use and availability, EURO cooling and heating, Centro Studi Galileo; <www.eurocooling.com>.
- [9] <www.prod.exxonmobil.com/lubes/marine/products/mn\_ synthetic\_lubricants.html>.
- [10] <www.cromptoncorp.com/lubricants-grease.html>.
- [11] <www.ecompressedair.com/lubricant.shtml>.
- [12] H. Ikeda, J. Yagi, Y. Kawaguchi, Evaluation of various compressor lubricants for a carbon dioxide heat pump system, in: Sixth IIR G Lorentzen Natural Working Fluids Conference, Glasgow, UK, Aug. 29–Sep. 1, 2004.
- [13] A. Adhvaryu, S.Z. Erhan, Epoxidized soybean oil as a potential source of high temperature lubricants, Ind. Crop. Prod. 15 (2002) 247–254.
- [14] <www.lubricationtechnology.com/products.htm>.
- [15] <www.miller-stephenson.com/>.
- [16] P.J. John, S.V. Prasad, A.A. Voevodin, J.S. Zabinski, Calcium sulfate as a high temperature solid lubricant, Wear 219 (1998) 155–161.
- [17] D. Feng, J. Zhou, W. Liu, Q. Xue, The thermal stability and lubricity of zinc thiomolybdenate at temperatures up to 500 °C, Wear 246 (2000) 68–73.
- [18] D. Feng, W. Liu, Q. Xue, The lubrication mechanism of cerium dithiomolybdate from room temperature to 600 °C, Mater. Sci. Eng. A326 (2002) 195–201.