

A Cascade Refrigeration System Using Mixture of Carbon Dioxide and Hydrocarbons for Low Temperature Applications

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Abstract: Various binary mixtures of carbon dioxide and hydrocarbons, especially propane or ethane as alternative natural refrigerants to Chlorofluorocarbons (CFCs) or Hydrofluorocarbons (HFCs) are presented in this study. Their environmental performance is friendly with an Ozone Depletion Potential (ODP) of zero and Global Warming Potential (GWP) <20. Experimental studies for some binary mixtures of carbon dioxide and propane or ethane were performed at low temperature circuit in a cascade refrigeration system. The mixture of carbon dioxide and propane at the optimal composition 70:30 in the mass fraction was reached at an evaporating temperature of -68°C. For temperatures <-70°C then a mixture of carbon dioxide and ethane was used. The optimal composition of carbon dioxide and ethane equaling 66:34 in the mass fraction was reached at an evaporating temperature of -75°C.

Key words: Refrigerant, binary mixture, carbon dioxide, propane, ethane, cascade

INTRODUCTION

For >50 years, CFCs were considered to be the perfect refrigerants for their good properties; being stable, non-flammable, inexpensive to produce and exhibiting low toxicity. Since, the Montreal protocol, the production and consumption of CFCs and of other ozone-depleting chemicals have been almost phased out in most industrialized countries.

There are however, only a small number of alternative refrigerants that can be considered for the low-temperature application range between -40°C to -80°C. Refrigerants R13 and R503 were possibilities for this range but their future use has been capped because of their contribution to the ozone depletion. Possible replacements such as R23, R116 and their derivatives, R508a and R508b have limited value because of their contribution to the greenhouse effect (Schon, 1998). It can be seen that the use of HFCs, once viewed as the long-term replacement for CFCs are now being questioned. Several countries do not consider HFCs as the final solution because concerns about global warming have intensified and some countries have already issued regulations relating to the use of refrigerants. Denmark has banned the use of R23 since 2006 (DEPA, 2002) and there are reports that Austria and Switzerland may follow suit (FOEFL, 2002). The appearance of these bans has reinforced the need to seek new and alternative refrigerants. Natural refrigerants such as ammonia,

hydrocarbon and Carbon dioxide are widely considered to be the best retrofit refrigerants to meet the future demand of long-term, environmental-friendly refrigerant (Lorentzen, 1995). These substances are non-ozone depleting and do not contribute to the greenhouse effect. It is therefore apparent that the research for alternative refrigerants should be directed towards natural refrigerants.

Despite their high flammability, hydrocarbons have excellent thermophysical properties compared with halocarbons. Alsaad and Hammad (1998), Hammad and Alsaad (1999) and Somchai and Nares (2005) have successfully demonstrated the use of hydrocarbon mixtures of propane-butane-isobutene in domestic refrigerators. Halimic *et al.* (2003) have shown that HC290 (propane) gives best performance when compared to R410a and R134a. Carbon dioxide (CO₂/R744) has no harmful effects on the environment and is non-flammable and non-toxic.

It is compatible with normal lubricants and common machine construction materials. It is easily available and independent of supply monopoly. It has a lower compression ratio compared with conventional refrigerants. Lee *et al.* (2006) has successfully experimented with the NH₃/CO₂ cascade refrigeration system. However, it has some disadvantages such as high pressure and high triple-point temperature (216.58 K) which prevents it from operating in vapor compression cycles intended for use at lower temperatures. An

obvious solution to overcoming this drawback could be a blend containing carbon dioxide. Nicola *et al.* (2005) proposed a binary mixture of carbon dioxide and HFCs as working fluids for the low-temperature circuit in the cascade refrigeration cycle. Using the Carnahan Starling De Santis (CSD) Equation of State (EoS), they have successfully shown that the mixture of carbon dioxide (R744) with HFCs is an attractive option for the low-temperature circuit of cascade systems operating at temperatures approaching 200 K (Nicola *et al.*, 2005). Kim *et al.* (2008) and Niu and Zhang (2007) proposed a new binary mixture of R744 and R290 as an alternative natural refrigerant to CFCs.

Niu and Zhang (2007) conducted experimental studies for this mixture and R13 were performed on a cascade refrigeration system with modification to the capillary in a low-temperature circuit. COP and refrigeration capacity of this binary mixture were higher than those of R13; condensing pressure, evaporating pressure, compression ratio and discharge temperature were also higher than that of R13 when the high-temperature circuit of cascade refrigeration system was kept invariable.

However, the mixture of carbon dioxide and propane (R290:C₃H₈ at composition 71:29 in the mole fraction, it is a zeotrope binary mixture, is considered as a promising alternative refrigerant to R13 when the evaporator temperature is $>-72^{\circ}\text{C}$ (Niu and Zhang, 2007). Additionally, the zeotrope binary mixture is generating temperature glide (temperature different between the beginning and end of phase change process) up to 20 K which will make a problem in the heat exchangers. This high temperature glide will affect heat transfer performance in the condenser as well as in the evaporator.

In addition, research was conducted for only one specific composition, so the effect of changing the composition of energy input (performance) in the cascade refrigeration system is still unknown. On the other hand, a mixture of carbon dioxide with ethane (R170:C₂H₆) created a near-azeotrope mixture which blended perfectly in the two-phase region (Cox *et al.*, 2006). Therefore, this research proposes the binary mixture of R744 (carbon dioxide) with R170 (ethane) as the new promising solution for alternative natural refrigerants. This mixture creates low-temperature glides compared with that of the carbon dioxide and propane mixture.

Due to its significant application for low-temperature cascade refrigeration systems, industrial processes and material testing, pharmaceutical processes and storage and chemical/petrochemical processes and transporting, a series of tests need to be carried out to prove its potential as a promising refrigerant substitute for

low-temperature applications. Hence, the main aim of this research was to compare the performance of a mixture of carbon dioxide and propane with a mixture of carbon dioxide and ethane. The parameters compared included composition of the mixture, evaporating temperature, suction pressure and power required by the compressor.

MATERIALS AND METHODS

Carbon dioxide and ethane composition selection: For the low-temperature circuit, a high-pressure refrigerant with a high vapor density (even at low temperatures) was chosen (ASHRAE, 2006). For many years, R503, an azeotrope mixture of R13 and R23 was a popular choice but it is no longer available because of the negative environmental effects of CFCs and HFCs. Alternative refrigerants such as carbon dioxide or hydrocarbons, must be found to replace them. A comparison of the refrigerants is shown in Fig. 1.

To be able to replace R13 or R23, the thermodynamic properties, particularly pressure and the evaporating temperature must be similar. Figure 1 shows that the natural refrigerant carbon dioxide (FOEFL, 2002) has some disadvantages such as high pressure and high triple-point temperature (56.6°C) which prevents it from operating in vapor compression cycles intended for use at lower temperatures. When CO₂ was forced under pressure and the temperature tripled carbon dioxide dry ice was formed which of course was highly undesirable (Campbell *et al.*, 2007).

It was also noted that the use of the refrigerant propane $<-42^{\circ}\text{C}$ temperature would cause evaporation pressure below atmospheric pressure. It should not happen because important to prevent pressure in the refrigerating system is above atmospheric pressure to help keep the air is not drawn into the system. For ultralow temperature applications compared to R23, ethane has a better refrigeration effect (Rahadiyan, 2007) but it is highly flammable, so hydrocarbons mixed with

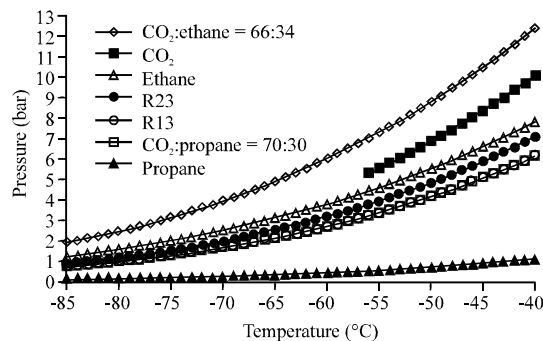


Fig. 1: P-T diagram comparing selected refrigerants

Table 1: Composition of charged refrigerant in mass fraction

Composition	CO ₂ (%)	C ₂ H ₆ (%)	C ₂ H ₄ (%)
I	100	-	-
II	70	30	-
III	66	34	-
IV	60	40	-
V	-	100	-
VI	70	-	30
VII	66	-	34
VIII	60	-	40
IX	-	-	100

carbon dioxide are expected to reduce its flammability and improve the thermophysical properties of carbon dioxide. Studies of binary refrigerant mixtures of carbon dioxide and hydrocarbons as alternatives to R13 for a low-temperature cascade refrigeration system have already been undertaken.

One of them was conducted by Niu and Zhang (2007) who proposed a binary mixture of carbon dioxide and propane (79:21 in mole fractions or 70:30 in mass fraction) as an alternative natural refrigerant for R13. On the other side, a blend of carbon dioxide and ethane producing an azeotrope mixture at -80°C in the composition 66:34 in mass fraction (Alhamid *et al.*, 2010) was examined. Figure 1 shows some of the carbon dioxide mixtures which were compared to R13 and R23; evaporation pressure differences were no >2 bars and still within acceptable limits for evaporating pressure in a compressor.

Experiment: Test equipment consisted of two refrigeration circuits, a high- and low-temperature circuit. The high-temperature circuit was charged with propane (C₃H₈). Meanwhile, the low-temperature circuit was charged with either a mixture of Carbon dioxide (CO₂) and propane (C₃H₈) or a mixture of Carbon dioxide (CO₂) and ethane (C₂H₆). Total mass of refrigerant charged in the low-temperature circuit was 100 g measured using a TIF 9010A digital refrigerant scale with accuracy ±0.5% of reading. Mass composition variations of mixtures are shown in Table 1.

The compressor for HTC is a Tecumseh hermetic type which was actually designed for R22 and can also be used for R290 with the capacity of 1 hp. The LTC compressor is also a Tecumseh hermetic compressor which has 1 hp capacity and was actually designed for R404a rather than for R13 or R23 low-temperature systems. The type of expansion valve is a manual expansion valve from Sporlan/AS-HS-B20.133 2X3 ODF.

The measured of temperatures and pressure at some points of system was shown in Fig. 2. The temperatures were measured with k type thermocouples with accuracy ±0.14% of reading. Pressure were measured with some Druck PTX 1400 pressure transmitter with accuracy

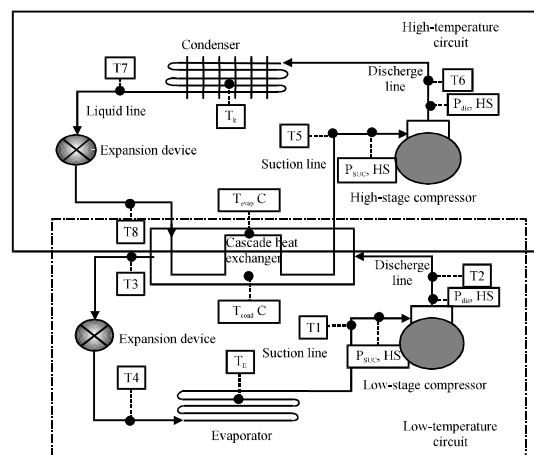


Fig. 2: Schematic diagram of cascade refrigeration system

combine non-linearity, hysteresis and repeatability ±0.15% typically, ±0.25% maximum Base Straight Line (BSL) definition. The Yokogawa power meter type W1010 with basic accuracy 0.2% of full scale detection of bands was used to measure current, voltage and overall power needed for the system. All input data was recorded through National Instruments Data Acquisition 9211 and 9203 at 2 sec intervals until reaching steady state.

RESULTS AND DISCUSSION

Characteristics of carbon dioxide and propane in the low-temperature circuit:

The experimental results for evaporating temperatures in varying mixtures of carbon dioxide and propane is shown in Fig. 3, the evaporating temperature decreased with decreasing carbon dioxide in the mixture where the lowest -72.5°C evaporating temperature was achieved at the 60:40 composition. However when the composition of propane was increased to 100%, the evaporating temperature reached only -47°C because the boiling point of propane is approximately -42.5°C. Standard refrigerants cannot operate at very low temperatures because their saturation pressure is too low under such conditions. If the saturation pressure is less than about 21 in Hg vac/4 psia (28 kPa), very little refrigerant vapor is drawn into the compressor. Vapor density is also extremely low at these pressures, so the mass of refrigerant through the system is very low.

The refrigerant used for the low temperature circuit of cascade systems generally has a saturation pressure at the low-temperature condition above atmospheric pressure to help keep air from being drawn into the system. The higher pressure cascade refrigerant because of its density will require a much smaller compressor to

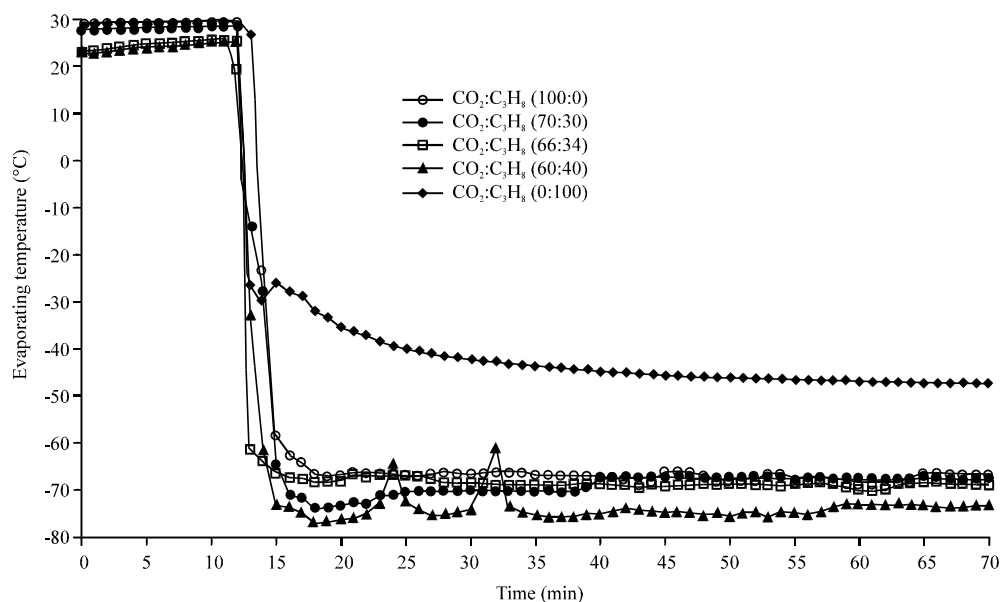


Fig. 3: Evaporating temperatures for CO₂:propane mixtures

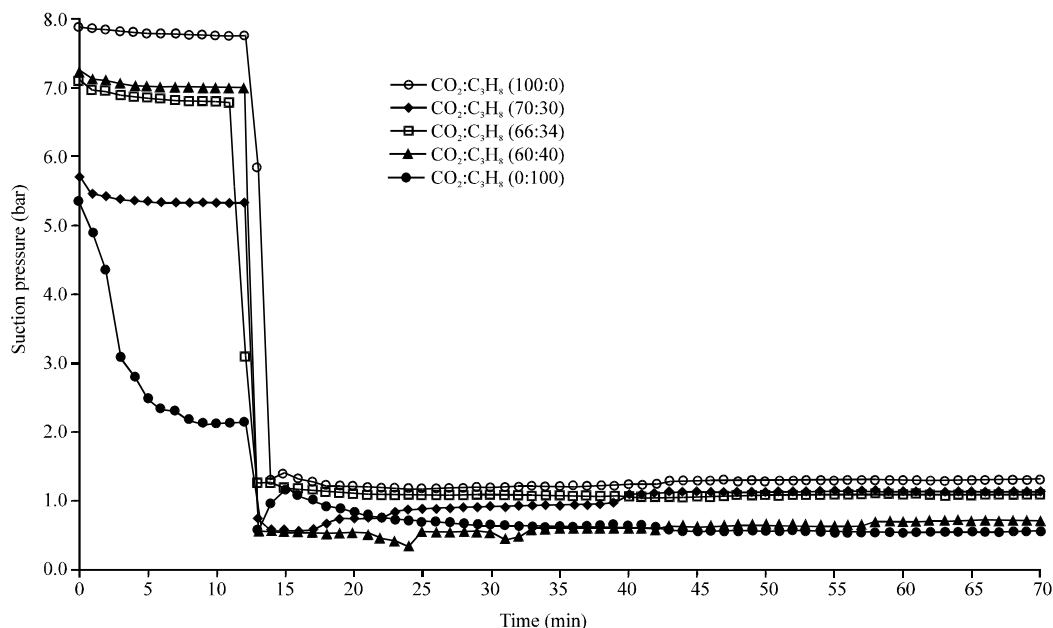


Fig. 4: Suction pressure of varying composition mixings of carbon dioxide and propane

provide the needed system capacity than if a standard refrigerant were used. The suction pressure for several mixtures of carbon dioxide and propane is shown in Fig. 4 and it can be seen that the composition of 60:40 and 100% propane has suction pressure under the atmospheric pressure (1 bar 101 kPa⁻¹). Therefore, although the composition of the evaporating temperature of 60:40 is lowest, the composition of 60:40 and 100% propane is not suitable for use in the low-temperature

circuit of the cascade refrigeration system. Figure 5 shows the compressor power in varying compositions. In the steady state for all compositions it is known that the greatest power input is when using carbon dioxide, as this has the highest suction pressure. Conversely, because propane has the lowest suction pressure, the compressor's power is the lowest. The mixture of carbon dioxide and propane with the smallest compressor power occurs precisely at the composition

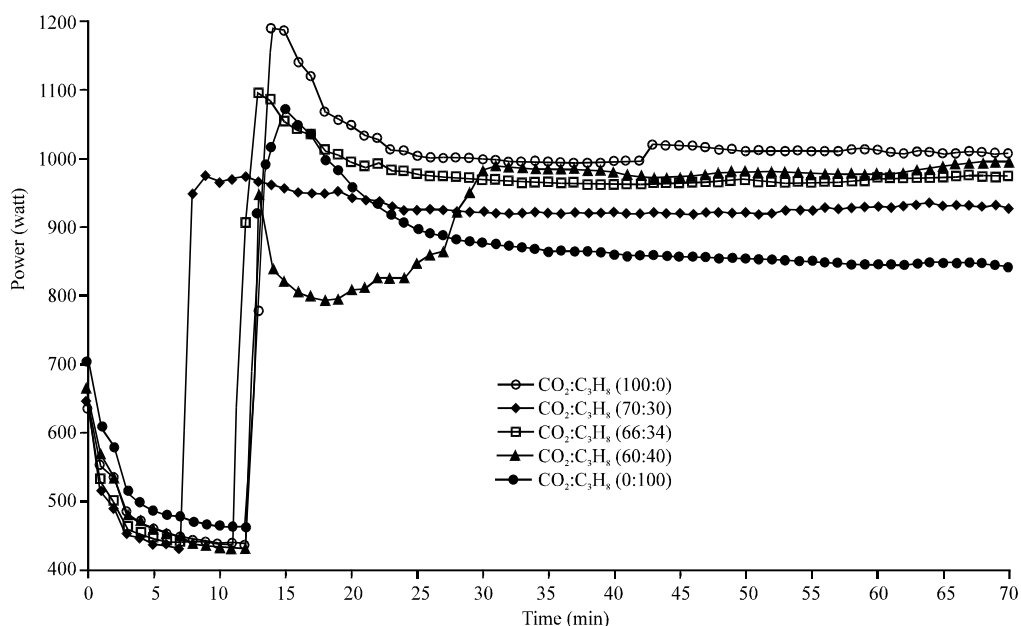


Fig. 5: Power compressors for CO₂: propane mixtures

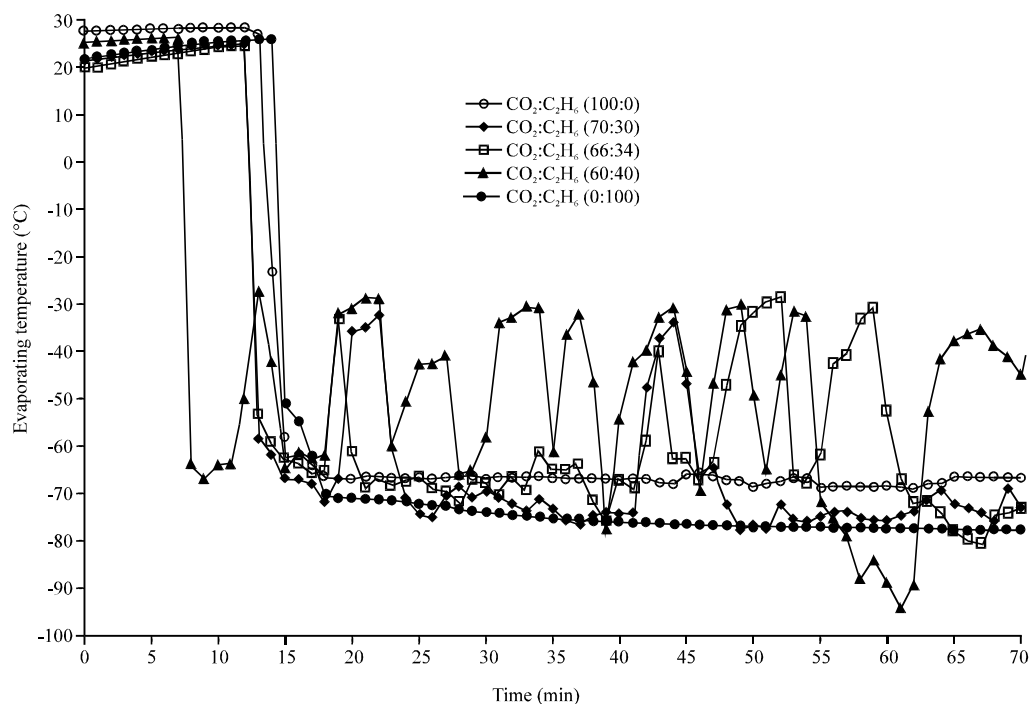


Fig. 6: Evaporating temperatures of varying compositions of carbon dioxide and ethane mixtures

of 70:30. Results of experiments identified a 70:30 mixture of carbon dioxide and propane as most optimal for the low-temperature circuit of the cascade refrigeration system. This is because the composition of the 70:30 produces an evaporating temperature of -68°C which is still above atmospheric pressure and requires little power compared to most other mixed compositions. This is similar to the

results of experiments conducted by Niu and Zhang (2007) who proposed a binary mixture of carbon dioxide with propane (79:21 in mole fractions or 70:30 in mass fraction) as a natural alternative refrigerant to replace R13.

Characteristics of carbon dioxide and ethane in the low-temperature circuit: Figure 6 shows the comparison

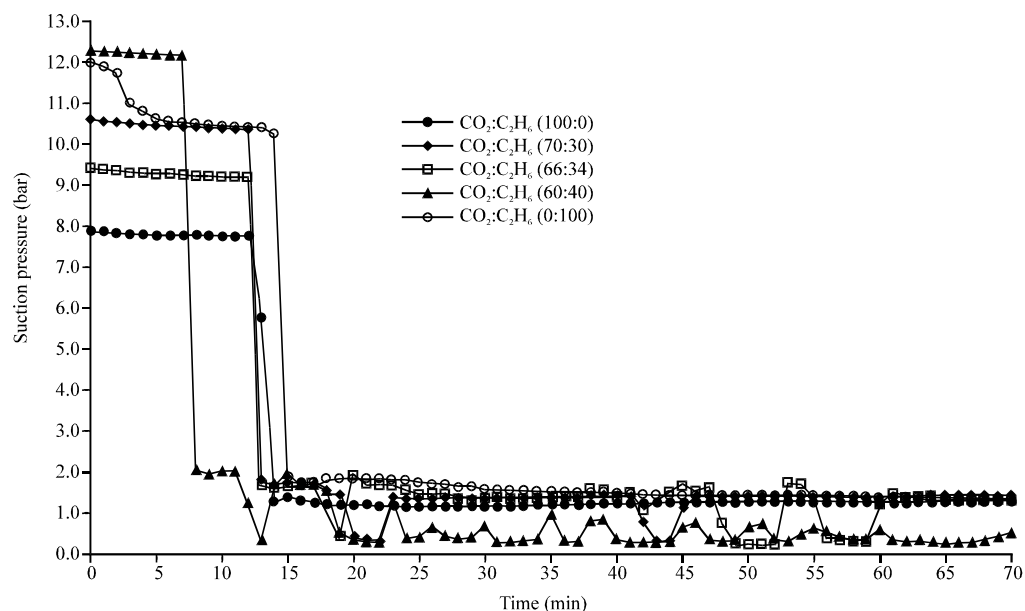


Fig. 7: Suction pressures of varying compositions of carbon dioxide and ethane mixtures

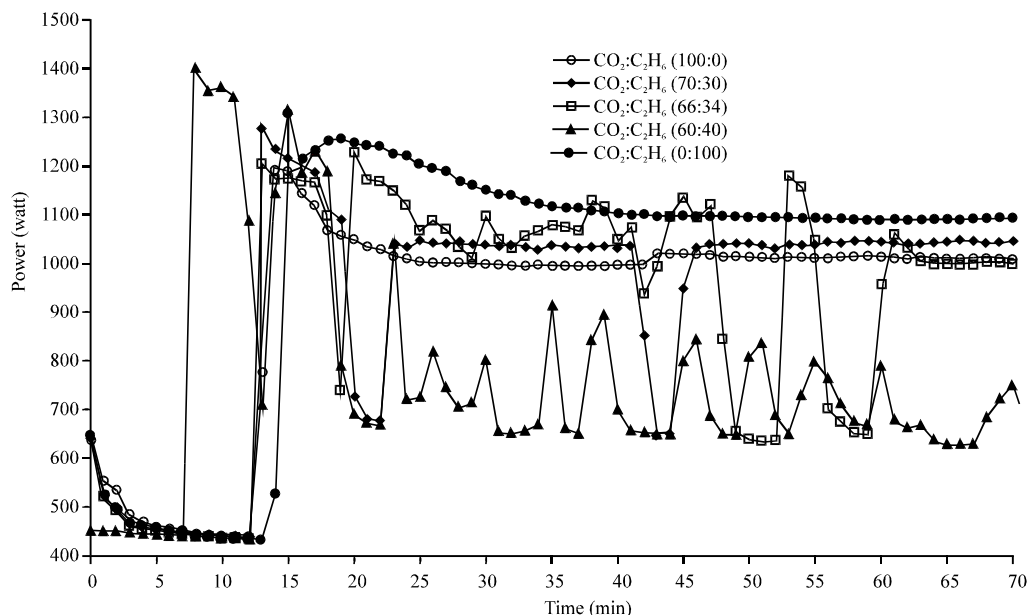


Fig. 8: Power compressors of varying compositions of carbon dioxide and propane mixture

of evaporating temperatures at varying compositions. The composition 100% ethane (C_2H_6) obtained a stable temperature because the boiling point of the refrigerant ethane was around $-80^{\circ}C$. The lower composition of carbon dioxide (the higher composition of ethane) produced a lower evaporating temperature as demonstrated by the composition 60:40. However, despite not reaching the lower evaporating temperature until $-94.86^{\circ}C$, this composition was not stable, probably

due to the formation of carbon dioxide dry ice at the expansion valve. When the level of carbon dioxide was increased so that the composition was 66:34, the evaporating temperature was approximately $-75^{\circ}C$ and began to stabilize after 65 min. This is because at 65 min, the mixture of carbon dioxide and ethane began to form an azeotrope. If the carbon dioxide level increased to form a 70:30 composition, it began to stabilize more quickly (at around 55 min) but the evaporating temperature was

higher at approximately -73°C . Based on the explanation, it is indicated that the 66:34 composition of the carbon dioxide and ethane mixture can be used to reach the evaporating temperature of -75°C but it takes time to form an azeotrope mixture.

The suction pressure for several mixtures of carbon dioxide and ethane is shown in Fig. 7. In steady state, suction pressure of all compositions is above atmospheric pressure (1 bar 101 kPa^{-1}) with the exception of the 60:40 composition. Therefore, although the composition of the evaporating temperature of 60:40 is lowest, the composition is not suitable for use in the low-temperature circuit of the cascade refrigeration system.

The composition of 100% carbon dioxide absorbs the greatest power, around 1000 watts (Fig. 8) caused by the requirements of refrigerant R744 for higher compression. Stability of the power required by the compressor is influenced by evaporating temperature as shown by the composition 70:30 which began to stabilize at 55 min, while the composition 66:34 began to stabilize after 65 min. The composition 60:40 was still not stable. This trend was similar to the trend for evaporation temperature (Fig. 6).

CONCLUSION

Several conclusions can be drawn from this study, including:

- The mixture of carbon dioxide and propane at the composition 70:30 has optimal performance when compared with the other mixtures of carbon dioxide and propane
- When the mixture of carbon dioxide and propane is at optimal composition of 70:30, it reaches evaporating temperature at -68°C ; suction pressure is above atmospheric pressure and compressor power is lowest compared with the other mixtures
- For temperatures $<-70^{\circ}\text{C}$, a mixture of carbon dioxide and ethane was used. Optimal composition of carbon dioxide and ethane was 66:34 in mass fraction showing that the evaporating temperature of -75°C began to stabilize after 65 min
- The operational parameter of the cascade refrigeration system including evaporating temperature, suction pressure and power is influenced by the composition of the refrigerant

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