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A COMBINED CHEMICAL STORAGE AND VAPOUR COMPRESSION HEAT PUMP USING $CH_3OH/CaCl_2$ and R12 REGRIGERANT

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SUMMARY

The work is concerned with the development of a chemical/compression heat pump designed to operate on the cheap rate "Economy 7" electricity tariff. The $CH_3OH/CaCl_2$ pair was used in the energy storage cycle and dichlorodifluoromethane (R12) was used as the refrigerant in the vapour compression cycle. In order to improve heat and mass transfer, as well as simplify construction of the generator/absorber, a mixture of metal wool and $CaCl_2$ was used. Heat pumping and regeneration phases were demonstrated successfully and the average coefficient of performance of the system was found to be about 2.1.

1. INTRODUCTION

There is growing interest in utilising energy storage systems for energy conservation. The potential for improved use of existing power stations through load shifting has encouraged electric utility companies in Europe and the USA to carry out research into energy storage[1]. Widespread use of energy storage systems would allow "levelling" of electric power curves, which currently peak in the mid afternoon and fall dramatically at night, so improving the efficiency of electricity generation.

The use of energy storage systems may also assist deceleration of the "Green-House Effect" by enabling electric power plant to run at a constant moderate load and so decrease gaseous emissions.

One of the most important measures of performance of an energy storage system is its energy storage density. The use of a chemical energy store based on solid-gas reactions is without doubt the best method for achieving a high energy storage density and if this were combined with a vapour compression heat pump designed to operate overnight using the cheap rate "Economy 7" electricity tariff, the combined system would have a sufficiently low running cost to make it economically attractive. Although equipment with an operating cycle similar to that of a chemical/vapour compression heat pump is used in distillation processes in the chemical industry, we are unaware of the development of a storage heat pump which uses this cycle.

This paper describes the development of a chemical storage/vapour compression heat pump which uses $CH_3OH/CaCl_2$ in the storage circuit and dichlorodifluoromethane (R12) in the vapour compression cycle. The heat pump is designed to operate on the cheap rate "Economy 7" electricity tariff and uses ambient air as a heat source.

2. BACKGROUND

This section provides a brief review of previous important work on chemical and vapour compression heat pumps.

2.1 Chemical Heat Pumps

A chemical heat pump operates using a cycle based on that of an intermittent absorption machine and a description of the early developments in chemical heat pump technology is given by Raldow(2). Chemical heat pumps use latent heat of absorption as their primary heating mechanism and this is provided by a dissociation reaction of the type:

$$AB(s,1) \Leftrightarrow A\ (s,1) + B\ (v) \quad (1)$$

where B is stripped as vapour.

A large range of storage temperatures is provided by the different reactions available.

Early work on chemical heat pumps was carried out using soluble refrigerant/absorbent pairs such as NH_3/H_2O and $H_2O/LiBr$. However, the volatility and high freezing point of water gave rise to practical difficulties and a search was made for new refrigerant/absorbent pairs. The salts NaSCN and $LiNO_3$, were considered as possible alternatives for use with NH_3. However, the high temperature lifts provided by the $NH_3/NaSCN$ and $NH_3/LiNO_3$ systems restricted their use to a small number of industrial applications. Other workers used chemical systems, such as $NH_3/CaC1_2$, $NH_3/SrC1_2$, $CH_3OH/CaC1_2$, H_2O/Na_2S, $H_2O/BaC1_2$ and $H_2O/MgC1_2$ but found that they gave rise to poor heat and mass transfer.

Taube[3], Wentworth[4] and Riffat[5] have carried out investigations with the aim of improving heat and mass transfer in solid absorbent beds. $NH_3/CaC1_2$ and $NH_3/SrC1_2$ were found to form mobile slurries in inert liquids such as n-heptanol and kerosene but energy storage densities were poor owing to the small solid content of these slurries. Other workers such as Abhat and Huy(6) and Bjurstrom(7) have adopted heat exchanger techniques in order to improve the heat and mass transfer of the solid-gas reaction.

A study of the literature suggests that the $CH_3OH/CaCl_2$ combination is the most suitable system for our heat pump. We chose to use CH_3OH on the grounds of cost, high latent heat of vaporisation, low operating pressure and safety. In addition the low freezing point (-98°C) of CH_3OH protects evaporator against freezing. The $CaCl_2$ absorbent was chosen on the basis of cost and performance and the combined $CH_3OH/CaCl_2$ system provides a temperature lift suitable for domestic application.

In order to improve generally poor heat and mass transfer in solid absorbent beds, as well as simplifying the construction of the system, a mixture of metal wool and $CaCl_2$ was used in the generator/absorber.

2.2 Vapour Compression Heat Pumps

A review of the early developments and applications of vapour compression heat pumps has been compiled by Von Cube(8). The performance of a heat pump is largely dependent on the type of heat source used. Various types of heat sources include air, water, soil and solar energy have been examined(9). More recently, the trend towards increased airtightness of house envelopes has encouraged researchers to investigate the use of exhaust air from mechanical ventilation systems as a heat source(10, 11).

A review of the different types of heat sources available identified air as the most suitable heat source for our type of heat pump. The choice was based on the general availability of the heat source and in particular, the possibility of using exhaust air from mechanical ventilation in domestic situations.

3. DESCRIPTION OF THE HEAT PUMP SYSTEM

The basic refrigerant circuit of the chemical storage heat pump is shown in Figure 1. The chemical energy store contains $CH_3OH/CaCl_2$ whilst the vapour compression circuit contains refrigerant R12.

The heat pump cycle has two main operational phases, namely regeneration and heat pumping. The regeneration phase occurs during the night hours when cheap electricity is available under the "Economy 7" tariff. Initially, the $CaCl_2/CH_3OH$ pair is chemically combined in the generator/absorber. As the compressor starts to operate CH_3OH vapour separates from $CaCl_2$, latent heat is re-cycled and CH_3OH is stored as a liquid in the accumulator.

The heat pumping phase occurs during the day. Warm exhaust air is chilled in the accumulator of the heat pump immediately prior to leaving the building and the extracted heat causes the CH_3OH liquid in the accumulator to boil. The CH_3OH vapour is then recombined with the $CaCl_2$ absorbent resulting in the emission of heat in the generator/absorber. This heat could be used to warm the interior air of the building and the domestic hot water.

4. CYCLE ANALYSIS

The pressure-temperature relationship for the absorption process is shown in Figure 2. The relationship for $CH_3OH/CaCl_2$ has been investigated by Bramlette and Mar[12] and experiments indicated that the overall stoichiometry is:

$$CaCl_2(s) + 2CH_3OH(v) \Leftrightarrow CaCl_2 2CH_3OH(s) \qquad (2)$$

The enthalpy and entropy for the above reaction were found to be 51.9 kJ/mole and 126 J/mole°C respectively.

The ideal cycle for the heat pump is shown in Figure 3 and its operational phases are described below:

i) Regeneration Phase

Compressor power input, $P = m\,(h_2 - h_1)$ (3)

where m = rate of refrigerant flow in the compression cycle (kg/s)

h = enthalpy per unit mass (kJ/kg)

The quantity of refrigerant desorbed from the generator/absorber equals that collected in the liquid accumulator and is given by:

$$m_g = m\,(h_2 - h_3)/K \quad (4)$$

where K = heat of absorption (kJ/kg)

A small heat input is required at the evaporator to ensure thermal balance. This is given by:

$$Q_e = m\,(h_1 - h_4) - m\,(h_2 - h_3)\,(h_6 - h_1)/K \quad (5)$$

ii) Heat Pumping Phase

Heat emitted in the generator/absorber is given by:

$$Q_g = m\,(h_2 - h_3)\,[1 - (h_{g6} - h_{g5})/K] \quad (6)$$

where h_g = enthalpy of saturated vapour (kJ/kg)

Heat required at the evaporator is given by:

$$Q_{ep} = m\,(h_2 - h_3)\,h_{fg5}/K \quad (7)$$

where h_{fg} = latent heat of evaporation (kJ/kg)

The coefficient of performance is given by:

$$C.O.P._H = \frac{(h_2 - h_3)\,[1 - (h_{g6} - h_{g5})/K]}{(h_2 - h_1)} \quad (8)$$

The design values for the prototype heat pump using the CH_3OH system are given in Table 1.

TABLE 1

Design values for the prototype heat pump

i) Regeneration Phase	
Evaporator, bar (°C)	2.84 (-15)
Condenser, bar (°C)	14.67 (55)
Absorbent, bar (°C)	0.72 (45)
Temperature lift, (°C)	- (70)
Enthalpies[13]	
h_1 (kJ/kg)	181
h_2 (kJ/kg)	217
h_3 (kJ/kg)	90
h_4 (kJ/kg)	90
K (kJ/kg) (Ref 12)	1622
ii) Heat Pumping Phase	
Evaporator, bar (°C)	0.72 (-15)
Absorbent, bar (°C)	0.72 (45)
Temperature lift (°C)	- (60)
h_{g5} (kJ/kg)	1028
h_{g6} (kJ/kg)	1082
$C.O.P_H$	3.42

5. DESIGN AND CONSTRUCTION

A prototype heat pump was constructed in our laboratory and consisted of a generator/absorber, a liquid accumulator, a compressor, a thermostatic expansion valve, an oil separator, a filter/drier and three heat exchanges.

The generator/absorber was constructed from a 0.04 m^3 capacity mild steel vessel, equipped internally with two heat exchangers. In order to improve heat and mass transfer in the generator/absorber, as well as simplify the construction of system, a mixture of aluminium wool and $CaCl_2$ was used in the generator/absorber. In addition, a number of perforated dip-tubes were employed in order to assist the transfer of methanol vapour to the bulk mass of the calcium chloride. The energy storage density for the $CH_3OH/CaCl_2$ system was estimated to be about 110kWh/m^3.

The liquid accumulator consisted of a 0.028m^3 mild steel vessel which was resiliently coupled to the rest of the system so that the quantity of liquid CH_3OH could be weighed at any time.

A semi-hermatic compressor, made by Proven Prestcold Ltd, was used and this operated on 0.75 kW single-phase with 2-cylinder contra flow. The oil separator was packed with discs of stainless steel gauze to intercept oil mist from the compressor and return it to the crankcase.

The electric motor of the compressor was controlled by pressure and time switches. A thermostatic expansion valve made by Danfoss Ltd was used as a refrigerant control valve. The components were connected by means of copper tubing and coupling and all vessels and connecting tubes were thermally insulated. Provision was made for evacuating the system prior to filling.

Bourdon tube gauges were used to measure pressures in the system and copper-constantan thermocouples were used for the measurement of temperature at various points in the circuit. The heat flow from the generator/absorber was measured by means of a water flowmeter and differential thermocouples. A digital pulse counting electricity meter was used to measure the power input to the compressor.

Measurements were recorded using a data logger and data were stored using a microcomputer.

6. HEAT PUMP TESTING

After construction, the system was leak tested and evacuated prior to filling. The energy storage circuit was charged with 20kg $CaCl_2$ and 0.015m^3 CH_3OH and the vapour compression circuit was charged with refrigerant R12.

Experiments were carried out to investigate the heat pumping and regeneration phases of the heat pump.

i) Heat Pumping Phase

During the initial heat pumping phase, the absorption of methanol vapour by $CaCl_2$ granules was slow and 25 hours were required for complete absorption . After the initial absorption, methanol was desorbed and a second absorption was demonstrated. The rate of absorption was large in the first 20-40 minutes and then fell to a constant rate. The rate of absorption of methanol depended on the heat output from the generator/absorber and on the temperature of air passing over the accumulator. When the temperature of the liquid accumulator was -2 ^oC, the core temperature of the generator/absorber was 32^oC and the water passed through the heat exchanger coil was heated by about 8^oC. The total amount of methanol in the system was absorbed in about 3-5 hours depending on the rate of removal of heat from the generator/absorber. The heat pumping phase was carried out under conditions of different heat output and results indicated that it would be possible to adjust the absorption time to allow use of the "Economy 7" electricity tariff.

ii) Regeneration Phase

Liquid methanol was collected during this phase. Temperature lifts in the range of 36-40^oC caused the desorption of 2 moles of methanol per mole of $CaCl_2$ in about 3 hours in accordance with theoretical prediction. The time required for complete desorption could be reduced if the temperature lift were increased to 45°C. The $C.O.P_H$ was found to be variable and depended on the rate of collection of methanol. The average value of the $C.O.P_H$ was found to be about 2.1.

After completion of the operational tests using the $CH_3OH/CaCl_2$ system, the heat pump was partially dismantled so that the components could be inspected. No visible signs of corrosion were found in either the generator/absorber or liquid accumulator vessels.

CONCLUSIONS

Experimental work showed that that chemical/compression heat pump operated in accordance with theoretical prediction. Heat pumping and regeneration phases were demonstrated and the $CH_3OH/CaCl_2$ system was found to provide a suitable temperature lift for domestic applications. The average $C.O.P_H$ of the heat pump system was found to be 2.1 and its operational cycle could be controlled to allow use of the "Economy 7" electricity tariff.

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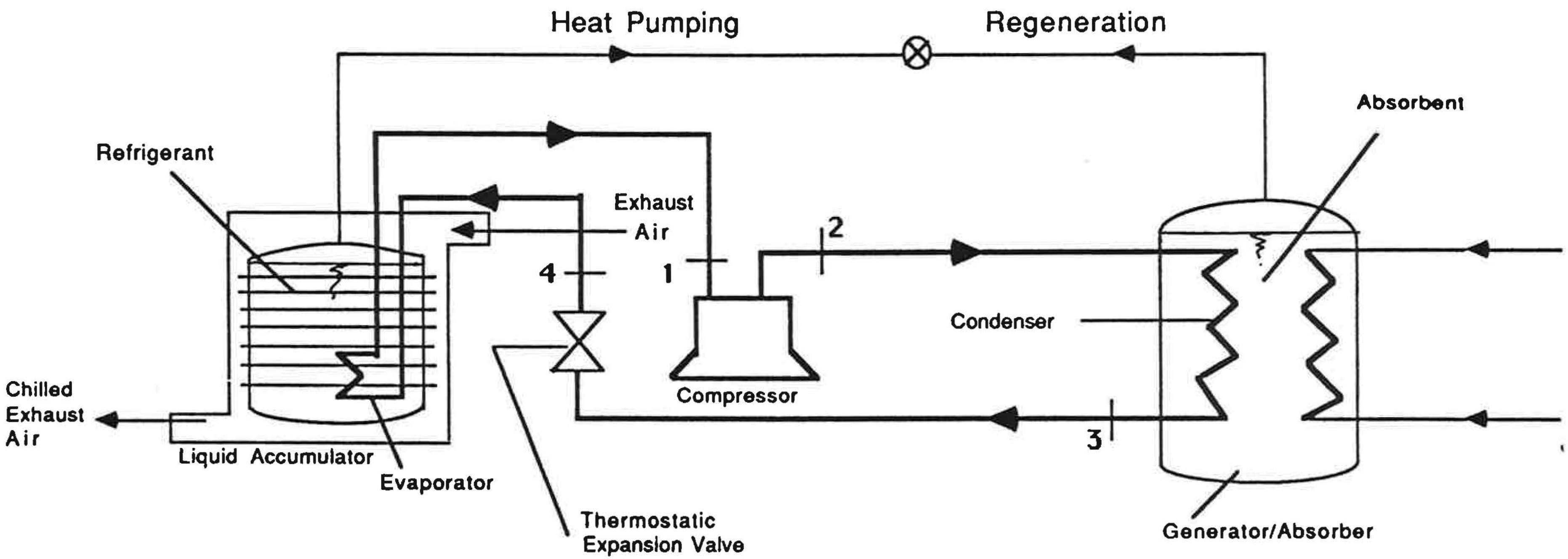
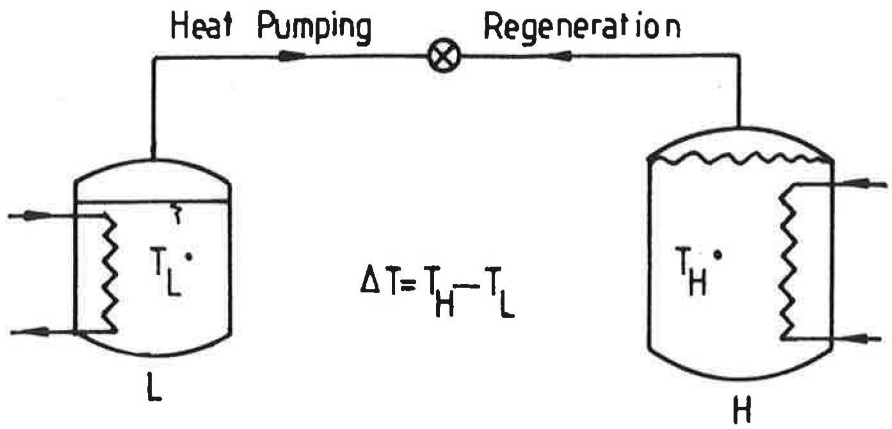
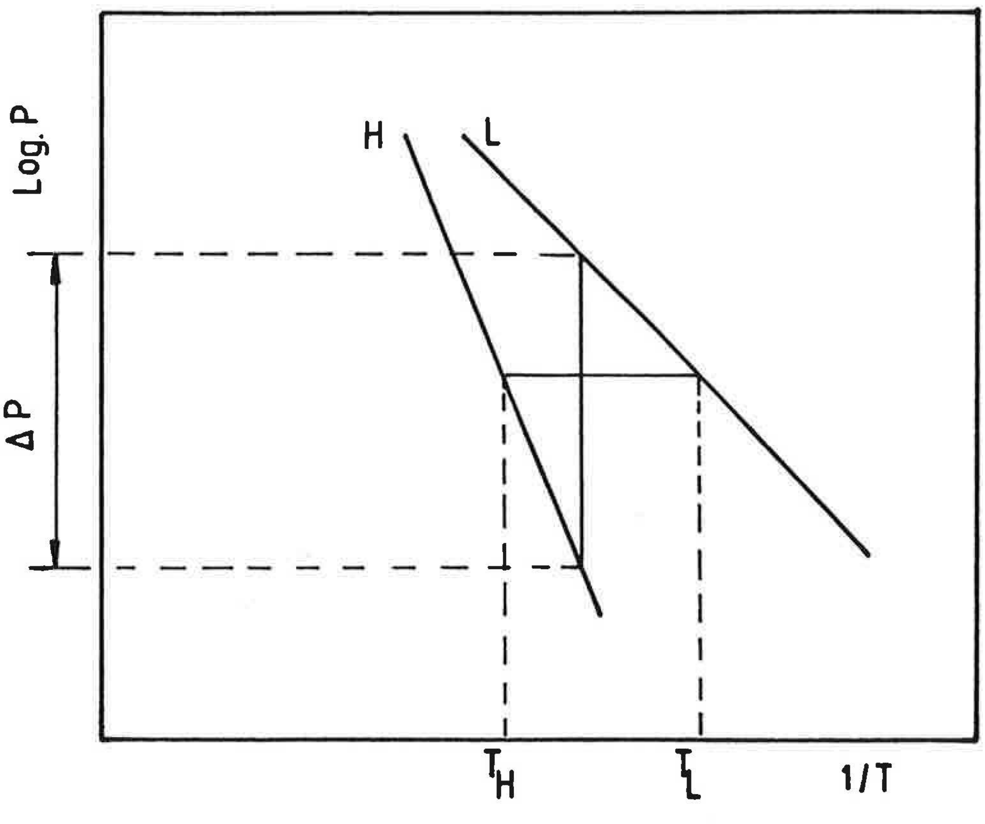
FIGURES

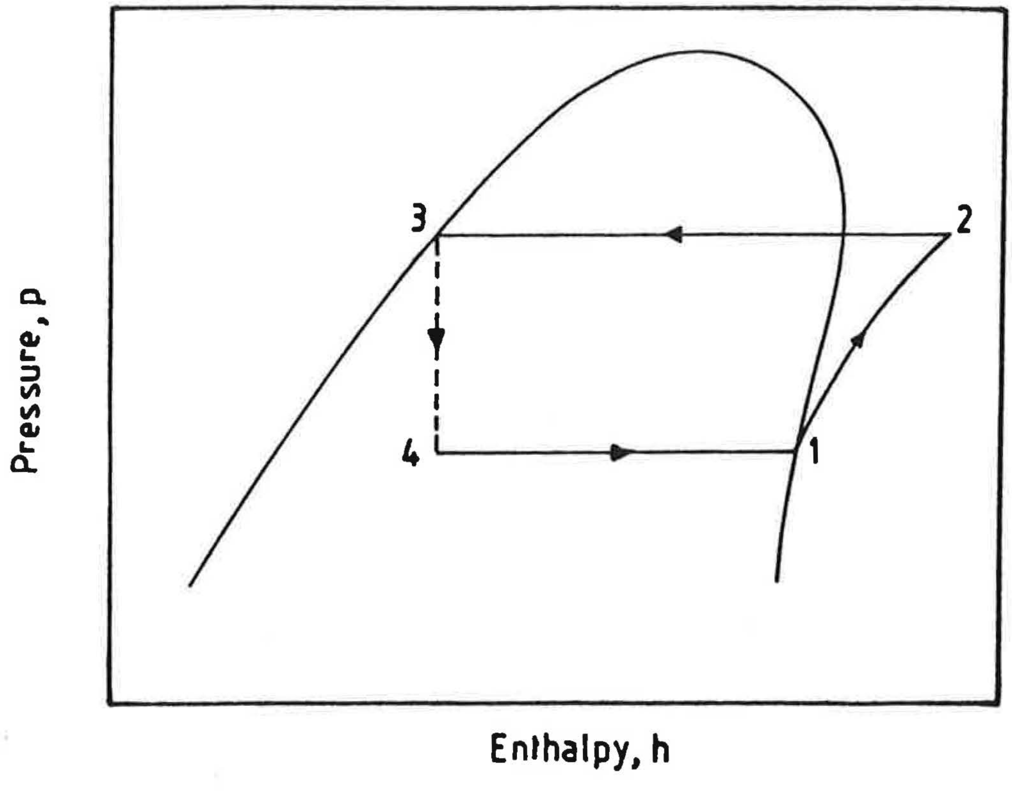

Heat Pumping
Regeneration
Absorbent
Refrigerant
Exhaust
Air
2
4
1
Condenser
Chilled
Exhaust
Air
Compressor
3
Liquid Accumulator
Evaporator
Thermostatic
Expansion Valve
Generator/Absorber



Heat Pumping
Regeneration
T_L
$\Delta T = T_H - T_L$
T_H
L
H



Log. P
H
L
ΔP
T_H
T_L
1/T


3
2
4
1
Pressure, p
Enthalpy, h