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The Use of Formaldehyde as a Refrigerant in Heat Pumps

Anita Kovač Kralj*
University of Maribor, Faculty of Chemistry and Chemical Engineering, Smetanova 17, Maribor, Slovenia

Abstract

A heating system sometimes needs a low temperature source such as low-pressure steam. The need for lower-temperature heat can be replaced using a heat pump. A heat pump is a machine or device that moves heat from one location to another location mechanically. Refrigerant within a heat pump is used as the working fluid. Different standard refrigerants (such as chlorofluorocarbons, hydro-fluorocarbon isobutene …) are cycled throughout the heat pump's system. When replacing the standard refrigerant (1,1,1,2-tetrafluoroethane; R-134a) within the heat pump with formaldehyde under the same compressor power, the efficiency should increase.

Heating with low pressure steam can be replaced by a heat pump under optimised compressor power (5 bar) by using formaldehyde as a refrigerant during the existing process. The use of formaldehyde as a refrigerant can enlarge the efficiency of a heat pump's system by about 80 % during an existing process.

Keywords: Formaldehyde; Heat pump; Lower temperature heat; Refrigerant

Introduction

Different standard refrigerants (such as chlorofluorocarbons, hydro-fluorocarbon isobutene …) are used as working fluids within heat pump systems.

Until the 1990s, these refrigerants were often chlorofluorocarbons such as R-12 (dichlorodifluoromethane), one of a class of several refrigerants using the brand name 'Freon'. Its manufacture was discontinued in 1995 because of the damage that CFCs (chlorofluorocarbons) were causing to the ozone layer if released into the atmosphere. One widely-adopted replacement refrigerant is the hydro-fluorocarbon (HFC) known as R-134a (1,1,1,2-tetrafluoroethane). Other substances such as liquid ammonia or occasionally the less-corrosive but flammable propane or butane, can also be used [1,2].

Since 2001, carbon dioxide, R-744 has increasingly been used by utilising the transcritical cycle. Hydro-chlorofluorocarbon (HCFC) R-22 is still widely used in residential and commercial applications. Hydrogen, helium, nitrogen, or plain air is used in the Stirling cycle, thus providing the maximum number of options regarding environmentally-friendly gases. More recent refrigerators are now exploiting the R600A, which is isobutane, does not deplete the ozone layer, and is friendly to the environment [1,2].

General Presentation of Heat Pumps

A heat pump is a machine or device that moves heat from one location (the 'source') to another (the 'sink' or 'heat sink') mechanically. Most heat pump technology moves heat from a low temperature heat source to a higher temperature heat sink [1,2]. Common examples are food refrigerators and freezers, air conditioners, and reversible-cyclic heat pumps for providing thermal comfort. Heat pumps can also operate in reverse, thus producing heat.

According to the second law of thermodynamics, heat cannot spontaneously flow from a colder location to a hotter area and so work is required to achieve this. Heat pumps differ as to how they apply this work when moving heat, but can essentially be thought of as heat engines operating in reverse. A heat engine allows energy to flow from a hot 'source' to a cold heat 'sink', extracting a fraction of it as work during the process. Conversely, a heat pump requires work to move thermal energy from a cold source to a warmer heat [1,2].

As the heat pump uses a certain amount of work to move the heat, the amount of energy deposited at the hot side is greater than the energy taken from the cold side by an amount equal to the work required. Conversely, for a heat engine the amount of energy taken from the hot side is greater than the amount of energy deposited in the cold heat sink, as some of the heat has been converted into work [1].

One common type of heat pump (Figure 1) works by exploiting the physical properties of an evaporating and condensing fluid known as a refrigerant [1].

The working fluid, in its gaseous state, is pressurised and circulated throughout the system by a compressor. On the discharge side of the compressor, the now hot and highly- pressurised gas is cooled within a heat exchanger, called a condenser. The condensed refrigerant then passes through a pressure-lowering device such as an expansion valve. This device then passes the low pressure, now (almost) a liquid refrigerant, on to another heat exchanger, then to an evaporator where the refrigerant evaporates into a gas via heat absorption. The refrigerant then returns to the compressor and the cycle is repeated [1].

Formaldehyde can be used as a refrigerant within a heat pump. This is quite a novel idea and it would be necessary to pilot it within a plant. Certain calculations are required before performing this task. Formaldehyde is toxic, however the refrigerant circulates within a closed system.

Formaldehyde as a Refrigerant

A heat pump needs only significant construction modifications when replacing standard refrigerant with formaldehyde. The standard refrigerant (1,1,1,2-tetrafluoroethane; R-134a) could be replaced within the heat pump by formaldehyde under the same compressor power

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***Corresponding author:** Anita Kovač Kralj, University of Maribor, Faculty of Chemistry and Chemical Engineering, Smetanova 17, Maribor, Slovenia; Tel: +44 1772 201201; E-mail: anita.kovac@um.si

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and parameters (mass flow=1.4 m^3/h). The heat pump, when using the standard refrigerant (R-134a -1,1,1,2-tetrafluoroethane), draws a 1.86 kW heat flow rate from the air (or another heat source within a plant; Table 1). The heat pump, when using formaldehyde as a refrigerant, needs only a 1.56 kW heat flow rate from the air (or another heat source within a plant - evaporator) for heating the refrigerant from 0°C to 5°C under 1 bar during a reversible cycle using a valve and an evaporator (Figure 1, Table 1). The compressor pushes the pressure up to 4 bar with a power of 22 kW and the outlet temperature rises to 60°C, giving 4.2 kW heat flow rate within the condenser using refrigerant R-134a. When using formaldehyde as a refrigerant, the outlet temperature rises to 146°C under the same pressure (4 bar) with a power of 49.8 kW, thus giving 34 kW heat flow rate within the condenser. For the easiest comparison, compression takes place using the same power of 22 kW. In this case, the presented case's pressure was pushed up to 1.95 bar (not to 4 bar), the outlet temperature was 70°C, and the heat flow rate within the condenser was 6.9 kW using the same outlet temperature from the condenser (50°C) when using formaldehyde (Table 1). The analysis was carried out by using the same mass flow with (1.4 m^3/h) standard value of refrigerant and in a condenser where total condensation did not take place.

The characteristics of formaldehyde as a refrigerant should be noted as being of higher efficiency, producing additional savings during critical times:

The evaporator needs up to 11 % lower heat flow rate (Table 1)

The condenser delivers 64 % more heat flow rate when heating using the same compressor power (Table 1).

The technical principle was checked by using an Aspen Plus simulator [3], which includes real thermodynamically properties. The simulated results were in good approximation with the real results [4] but should still be checked using a pilot plant.

Different analyses took place for formaldehyde as a refrigerant using the same evaporator heat flow rate (Φ_{ev} =1.65 kW) and different pressure (p) within the compressor, different compressor power (P_{com}), different inlet temperature of the condenser (T_{co}), and different heat flow rate of the condenser (Φ_{co}; Table 2). The outlet temperature of the condenser was always the same (50°C).

The compressor power (P_{com}; Eq. 1) and heat flow rate of the condenser (Φ_{co}; Eq. 2) can be denoted by mathematical quadratic equations depending on the pressure within the compressor (p) using parameters from Table 2, and quadratic extrapolation:

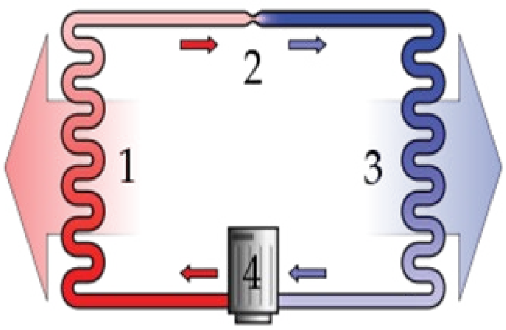

Figure 1: A simple stylized diagram of a heat pump's vapour-compression refrigeration cycle (Perry and Green, 1997): 1) condenser, 2) expansion valve, 3) evaporator, 4) compressor.

Parameters	1,1,1,2-tetrafluoroethane	Formaldehyde
Inlet of evaporator	0°C, 1 bar, gas	0°C, 1 bar, gas
Heat flow rate of evaporator, Φ_{ev}/ kW	1.86	1.65
Outlet of evaporator	5°C, 1 bar, gas	5°C, 1 bar, gas
Power of compressor, P_{com} /kW	22	22
Inlet of condenser	60°C, 4 bar, gas	70°C, 1.95 bar, gas
Heat flow rate of condenser, Φ_{co}/kW	— 4.2	— 6.9
Outlet of condenser	50°C, 4 bar,_mixed phase	50°C, 1.95 bar,_mixed phase

Table 1: Comparison between 1,1,1,2-tetrafluoroethane and formaldehyde using the same compressor power, and without total condensation in the condenser

Pressure (p) /bar	***Compressor power (P_{com})/kW***	***Heat flow rate of condenser (Φ_{co}) /kW***	***Inlet temp. of condens. / °C***
2	22.9	7.8	72
3	38.1	23.0	115
4	49.8	34.7	146
5	59.4	44.2	171
6	67.6	52.4	191

Table 2: Other parameters when using formaldehyde as a refrigerant, but without total condensation within the condenser.

$$P_{com} = - 1.4\, p^2 + 21.92\, p - 15.27 \qquad (1)$$

$$\Phi_{co} = - 1.425\, p^2 + 22.065\, p - 30.565 \qquad (2)$$

Mathematical assumptions were obtained using Aspen Plus.

The same analysis was carried out using total condensation and the same compressor power (Table 3). When exchanging 1,1,1,2-tetrafluoroethane with formaldehyde using the same compressor power, and with total condensation within the condenser:

The evaporator needed 11 % lower heat flow rate (Table 3)

The condenser delivered up to 82 % more heat flow rate when heating using the same compressor power (Table 3).

Different parameters were analysed with total condensation using formaldehyde as a refrigerant, the same heat flow rate of the evaporator (Φ_{ev} =1.65 kW), different pressure (p) within the compressor, different compressor power (P_{com}), different inlet temperature of the condenser (T_{co}), and different heat flow rate of the condenser (Φ_{co}; Table 4). The outlet temperature of the condenser was always the same (20°C).

The compressor power (P_{com}) and heat flow rate of the condenser (Φ_{co}) can be denoted by mathematical quadratic equations depending on the pressure within the compressor (p), and with total condensation (Eqs. 3, 4) using the parameters from Table 4, and quadratic extrapolation:

$$P_{com,\,tot} = - 0.449\, p^2 + 13.05\, p + 5.4 \qquad (3)$$

$$\Phi_{co,tot} = - 0.449\, p^2 + 13.05\, p + 201.2 \qquad (4)$$

All results are presented on the basis of the same compressor power.

The NLP Model

The basis of the optimization model is the replacement of low temperature steam with a heat pump under a different compressor power. It is important as to which refrigerant is flowing within the heat

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pump. This optimisation model has been developed for formaldehyde using a nonlinear programming (NLP) model [5]. Optimisation could increase annual profit.

The parameters within the hybrid model are simultaneously optimised using GAMS/MINOS software [5]. This NLP can be solved using a large-scale reduced gradient method (eg. MINOS). This model quickly provides good results. This NLP model uses simple quadratic equations from 3 to 4, and with total condensation. The objective function (Eq. 5) of the NLP model is to maximise the annual profit in EUR, V; it includes savings of low pressure steam over 5 years when replacing with a heat pump. Price of heat (C_{heat}) is 80 EUR/(kW·a). The cost of a heat pump is denoted by C_{pu} (C_{pu} =500 EUR/kW), depending on the compressor power (P_{com}).

Maximal additional annual profit (in EUR) is defined by Eq. 5:

$$V_{max} = C_{heat}\,\Phi_{co}\,5 - C_{pu}\,P_{com} \qquad (5)$$

The replacement of low temperature steam with a heat pump was tested during formalin production.

Case Study

The existing formalin is produced from methanol and air (Figure 2). They are mixed within a vessel C4 and column C3/C5, heated within heat exchangers E2 and E4, and react within the reactor RE through a silver catalyst bed, where the conversion of methanol to formaldehyde takes place (oxidation and dehydrogenation):

$$2\,CH_3OH + O_2 \rightarrow 2\,H_2CO + 2\,H_2O$$

$$CH_3OH \rightarrow H_2CO + H_2$$

The silver-based catalyst is usually operated at a higher temperature of about 650°C. The reactive gases are cooled and enter the absorption tower (C1), where the absorption of formaldehyde takes place over a counter-flow of four stages by means of aqueous formaldehyde solution and cold de-mineralised water (inlet stream water). The gaseous formalin produced is absorbed in water in C1 and is produced as C2 bottoms. The non-reactive methanol can be purified within a distillation column and is recycled within a vessel C4 [6]. Although formaldehyde is a gas at room temperature, it is readily soluble in water, and is more commonly sold as a 37 % solution in water known by trade-names such as formalin or formol. The process was integrated [4] but we needed only hot utilities for the heat exchanger E6 (Table 5). This low pressure steam could be replaced by a heat pump using formaldehyde under different compressor power.

Parameters	1,1,1,2-tetrafluoroethane	Formaldehyde
Inlet of evaporator	0°C, 1 bar, gas	0°C, 1 bar, gas
Heat flow rate of evaporator, Φ_{ev}/ kW	1.86	1.65
Outlet of evaporator	5°C, 1 bar, gas	5°C, 1 bar, gas
Power of compressor, P_{com} /kW	59.4	59.4
Inlet of condenser	142°C, 30 bar, gas	171°C, 5 bar, gas
Heat flow rate of condenser, Φ_{co}/kW	— 139.8	— 255.2
Outlet of condenser	20°C, 30 bar, liquid phase	20°C, 5 bar, liquid phase

Table 3: Comparison between 1,1,1,2-tetrafluoroethane and formaldehyde using the same compressor power, and with total condensation within the condenser.

Pressure (p)/bar	***Compressor power (P_{com})/kW***	***Heat flow rate of condenser(Φ_{co}) /kW***	***Inlet temp. of condens. / °C***
5	59.4	255.2	171
6	67.5	263.3	191
7	74.7	270.5	209
8	81.0	276.8	225

Table 4: Other parameters using formaldehyde as a refrigerant, and with total condensation within the condenser.

The optimisation model (from chapter 4) used equations 3, 4 and 5. An optimisation model was selected with a heat pump of 5 bar compression power, which replaced the low –pressure steam within the E6 heat exchanger. The compressor power (P_{com}) was 17.8 kW with a lower mass flow of formaldehyde refrigerant (0.42 m^3/h). The heat flow rate within the condenser was 76 kW (Φ_{co}) at 22°C outlet temperature, with total condensation within the condenser. By using the existing process, 30.4 kEUR could be saved regarding low pressure steam over 5 years (Eq. 5; $C_{heat}\,\Phi_{co}\,5$). The cost of the heat pump was 8.9 kEUR (Eq. 5; $C_{pu}\,P_{com}$). The contingency cost, electricity and modification costs were estimated to be about 10 kEUR. The total profit over 5 years would be 11.5 kEUR. The annual profit would be 2.3 kEUR.

Conclusions

A heat system was needed as a low temperature source, similar to low pressure steam, which could be replaced by a heat pump using formaldehyde as a refrigerant. Formaldehyde as a refrigerant can be worked with higher efficiency and additional savings during critical times with total condensation when compared with the standard (1,1,1,2-tetrafluoroethane; R-134a):

The evaporator needs up to 11 % lower heat flow rate

The condenser would deliver up to 82 % more heat flow rate for heating using the same compressor power (59.4 kW).

The optimised working of a heat pump using formaldehyde would be at a pressure of 5 bar. The optimised 5 bar heat pump would be used within an existing formalin process. Heating with low pressure steam could be replaced by a heat pump under optimised compressor power (5 bar). The total profit over 5 years would be 11.5 kEUR. The annual profit would be 2.3 kEUR.

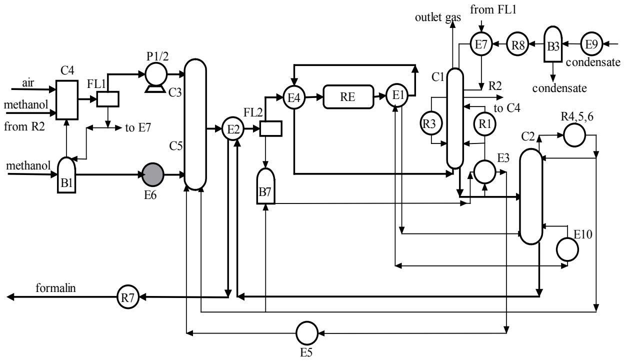

Figure 2: Formalin process flow diagram.

™Stream	***T_{in}/°C***	***T_{out}/ °C***	***I/kW***
E6	15	54	76

Table 5: Process stream.

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