Application of the Second Law Analysis to a Heat Exchanger Working with Ethanol/Water Ice Slurry

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Abstract

The use of ice slurries as secondary refrigerants is a very promising technology. The aim of this paper is to evaluate the contribution of second law analysis to the study of a phase changing secondary refrigerant in cooling systems. The first step of the work presented here consists of two parts: the first involves the calculation of enthalpies and entropies and the second is an entropy/exergy analysis of a heat exchanger. This work attempts to provide a thermodynamic criterion in order to choose the kind of fluid and the inflow conditions that are more suitable for a particular application. It presents the establishment of the method and the results that have been obtained for an ethyl alcohol-water mixture.

Keywords: Ice slurry, ethanol-water ice slurry, exergy, binary mixture, second law analysis, specific entropy.

1. Introduction

Secondary refrigerants are used in indirect refrigeration systems to transport heat from the cooling utilisation to the cooling production. Over the last few years, a new class of transport fluid has been developed. Two-phase solutions, known as ice slurries composed of water, an additive (for example ethanol (ethyl alcohol)) and very small ice crystals are very interesting. The latent heat of fusion enables large cooling capacities and more stable temperature conditions to be obtained. One of the main advantages of secondary refrigeration systems is a lower impact on the environment thanks to the reduced risk of primary refrigerant leakage, due to shorter piping, and reduced charge amount.

A number of water solutions may be used for ice slurry applications. For these binary mixtures, the enthalpy change depends on the kind of solution, the concentration of the freezing point depressant substance, and the temperature (i.e. ice mass fraction). To make the choice of these parameters easier for a given application, entropy analysis has already been applied to cold storage with phase-change (Strub and Bedecarrats, 1999, 2000).

The studied system is a heat exchanger through which an ice-slurry is flowing and melting. The open thermodynamic system is in thermal contact with a heat reservoir of which the temperature represents a particular application. The heat transfer across the reservoir-fluid temperature difference is the cause of irreversibilities.

Because our objective is second law analysis of ice slurry behaviour, particular attention is paid to the ice fraction. The enthalpy calculation is based primarily on the previous works of Melinder (1997, 2001, 2002). The specific entropy definition is then introduced and the values of specific entropy for the two-phase ethanol/water mixture are calculated. The calculations and the diagrams for enthalpy and entropy versus the ice fraction are an originality of the paper. The second one lies in the entropy/exergy analysis of the heat exchanger mentioned above. It is developed in the second part where the entropy generation values are determined versus all the main parameters of the ice slurry. At the end, this paper proposes a thermodynamic criterion to determine the best choice for the inlet ice fraction range for cooling. The method presented in the paper is applied to an ethanol–water solution.

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2. Background

Aqueous binary ice slurries are defined through a set of different characteristics. The first one is the concentration of the ethanol (the solvent chosen in this paper) in the solution. This ratio is given by $C = m_a / m_s$, where m_a is the mass of alcohol, while m_s represents the mass of the solution. This concentration changes the freezing point temperature of the solution. As can be seen in the freezing point diagram for ethanol, *Figure 1*, the higher C is, the lower this temperature.
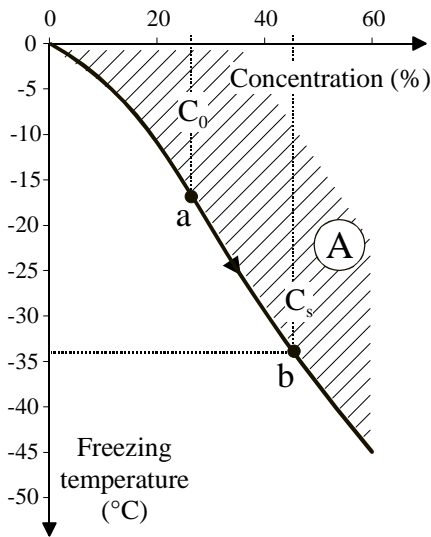

Figure 1. Freezing point diagram of ethanol/water solution.

Thus, a solution remains liquid as long as its properties are situated in the hatched area (A). In contrast, lowering the temperature of a solution at a given initial concentration C_0 below the solid-liquid equilibrium curve, leads to a partial crystallization of water present in the solution that starts at point "a". The binary mixture is then composed of ice at the final temperature and a more concentrated solution (C_s) at the same temperature (point b). The amount of ice in the secondary refrigerant is generally described through the ice fraction given by $i = m_i / m_0$, where m_i is the mass of ice and m_0 is the total mass of ice and solution.

As the sum of ice and the water remaining in the solution represents the amount of water that was initially in the solution at C_0, the last two equations can be combined to give $i = 1 - C_0 / C_s$. The ice fractions of the ethanol solution as a function of freezing point temperature and for different initial concentrations are given in *Figure 2*.

Ice slurries are used for energetic and particularly for cooling purposes and thermodynamic properties such as enthalpy for first law analysis and entropy for second law analysis are needed. Both expressions take the same general form given by

$$f = (1-i)f_s + i(f_i) \qquad (1)$$

where f can represent enthalpy as well as entropy. f_s integrates, if any, sensible as well as mixing transformation of the solution and f_i, sensible as well as latent transformations.
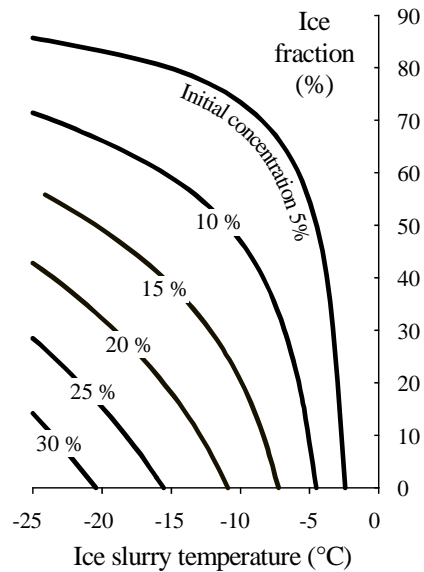

Figure 2. Ice fraction versus temperature for various initial concentrations.

The diagram in *Figure 3* illustrates the variation of enthalpy versus the temperature of ethanol/water solutions for various initial concentrations of ethanol. Considering the shapes of the curves, one can see that the enthalpy change is strongly dependent on the initial concentration and temperature of the solution (i.e. ice fraction). As can be seen, the available latent heat has its maximum at low concentrations of the additive (ethanol) and at a temperature just below the freezing point. So, just below 0°C, a small temperature change is sufficient to generate a high ice concentration and, thus, a large enthalpy difference that will give a large "heat transport capability". Higher concentrations of the additive will require a much larger temperature change to get the same effect. However, for a particular temperature application, it is not easy to choose the initial concentration C_0 and the ice fraction i (i.e. the ice slurry temperature entering the process). For example, to reach the cooling temperature

demand, two entering characteristics are possible: either a high initial concentration and a low ice fraction or a low initial concentration and a high ice fraction. Regarding the enthalpy diagram, these two possibilities cannot have the same thermodynamic efficiency. So an entropy analysis has been developed.
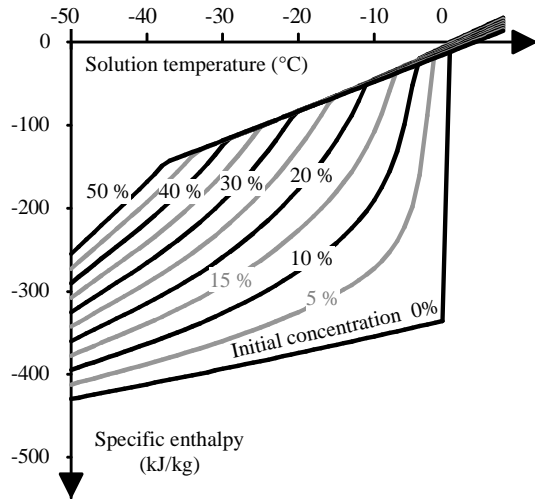

Figure 3. Enthalpy diagram of water/ ethanol solutions.

Because this study requires specific entropy values, their calculation for the two phase mixture has been carried out according to Eq. (1) and with the help of thermophysical properties from Prosim (Vacher and Guittard, 2002). The results are reported on *Figure 4*.

The global behaviour of the entropy curves reveals behaviour very similar to those for the enthalpy. This is quite unsurprising, since the changes in these thermodynamic properties are much more affected by the latent heat of fusion contained in h_i and s_i than by any other term of the preceding equations.
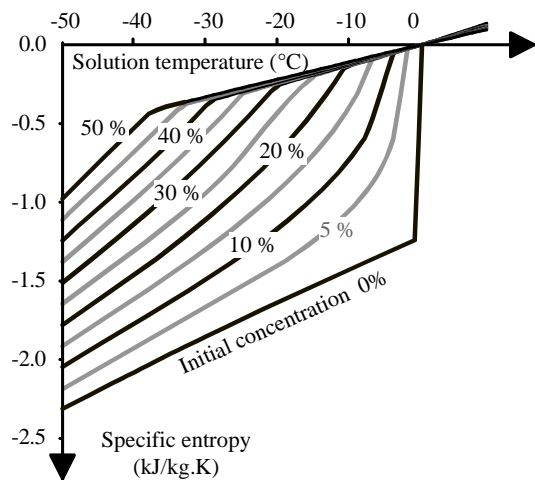

Figure 4. Entropy diagram of water / ethanol solutions.

3. Second Law Analysis of Heat Exchange with a Phase Changing Secondary Refrigerant.

Thanks to many previous works concerning the exergy/entropy analysis of machines (e.g., Feidt and Lang, 2001), cycles (e.g., Spinner et al., 2001) as well as elementary components (e.g., Bejan, 1996 and Bejan and Tondeur, 1998), an important literature in the second law analysis of systems has developed.

The thermodynamic system being studied here consists of a heat exchanger as illustrated in *Figure 5*. A given mass flow of ice slurry $\dot{m}$ at given concentration (C_0) and temperature (T_{in}) conditions, crosses a heat exchanger in order to cool a medium at a uniform temperature T_∞ as shown in *Figure* 5. The amount of heat flux transferred is denoted as $\dot{Q}$.
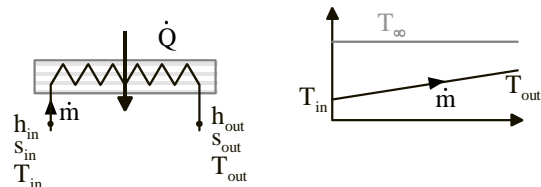

Figure 5. Illustration of the heat exchanger studied and the considered temperature profile.

Under the following assumptions:
- steady state operating conditions,
- entropy generation is due only to heat transfer between the ice slurry and the medium at T_∞ (the heat exchanger is insulated from the environment and the fluid does not undergo any pressure drop),
- kinetic as well as potential energy changes are neglected,

the energy and entropy balances yield

$$\begin{cases} \dot{Q} + \dot{m}\left(h_{in} - h_{out}\right) = 0 \\ \dfrac{\dot{Q}}{T_\infty} + \dot{m}\left(s_{in} - s_{out}\right) + \dot{P}(s) = 0 \end{cases} \quad (2)$$

Combining these two equations gives the expression for the entropy generation as a function of the thermodynamic properties of the refrigerant:

$$\dot{P}(s) = \dot{m}\left[\frac{\left(h_{in} - h_{out}\right)}{T_\infty} - \left(s_{in} - s_{out}\right)\right] \quad (3)$$

Values of the entropy generation per unit mass flow rate versus input temperature are presented in *Figure* 6. Each curve corresponds to a constant initial concentration of ethanol. The operating conditions corresponding to these results are summarized in TABLE I.

TABLE I. OPERATING CONDITIONS OF
THE RESULTS PRESENTED IN FIGURES 6-7

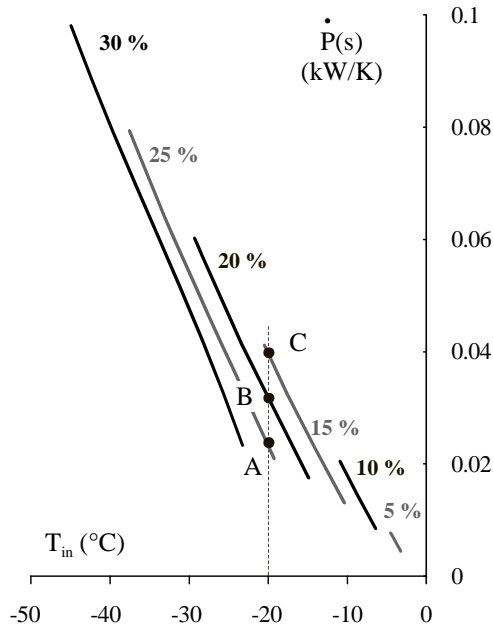| Specific enthalpy variation (kJ/kg)	100
Environment temperature T_0 (°C)	35
Temperature of the application T_∞ (°C)	0
Mass flow rate (kg/s)	1

Figure 6. Entropy production versus input temperature for various water/ethanol initial composition solutions.

For each curve, the highest input temperature corresponds to an output temperature equal to T_∞ while the last point corresponds to an input ice fraction of 50 %. Lowering the entropy generation requires both increasing the input temperature and, for a given temperature, using the highest available concentrated solution. This is clearly shown in the Figure 6 where detailed values taken at points A, B, and C are summarized in TABLE II.

These three points correspond to the same input temperature (-20°C). At such conditions, the lowest entropy generation occurs for the inlet conditions at point A. So, to operate with an input temperature of –20°C, it is better to use the fluid conditions represented by point A than those represented by point C. In other words and according to TABLE II, it is better to use ice slurry from a high concentrated solution (C_0 = 0.25) with a low ice fraction (i = 0.15) than to use ice slurry from a low concentrated solution (C_0 = 0.15) with a higher ice fraction (i = 0.49).

To integrate these results in a more global analysis, an exergetic balance is introduced. The destroyed exergy is derived directly from the entropy generation via

$$\dot{Ex}_d = T_0 \dot{P}(s) \qquad (4)$$

while the exergy change of the fluid entering the system is given by:

$$\Delta \dot{Ex} = \dot{m}\left[h_{in} - h_{out} - T_0 \left(s_{in} - s_{out} \right) \right] \qquad (5)$$

The exergetic efficiency compares these two quantities by the exergetic efficiency $\eta_{ex} = 1 - \dot{Ex}_d / \Delta \dot{Ex}$ whose values are presented in *Figure 7*.

TABLE II. DETAILS OF POINTS A, B AND C
IN FIGURES 6 - 7

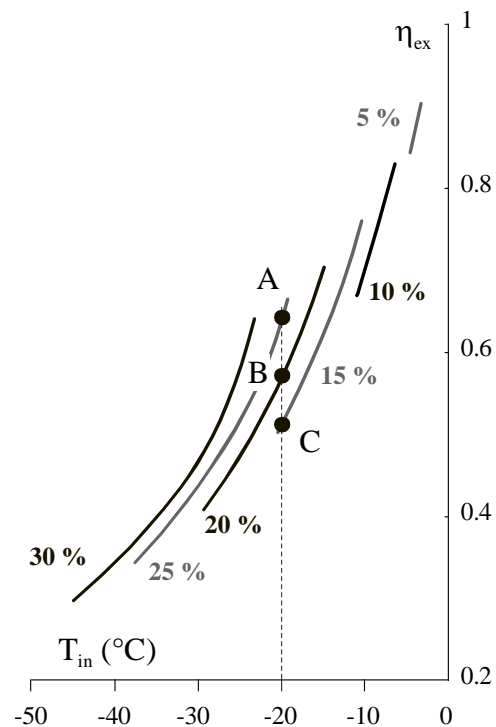|	**A**	**B**	**C**
C_0 [%]	25	20	15
T_{in}/C_{in} [°C/%]		−20 / 29.4	
i [%]	15	32	49
T_{out} [°C]	−4.8	−12.28	−11.0
$\dot{P}(s)$ [kW.K^{-1}]	0.023	0.031	0.04
$\Delta \dot{Ex}$ [kW]	20.0	22.5	24.8
$\dot{Ex}_d$ [kW]	7.19	9.65	12
η_{ex} [%]	64	57	50

Figure 7. Exergetic efficiency versus input temperature for various water/ethyl alcohol initial composition solutions.

The same conclusions can be drawn from the variations of η_{ex} shown in *Figure 7*. In order to produce a cooling effect (at 0°C in our example) efficiently, ice slurry with a high initial

concentration of the additive is preferable. For a given inlet temperature, the highest values of η_{ex} are found with the highest values of C_0. When C_0 is fixed, η_{ex} decreases with the increase in ice fraction, which means a decrease in the inlet temperature. If the input temperature is -20°C, point A is still preferred from an exergetic efficiency point of view.

It is interesting to note that

$$\eta_{ex} = 1 - \frac{\dot{Ex}_d}{\Delta\dot{Ex}} = \frac{\Delta\dot{Ex} - \dot{Ex}_d}{\Delta\dot{Ex}} \qquad (6)$$

where

$$\Delta\dot{Ex} - \dot{Ex}_d = \dot{m}(h_{in} - h_{out})\left(1 - \frac{T_0}{T_\infty}\right)$$
$$= \dot{Q}\left(\frac{T_0}{T_\infty} - 1\right) \qquad (7)$$

The denominator of η_{ex} is the exergy change of the fluid across the heat exchanger and represents the work that would be required to cool down, in a reversible way, the ice slurry from outlet to inlet conditions. On the other hand, the numerator represents the minimum amount of work that is necessary to provide the cooling $\dot{Q}$, i.e. the work consumed by a reversible refrigeration machine operating between T_∞ and T_0.

4. Conclusions and Analysis

Knowing the thermophysical properties of ice slurries is not sufficient to find the best kind of fluid for a particular cooling application. Not only the kind of additive but also the initial concentration and the ice fraction must be defined. To aid in the selection, an entropy analysis was used. Preliminary to this, specific entropy was introduced and calculated for a binary water-ethanol solution. Entropy generation and exergetic efficiency were then calculated for different initial concentrations and different ice fractions. The results show that concentrated solutions without ice are preferable to less concentrated solutions with an important ice fraction. As is well known, this fluid is powerful for low concentrations and well-adapted for cooling temperatures near the freezing point. It is why the exergetic efficiency reaches values near 1 at a low concentration and for a cooling application at 0°C.

This work will soon be extended to other kinds of solutions and results compared between each other. Hence, for a fixed cooling temperature, the different exergetic efficiencies will permit one to select a particular kind of fluid.

Of course, it is obvious that minimization of exergy destruction may lead to impractical constructions. This study contributes to the selection of the inlet conditions of the ice slurry flowing into the heat exchanger when the refrigeration application temperature and heat rate are specified. An improvement can be achieved with supplementary constraints like surface and cost.

Lastly, approach being persued by the authors presently is the integration of transfer properties (heat transfer as well as pressure drop coefficients) into the global exergetic analysis, in order to point out the major sources of exergy destruction and to optimize heat exchangers when refrigeration applications involving ice-slurries are concerned.

Nomenclature

C	concentration	[-]
m	mass	[kg]
T	temperature	[K]
s	specific entropy	[J.kg^{-1}.K^{-1}]
h	specific enthalpy	[J.kg^{-1}]
$\dot{Q}$	heat flux	[W]
$\dot{m}$	mass flow	[kg.s^{-1}]
$\dot{P}(s)$	entropy generation	[W.K^{-1}]
η_{ex}	exergetic efficiency	[-]
i	ice fraction	[-]
$\dot{Ex}$	exergy flow rate	[W]

Subscripts

in	input
out	output
∞	application conditions
0	environmental conditions.
s	solution
a	alcohol
i	ice

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