COMPARATIVE OF ALCOHOLS DERIVED FROM RENEWABLE AND NON-RENEWABLE RESOURCES AS ANTIFREEZE ADDITIVE IN ICE SLURRY

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Abstract. *The ice slurry is one of the new technologies of secondary coolant applied in indirect refrigeration system with cool thermal storage. It is a two-phase fluid composes by water, antifreeze and ice microcrystals in suspension. The alcohols are the most commonly used antifreeze because they reduce the melting point of water in solution, they are completely soluble and they have low or no corrosive activity. The feedstocks for the manufacture of alcohols include renewable and non-renewable energy sources, especially ethanol and propylene glycol obtained from the respective sources. Thus, this paper evaluates the use of alcohol cited as antifreeze additives in the ice slurry to working temperature of -15 °C and 10% concentration of ice crystals, examining the thermophysical properties of the ice slurries (alcohol concentration, density, heat of fusion, thermal conductivity and dynamic viscosity). The results show the main differences between the use of alcohols from renewable and non-renewable resources are the dynamic viscosity and concentration reduced of ethanol (respectively -26% and -21% compared to ice slurry with propylene glycol). The differences among the other properties are not significant. Thus, ethanol shows its potential as antifreeze, requiring less quantity and power pumping of the ice slurry. Although it is corrosive, ethanol has a great advantage to be derived from renewable sources and environmentally correct.*

Keywords*: Ice Slurry, Thermophysical Properties, Ethanol, Propylene Glycol, Renewable and Non-Renewable Resources.*

1. INTRODUCTION

Industrial refrigeration and air conditioning processes that operate by indirect expansion systems with thermal storage use secondary fluids to transport the coolness from the thermal storage tank to the refrigeration site. The selection of this fluid is extremely important for the thermal efficiency of the heat transfer process. The main thermophysical properties involved in the selection are melting point, bulk density, specific heat, thermal conductivity and dynamic viscosity (Dinçer, 2003; Stoecker, 1998).

The secondary fcoolant composed of water and alcohol antifreeze are the most used, but they are not fluid that has no thermal storage effect. As much as they have a high specific heat combined with a high density, this value will always be less than ones of pure water for temperatures above 0 °C. The need to increase the thermal efficiency of fluid through the thermal storage promoted the development of new secondary fluids that could change phase during the flow, principle widely applied to the primary refrigerant fluid.

The thermal conductivity of a fluid can be improved if there is heat transfer in the form of latent heat of fusion, which is only possible with the introduction of phase change materials in the solution. The main distinction is in the ice slurry: a suspension of ice crystals dispersed in a carrier fluid composed of water and antifreeze (Melinder, 2007).

The ice slurry is a suspension of ice crystals dispersed in a carrier fluid comprising water and an antifreeze. These ice crystals act as phase change materials - PCM - which has the advantage of its latent heat of fusion as an energy resource. The thermophysical properties of the ice slurry are a function of geometry and size of the crystals with a diameter smaller than 1 mm (Egolf, Kauffeld, 2005).

The main attraction of the ice slurry is its high cooling capacity, resulting in reducing the size of the thermal energy tank, the mass flow in heat exchangers and pipe diameter (Melinder, 2007). Being a theme relatively new, there are several studies analyzing its characteristics. The thermophysical properties of the ice slurry are a function of ice applied, of antifreeze and of ice crystals concentration.

Environmental concerns are widely considered in new projects or upgrading existing systems. A heat transfer fluid can not harm the environment, since large quantities are demanded in industrial systems.

The antifreeze most widely used in ice slurry are ethanol and propylene glycol. The application of ethylene glycol is in disuse due to its toxicity, despite it having excellent thermophysical properties, being replaced by other alcohols. Propylene glycol and ethylene glycol alcohols are derived from petrochemical industries, i.e., by non-renewable sources and high impact on the environment. Ethanol is a product obtained by fermentation of carbohydrates of plant origin, which its production is sustained in the use of agricultural biomass and renewable.

Ethanol, unlike propylene glycol and ethylene glycol, which is corrosive, a factor that limits their application in large scale. The addition of anti-corrosion fluids is an additional cost in the use of ethanol; however, the commercial value of anhydrous ethanol is much less than the amount of pure propylene glycol.

The limited use of ethanol as antifreeze is based on studies conducted by Melinder (2007), it was found that when in solution with water to form a single secondary fluid has thermophysical properties inferior to other alcohols. However, the use of ethanol in ice slurry shows satisfactory properties but not compared with the use of propylene glycol, which is the alcohol used as antifreeze more today.

The purpose of this study is to compare ice slurries with ethanol and propylene glycol, quantifying the differences among thermophysical properties to check the feasibility in the use of ethanol, an alcohol derived from renewable sources.

2. METHODOLOGY

Data on the thermophysical properties of ice slurries with ethanol and propylene glycol were obtained using SecCool, a program developed by the Department of Mechanical Engineering at the University of Denmark, which contains a library with the physical properties of secondary fluids based mainly on the experimental parameters of ASHRAE (American Society of Heating, Refrigeration and Air-Conditioning Engineers), and Ake Melinder, researcher in the Department of Energy Technologies of the Royal Institute of Technology of Sweden.

For comparison, the solutions were analyzed at a temperature of -15 °C, where corresponding to the ice slurry tends to solidify, the value quoted for depending on the concentration of antifreeze. This analysis of temperature is within the levels committed in cold thermal storage systems. The ice mass content in ice slurries is 10%.

With the data from these conditions, it is measured in percentage terms the difference among their thermophysical properties: concentration of antifreeze, density, heat of fusion, thermal conductivity and dynamic viscosity. These properties are related to the ability to transfer heat and its resistance to flow, considering their thermodynamic and kinetic effects.

Therefore, with these data, a table has been developed to verify and explore the influence of alcohol in each ice slurry.

3. RESULTS AND DISCUSSIONS

From the data obtained in SecCool is shown in table 1 the numerical values of the thermophysical properties of fluids analyzed and their respective differences between the ice slurry with propylene glycol (PG) and ethanol:

Table 1: Thermophysical Properties of Ice Slurries with Ethanol and PG

Property	**Ice Slurry - Ethanol**	**Ice Slurry - Propylene Glycol**	**% IS-Ethanol/ IS-PG**
Alcohol Concentration (%)	24,36	32,92	-26,00
Density (kg/m³)	969,2	1025,3	-5,47
Heat of Fusion (kJ/kg)	39,83	38,95	2,26
Thermal Conductivity (W/m.K)	0,4989	0,4945	0,89
Dynamic Viscosity (cP)	21,32	27,13	-21,42

Each property evaluated will be discussed below:

3.1. Alcohol Concentration

Melinder (2007) found in his research that the addition of antifreeze in the water reduces its thermophysical properties in favour of reducing the melting point of water. These decrements are proportional to the concentration of antifreeze, i.e., the less alcohol cause better thermophysical properties in the solution, and consequently lower costs.

For the same minimum working temperature of the ice slurry, ethanol exerts its effects on the colligative properties of water. Even in single-phase solution with water, ethanol is more efficient than the propylene glycol to reduce the melting point. This is due to lower molar mass of ethanol (46 kg/kmol) compared to propylene glycol (76 kg/kmol) that best fits the small molecular weight of water (18 kg/kmol), resulting in stronger intermolecular interactions.

3.2. Density

Density is defined as the amount of mass existing in a unit of volume. It is desirable that secondary fluids also have the highest bulk density possible, since, in addition to decreasing the size of thermal storage tanks, they show more efficient heat transmission properties, in terms of thermal diffusivity properties (Baehr, Stephan, 2006).

Checking the data and their percentage differences, it found that the solution with ethanol is less dense due to the lower density of pure ethanol in relation to pure propylene glycol, respectively 789 kg/m³ and 1036 kg/m³ at 20 °C, which corresponds a difference of -23.84% ethanol compared to pure propylene glycol.

Even with this divergence between the densities of pure alcohols, when in solution with ice slurry the densities do not become insignificant, a difference of only -5.47% from the ice slurry with ethanol on the ice slurry with propylene glycol. Thus, the two solutions are considered equivalent in the density.

3.3. Heat of Fusion

The heat of fusion, also known as the enthalpy of fusion, is the change in enthalpy resulting from the addition or removal of heat from 1 kg of a substance to change its state from a solid to a liquid (melting) or the reverse processes of freezing.

The heat of fusion is more an energy resource for the fluid, where the heat absorbed by ice crystals causes greater heat flow, besides serving as a element of thermal energy storage.

Looking at the data for this property, there is no difference when using ethanol or propylene glycol, as this property is intrinsically linked to the own ice crystals dispersed in the fluid, not modified by the action of antifreeze.

3.4. Thermal Conductivity

Thermal conductivity is a transport property characteristic of each substance, indicating the rate at which a given material can transport energy under certain conditions of geometry and temperature. The mechanism of heat transfer in a solid is well defined and occurs by means of vibrations in its crystalline structure. In the case of metals, it is complemented by the movement of free electrons present in the network. The thermal exchange mechanism in liquid substances is similar to that of gases, that is, it occurs by molecular collisions and molecular diffusion (Çengel, 2007).

The ice slurry is a biphasic system in which the mechanisms involved in heat transfer are different from single-phase fluid: while for single-phase fluid the heat transfer is through exchange of sensible heat until it reaches the melting point or boiling the fluid; in ice slurry, there is heat exchange of sensible and latent heat, characterized as a heat transfer in a multiphase system, i.e., liquid phase (water-antifreeze) and solid phase (ice). The latent heat absorbed by ice crystals is higher than the sensible heat absorbed by the single-phase solution and is proportional to the mass concentration of ice.

The thermal conductivity on multiphase system is related to the fine ice particles dispersed in the carrier fluid and depends on its size, and it is function the area of heat transfer by ice crystals (Ticona, 2007). So thermal conductivity property of ice slurry is associated with ice crystals, because the latent heat of fusion and the biggest area of heat exchange are crucial for greater efficiency in heat transmission, and antifreeze added.

In this study, it found that there are not differences between the thermal conductivities of the ice slurry with ethanol and propylene glycol. At 25 °C, pure ethanol and propylene glycol have thermal conductivity of 0.18 W/m.K and 0.22 W/m.K (Dow Chemical, 2010), respectively. This difference is 10%, however, between ice slurries is a difference of 0.9%.

The explanation for this difference is negligible that even pure ethanol has lower thermal conductivity, its concentration in the ice slurry is less, hence the effect of the decrease of thermophysical properties is also smaller. This ensures its direct competition with propylene glycol in the influence of the properties as a function of the concentration of antifreeze.

3.5. Dynamic Viscosity

Dynamic viscosity is a transport property related to internal outflow resistance caused by cohesive forces between fluid molecules (Çengel, Cimbala, 2007). Ice slurry is analyzed as a multiphase system, showing different behavior from that exhibited by single-phase fluids submitted to outflow.

Unlike single-phase fluids, multiphase fluids require greater outflow velocities, mainly to sustain solid particles in suspension. Single-phase fluid outflow fluid is homogeneous for all velocities imposed, unlike multiphase fluids, which have heterogeneous behavior, exhibiting rheologic properties of non-Newtonian fluids (Crowe, 2006).

Ice slurry, a non-Newtonian fluid, is treated rheologically as a stable viscoplastic fluid (Niezgoda-Zelasko, Zelasko, 2009). Single-phase systems behave like a Newtonian fluid, with constant dynamic viscosity for a given pressure and temperature. Multiphase systems do not have constant dynamic viscosity, that is, there is no constant relationship between shear stress and shear rate. Moreover, temperature and pressure are considered to determine multiphase fluid viscosity (Chhabra, Richardson, 2008).

This analysis it is considered that the pressure conditions are the same for all fluids. The dynamic viscosity of the ice slurries analyzed is the apparent viscosity, whereas the ice slurries behave like a Newtonian fluid.

The high numbers of viscosities of the ice slurries are related to the size and geometry of ice crystals and their interactions with the carrier fluid (water + alcohol). Although they are microscopic crystals, they directly influence the viscosity and the difficulty of pumping.

The difference between the viscosity of the ice slurries with ethanol and propylene glycol is related to the viscosity of each pure alcohol. The viscosities of ethanol and propylene glycol are respectively, at 25 °C, 1.04 cP and 48.6 cP (Dow Chemical, 2010).

These values for pure alcohols and their concentrations directly influence the viscosity of the ice slurries. Thus, ice slurry with ethanol (which has lower viscosity and less pure concentration) is 21.4% lower viscosity than the ice slurry with propylene glycol.

Therefore, for the same flow conditions, the ice slurry with propylene glycol is needed more power for pumping and flow conditions more complex than the ice slurry with ethanol.

4. CONCLUSIONS

Analyzing the thermophysical properties of the ice slurries with ethanol and propylene glycol, it was seen that no property in the ice slurry with ethanol was lower than the one with propylene glycol.

The properties of pure ethanol and propylene glycol are very diverse, and each alcohol affect the thermophysical properties of water accordant their properties and intermolecular interactions.

With the lower concentration of ethanol in the ice slurry, and the thermodynamic properties of water transport are a little altered, unlike propylene glycol which significantly increases the viscosity and requires greater concentration to achieve the reduction of the melting point of water.

The large difference in viscosity between slurries using ethanol and propylene glycol is related to the energy consumption of each fluid pumping, in which ice slurry with ethanol requires less pumping power implies that a fluid for better energy efficiency.

Because ethanol comes from renewable energy sources, its use is more feasible in technical, economic and environmental fields; unlike propylene glycol which is obtained by the petrochemical industries (non-renewable) at a price effectively higher than ethanol.

The fact that ethanol be corrosive not necessarily in the disposal of its use, because the addition of anticorrosion additives or corrosion inhibitors to circumvent this problem, valuing it as viable for antifreeze in ice slurry.

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