

## EFFECTS OF ADDITION GLYCEROL CO-PRODUCT OF BIODIESEL IN THE THERMOPHYSICAL PROPERTIES OF WATER-GLYCEROL SOLUTION APPLIED AS SECONDARY COOLANT

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**Abstract.** *This paper evaluates the effects of glycerol concentration on thermophysical properties of water-glycerol solution applied as a secondary coolant in refrigeration systems by expansion-indirect. The processing of triglycerides for biodiesel production generates glycerol as co-product and there are concerns of environmental and economic order on the surplus of glycerol. The addition of glycerol in water alters the colligative and thermophysical properties (melting point, mass, specific heat, thermal conductivity and dynamic viscosity). There are studies that prove the feasibility of using glycerol as an additive and this paper has the goal to verify the changes on properties compared with pure water. This comparison was made from data obtained by the software simulation and they analyzed using graphs and tables. It was shown that glycerol increases the density and dynamic viscosity, and reduces the specific heat and thermal conductivity. This behavior of water-glycerol solution is proportional to the mass concentration of glycerol and it is justified because the glycerol has low values of specific heat, thermal conductivity and high viscosity when compared with water. Despite the losses in the thermophysical properties, glycerol shows its potential application, because of the cryoscopic effect and it is a non-toxic substance at low cost.*

**Keywords:** *Secondary Coolant, Glycerol, Thermophysical Properties, Biodiesel*

### 1. INTRODUCTION

Glycerol (1,2,3-propanetriol) is an alcohol trihydric alcohol, odorless, colorless, sweet taste and hygroscopic. It is obtained through processes of reactions with fatty acids, or from the synthesis of propylene from petroleum. Glycerol has the following thermophysical properties (table 1):

Table 1. Thermophysical Properties of Glycerol at 20 °C (Çengel, 2007)

Density	1,264 kg/m <sup>3</sup>
Specific heat	2.386 kJ/kg.K
Thermal conductivity	0.2860 W/m.K
Dynamic viscosity	1,519 cP
Melting Point	18.2 °C
Boiling Point	290 °C

Glycerol has infinite solubility in water and alcohols (Solomons, Fryhle, 2007), slightly soluble in diethyl ether, ethyl acetate and dioxane, and insoluble in hydrocarbons (Knothe et al, 2005). By owning these properties, glycerol is used as feedstock in various industrial applications, especially in the pharmaceutical, biochemical and food industries. The term "glycerin" is applied to the glycerol containing certain impurities: to levels below 5%, glycerin is considered purified and above 5% is considered crude, requiring filtration and purification to be marketed (Bertozzo et al, 2009).

Currently, large quantities of glycerol are produced by the biodiesel manufacture, a co-product of the process. As biodiesel production is up, the excess of glycerol is a factor uneasy. The market is not prepared to absorb this large surplus, despite its growing demand as feedstock in processing industries. There are concerns about what to do with this co-product and may generate serious environmental and economic problems (Knothe et al, 2005).

For each 100 kg of biodiesel produced, there is 10.5 kg of glycerol as a co-product (Pagliaro, Rossi, 2008). In 2007, Brazil produced over 400 million liters of biodiesel, almost 50 million liters of glycerin. The Brazilian production in 2009 was 1.6 billion liters of biodiesel, generating 200 million glycerin only in Brazil (Anp, 2010).

The future of this excess of glycerol is not yet defined and several studies are being developed. Knothe et al (2005) explain, "Glycerol is seldom seen in the crystallized state because of its tendency to supercool and its pronounced freezing point depression when mixed with water". Because it is an alcohol with low vapor pressure, glycerol alters the colligative properties of water, increasing its boiling point and lowering the melting point in solution (Dow Chemical, 2010). A mixture of 66.7% and 33.3% glycerol water mixture forms a eutectic freezing point with a minimum temperature of -46.5 °C. In figure 1, it is shown graphic temperature versus mass concentration for glycerol:

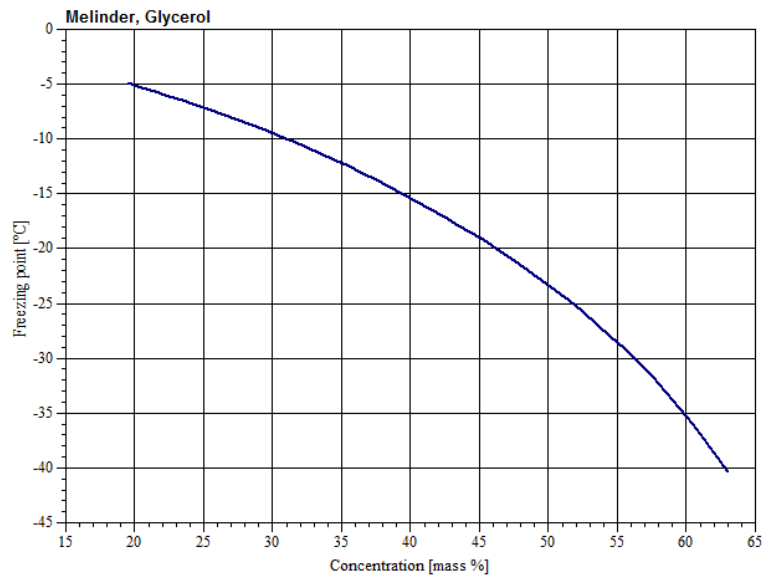


Figure 1. Phase change curve (melting point) as a function of the concentration of glycerol.  
Source: SecCool Software.

These properties are desirable in a heat transfer fluid (Fink, 2003) and, according to Medeiros and Barbosa (2010) is possible the use of glycerol as an additive in thermal fluids, mainly as antifreeze in refrigeration processes by expansion-indirect, forming with the water a secondary coolant.

The use of secondary coolants in indirect cooling systems is expanding due to the possible implementation of cool thermal storage, supported by policies for efficient use of electricity (ASHRAE, 2008; Procel, 2006). The use of glycerol as an antifreeze is incipient, because there are already established antifreeze additives available in the market, for example, ethylene glycol. The attractiveness of the glycerol is justified because it is a nontoxic compound with properties similar to others alcohol additives, and with high availability at low cost (Pagliaro, Rossi, 2008).

Secondary coolants should show good thermodynamic and transport properties, and other factors, such as being nontoxic, nonflammable, chemically stable, with little or no corrosion activity (Dincer 2003; Stoecker, 1998). The main thermophysical properties for secondary coolants are melting point, density, specific heat, thermal conductivity and dynamic viscosity. Water has thermophysical properties that satisfy its full use as a secondary fluid, except for the fact that its melting point occurs at 0 °C. Refrigeration processes require temperatures lower than the melting point of water (Dossat, Horan, 2001), and water-glycerol solution lets be employed in these lower temperatures from cryoscopic effect.

Ideal for a secondary fluid is that it has high density, specific heat and thermal conductivity, and low values for the melting point and dynamic viscosity (Melinder, 2007). The addition of antifreeze in the water reduces the thermophysical properties of the solution compared to pure water: there are losses in the thermal conductivity and specific heat (ASHRAE, 2009, Melinder, 2007). These losses cause fluid in a lower thermal inertia, reducing the ability to transfer heat and thermal energy storage.

Thus, this study analyzes and quantifies the changes in thermophysical properties that glycerol causes when in solution with water, analyzing the effects depending on the concentration of alcohol, assuming that the larger its quantity the lower the melting temperature of the solution.

## 2. METHODOLOGY

The data about thermophysical properties of secondary coolants and ice slurries were obtained by SecCool, software developed by the Department of Mechanical Engineering at University of Denmark. This software contains a library with thermophysical 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 at the Department of Energy Technology at Royal Institute of Technology in Sweden.

The samples, water-glycerol solutions, were classified from the mass concentrations of glycerol, that ranging between 20% and 50%, with intermediate values of 30% and 40%. These concentration values correspond to most commercial applications of secondary fluids in thermal storage systems. The properties become separated in thermodynamic properties and transport properties. The thermodynamic properties are density and specific heat, and

transport properties are thermal conductivity and dynamic viscosity. These properties were compared with the properties of pure water, reference for research.

The qualitative analyses refer to the graphs, by SecCool, containing each thermophysical property behavior versus glycerol concentration, in the temperature between -25 °C and 10 °C. The quantitative analyses are from numerical values of properties at temperature of 1 °C, investigating the removal of the properties relative to pure water.

Graphics and tables were made to verify and to explore the changes in thermophysical properties caused by the addition of glycerol in water.

### 3. RESULTS AND DISCUSSION

From the data obtained in the SecCool, numerical values of the thermophysical properties of fluids analyzed are shown in Table 2:

Table 2. Thermophysical properties of the samples. Source: SecCool Software

Sample at 1 °C	Melting Point (°C)	Density (kg/m <sup>3</sup> )	Specific heat (kJ/kg.K)	Thermal Conductivity (W/m.K)	Dynamic Viscosity (cP)
Pure Water	0.00	999.9	4.213	0.5642	1.731
Water/Glycerol-20%	-5.12	1,051.5	3.826	0.4985	3.282
Water/Glycerol-30%	-9.48	1,077.9	3.610	0.4665	4.647
Water/Glycerol-40%	-15.39	1,106.8	3.358	0.4339	7.532
Water/Glycerol-50%	-23.32	1,135.6	3.127	0.4039	13.32

The melting point for all water-glycerol solutions are below the pure water, because, as previously mentioned, the glycerol lowers the melting point by cryoscopic effect due to its low vapor pressure and higher intermolecular interaction with water

With these data, except the melting point, each thermophysical property was analyzed separately according to the concentration of glycerol, checking its influence on the solutions.

#### 3.1 Density

As can be seen in Table 2, the density of water at a temperature of 1 °C is 999.9 kg/m<sup>3</sup>. The solutions were higher for the same temperature, and the increment is proportional to the mass concentration of glycerol

For the purpose of initial comparison, the density of pure glycerol is 1,264 kg/m<sup>3</sup> at 20 °C (Çengel, 2007). The water at this temperature shows density of 998.3 kg/m<sup>3</sup>, by SecCool Software. One can say a priori that glycerol alters the density to be denser than water, even in small quantities.

Based on this initial premise, the result for the density of each sample was expected. It was found that with the minimum concentration in mass (20%), the water-glycerol density is increased 5.16%; with the maximum concentration of 50%, the increase is 13.57%.

Figure 2 represents the curves of density variation for each concentration of glycerol from melting point to 10 °C of each sample. It is noticed that the curves of the water-glycerol density are equidistant from each other. The curves showed a slight incline, which density tends is function temperature, but this variation is very small and can be neglected without many problems.

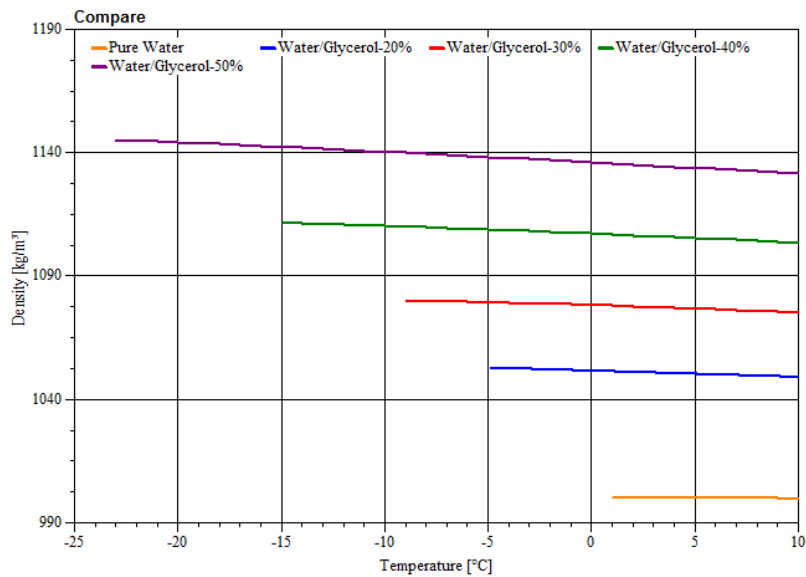


Figure 2. Density variation of the samples. Source: SecCool Software.

### 3.2 Specific Heat

One of the most relevant properties in thermodynamics is the specific heat. It is the energy required to raise the temperature of a unit mass of a substance by one degree (Çengel, Boles, 2006). The value of the specific heat of substances is a direct function of temperature, but variations caused by the effect of temperature are small, and in some cases be neglected. The specific heat undergoes abrupt change in value when a substance changes phase.

The numerical value for the specific heat for each solution is critical for selection and use as secondary coolant. In this study, we analyzed the variation of that property in relation to the concentration of glycerol used. Figure 3 is shown the curves of specific heat for each concentration of alcohol.

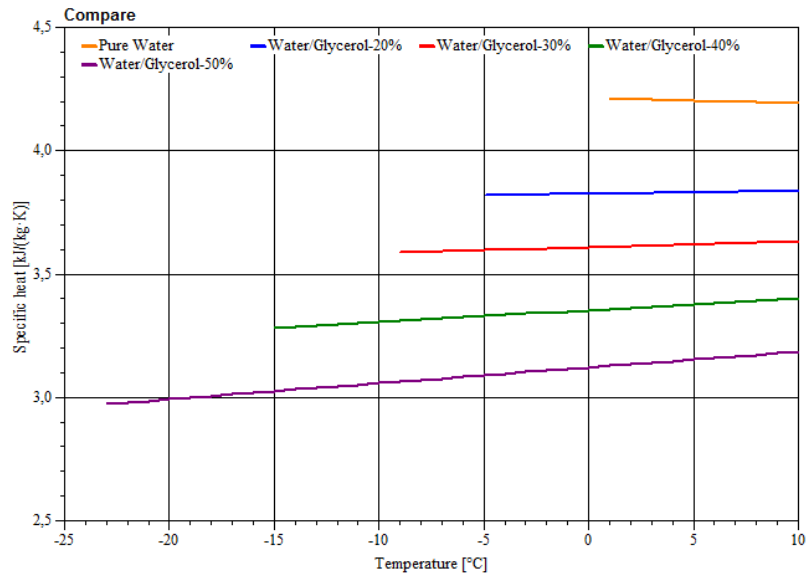


Figure 3. Curves of specific heat of each sample. Source: SecCool Software.

Evaluating the data in table 2 and the curves of Figure 2, it appears that the greater the mass concentration of glycerol increased the reduction of specific heat. Considering the values of specific heat at the temperature of 1 °C (Table 2), the largest reduction is 25.78% to 50% glycerol, and the lowest is 9.19% to 20% glycerol.

These reductions in the specific heat heater modify the effect of the solutions, thus having a lower thermal inertia. The specific heat of solutions varies with temperature, and this effect was stronger for 50% concentration.

### 3.3 Thermal Conductivity

Thermal conductivity is a transport property characteristic of each material, which indicates the rate at which a given material can transport energy under certain conditions of geometry and temperature. The mechanism of heat transfer in fluid condition is more difficult to describe because they are not yet well defined (Incropera et al, 2006). It is estimated that the mechanism of heat transfer fluids is similar to those of gases, or by molecular collisions and molecular diffusion (Çengel, 2007)

Besides the effects of the status of the material, the thermal conductivity is a function of temperature too. For non-metallic liquids, the thermal conductivity generally decreases with increasing temperature. The water and pure glycerol are examples of exceptions to the rule, which their behavior is different from the vast majority of liquid fluids.

In the case of fluids analyzed, the variation of the thermal conductivity of the mixture is a function of the concentration of glycerol for a given temperature. In all samples, the numerical value of thermal conductivity decreased with increasing mass concentration of glycerol (Figure 3).

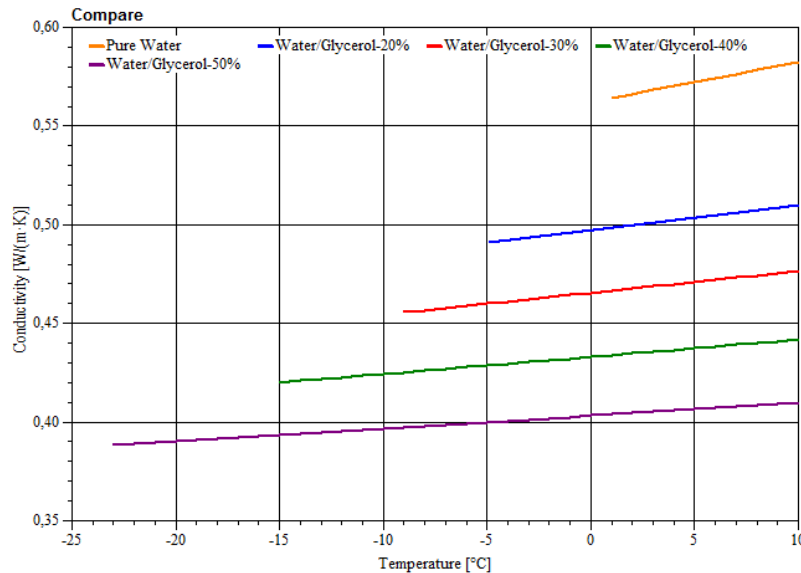


Figure 3. Thermal Conductivity of all samples. Source: SecCool Software.

The pure glycerol at 20 °C has a thermal conductivity 52.31% smaller than the thermal conductivity of water at the same temperature (0.5997 W/mK). Thus, observing the graph above, one sees that the more glycerol is added the greater the reduction in thermal conductivity. At the concentration of glycerol 20%, the difference between their values is 11.64%. For 50% glycerol, the difference grows to 28.41% when compared to pure water.

In all the curves shown in Figure 3 as the temperature decreases the thermal conductivity is reduced due to lower molecular vibration of molecules.

### 3.4 Dynamic Viscosity

The dynamic viscosity is a transport property related to the internal resistance to fluid flow caused by cohesive forces between the fluid molecules (Çengel, Cimbala, 2007). It directly influences the flow conditions and the pumping power: the lower the viscosity, less energy is required for this flow.

Water has a dynamic viscosity of 1.00 cP at 20 °C, while the glycerol at the same temperature has a viscosity of 1,519 cP. This abrupt difference in viscosity will directly influence the viscosity of water-glycerol solution, causing it to provide high values of viscosity.

Observing the data in Table 2, for concentration of glycerol 20%, the gain in viscosity is 89.60%, at 1 °C. For water/glycerol-50%, the increase in dynamic viscosity at the same temperature reaches the incredible 669.5%! Figure 4 is shown the curves of dynamic viscosity in a semi-log graphic:

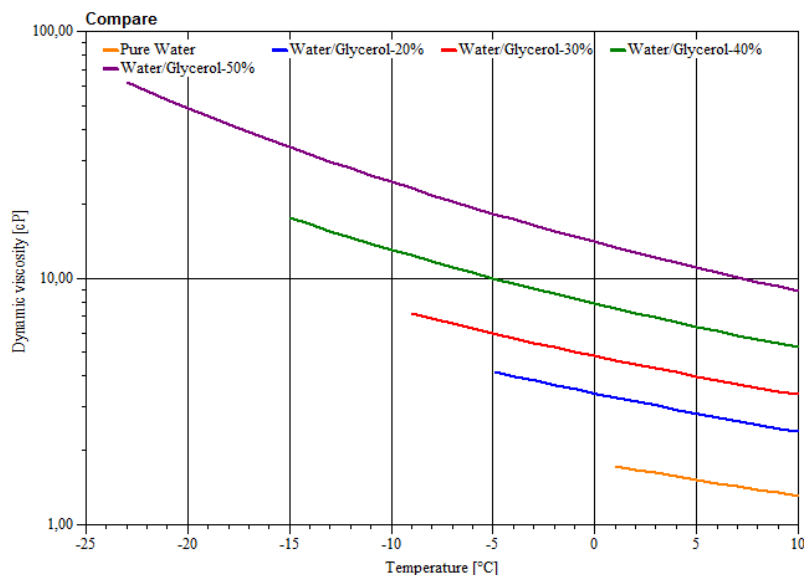


Figure 4. Dynamic viscosity of the samples, semi-log graph. Source: SecCool Software

The situation is further complicated when referring to temperature decreases in the viscosity increases considerably. The increased viscosity, inversely proportional to temperature, it becomes more evident when the concentration of glycerol increases. This is true because the viscosity of glycerol at 20 °C is “only” 1,500 times larger than that of water.

This high viscosity of the solutions requires a high power pumping, requiring higher energy consumption and more expensive pumps, resulting in a higher cost in pumping.

#### 4. CONCLUSIONS

With the growing demand for green energy, biodiesel comes as an ecologically correct fuel. However, the large production of glycerol resulting from the obtaining process of biodiesel raises many concerns about the final fate of this product.

There are no still routes defined for the full use of glycerol, thus resulting in many alternatives to its use. The application as an additive modifier of the colligative properties of water is one possible path, especially in the growing field of industrial refrigeration.

Therefore, it was shown that the changes that glycerol causes the water are acceptable considering the physicochemical nature of the product, justified since the glycerol compared with water, have low values of specific heat, thermal conductivity and a high viscosity. The only exception is the dynamic viscosity, which is quite higher, resulting in increased energy costs.

In this context, the characterization of thermophysical properties discussed above, on cryoscopic effect, enhances the water-glycerol solution as a secondary coolant, leading to the attainment of a more detailed study on the technical and economic feasibility for commercial application glycerol as an additive for thermal fluids.

#### 5. ACKNOWLEDGEMENTS

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