

Resurseffektiva kyl- och värmepumpssystem samt kyl- och värmelager

P03: Adsorption corrosion inhibitors, green corrosion inhibitors and alternative secondary fluids for indirect refrigeration system

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Förord

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Sammanfattning

Flertalet typer av köldbärare är vattenbaserade lösningar av organiska eller oorganiska ämnen (t.ex. alkoholer eller salter) och har använts länge i olika indirekta kylsystem och värmepumpar. Kommersiella köldbärare är komplexa blandningar som innehåller korrosionsinhibitorer, pH-justerande medel, antioxidanter, antiskummedel, stabilisatorer, färgämnen m.m. Dessa tillsatser har en mindre väl känd inverkan på köldbärarens termofysikaliska egenskaper. Tyvärr har många av de idag använda köldbärarna korrosiv karaktär men det är möjligt att minimera korrosionsriskerna genom att använda rätt typ av inhibitorer.

Ett av målen i projektet var att fortsätta utvecklingen av en alternativ och mer miljövänlig typ av alkoholbaserad köldbärare, en optimal blandning av etanol (EA) och isopropanol (PA), som ger högre flampunkt och bättre termofysikaliska egenskaper. De erhållna resultaten av dessa studier visar att blandningar med upp till 2 vikt-% isopropanol och 1 vikt-% butanol (EA18 + PA1.6 + BA0.4) och (EA18.4+PA1.6), ger bäst termofysikaliska egenskaper. Denna studie visar att den kemiska karaktären och koncentrationen av olika denatureringsmedel kan påverka de termofysiska egenskaperna. Speciellt etanol med 1.6 vikt-% isopropanol (EA18.4+PA1.6) visade bäst egenskaper med avseende på värmeöverföring (9% högre) och tryckfall (3 % lägre) jämfört med EA20. Blandningen EA18 + PA1.6 + BA0.4 ger upp till 10 % högre värmeöverföringskoefficient och 2.7 % lägre tryckfall än EA20. Dessa resultat hjälpte att i en svensk kommersiell produkt justera koncentrationen av isopropanol (7-9 vikt-%) och 2 vikt-% n-butanol till 8 vikt-% isopropanol och 2 vikt-% n- butanol.

Ett annat mål var att undersöka olika typer av adsorberande och traditionella (oxidbildande) korrosionsinhibitorer kompatibla med etanolbaserade köldbärare. Resultaten visar att vissa korrosionsinhibitorer har en negativ påverkan på egenskaper som fryspunkt, värmeledningsförmåga och specifik värmekapacitet men inte viskositet vilket man trodde förut. Denna studie visar att bensotriazol och 2-merkaptobensotiazol verkar vara de mest lovande korrosionsinhibitorerna för etanolbaserade köldbärare. En mer miljövänlig korrosionsinhibitor som natriumglukonat verkar ha väl stor inverkan på värmeledningsförmåga (14% lägre) och kanske inte borde använda alls. Dessa studier hjälpte till att se en koppling mellan molekylstruktur och koncentration av olika oorganiska och organiska korrosionsinhibitorer. Dessutom hjälpte studien att lansera en bioetanol produkt med bensotriazol som korrosionsinhibitor. Tester av värmeledningsförmåga för korroderade kopparprover visade att provet behandlat med natriumbensoat hade en lägre värmeledningsförmåga ca. 364 (± 1.5) W·K⁻¹·m⁻¹ vid en temperatur av 25 °C, vilket var ca 8% lägre än referensen. Ytterligare studier rekommenderas för att undersöka andra metaller inkl. aluminium för att jämföra resultaten.

Tester gjordes för olika syntetiska oljor (isoparaffiner) för att analysera hur sammansättning, fraktioneringsmetoder och molekyllängden kan påverka slutproduktens termofysikaliska egenskaper. Det visade sig att molekyllängden kan påverka tillämpningsområdet signifikant och korta kedjade isoparaffiner är de mest lämpliga för tillämpningar vid låga temperaturer. Ytterligare tester utfördes för att välja ut de mest lovande isoparaffinblandningarna för olika applikationer och de första kommersiella isoparaffinbaserade produkter lanserades på den svenska marknaden under projektet. Resultaten visade att den nya generationen av isoparaffiner med frystemperaturen på -50 °C eller lägre vid mycket låga temperaturer hade signifikant lägre viskositet (mellan 75% och 98%) jämfört med 60 vikt-% propylenglykol och 60

vikt-% etylenglykollösning. Således kan isoparaffiner bli ett intressant alternativ för kyltillämpningar vid mycket låg temperatur.

Resultaten visar att olika typer av katjoner (t.ex. litium, natrium, ammonium, cesium) påverkar egenskaper på olika sätt och mer forskning behövs för att hitta framtidens köldbärare. Bland alla undersökta alternativa formiatsalter och acetatsalter visades cesiumformiat ge längst viskositet och ammoniumformiatlösningar ger bäst prestanda vid låga temperaturer genom att ge låg viskositet samt hög specifik värmekapacitet och värmeledningsförmåga. Cesiumacetat visade sig vara ett bra och billigare alternativ till cesiumformiat. Goda egenskaper hos cesiumacetat är hög densitet och låg viskositet men värmeövergångstalet är ca. 16% lägre än cesiumformiat. Dessutom visade sig cesiumformiat vara minst korrosiv bland alla formiat- och acetatsalter.

Utredningen av de viktigaste termofysikaliska egenskaperna för blandningar av kaliumacetat, kaliumformiat, propylenglykol och etylenglykol med vatten slutfördes också. Resultaten visar några avvikelse jämfört med referensdata baserade mest på kommersiella produkter med olika additiver och kan bidra till förbättring av tabeller för rena blandningar med vatten samt komplettera data för vissa koncentrationer.

Summary

Most types of secondary fluids are aqueous solutions of organic or inorganic substances (e.g. alcohols or salts) and have been used for a long time in different indirect refrigeration systems and heat pumps. Commercial secondary fluids are complex mixtures that also contain corrosion inhibitors, pH adjusting agents, antioxidants, antifoams, stabilizers, dyes, etc. The effect of these additives on the thermophysical properties of the secondary fluids have been little known. Many of the currently used secondary fluids have unfortunately a corrosive character, but it is possible to minimize corrosion risks by using the correct corrosion inhibitor.

An important objective of the project was to continue the development of an alternative and more environmentally friendly type of alcohol based secondary fluids, an optimal mixture of ethyl alcohol (EA) and propyl alcohol (PA), which should give higher flash point and better thermophysical properties. The results of these studies showed that mixtures with up to 2 wt-% of propyl alcohol (EA18 + PA1.6 + BA0.4) and (EA18.4+PA1.6) give the best thermophysical properties , ie. highest heat transfer (up to 9 %) and lowest pressure drop (up to 3 %) compared to pure ethyl alcohol - water. The obtained results show that the chemical nature and concentration of different denaturing agents with ethyl alcohol can affect the thermophysical properties. Blend EA18 + PA1.6 + BA0.4 gives the best properties, ie. highest heat transfer (up to 10%) and lowest pressure drop (up to 2,7 %) than EA20. These results helped adjust a concentration of propyl alcohol (7-9 wt-%) and 2 wt-% n-butyl alcohol in a Swedish commercial product to exactly 8 wt-% propyl alcohol and 2 wt-% n-butyl alcohol.

Another important goal was to investigate different types of adsorption and traditional (oxide forming) corrosion inhibitors compatible with water - ethyl alcohol based secondary fluids. Results show that some corrosion inhibitors significantly affect properties such as freezing point, thermal conductivity and specific heat capacity but not viscosity as previously thought. This study showed that benzotriazole and 2mercaptobenzothiazole appear to be the most promising corrosion inhibitor for ethyl alcohol based secondary fluids. More environmentally friendly corrosion inhibitors like sodium gluconate appear to have a significant effect on thermal conductivity (14%) lower thermal conductivity) and should not be used at all. These studies helped to understand a relation between molecule structure and concentration of various inorganic and organic corrosion inhibitors as well as helping one of project partners to create a commercial alcohol product with benzotriazole as a corrosion inhibitor. The thermal conductivity tests for corroded copper specimens showed that specimen treated with sodium benzoate had a thermal conductivity of 364 (± 1.5) W K⁻¹ m⁻¹ at temperature of 25 °C, which was about 8 % lower than the references of untreated copper specimen. Further studies are suggested to investigate other metal alloys and aluminum in order to compare the results.

The tests were conducted for different synthetic iso-paraffins to analyse how composition, fractionation methods and molecular weight can affect the thermophysical properties of the final product. It was found that the molecular weight can significantly affect the thermal properties and short chained iso-paraffins are the most suitable for low temperature applications. Further tests helped to select the most promising iso-paraffin blends for different applications and during the project the first commercial iso-paraffin based products were launched on the Swedish market. The results showed that the new generation of iso-paraffins with a freezing temperature of -50 °C or less at these very low temperatures had significantly lower viscosity (between 75 and 98 %) compared to 60 wt-% propylene glycol and 60 wt-% ethylene glycol solution. Thus, iso-paraffins can be an interesting alternative for cooling applications with very low temperatures.

The results showed that different types of cation (e.g lithium, sodium, ammonium, and cesium) can affect properties in different ways and more research is needed to find future salt based secondary fluids. Among all the investigated alternative formate and acetate salts, cesium formate and ammonium formate solutions showed the best performance at low temperatures by providing the lowest viscosity in case of cesium formate and low viscosity, high specific heat capacity and thermal conductivity in case of ammonium formate. Cesium acetate proved to be a good and cheaper alternative to cesium formate. The good thermophysical properties of cesium acetate are high density and low viscosity but the heat transfer is about 16% lower than cesium formate. In addition, cesium formate was found to be least corrosive among all formate and acetate salts tested.

The investigation of the most important thermophysical properties of mixtures of potassium acetate and potassium formate was completed. The results showed some deviation with reference data that are mostly based on commercial products with different additives. Moreover, these data may contribute to the improvement of tables for pure mixtures of potassium formate, potassium acetate, propylene glycol and ethylene glycol and provide data for specific concentrations.

NOMENCLATURE

$\Delta H'$	head loss (m·m ⁻¹)
BA	n-butyl alcohol
BHE	Borehole Heat Exchanger
BTA	benzotriazole
BtL	Biomass to Liquid
С	concentration (%)
CMC	Critical Micelle Concentration (-)
ср	specific heat capacity (J·kg ⁻¹ ·K ⁻¹)
CsAc	cesium acetate
CsF	cesium formate
DSC	Differential Scanning Calorimetry
EA	ethyl alcohol
EG	ethylene glycol
f	freezing
GSHP	Ground Source Heat Pump
GtL	Gas to Liquid
h	heat transfer coefficient (W·m ⁻² ·K ⁻¹)
k	thermal conductivity (W·m ^{-1.} K ⁻¹)
KAc	potassium acetate
KF	potassium formate
LiF	lithium formate
Μ	mole
MA	methyl alcohol
MBTA	2-mercaptobenzothiazole
MEK	methyl ethyl ketone
MIBK	methyl isobutyl ketone
NaF	sodium formate
NH4Ac	ammonium acetate
NH4F	ammonium formate
PA	propyl alcohol
PE	Polyethylene
PG	propylene glycol
Re	Reynolds number (-)
SB	sodium benzoate
SG	sodium gluconate

SM	sodium molybdate
Т	temperature (°C)
wt-%	weight concentration (-)
μ	dynamic viscosity (mPa·s)
ρ	density (kg·m ⁻³)

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Background

Royal Institute of Technology, Energy Technology, Department of Applied Thermodynamics, has for more than 20 years been an international leader in the field of refrigeration systems and heat pumps. An international handbook by Åke Melinder about thermophysical properties of secondary fluids has been published in English for the International Institute of Refrigeration, IIR and the Swedish Society of Refrigeration. Several Swedish and English reports, scientific publications and books have also been produced and part of the work was funded by the Swedish Energy Agency. To help to design and build energy efficient indirect systems employees at the department at KTH and a number of experts from the refrigeration sector have produced a handbook (in both Swedish and English) that deal with different aspects of indirect refrigeration systems with secondary fluids.

Another project supported by Kylbranschens Samarbetsstiftelse, KYS, Energy Administration EFFSYS+ and various industrial partners have conducted research on the impact of corrosion inhibitors and other additives on the heat transfer and thermophysical properties of various secondary fluids used in the indirect cooling systems. This research has resulted in better knowledge of different secondary fluids without additives and ethyl alcohol with the addition of denaturing products.

Introduction

One method to significantly reduce the refrigerant charge is to use an indirect refrigeration system with a secondary fluid circuit (Palm 2007). Other advantages of the indirect refrigeration systems are: low risk of refrigerant leakage; the primary refrigerant system is placed in the machine room; easy and precise control; no oil recovery problems; natural refrigerants such as ammonia and hydrocarbons can be used; easy maintenance and no technical limitations on the distance.

A secondary fluid is a medium used to transport and transfer heat between two bodies due to temperature difference. Water is the most common type of secondary fluid, but it cannot be used when the operating temperature is below +3 °C due to its high freezing temperature of 0 °C (Aittomäki and Kianta, 2003). However, various freezing point depressants can be added to water, e.g.; ethyl alcohol, methyl alcohol, ethylene glycol, propylene glycol, calcium chloride, potassium acetate, potassium formate and potassium carbonate. Commercially available secondary fluids are complex mixtures containing corrosion inhibitors, pH adjusting agents, antioxidants, anti-foaming agents, stabilizers, colorants, etc. These additives can stabilize and improve the fluid performance but also affects the thermophysical properties.

Unfortunately, many of the currently used secondary fluids have corrosive nature but it is possible to minimize corrosion risks by using the right inhibitors. Additives stabilize and improve performance in some respects, but affect the secondary fluid's thermophysical properties in a way that is not well known. Additionally, new type of adsorption corrosion inhibitors belonging to the so-called "green corrosion inhibitors group" that are in 100% organic/plant based are being introduced. Plants are sources of naturally occurring substances with complex

molecular structures that have different chemical, biological and physical properties. These naturally occurring substances are used because they are environmentally acceptable, cost-effective and are easy to find in nature. These advantages are the reason for the use of extracts of some plants and products as corrosion inhibitors for metals. Various plant extracts that can be used as the corrosion inhibitors are generally called green corrosion inhibitors.

Ethyl alcohol (ethanol) based aqueous solutions are commonly used secondary fluids in geothermal heat pumps in Sweden. The available ethyl alcohol based commercial products contain up to 12% denaturing agents but no corrosion inhibitors. Measurements recently performed at KTH shows that the presence of these additives in ethyl alcohol enhanced the thermophysical properties, in particular the specific heat capacity, thermal conductivity and dynamic viscosity. So far, ethyl alcohol based secondary fluids in Sweden have not contained corrosion inhibitors. Further studies are needed to find suitable corrosion inhibitors that can be used instead of or together with denaturation products to effectively protect the system against corrosion.

Alternative secondary fluids such as environmentally friendly synthetic iso-paraffins and ionic liquids (different formate and acetate salts) were explored. The first results show that these iso-paraffins have a low dynamic viscosity at low temperatures and have wider operating temperature range compared to aqueous solutions of glycols as well as silicone oils. Synthetic iso-paraffins can be an interesting alternative to expensive silicone oils as heat transfer fluids at low temperatures. Advantages of isoparaffins are non-corrosive nature, a relatively high flash point and lubrication properties. Some types of complex organic salts of formate and acetate was tested. Initial results show that organic acetate salt can have better properties than potassium acetate.

Objectives

For the project, the following goals and objectives were formulated:

1. Validate properties of ethyl alcohol and propyl alcohol mixtures by measuring the thermophysical properties.

2. Identify and test potential adsorption corrosion inhibitors and green corrosion inhibitors compatible with ethyl alcohol as well as to investigate potential green corrosion inhibitors to replace dangerous corrosion inhibitors belonging to the Carcinogenic Mutagenic and Reprotoxic (CMR) group.

3. Validate the effect on the heat transfer process of corrosion inhibitors that form physical barriers and adsorption corrosion inhibitors.

4. Validate the thermophysical properties of various synthetic iso-paraffins and organic salts with applications at both low and high temperatures.

5. Complete measurement and investigation of the major thermophysical properties of glycols and salts with additives.

6. Help manufacturers to improve their products by providing the thermophysical properties of commercially available secondary fluids products with different additives and corrosion inhibitors, and to provide more information to customers as a basis for dimensioning of indirect refrigeration systems and their components.

Methodology

The investigation of different thermophysical properties of secondary fluids such as freezing point, density, specific heat capacity, thermal conductivity and dynamic viscosity has been carried out at the KTH Royal Institute of Technology, Department of Energy Technology, Division of Applied Thermodynamics and Refrigeration.

Freezing point measurements

The measurements of the freezing point were performed using two different methods: lab build apparatus and differential scanning calorimeter (microDSC evo7 from Setaram Instrumentation). Firstly, the freezing point temperatures of different samples was tested using the lab build freezing apparatus consisting of Sanyo Ultra Low freezer (temperature range between -15 and -90 °C), an Agilent 34970A Data Acquisition unit, a computer connected to the acquisition unit and a freezing unit specially designed at KTH for these kind of tests.

The freezing unit consists of nine identical plastic containers (volume 100ml) arranged in the circle, fitted to a Plexiglas plate and enclosed from the top with a closing plate as shown in Fig.1. The whole section is supported by four metal legs and a bottom plate to ensure that containers are not directly in contact with the bottom of the freezer. Additional two thermocouples are attached to the freezing unit to measure the conditions in the freezer during each test. All eleven thermocouples are calibrated with accuracy of $\pm 0.1^{\circ}$ C and all tests are repeated three times. The sample temperature is recorded every second until it reaches the complete solidification (freezing) and freezer temperature is set max 5K below the expected freezing point. In this way the freezing point temperature is predefined and later more accurate long tests using microDSC are conducted.



Fig. 1 The lab build freezing apparatus.

The Differential Scanning Calorimetry (DSC) method is used to measure both the freezing point as well as specific heat capacity with higher accuracy. The measurements are carried out using a microDSC evo7 model from Setaram Instrumentation shown in Fig.2.



Fig. 2 microDSC evo7 Setaram Intsrumentation.

Differential Scanning Calorimetry (DSC) method is a thermo-analytical technique in which the difference in the amount of heat required to increase the temperature of sample and reference is measured simultaneously. First, the water sample was tested in order to define the testing parameters, using continuous standard zone mode at four different heating and cooling scanning rates: 0.025; 0.05; 0.1 and 0.15 K min⁻¹. The difference in results for the three first scanning rates was only 0.01 K, thus, the scanning rate of 0.1 K min⁻¹ was chosen. The sample volume was always kept constant (750µl) and each test was repeated three times. The accuracy of temperature measurements for the instrument according to the manufacturer is set to be \pm 0.1 K. Each sample was subjected to two cooling (freezing) and heating (melting) cycles to compare the temperatures and the latent heat of fusion.

Specific heat capacity measurements

The specific heat capacity was measured as well using microDSC evo7 from Setaram Instrumentation. All tests were performed in cp continuous mode with heating scanning rate of 0.05 K·min⁻¹ in the temperature range between -45 and 40 °C and the sample volume was always kept constant (750 μ l). The experimental results for water were up to 1.5 % higher than tabulated NIST data and the standard deviation for five tests for water was about 24 J·kg⁻¹·K⁻¹ in whole temperature range.

Density measurements

The density measurements were performed using both pycnometers and aerometers in this project. Aerometer, as shown in Fig.3, is relatively simple instrument that is designed to measure the density and weight of a liquid at 15.6 and 20 °C according to ISO 17025 with accuracy ± 0.01 g·ml⁻¹. The working principle of an aerometer is based on Archimedes' law, which states that the upward force of a body immersed in liquid will equal the mass of the liquid that is displaced. Due to the fact that the weight within the aerometer is constant it is possible to measure the density of liquids based on how deep the device sinks into the element (the deeper the aerometer sinks into the liquid, the greater the density and weight). The density is determined by making note of where the scale penetrates the surface of the tested fluid (note: minimum sample volume is 200 ml). Note that the accuracy of the density measurement using aerometers is set to be ± 1 %.



Fig.3 Aerometer placed in tested liquid.

Fig.4 Different types of pycnometers.

A pycnometer, as shown in Fig.4, is another way to obtain accurate measurements of relative density with a high accuracy. The pycnometer or specific gravity bottle is a flask with a stopper that has a capillary tube through it. This fine hole in the stopper releases a spare liquid and removes air after closing. The specific volume of the pycnometer is determined according to DIN ISO 3507 with tolerance ±0.001cm³. The pycnometer uses a working liquid with well-known density, such as distilled water to define the volume. By knowing the volume and measuring mass of empty and full pycnometer with high accuracy analytical balance Mettler Toledo with accuracy ±0.0001g it is possible to determine the density of the liquid sample at 20 °C. In this project, three different pycnometers were used depending on the sample volume: 25ml, 50ml or 100ml. Moreover, a pycnometer with thermometer was used to determine the density of solutions in the temperature range between 10 and 25 °C. Later, the experimental results can be fitted to a function in order to extrapolate values in the desired range between the freezing point and 40 °C with the help of literature values. The accuracy of the density measurement using calibrated pycnometer is set to be ± 0.2 %.

Dynamic viscosity measurements

A Brookfield rotational viscometer DV-II Pro with special low viscosity adapter (UL-adapter), shown in Fig.5, was used to perform dynamic viscosity measurements in the temperature range between -17 and 40 °C with the instrument accuracy of ± 1 % in the full temperature range.



Fig.5 Brookfield rotational viscometer DV-II Pro with UL-adapter.

The working principle of the rotational viscometer is to drive a spindle immersed in the test fluid through a calibrated spring (calibration is performed before each test). The viscous drag of the fluid against the spindle is measured as the spring deflection with a rotary transducer. The measurement range of a rotational viscometer is determined by the rotational speed of the spindle, the size and shape of the spindle, the container the spindle is rotating in, and the full scale torgue of the calibrated spring. In this project all measurements were done using the same UL-adapter and spindle to reduce the uncertainty of measurements (Brookfield, 2010). The dynamic viscosity result is obtained as the slope of shear stress versus shear rate function for the range of torque between 10 and 90 %. Moreover, the measurements were performed starting from 2K above the freezing point temperature of sample and taken each 5K until the temperature of 40 °C. It is important to underline that in case of very low viscosity fluids it was not possible to run tests up to 40 °C temperature. The tests were conducted using a written program having 12 rotational speed steps taking 20 measurements for each one and repeated twice to obtain higher accuracy of results. Afterwards, the experimental data were analysed by plotting the shear stress versus shear rate to read the dynamic viscosity as the angle of the linear function (Newtonian fluid behaviour).

Thermal conductivity measurements

Thermal conductivity tests were carried out using a Transient Plane Source (TPS) method, with a Hot Disk Thermal Constants Analyser TPS-2500S having the accuracy of ± 2 %, shown in Fig. 6. When performing a thermal conductivity measurement the plane Kapton sensor is fitted between two pieces of the sample, as shown in Fig.7. Note that the density and specific heat capacity are input values for post processing of thermal conductivity results since knowledge of the volumetric heat capacity, pcp, decreases the measurement error below 2 %. Due to the fact that sample volume is kept rather high (10 ml) the error of measurement was further decreased to 0.7 %. The standard deviation for 18 tests at one given temperature for each sample (between 6 and 16 different temperatures in total) gave a standard deviation between 0.0006 and 0.0036 W·m⁻¹·K⁻¹ and standard error of 0.00086 %.

The Hot Disk sensor consisted of an electrically conducting pattern in the shape of a double spiral, which had been etched out of a thin metal foil. By passing an electrical current high enough to increase the temperature of the sensor between a fraction of a degree up to several degrees, and at the same time recording the resistance (temperature) increase as a function of time, the sensor is used both as a heat source and as a dynamic temperature sensor (HotDisk, 2016). A Kapton sensor 7577 with radius 2.001 mm suitable for testing liquids was chosen in this project. Moreover, the sample volume was kept constant, 10 ml, and all tests were conducted in the temperature range between -35 and 40 °C.



Fig. 6 Hot Disk Thermal Constants Analyser TPS-2500S. Fig. 7 Sample holder with Kapton sensor.

The tests were taken starting from the temperature that was 2K above the freezing point up to 40 °C with a step temperature increment of 5 K. Each sample was tested 6 times at given heating power and testing time for better accuracy (totally 18 measurements at each testing temperature).

Corrosion tests

The corrosion tests following ASTM Standard G1–03 and ASTM standard NACE TM0169/G31(12a) (ASTM, 2017 a, b) were performed for the most commonly found metal alloys in the indirect refrigeration system such as: stainless steel grade 316L, brass (copper content 65 %), carbon steel grade 312, copper 99.95 % and aluminum 3300 series. The objective of these tests was to validate the effectiveness of the proposed corrosion inhibitors compatible with ethyl alcohol commercial solutions as well as evaluate the corrosiveness of the alternative organic salts.

The applied ASTM standard is taking into account various factor, such as: liquid sample volume, metal specimen isolation from ambient, circulation of air, temperature control and other parameters. Thus, around 100 identical shape and size specimens (30 mm length, 30 mm width and 1.5 mm thickness) of different materials were corroded during the period of 8 weeks as shown in Fig.8.



Fig. 8. Ongoing corrosion tests.

The visual conditions of the metallic specimen were checked and noted every week. Later the corrosion rate was calculated, using equation 1, to give the corrosion rate for every metal specimen in a specific secondary fluid sample.

$$Corrosion \, rate = \frac{K \cdot (m_{sample_{old}} - m_{sample_{new}})}{A_{sample} \cdot t_{exposure} \cdot \rho_{sample}} \, [mm \cdot year^{-1}]$$
(1)

Where:

Corrosion rate – the rate at which the metal corrodes, on a yearly basis (mm·year⁻¹).

K – arbitrary constant to determine the output time unit, K = 8760.

m_{sample old} – the initial mass of the metal specimen (kg).

 $m_{\text{sample new}}$ – the mass of the metal specimen at the end of a corrosion test after a determined number of hours (kg).

 A_{sample} – the initial surface area of the metallic sample (m²).

texposure – the exposure time of the metal specimen in hours (h).

 ρ_{sample} – the initial density of the metal specimen obtained by knowing the volume and the initial mass (kg·m⁻³).

Results

The results are presented according to the given objectives in this report.

Objective 1: Alternative ethyl and propyl alcohol blends

Methyl and ethyl alcohol based secondary fluids are commonly used in various indirect refrigeration systems due to relatively good thermophysical properties. Methyl alcohol (methanol) is toxic and therefore not permitted to be used as secondary fluid in most of Europe. Aqueous solutions of ethyl alcohol (ethanol) are the most common secondary fluids used in Sweden and other Scandinavian countries. Geological Survey of Sweden (SGU) and the Swedish Environmental Protection Agency highly recommend ethyl alcohol based secondary fluids for the ground source heat pumps application (SGU, 2008). Due to safety regulations and flammability risks the ethyl alcohol based secondary fluids are usually not exceeding 30 wt-%, corresponding to a freezing point of about -20 °C. The concentration is usually chosen to give a freezing point 8-10 K below the normal operating temperature in order to prevent freezing problems (Melinder, 2009). The commercially available ethyl alcohol based products in Sweden are distributed as 90 - 95 wt-% ethyl alcohol concentrate, including up to 12 wt-% of denaturing agents but no corrosion inhibitors.

European Union regulations strictly define the types and concentrations of the denaturing agents used to prevent from drinking e.g.: acetone, methyl alcohol, propyl alcohol (2-propanol), n-butyl alcohol (n-butanol), methyl ethyl ketone and methyl isobutyl ketone (EUR-Lex, 2013). The most common denaturing agents in Sweden are: 7-9 wt-% propyl alcohol and 2 wt-% n-butyl alcohol. Both propyl and butyl alcohols are considered to be environmentally friendly due to the fact that they occur naturally as fermentation products. Ethyl alcohol is expected to biodegrade rapidly in all environments with predicted half lifetime ranging from 0.1 to 10 days while propyl and butyl alcohols have longer degradation time up to 28 days (Ignatowicz et al., 2015). Recent measurements performed at KTH showed that presence of small amounts of especially propyl alcohol in the solution had a positive impact on specific heat capacity, thermal conductivity, and dynamic viscosity (Ignatowicz et al., 2014). Thus, a question has been raised if blends of only ethyl alcohol and propyl alcohol or only propyl alcohol could become an alternative type of secondary fluid.

In this study five different ethyl alcohol and propyl alcohol solutions were tested. The total concentration of all alcohols was set to be 20 wt-% to investigate the effect of increasing concentration of propyl alcohol on thermophysical properties and the results were publish as two conference articles at 24th IIR International Congress of Refrigeration 2015 (Ignatowicz et al., 2015) and 12th IIR Gustav Lorentzen Natural Working Fluids Conference 2016 (Ignatowicz et al., 2016a).

Ethyl and propyl alcohol blends were prepared by first mixing absolute (99.5 %) ethyl alcohol with 99.9 % pure propyl alcohol (2-propanol) in the given weight proportion and later diluting to concentration of 20 wt-% using distilled water. Since the concentration of propyl alcohol additive was not exactly stated by the different producer, it was decided to use the recommended concentration of 8 wt-%, which at the same time is an average value for the range between 7 wt-% and 9 wt-%. The same method was applied when preparing reference samples of 20 wt-% ethyl and propyl alcohol and all investigated blends are summarized in Table.1.

Sample	Concentration of ethyl alcohol (wt-%)	Concentration of propyl alcohol (wt-%)		
EA20	20	0		
EA18.4+PA1.6	18.4	1.6		
EA18+PA2	18	2		
EA15+PA5	15	5		
EA10+PA10	10	10		
EA5+PA15	5	15		
PA20	0	20		

Table 1. Concentration of ethyl and propyl alcohol blends.

The freezing point results showed that the solution of 20 wt-% propyl alcohol (PA20) had 2.4 °C higher freezing point than the solution of 20 wt-% ethyl alcohol (EA20). Thus, different blends of the two alcohols can as a result have freezing point between -10.92 °C and -8.52 °C. Measurements showed that the increment of the concentration of propyl alcohol in blend results in higher freezing point. Therefore, a high of propyl alcohol affects the freezing point of the alcohol blends negatively and smaller concentrations are recommended.

Fig.9, summarizes all changes in all thermophysical properties in percentage related to increased concentration of propyl alcohol in ethyl and propyl alcohol blend. Note that 20 wt-% ethyl alcohol solution is the benchmark for comparison of different alternative ethyl and propyl alcohol blends.



Fig. 9. Percentage change in thermophysical property due to variating concentration of propyl alcohol.

Among all tested blends only two blends of ethyl and propyl alcohol (EA18.4+ PA1.6) and (EA18+PA2) seems to match all requirements, having low dynamic viscosity, high thermal conductivity and high specific heat capacity, making it an interesting alternative secondary fluid. The presence of propyl alcohol in blends seems to improve the specific heat capacity in the full temperature range. A higher concentration of propyl alcohol gave higher specific heat capacity. The highest results were obtained for PA20 by up to 5.6 %. EA18+PA2 had the highest thermal conductivity values, 1 % higher than EA20. Blends having a propyl alcohol concentration higher than 5 wt-% had lower thermal conductivity values compared to experimental results for EA20.

These results suggest that the n-butyl alcohol used in commercial ethyl alcohol based secondary fluids could preferably be replaced by the same amount of propyl alcohol. In this way the European Union regulation regarding denaturing agents for ethyl alcohol could still be fulfilled. Therefore, further studies were conducted to investigate the performance of two alternative alcohol blends in terms of the pressure drop and heat transfer in the borehole heat exchanger (BHE). Moreover, a comparison with the commercially available product having two denaturing agents in form of propyl alcohol ad n-butyl alcohol (EA18 + PA1.6 + BA0.4) was performed. It is important to note that all investigated blends had rather similar freezing point temperature.

Measurements showed that any changes in the alcohol concentrations affect slightly the density of alternative blend and EA18+PA1.6+BA0.4 had the highest density among all tested blends as shown in Fig.10. Additionally, the results of dynamic viscosity measurements showed that the presence of both propyl and n-butyl alcohols can significantly decrease the dynamic viscosity compared to EA20 in full temperature range as seen in Fig.11. The most promising blend seems to be EA18.4+PA1.6 having the lowest dynamic viscosity by up to 8 % at temperature of -10 °C. Moreover, the alcohol blend representing commercial product (EA18+PA1.6+BA0.4) has slightly higher dynamic viscosity than EA18.4+PA1.6. Additionally, n-butyl alcohol is affecting more positively the dynamic viscosity at operating temperatures higher than 10 °C. Thus, only small concentrations of the propyl alcohol (up to 1.6 wt-%) have a positive effect on the dynamic viscosity.

Fig.12 presents the results of the thermal conductivity measurements. As can be seen, both propyl and n-butyl alcohol are affecting positively the thermal conductivity when compared to EA20. Both EA18+PA1.6+BA0.4 and EA18.4+PA1.6 seem to be the best performing alcohol blends. The presence of n-butyl alcohol in EA18+PA1.6+BA0.4 blend results in higher thermal conductivity by up to 1.15 % than EA20. Additionally, EA18+PA2 has higher thermal conductivity by up to 1 % compared to result obtained for EA20.

Fig. 13 presents the results of the specific heat capacity measurements. The specific heat capacity measurements showed similar tendency for both propyl and n-butyl alcohols. EA18+PA1.6+BA0.4 has the highest specific heat capacity by around 2 % in the temperature range between -10 and -5 °C and EA18+PA2 by around 1.8 % in temperature range between -5 and 30 °C than EA20. Thus, the presence of small amount of n-butyl alcohol in alcohol blend has the biggest influence for the low temperature application.









Fig.11 Dynamic viscosity results.



Fig.13 Specific heat capacity results.

Fig. 14, presents the convection heat transfer coefficients calculated using equations 7 and 8 found in (Ignatowicz et al., 2016a) for two different pipe sizes and typically used flow rates in found in Borehole Heat Exchangers, BHEs taking into consideration experimentally obtained thermophysical properties. The alcohol blends performance was investigated at the operational temperature of 0 °C. In all cases EA18+PA1.6+BA0.4 gives the highest convection heat transfer coefficient although EA18.4+PA1.6 gives values only about 2 % lower. EA20 gives the lowest convection heat transfer coefficient in all cases. As seen, for the same flow rates, the convection heat transfer coefficients are lower for PE50 pipes than for PE40 pipes due to lower average velocities of the fluid. This may also lead to the establishment of the laminar flow regime in pipes and that should be avoided from the heat transfer perspective as shown in Fig. 14(a) and 14(b) for 0.4, 0.5 and 0.6 l·s⁻¹ flow rates.



(a) PE40 x 2.4 mm

(b) PE50x2.9 mm





(a) PE40 x 2.4 mm

(b) PE50 x 2.9 mm

Figure 15. Linear head losses per meter vs Reynolds number at different flow rates (T = 0 °C).

Moreover, the heat transfer area is larger in PE50 pipes than in PE40 pipes. Lower velocities also imply lower pressure drops as seen in Fig.15 presenting the head loss per meter of pipe as the function of Reynolds number for PE40 (a) and PE50 (b) pipes. For the flow rate of 0.6 l·s⁻¹, the pressure drop along a 500 m PE40 U-pipe, i.e. with a total length of 1000 m would be about: 213.5 kPa (EA18.4+PA1.6); 214 kPa (EA18+PA1.6+BA0.4); 218 kPa (EA18+PA2) and 220 kPa (EA20). In the configuration with a PE50 U-pipe, the pressure drops was 73.7 kPa (EA18.4+PA1.6); 74 kPa (EA18+PA1.6+BA0.4); 75 kPa (EA18+PA2) and 76 kPa (EA20). The trends for the convection heat transfer coefficients and head losses were the same for temperatures of 5°C and -5°C. It may be of interest to notice that the thermal entry length varies from 230 to 372 m for laminar flow regimes.

Thus, the alcohol blends EA18+PA1.6+BA0.4 and EA18.4+PA1.6 presented the best characteristics in terms of the heat transfer and pressure drop in this study compared with EA20. Both blends were giving higher heat transfer coefficient by 9% (EA18+PA1.6+BA0.4) and 8 % (EA18.4+PA1.6) than pure EA20. Both blends were giving lower pressure drop than EA20 by up to 2.7 % (EA18+PA1.6+BA0.4) and 3 % (EA18.4+PA1.6). Moreover, EA18+PA1.6+BA0.4 gave 1.4 % higher heat transfer coefficient and EA18.4+PA1.6 gave lower pressure drop by up to 0.4 % when these two blends are compared to each other. If the existing secondary fluid in all Swedish Ground Source Heat Pumps, GSHPs, would be change to blend EA18.4+PA1.6 an annual energy saving for pumping power of around 0.5 GWh could be achieved.

It is important to underline that in other European countries, like Switzerland and Finland, commercial products containing a mixture of two ketones are used for GSHP application. In Switzerland the commercial ethyl alcohol product contains 2 vol-% methyl ethyl ketone and 0.5 vol-% methyl isobutyl ketone (Alcosuisse, 2014). Whereas, in Finland commercial products contain up to 1.8 vol-% methyl ethyl ketone and 2.7 vol-% methyl isobutyl ketone (Altia Plc. 2012). Instead, in North America the most

common denaturing agents for ethyl alcohol based secondary fluid are methyl alcohol (methanol) (3.76 - 10 wt-%) (Lyondell, 2003) and pine needle oil (up to 0.5 vol-%) (Government of Canada, 2016).

The chemical character of these denaturing agents can in different ways affect the thermophysical properties. Thus, it was decided to investigate the thermophysical properties of different commercially available alcohol blends in Europe and United States and results were published as a conference article in IGSHPA Technical/Research Conference and Expo Denver 2017 (Ignatowicz et al., 2017a).

As reported, the presence of two ketones had a strong effect on the freezing point. Methyl, propyl and n-butyl alcohols used as denaturing agents increased the density while methyl ethyl and methyl isobutyl ketones decreased the density values compared to pure EA20 as shown in Fig.16. Additionally, different denaturing agents were positively affecting the dynamic viscosity in most cases and EA18+MA2 had the lowest dynamic viscosity by up to 12 % as presented in Fig.17. EA18+PA1.6+BA0.4, EA20+MEK2+MIBK0.5 and EA17.5+PA2+BA0.5 had as well lower dynamic viscosity than EA20 at the temperature of -8 °C by up to 8 %, 7 %, and 3.5 % respectively. Only EA20+MEK1.8+MIBK2.7 had the dynamic viscosity higher by up to 2 % compared to pure EA20.

Moreover, different concentrations of propyl and n-butyl alcohol were affecting in different way the thermal conductivity and EA18+PA1.6+BA0.4 showed higher thermal conductivity than EA20 as seen in Fig. 18. The presence of denaturing agents in form of ketones decreased the thermal conductivity in full temperature range. Methyl alcohol as denaturing agent did not increase the thermal conductivity value and EA18+MA2 sample had almost the same thermal conductivity values compared to reference EA20 data.



Fig. 16 Density results.

Fig. 17 Dynamic viscosity results.



Fig. 18 Thermal conductivity results.

Fig.19 Specific heat capacity results.

Fig.19 presents the results of the specific heat capacity measurements. EA17.5+PA2+BA0.5 had the highest specific heat capacity, by up to 2.5 % than EA20 and by up to 1.5 % than EA18+PA1.6+BA0.4. EA20+MEK2+MIBK0.5 and EA20+MEK1.8+MIBK2.7 showed very similar results and gave by up to 1.5 % higher specific heat capacity. EA18+MA2 had higher specific heat capacity by up to 1.2 % compared to EA20 and EA18+PA1.6+BA0.4 had higher specific heat capacity only in temperature range between -10 and 0 °C compared to ethyl alcohol samples with ketones and methyl alcohol, which is the most important operational temperature range for Swedish GSHPs.

Summarizing, the results showed that the commercial product commonly used in Sweden (EA18 + PA1.6 + BA0.4) has the best thermophysical properties among different ethyl alcohol based products found in Europe when taking into consideration all thermophysical properties. Pure methyl alcohol solution, MA20, poses better thermophysical properties than EA18+MA2 and the lowest viscosity among all investigated alcohol blends but special care needs to be taken due to high toxicity. However, EA18+MA2 does not have good thermophysical properties compared to other ethyl alcohol blends and products containing small amounts of propyl and butyl alcohol.

GSHPs in other European countries could benefit by shifting from the ethyl alcohol based blends containing denaturing agents in the form of ketones to blends of alcohols presented in this study and an overall improvement of the heat transfer without affecting the pressure drop could be obtained. Therefore, the comparison of performance of different commercially available alcohol blends in Europe were conducted and the results were published as a conference article 12th IEA Heat Pump Conference 2017 (Ignatowicz et al., 2017d).

This study showed that the product commonly used in Sweden (EA18+PA1.6+BA0.4) presents the best characteristics in terms of higher heat transfer (up to 10 %) and lower pressure drop (up to 2.7 %) among different commercial products. EA20+MEK2+MIBK0.5 used in Switzerland showed second best performance in terms of higher heat transfer (up to 5 %) and lower pressure drop (up to 2 %). Moreover, EA17.5+PA2+BA0.5 and EA20+MEK1.8+MIBK2.7 present the worst performance both in terms of lower heat transfer and higher pressure drop. EA20+MEK1.8+MIBK2.7 gave by up to 8 % lower heat transfer and by up to 0.5 % higher pressure drop. EA17.5+PA2+BA0.5 gave by up to 3 % lower heat transfer and by up to 1 % higher pressure drop than EA20.

Fig.20 and 21, present the convection heat transfer coefficients calculated using methodology found in (Ignatowicz et .al.2017b) for two different pipe size and typically used flow rates (between 0.4 and 0.6 l·s⁻²) found in BHEs taking into account experimentally obtained thermophysical properties for the operational temperature of -5 °C. The performance of different ethyl alcohol based secondary fluids with different denaturing agents was investigated at the operational temperatures of -5, 0 and 5 °C. In all cases EA18+PA1.6+BA0.4 gives the highest convection heat transfer coefficient although EA20+MEK2+MIBK0.5 gives values only about 6 % lower. EA20+MEK1.8+MIBK2.7 gives the lowest convection heat transfer coefficient in all cases. In all cases EA20 is performing better than EA20+MEK1.8+MIBK2.7 and EA17.5+PA2+BA0.5. As seen, the convection heat transfer coefficients are lower for PE50 pipes than for PE40 pipes for the same flow rates due to lower average velocities of the secondary fluid. This may also lead to the establishment of the laminar flow regime in pipes which from the heat transfer perspective should be avoided. The trends for the convection heat transfer coefficients and head losses were the same for other operational temperatures.



Fig.20 Convection heat transfer coefficient vs Re number at different flow rates in PE40 x 2.4 mm BHE.



Fig.21 Convection heat transfer coefficient vs Re number at different flow rates in PE50 x 2.9 mm BHE.

The pressure drop along a 250 PE40 U-pipe, i.e. with a total length of 500 m for the different flow rates was the smallest for EA18+PA1.6+BA0.4 and EA20+MEK2+MIBK0.5 as shown in fig. 22 and 23.



Fig.22 Pressure drop at different flow rates in PE40 x 2.4 mm BHE.



Fig.23 Pressure drop at different flow rates in PE50 x 2.9 mm BHE.

Thus, the product commonly used in Sweden (EA18+PA1.6+BA0.4) presents the best characteristics in terms of higher heat transfer (up to 10 %) and lower pressure drop (up to 2.7 %) among different commercial products. EA20+MEK2+MIBK0.5 used in Switzerland showed second best performance in terms of higher heat transfer (up to 5 %) and lower pressure drop (up to 2 %). Moreover, EA17.5+PA2+BA0.5 and EA20+MEK1.8+MIBK2.7 present the worst performance both in terms of lower heat transfer and higher pressure drop. EA20+MEK1.8+MIBK2.7 gave by up to 8 % lower heat transfer and by up to 0.5 % higher pressure drop. EA17.5+PA2+BA0.5 gave by up to 3 % lower heat transfer and by up to 1 % higher pressure drop than EA20.

Objective 2: Potential corrosion inhibitors compatible with ethyl alcohol

Currently available commercial ethyl alcohol based secondary fluids in Sweden and other Nordic countries contain up to 12 wt-% denaturing agents (in concentrate alcohol) in form of propyl alcohol and n-butyl alcohol but no corrosion inhibitors. A search for potential corrosion inhibitors compatible with alcohols was one of the objectives suggested by the industrial project partners. Thus, this study was conducted due to a growing need to provide protection against corrosion and to extend the lifetime of the system. Results were published as a conference paper during 12th IIR Gustav Lorentzen Natural Working Fluids Conference 2016 (Ignatowicz et al., 2016b).

A corrosion inhibitor is a substance which reduces the rate of corrosion when added to the corrosive environment in a suitable concentration, without changing significantly the chemical composition of the secondary fluid. The corrosion inhibitor is effective when present in small concentrations. Although organic inhibitors are very suitable for the corrosion protection, many of these corrosion inhibitors are expensive or toxic. Thus, the goal was to use green, cheap and environment-friendly compounds such as plant extracts. Numerous studies showed that these compounds are very good alternatives for the protection of metals in acidic solutions. Nevertheless, the extractions methods and preservation of active substances from plants as well as availability of some specific plants were more complicated than expected.

The choice of Aloe Vera was based on the research by (Singh et al., 2016). This study reported that Aloe Vera extract gave more than 90% inhibition efficiency and lowest corrosion rate at optimum concentration of 200 ppm for mild steel in hydrochloric acid medium. It is important to underline that Aloe Vera gel consists primarily of water and polysaccharides (pectins, hemicelluloses, glucomannan, acemannan, and mannose derivatives as well as amino acids, lipids, sterols (lupeol, campesterol, and b-sitosterol), tannins, b-carotene, Vitamin B12, Vitamin E (a-tocopherol) and enzymes. Thus, these plant extracts are susceptible to microbial attack and different preservatives such as benzoates are required. Moreover, the most recommended storage conditions are at the maximum temperature of 4 °C, which in a way limits the application of Aloe Vera extracts as additives for ethyl alcohol based secondary fluids. Some of the attempts were made in the lab to produce a stable product but more research is needed to further improve the preservation method as well as increase the temperature stability range.

Therefore, it was decided to work with more stable substances such as sugars that as well are environmentally friendly, effective and non-toxic corrosion inhibitors. Among the sugars, sodium gluconate (SG) used in food industry and a well known corrosion inhibitor for protection of iron and mild steel was investigated.

Another good candidate was sodium benzoate (SB), which is widely used as the food preservatives as well as anodic inhibitors for ferrous materials (Rammelt et al. 2008). The most important advantages of sodium benzoate are safety and high solubility in water. Moreover, sodium benzoate in chloride solutions can induce pitting of the carbon steel and adding sodium gluconate eliminates this susceptibility. Thus, the blends of 1.5 % sodium gluconate with sodium benzoate are suggested for the protection of carbon steel (Lahodny-Šarc et al. 2000). Additionally, sodium benzoate is very often combined with other corrosion inhibitors such as benzotriazole (BTA) to provide a better protection. Benzotriazole and its derivatives are known as excellent

inhibitors for copper and its alloys and carboxylates, such as benzoates, are very good corrosion inhibitors for ferrous metals. Therefore, a combination of both corrosion inhibitors is often applied to improve the multi-metal protection. Synergistic inhibition gives an improved performance of the mixture of corrosion inhibitors compared with the individual corrosion inhibitors and can lead to a decrement of the required concentrations (Ramelt et al.2008).

2-mercaptobenzothiazole (MBTA) was another interesting corrosion inhibitor that was selected due to the fact that both 2-mercaptobenzothiazole and its derivatives are widely used as the corrosion inhibitor for copper and its alloys in cooling systems and heat exchangers. 2-mercaptobenzothiazole is not soluble in water but has a high solubility in alcohols, which makes it a good corrosion inhibitor for the ethyl alcohol based secondary fluids.

Moreover, sodium molybdate (SM) as the most broadly applicable inhibitor for protection of both ferrous and nonferrous metals and its very low toxicity (Polo et al., 2002) was chosen. Two patents by Bayes and Lamprey were issued in 1939 describing the utilization of soluble sodium molybdate as corrosion inhibitor in alcohol - water antifreeze mixtures to protect the automobile cooling systems.

Finally, different non-toxic standard oxide forming (sodium gluconate, sodium molybdate,) and as well as adsorption type corrosion inhibitors (sodium benzoate, benzotriazole, 2-mercaptobenzothiazole) for ethyl alcohol based secondary fluids were studied. Unfortunately, suitable concentrations of selected corrosion inhibitors for alcohol solutions were not found except for sodium molybdate. Therefore, it was decided to use same concentrations as the ones found in literature for protection of different water systems.

Results showed that the different corrosion inhibitors can affect the thermophysical properties of 25 wt-% and 30 wt-% ethyl alcohol based secondary fluid even when added in small concentrations. Note that for both types of concentrations, the same amount of corrosion inhibitor was added to investigate the effect of each corrosion inhibitor on the thermophysical properties. As seen in table 2, the presence of corrosion inhibitor can have a positive effect and decrease the freezing point. The highest change was observed for solutions containing sodium molybdate (SM) and sodium benzoate (SB) while sodium gluconate (SG), benzotriazole (BTA) and 2-mercaptobenzothiazole (MBTA) had the smallest effect.

Sample	T _f exp (°C)	T _f ref (°C)	Diff. (K)	Sample	T _f exp (°C)	T _f ref (°C)	Diff. (K)
EA25	-15.46	-15.45	0.01	EA30	-20.40	-20.50	0.1
EA25 + 0.01M SG	-15.91	-15.45	0.46	EA30 + 0.01M SG	-20.69	-20.50	0.19
EA25 + 0.02M BTA	-15.59	-15.45	0.14	EA30 + 0.02M BTA	-20.68	-20.50	0.18
EA25 + 0.02M SM	-16.75	-15.45	1.3	EA30 + 0.02M SM	-21.58	-20.50	1.08
EA25 + 0.1M SB + 0.1M BTA	-16.81	-15.45	1.36	EA30 + 0.1M SB + 0.1M BTA	-24.52	-20.50	4.02
EA25 + 0.2 M SB	-17.15	-15.45	1.7	EA30 + 0.2 M SB	-23.49	-20.50	2.99
EA25 + 1.5%SG+SB	-16.24	-15.45	0.79	EA30 + 1.5% SG+SB	-22.40	-20.50	1.9
EA25 + 0.01M MBTA	N/A	N/A	N/A	EA30 + 0.01M MBTA	-20.41	-20.50	0.09

Table 2. Freezing point results for ethyl alcohol solutions with corrosion inhibitor.

Moreover, the corrosion inhibitors seem to increase the density of solutions having lower ethyl alcohol concentration as seen in Fig.25. The results for 30 wt-% solutions (EA30) did not show the same tendency and only solutions containing sodium gluconate (SG), 2-mercaptobenzothiazole (MBTA) and benzotriazole (BTA) had lower density.



Fig. 25. Density results for: (a) EA25; (b) EA30 solutions with corrosion inhibitors.

Additionally, the presence of corrosion inhibitor in EA30 samples had no significant effect on the dynamic viscosity value as shown in Fig.26. Only EA25 + 0.01 SG sample had lower dynamic viscosity in the temperature range between -13 and -5 °C by up to 10 %. The presence of sodium gluconate and sodium molybdate affected the dynamic viscosity of low concentration ethyl alcohol solutions only.

All studied corrosion inhibitors had negative effect on the thermal conductivity in full temperature range in all ethyl alcohol solutions. The lowest decrement in thermal conductivity value was observed for ethyl alcohol based solutions containing 2-mercaptobenzothiazole and benzotriazole by up to 7 %. The presence of sodium gluconate decreased the most thermal conductivity by up to 14 % for EA30 + 0.01M SG at the temperature of 0 °C as seen in Fig.27.



Fig. 26. Dynamic viscosity results for: (a) EA25; (b) EA30 solutions with corrosion inhibitors.



Fig. 27. Thermal conductivity results for: (a) EA25; (b) EA30 solutions with corrosion inhibitors.

Fig.28 presents the specific heat capacity results. Ethyl alcohol based secondary fluids containing sodium gluconate (SG), benzotriazole (BTA) and sodium molybdate (SM) had higher specific heat capacity than the pure ethyl alcohol solutions. Sodium gluconate gave higher specific heat capacity and its effect seems to diminish at the higher concentration of ethyl alcohol. Similar observations were made for the solutions containing benzotriazole and sodium molybdate. The presence of benzotriazole, 2-mercaptobenzothiazole and sodium molybdate seems to increase the specific heat capacity the most. The lowest specific heat capacity was observed for samples containing sodium benzoate and the decrement by up to 2 % for EA30 + 0.2M SB was reported.



Fig. 28. Specific heat capacity results for: (a) EA25; (b) EA30 solutions with corrosion inhibitors.

Summing up, both benzotriazole and 2-mercaptobenzothiazole seem to be the most promising corrosion inhibitors for 30 wt-% ethyl alcohol based secondary fluids when thermophysical properties are considered. Both corrosion inhibitors seem to decrease the thermal conductivity least, increase the specific heat capacity and do not affect the dynamic viscosity. Moreover, these two corrosion inhibitors could be applied together for protection of copper and its alloys as well as mild steel. Consequently, the immersion corrosion tests were as well performed to validate the effectiveness of investigated corrosion inhibitors at proposed concentrations and results are shown in fig. 29 - 33.



Fig. 29. Corrosion results for stainless steel 316L.



Fig. 30. Corrosion results for carbon steel 312.



Fig. 31. Corrosion results for aluminum 3300 series.







Fig. 33. Corrosion results for brass.

Experiments showed that most of proposed corrosion inhibitors decreased the corrosion rate significantly compared to pure 30wt-% ethyl alcohol based solution. Sodium gluconate showed high inhibition efficiency in case of stainless steels, cast iron, brass and copper but not aluminum. Whereas, benzotriazole seemed to be the perfect corrosion inhibitor for all alloys except cast iron. Sodium molybdate showed as well very good performance for all alloys except copper. Actually, only the proposed blend of sodium benzoate and benzotriazole seems to provide a good corrosion protection for aluminum, ferrous and copper alloys. 2-mercaptobenzothiazole proved to be very effective corrosion inhibitor but should not be used due to high instability in water based solution and recrystallization. These studies helped to understand a link between molecule structure and concentration of various inorganic and organic corrosion inhibitors as well as helping one of project partners to create a commercial alcohol product with benzotriazole as a corrosion inhibitor.

Objective 3: Effect of different corrosion inhibitors on the heat transfer

A corrosion inhibitor is a substance which reduces the rate of corrosion when added to the corrosive environment in a suitable concentration, without changing significantly the chemical composition of the base fluid. The corrosion inhibitor is, as a rule, effective when present in small concentrations and the goal is usually to produce a protective film on the metal surface. This can take the form of a very thin monomolecular layer (film) of adsorbed corrosion inhibitor. Another alternative is formation of the protective oxides by chemical reaction between the metal and the inhibitor, possibly with corrosion products (metal oxides) being involved. A further possibility is that a thick coating (> 100 nm) of the inhibitor forms on the metal surface, often called oxide-forming inhibitors.

Adsorption (surfactant) corrosion inhibitors are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic group (water insoluble component called "tail") and hydrophilic group (water soluble component called "head") as shown in Fig.34.



Fig.34 Adsorption (surfactant) corrosion inhibitor (Malik et al., 2011).

In the polar solvent such as water, amphiphilic surfactant corrosion inhibitor monomers assemble in such way that their hydrophobic tails group in the core of micelle and the polar head groups face outwards into the polar bulk solution and locate at the micelle-water interface. The adsorption of corrosion inhibitor onto metallic surfaces typically occurs in four distinct steps. Initially, below the critical micelle concentration (CMC), surfactant corrosion inhibitors are monomers that adsorb little onto the surface. As the CMC is approached, the formation of the aggregates so-called semi-micelles or hemi-micelles may start, although the metal surface remains partially coated with the film.



Fig.35 Schematic representation of the adsorption process on metal surface (Malik et al., 2011).

In the last phase, at the CMC, a monolayer of corrosion inhibitor molecules covers the entire surface as shown in Fig.35. Adsorption of corrosion inhibitor molecules on the metallic surface involves the removal of the absorbed water molecules replacing them with the inhibitor molecules, thus water is no longer in direct contact with metal. The thickness of the protective film layer is very small and dependent on the length of corrosion molecules (usually 2-6 nm) in case of some bilayers (Malik et al., 2011).

The potential application of adsorption (surfactant) corrosion inhibitors has been studied widely in the last few years. It was found out that adsorption on the metal surface and micelle formation is extremely critical to corrosion inhibition. Various factors can affect the CMC value: temperature, the length of hydrocarbon tail, the existence of salts and other additives, thus each corrosion inhibitor have a specific CMC value (Malik et al., 2011). It is apparent that corrosion efficiency of adsorption corrosion inhibitors increases with increased concentration and decreases with increased the temperature. Adsorption corrosion inhibitors having low CMC value tend to have higher efficiency and can be added at smaller concentrations making it more cost effective.

Therefore, adsorption corrosion inhibitors such as sodium benzoate, benzotriazole and 2-mercaptobenzothiazole seem to be more effective method of corrosion protection than the ones building oxide layer on metal surface. Some standard corrosion inhibitors that create an oxide layer on metal surface had already been phased out due to health and environmental concerns e.g. phosphates, nitrates, nitrites, amines, amides and borates. This situation creates a need for a search for alternative corrosion inhibitors being more effective, less harmful and requiring lower concentration levels. Adsorption corrosion inhibitors could be an interesting alternative as highly-effective and low concentration demanding corrosion inhibitors. There is no research done so far about the influence of standard oxide forming and adsorption corrosion inhibitors on heat transfer process. Therefore, this project is the first attempt to study the thermal properties of modified surfaces such as protective metal oxides.

It was decided to work with copper as the highly thermal conductive material among all investigated metals in this study in order to detect the variations in thermal conductivity properties. Moreover, ethyl alcohol 30 wt-% solutions containing different types of oxide forming as well as adsorption (surfactant) corrosion inhibitors were chosen in order to compare the results with other corrosion results presented in section 2. The identical metal specimens were copper discs (copper purity 99.95%) having 50 mm diameter and 30 mm thickness. Both flat surfaces were prepared according to ASTM standards G1–03 and later corroded according to ASTM Standard NACE TM0169/G31–12a. The total corroding time for 18 metal specimens was 3 months. In order to obtain reproducible results two specimens were place d in same solution. The specimen weight and dimensions were measured and documented before and after the tests. Fig.36 presents the specimens after 3 months time immersion corrosion tests.



Fig. 36. Oxide formation on copper specimens after two months immersion corrosion test.

As seen in fig.36, only specimen no.1 immersed 30 wt-% ethyl alcohol solution with 0.2 M sodium benzoate showed the most pronounced type of coper oxide on its surface. It was actually very surprising result since sodium benzoate is one of the adsorption corrosion inhibitors investigated in this project. Previously reported results suggested that sodium benzoate is the most suitable corrosion inhibitor for ferrous alloys and the least efficient in case of copper and its alloys as shown in section 2. Surprisingly, adsorption corrosion inhibitor, such as sodium benzoate, due to its inefficiency was pronouncing the corrosion rate and formation in thicker oxide. Moreover, other copper specimens did not develop an even type of metal oxides on their surfaces after the visual investigation but were still included in this study. Especially, specimens treated with benzotriazole (specimens no.4 and 5) had unchanged shiny surface. Note that part of the copper oxide was damaged during removing specimen from the solution. Therefore, it was decided to test the part of specimen no.1 were still there was oxide. Other specimens did not suffer any damages handling procedures.

The thermal conductivity tests for all nine specimens were performed using Hot Disk Thermal analyser TPS 2500S instrument and sensor 5501 (6.403mm) was chosen in this study. Firstly, the thermal conductivity tests of reference non-corroded copper specimens was performed. The thermal conductivity reference value of 400.1 WK m⁻¹ for pure copper (purity higher than 99.9%) at room temperature was found in (Raab et al., 2016). The measured thermal conductivity value for untreated copper specimen was about 395 (± 2) W·K⁻¹·m⁻¹ at temperature of 25 °C and showed rather good agreement (only 1.25 % lower value) with the reference values. Afterwards, the other nine specimens were tested and the experimental results did not show any significant change in thermal conductivity value for specimens no.2 – 9. Only specimen no.1 showed lower thermal conductivity of 364 (± 1.5) W·K⁻¹·m⁻¹ at temperature of 25 °C, which was about 8 % lower than the untreated copper reference specimen. The reference thermal conductivity value for copper oxide was not found. Further studies are suggested to investigate other metal alloys and aluminium in order to compare the results. Nevertheless, ferric oxide instability might be a limiting factor as well and only aluminium specimens with stable oxides could be tested.

Objective 4.1: Iso-paraffins as low temperature secondary fluids

Ethylene and propylene glycol water based secondary fluid solutions are very popular due to their low corrosive character, low freezing point, high boiling point and low fire hazards. Ethylene glycol has better thermophysical properties compared to propylene glycol but is more poisonous. Thus, propylene glycol water based secondary fluid is the most common substitute for ethylene glycol. The biggest disadvantage of propylene glycol solutions is its very high viscosity at low temperatures, which results in higher pumping power and lower system performance.

An alternative to propylene glycol solutions could be non-aqueous saturated hydrocarbon mixtures (n-paraffins, cycloalkanes and silicone oils) that have significantly lower viscosity and give lower pumping power at very low temperatures but poor thermal conductivity and energy transport capability compared to water based solutions (Melinder, 2010). One of the most recent technologies for synthesis of liquids from biomass is the biomass to liquid (BtL) technology. The obtained synthetic liquid is environmentally friendly due to lower carbon dioxide emission during the production process (Triantafyllidis et al., 2013). Another way of synthesis of paraffins from syngas (modified Fischer-Tropsch synthesis) can result in sulfur-free, nitrogen-free, and aromatic-free final products (Qihang et al., 2016). The first reports about iso-paraffin used as heat transfer fluid in transformers were found in (Krawiec and Leath, 2011). The results showed that iso-paraffins had better heat transfer properties in terms of higher thermal conductivity and specific heat capacity than the conventional cycloalkane (naphthenic) liquids. Another advantage of iso-paraffins is rather short decomposition time by up to 71 % compared to 56 % for naphthenic after 22 days as reported by Vieira et al., (2009). Moreover, iso-paraffins are non-corrosive fluids compared to propylene glycol water based solutions and compatible with all metals and most of the polymer materials.

One of the aims of this project was to propose a new generation of synthetic iso-paraffins having better thermophysical properties compared to existing synthetic products for very low temperature applications. Totally 42 different GtL and BtL type iso-paraffin mixtures were tested and the two most promising iso-paraffin mixtures (isoparaffins 1 and iso-paraffin 2) having different composition and operating temperature ranges were presented in the conference article (Ignatowicz et al., 2017c) at the 5th IIR International Conference on Thermophysical Properties and Transfer Processes of Refrigerants 2017. The obtained experimental results were compared with two reference water based solutions of 60 wt-% ethylene glycol (EG 60 %) and 60 wt-% propylene glycol (PG 60 %) having the freezing point of -50 °C. Fig.37 presents the experimental results for both iso-paraffin mixtures showed the lowest density among all samples. As seen in Fig.38, PG 60 % had the highest dynamic viscosity and kinematic viscosity. Iso-paraffin 1 had the lowest viscosity at temperature of -50 °C by up to 98 % and 86 % compared PG 60 % and EG 60 %, respectively. Additionally, isoparaffin 1 had about three times higher viscosity than water at the temperature of 0 °C. Similar results were obtained for iso-paraffin 2 mixture and lower viscosities by up to 97 % and 75 % compared to PG 60 % and EG 60 % were observed at the temperature of -50 °C. Moreover, iso-paraffin 2 was about four times more viscous than water at temperature of 0 °C.



Furthermore, iso-paraffin 1 had lower thermal conductivity by up to 40 % and 45 % compared to PG 60 % and EG 60 % solutions at temperature of -50 °C, respectively. Similar results were obtained for iso-paraffin 2 and lower thermal conductivity value by up to 46 % and 51 % at the temperature of -50 °C was reported compared to PG 60 % and EG 60 % solutions as presented in Fig.39. Both iso-paraffin mixtures had lower specific heat capacity than glycol solutions as shown in Fig.40. Iso-paraffin 2 had lower specific heat capacity by up to 34 % and 24 % than PG 60 % and EG 60 % at temperature of -50 °C. Whereas, iso-paraffin 1 had lower specific heat capacity by up to 36 % and 26 % than PG 60 % and EG 60 % at the temperature of -50 °C, respectively.



This study helped to select the most promising iso-paraffins blends for different applications and the first commercial iso-paraffin based products were launched on the Swedish market.

Objective 4.2: Alternative formate and acetate salts

Potassium organic salts like formates and acetates are known as environmentally friendly secondary fluids. The most important advantages of salts compared to aqueous solutions of alcohols and glycols are good thermophysical properties, low toxicity and non-flammability. One of the objectives of the project was to investigate properties of different formate and acetate salts at low temperatures in order to propose new blends of formate salts that could be used as secondary fluids for low temperature applications. Some of these results for alternative formates were published as a conference article at 5th IIR International Conference on Thermophysical Properties and Transfer Processes of Refrigerants 2017 and more publications are planned in future.

In this study, formate salts solutions such as copper formate, sodium formate, lithium formate and ammonium formate were investigated since data regarding the freezing point and possible thermophysical properties were mostly not available. Nevertheless, formate salts such as sodium formate (NaF), potassium formate (KF) and cesium formate (CsF) have been used as drilling and completion fluids for the oil industry since early 1990's. These alkali metal formate salts have very high solubility levels in water and create dense, thermally stable and relatively low viscous alkaline solutions ideally suited for extreme conditions (Downs, 1992; Downs, 1993). Studies showed that potassium formate, sodium formate and cesium formate in solution can exert a structuring effect on surrounding water molecules making water more ice-like in nature, making them more stable at high temperatures (Valizadeh and Nasiri, 2012). A drawback of these highly concentrated formate blends (between 40 and 97 wt-%) is rather high crystallization temperature (temperature above 8 °C) limiting its use only to high temperature and high pressure applications (Caenn et al., 2016). The thermophysical properties in the temperature range between 10 and 70 °C for highly concentrated blends of cesium formate, potassium formate and sodium formates; sodium formate and potassium formate; cesium formate and potassium formate as well as sodium formate have been found in (Cabot Corp, 2016).



Fig.41 Freezing point results.

Fig.41 presents the results of freezing point measurements for selected formate solutions. In this study the additive concentration of different formate salts were chosen to achieve about the same freezing points as KF 28.9 % (T_f = -20 °C) and KF 36.8% (T_f = -30 °C). Moreover, 42 wt-% ammonium formate solution had the lowest freezing point of about -38 °C. The results obtained for NaF 30% were slightly higher (0.8 K) than reference value reported in Cabot Corp (2016). Note that the concentration of sodium formate salt was higher than at eutectic point. Additionally, the chosen additive concentrations of lithium formate (LiF 29% and LiF 36%) gave higher freezing points of -18.45 °C and -28 °C, which can result in slightly better properties. 38 wt-% lithium formate solution had the lowest freezing point of about -31 °C.

Fig. 42 and 43 present the results of density and dynamic viscosity for selected salt solutions. As seen, the experimental result for water and KF 29% were slightly lower (by up to 0.15 %) than the reference value. Though results for KF 36.8% were up to 1 % lower that the reference values although the freezing point result did not indicate any significant difference in the concentration. Note that data for potassium formate solution having the freezing point of -20 °C and -30 °C in Melinder (2007) and Melinder (2010) are based on commercial product properties containing other salts and additives. The lowest density was obtained for NH₄F solutions and the highest for KF and NaF solutions. The experimental results and curve pattern for NaF 30% at temperature 10 °C were in very good agreement with reference value (Cabot Corp, 2016).

The obtained viscosity results for both KF 29% as well as KF 36.8% were slightly lower by up to 5 % than reference values based on commercial products found in Melinder (2007) and Melinder (2010). Moreover, no experimental data for pure potassium formate, lithium formate, sodium formate as well as ammonium formate solution having the freezing point of -20 and -30°C were found. The results obtained for water were higher by up to 3 % than NIST reference values. The dynamic viscosity results for LiF 29%, LiF 36% as well as NaF 30% were two to three times higher than the other fluids, which is a serious drawback. Nevertheless, the dynamic viscosity of NH₄F 26% was about 1.35% lower than KF 29%. Similar result was obtained for NH₄F 34% and lower dynamic viscosity by up to 2.5 % than KF 36.8% was obtained. Moreover, results for LiF 36% sample are incomplete due to some crystal formation at temperatures below 0 °C when fast cooling rates were applied.



Fig. 42 Density results.

Fig. 43 Dynamic viscosity results.

Fig. 44, presents the results of the thermal conductivity measurements. It is important to underline that the comparison of different formate salt blends is based on the experimental results obtained for KF 29% and KF 36.8%. As seen, the obtained results for KF 29% were slightly lower than reference (Melinder, 2007; Melinder, 2010), whereas KF 36.8% results were by up to 5% lower compared to the reference values. The difference between experimental and reference results could be explained by the fact that the reference values for KF 36.8% are interpolated values based on the available data for commercial products. The experimental results for NaF 30% in the temperature range between 10 and 30 °C were in good agreement with the reference (Cabot Corp, 2016). Moreover, it was not possible to test NaF 30% sample at temperatures below 0 °C due to crystal formation and only experimental results for temperatures higher than 0 °C were presented in this study. Both LiF 29% and LiF 36% were giving higher thermal conductivity values by up to 1 % and 4 % compared to experimental results for KF 29% and KF 36.8%, respectively. NH₄F 26% had lower thermal conductivity values at lower temperatures by up to 1 % compared to KF 29%. Instead, NH₄F 34% gave higher values by up to 1 % at lower temperatures compared to experimental results obtained for KF 36.8%.



Fig. 45, shows the results of the specific heat capacity measurements. As seen, LiF 29 % and NH₄F 26% had higher specific heat capacity than KF 29% at the temperature of -15 °C by up to 13 % and 10 %, respectively. Note that NaF 30% and LiF 36% solutions showed high susceptibility of crystal formation below 0 °C when fast cooling rate was applied. Thus, the possible application is rather limited to higher temperatures only. Additionally, LiF 36% and NH₄F 34% showed higher specific heat capacity than KF 36.8% by up to 14 % and 11 % at temperature -25 °C, respectively.

Among all formate salts examined, ammonium formate solution showed the best performance at low temperatures by giving lower dynamic viscosity as well as higher specific heat capacity and thermal conductivity. Sodium formate and lithium formate solutions had two to three times higher dynamic viscosity than other formate salts and cannot be recommended for low temperature applications despite high specific heat capacity and thermal conductivity values. Highly concentrated solutions of lithium formate and sodium formate were recrystallizing at lower temperatures, thus, their possible application is mainly limited to higher temperatures. Additionally, the measured properties for both potassium formate solutions were slightly different from reference values. As seen, different type of cation in the formate salt can result in different properties and similar results were found for chloride salts. Thus, further studies were conducted to investigate cesium formate and different acetate salts such as ammonium acetate and cesium acetate.

Due to the lack of the freezing point data the first very step was to prepare solutions of varying concentrations each 10wt-% in order to develop the freezing curves. Afterwards, representative solutions with three different freezing temperatures of -10, -20 and -30°C were investigated. The freezing curves of each salt solution are reported in Fig. 46. Dashed lines indicate the reference values found in (Melinder, 2007).



Fig.46 Experimental freezing point results for alternative salts.

Fig. 46 shows that the lowest temperature of about -75 °C was reached for 60 wt-% cesium acetate (CsAc) solution while 80 wt-% cesium formate (CsF) water based solution gave the freezing point of around -66 °C. On the other hand, the thermal conductivity as well as specific heat capacity values tend to decrease with increasing salt concentration. Moreover, higher salt concentration in a solution results in higher dynamic viscosity and higher pumping power, consequently. Note that potassium acetate was excluded from this study because it poses poorer thermophysical properties than potassium formate.

Fig. 47 shows the density results obtained for cesium formate, cesium acetate, ammonium formate, ammonium acetate and sodium formate. It is important to underline that sodium formate (NaF) had rather high lowest freezing point temperature and only a solution of 15 wt-% having the freezing point of -10 °C is presented in this study. As seen, cesium formate solutions have higher density than cesium acetate solutions due to the significantly higher concentrations of cesium salt. Additionally, potassium formate solutions have higher density compared to sodium formate, ammonium formate and ammonium acetate solutions.



Fig.47 Density results for selected concentrations.

Fig. 48, 49 and 50 present the results of dynamic viscosity measurements for solutions having the freezing point temperature of -10, -20 and -30 °C, respectively.



As seen, similar trends were observed for chosen salts solutions having different freezing point temperatures. Results show the outstanding low viscosity results obtained for all cesium formate solutions. KF 19% and NH₄F 16% solutions had higher viscosity at temperature of -8 °C by 12 % and 16 %, respectively. Furthermore, CsAc 30% had higher viscosity by up to 41 % compared to CsF 32%. NaF 15 % and NH₄Ac 17% had the highest viscosity values among all tested samples. Similar tendencies were obtained for -20 °C freezing point solutions. Both KF 29% and NH₄F 26% had higher viscosity than cesium formate at temperature of -18 °C by 19% and 17%, respectively. CsAc 41% had higher viscosity values among all tested samples. Additionally, KF 36.8% and NH₄F 34% had higher dynamic viscosity at temperature of -18 °C by up to 33% and 34%, respectively. CsAc 48.5% had higher viscosity by up to 87% compared to CsF 54%. Again, NH₄Ac 34.6% showed the highest viscosity values.



Fig. 51, 52 and 53 show the results of thermal conductivity tests. As seen, NaF 15%, KF 19% and NH₄F 16 wt-% had the highest thermal conductivity values. CsAc 30% had the lowest thermal conductivity than KF 17.9% by up to 10% at temperature of -8 °C. Moreover, KF 29% and NH₄F 26% had the highest thermal conductivity among solutions having the freezing point of -20 °C. CsAc 41% and CsF 44 wt-% has the lowest thermal conductivity than KF 29% at temperature of -18 °C by up to 16% and 11%, respectively. Similar results were observed among solutions having the freezing point of -30 °C. Again, KF 36.8 wt-% and NH₄F 34% had the highest thermal conductivity thermal conductivity among all investigated solutions. CsAc 48.5% and CsF 54% had lower thermal conductivity than KF 36.8% at temperature of -28 °C by up to 30% and 13%, respectively.



Fig. 54, 55 and 56 present the results of specific heat capacity measurements. As seen, CsF 32% had 5% lower specific heat capacity than KF 19%. NH₄Ac 17%, NaF 15% and NH₄F 16% secondary fluids had the highest specific heat capacity thank KF 19% by up to 8%, 6.5% and 6% respectively. Moreover, CsF 32% and CsAc 41% had the lowest specific heat capacity than KF 19% by up to 18% and 5%, respectively.



Similar tendencies were observed for solutions having the freezing point of -20 °C and -30 °C. NH₄Ac 27% and NH₄F 26% had the highest specific heat capacity than KF 29% by up 11 % and 10 %, respectively. Whereas, CsF 44 wt-% and CsAc 41% had the lowest specific heat capacity than KF29% by up to 26 % and 19 %, respectively. NH₄Ac 34.6% and NH₄F 34% among all solutions having the freezing point of -30 °C had again the highest specific heat capacity thank KF 36.8% by up to 12 % and 11 %, respectively. CsF 54% and CsAc 48.5% had lower specific heat capacity than KF 36.8% by up to 30 % and 3.8 %, respectively.



Fig.56 Specific heat capacity ($T_f = -30$ °C).

In order to evaluate the heat transfer abilities of selected alternative salts and propylene glycol solutions, a numerical study aimed at comparing the Reynolds numbers, heat transfer coefficients and pumping power in a U –pipe type was carried out. Summary for some results of this performance study are presented in Fig.57, 58 and 59. The detailed description of methodology can be found in MSc. Thesis report by Barcarolo, 2018. In this comparison study the following parameters were assumed:

- Cooling capacity of the evaporator: Q = 12500 W
- Mean velocity in the U-pipe: w = 0.416 m/s
- Internal pipe diameter: di = 35 mm
- Total length of the pipe: L = 500 m

As seen, propylene glycol has a very low value because the fluid is still in laminar flow regime, whereas the other secondary fluids are already in turbulent flow regime. Fig. 57 points out the good heat transfer coefficient of CsF 32%, which is higher than KF 19% and just 1.2 % lower than water at the temperature of 0 °C. KF 19%, NH₄F 16%,

NaF 15% and NH₄Ac 17% had the worst heat transfer coefficient compared to water by up to 10%, 14.5%, 18% and 36 %, respectively.



Fig. 57 Heat transfer coefficient and pumping power for solutions with Tf -10 °C.

Moreover, the pumping power results showed that PG 25.4% was in the laminar flow conditions and at temperatures higher than 0 °C. NH₄F 16%, solution turned out to be the best fluid and needed the least pumping power to transport the same amount of heat. The second best performing solution was KF 19% while NH₄Ac 17%, CsF 32% and CsAc 30% solutions gave the highest pumping powers.

Fig. 58 presents both heat transfer coefficients and pumping power results for solutions with the freezing point of -20 °C. As seen, KF 29% solution had the highest heat transfer coefficient among all salts. NH₄F 26% had about 22 % lower heat transfer coefficient compared to KF 29%. NH₄Ac 27 wt-% had the lowest heat transfer coefficient by up to 55 % lower than water. Both CsF 32% and CsAc 30% had rather similar values. Moreover, the low pumping power of NH₄F 26 % by up to 10 % compared to KF 29% needs to be pointed out. The worst performing salt based secondary fluid was again PG 39.39 having the pumping power about 66 % higher than water. CsF 44%, NH₄Ac 27% and CsAc 41% had higher pumping power compared to KF 29% by up to 21 %, 24 % and 34 %, respectively.



Fig. 58 Heat transfer coefficient and pumping power for solutions with Tf -20 °C.



Fig. 59 Heat transfer coefficient and pumping power for solutions with Tf -30 °C.

Fig. 59 show both the heat transfer coefficient and pumping power results for alternative salt solutions with the freezing point of -30 °C. The highest heat transfer coefficient was obtained for CsF 54%, which is about 14 % lower than water. KF 36.8% showed lower heat transfer coefficient compared to CsF 54% and water by up to 11 % and 25 %, respectively. Similarly NH₄Ac 34.6% had the worst heat transfer coefficient than water by up to 68 %. Furthermore, NH₄F 34% and CsAc 48.5% had lower heat transfer coefficient than water by up to 30% and 42%, respectively. The lowest pumping power was obtained for NH₄F 34 wt-% among all salt solutions (about 24% lower compared to water). The worst performing secondary fluid was CsAc 48.5% and NH₄Ac 34.6% with higher pumping power than water by up to 64 % and 54 %, respectively. Additionally, CsF 54% solution had about 18% higher pumping power compared to KF 36.8%.

Summing up, among all the investigated alternative formate and acetate salts, cesium formate and ammonium formate solutions showed the best performance at low temperatures by providing the lowest viscosity in case of cesium formate and low viscosity, high specific heat capacity and thermal conductivity in case of ammonium formate. Cesium acetate proved to be a good and cheaper alternative to cesium formate, which maintained its good properties with high density and low viscosity but about 16% lower heat transfer than cesium formate. In addition, cesium formate and cesium acetate was found to be least corrosive among all formate and acetate salts tested. Unfortunately, both ammonium salts were the most corrosive especially toward copper and copper alloys and might be considered as the limiting factor for further investigations.

Objective 5: Validation of thermophysical properties of glycols and organic salts

The goal of the project was to complete the results for pure solutions of potassium formate, potassium acetate, propylene glycol and ethylene glycol. An extensive study of different secondary fluids and a critical evaluation of previously reported thermophysical properties mostly available for commercial products were presented in works by (Melinder, 1998; Melinder, 2006 and Melinder, 2010). Therefore, different concentrations corresponding to a given freezing points were prepared and tested in the lab.

Objective 5.1 Propylene glycol and ethylene glycol

In this study pure solutions of propylene glycol and water with respective freezing points of: – 10, -20, -30; -40 and -50 °C. Note that analytical grade propylene glycol (purity 99.9%) was used to prepare solutions. The freezing point and density results were in very good agreement with references found in (Melinder 1998; Melinder 2007; Weast et al., 1986-87) as seen in Fig.60. The measurement error was around 0.1 % compared with reference values.



As seen in Fig. 61, there were some differences observed in results for highly concentrated solutions of propylene glycol i.e.: 48.82 wt-% (PG 48.82%), 52 wt-% (PG 55%) and 60 wt-% (PG 60%). Especially the experimental results for PG 55% and PG 60% were lower than references by up to 9% and 8.5 %, respectively. Results for PG 48.84% was about 5 % lower compared to references. Note that the reference values are based on both pure solutions and commercial products as well as availability of

data for higher concentrations is rather limited to mostly commercial products containing different additives, which might affect the properties.



Fig. 62 and 63 presents the results of the thermal conductivity and specific heat capacity. As seen, the thermal conductivity results differ by up to $\pm 2\%$. The possible explanation can be again the source data for reference values. In most cases, the thermal conductivity results were lower than the estimated reference values for concentrations giving the freezing point of -10, -20,-30 and -50 °C. Surprisingly, only PG 55 solution was in very good agreement with the estimated properties found in Melinder, (2010). Additionally, the specific heat capacity results were not in agreement with any references found in literature. The shape of curves were more pronouncing with increasing concentration similarly to alcohol and salt type secondary fluid. Moreover, the experimental values are higher than ones published before. The possible explanation behind these differences could be the source data, the purity of tested solutions as well as the measurement temperature ranges applied. Similar inconsistencies were found for specific heat capacity results for ethylene glycol solutions giving the freezing point of -10, -20, -30, -40 and -52°C. It is important to underline that the freezing point and density results were in very good agreement with reference values found in (Weast R.C. et al., 1986-1987, Melinder, 1998 and Melinder, 2010) as shown in fig.64.

Fig.65 and 66 below present the dynamic viscosity and thermal conductivity results. As seen, the measurements for higher concentrations are in very good agreement (\pm 1%) with the reference values. The possible explanation can be the fact that these concentrations of based on some measurements published in (Melinder, 1998). Moreover, the results for specific heat capacity are very similar to propylene glycol solutions and hard to compare with reference values.







Objective: 5.2 Potassium formate and potassium acetate

The objective of this study was to complete the thermophysical properties for organic salt used as secondary fluids. The currently available data are mostly based on the commercially available products containing additives and other salts. Thus, it was crucial to investigate properties of pure potassium formate and potassium acetate solutions in order to develop the pure salt solutions database for the refrigeration industry. A high quality data are required when searching for new solutions and improving the existing secondary fluids. This study was conducted in parallel with investigation of other formate and acetate salts as low temperature alternative secondary fluids (section 4.2). Additionally, these two studies can lead to creation a new benchmark for comparison of properties and help in developing new generation of formate and acetate salts blends.

The freezing point for different solutions of potassium formate and potassium acetate were in rather good agreement with references found in (Melinder 1998; Melinder 2007; Melinder 2010) as seen in Fig.46. Some of the concentrations found in references were too high and some dilutions were made to reach the desired freezing point temperatures. Fig. 68 and 69 presents the density and dynamic viscosity results for solutions with respective freezing point temperatures of -10, -20, -30, -40 and -50 °C. The measurement are in very good agreement with only two solutions of 29 wt-% and 42 wt-% potassium formate. Other experimental density results are lower by up to 2 % compared to references. The possible reason of these significant differences is the reference data based on some commercially available products containing different additives and other salts that can change the properties. As seen, the obtained results for all potassium formate solutions were lower by up to 5 % than reference values presented in (Melinder, 2007; Melinder 2010). Note that the reference values for dynamic viscosity are only based on data found for commercial products containing additives that may affect the dynamic viscosity in different ways. Moreover, no experimental data for pure solutions of potassium formate were found. Thus, this study provides the first data for pure solutions of potassium formate with water at different concentrations and temperatures.

Fig. 70 and 71 present result of the thermal conductivity and specific heat capacity results. As seen, the obtained results for different potassium formate solutions were lower between 1 and 5 % than reference values found in (Melinder, 2007; Melinder; 2010). The highest difference between experimental and reference results could be explained by the fact that the reference values for KF 36.8 % are interpolated values based on the available data for commercial products. The specific heat capacity experimental results were higher between 1 and 4 % than reference values. Note that the shape of specific heat capacity curve is changing with increasing concentrations in a similar way as it happens for other type solutions such as alcohols, glycols or salts. Moreover, similar results were obtained for different solutions of potassium acetate.



Fig.70 Thermal conductivity results.

Fig.71 Specific heat capacity results.

Fig. 72 and 73 presents the density and dynamic viscosity results for solutions with respective freezing point temperatures of -10, -20, -30, -40 and -50 °C. The measurement are in very good agreement with only one solution of 18.5 wt-% potassium acetate and similar curve shape was reported by (Melinder, 1998). Other experimental density results are lower by up to 3 % compared to references. Moreover, the shape of density curve is changing with the concentrations and similar observations were made during measurements for other salts. As seen, the obtained dynamic viscosity results for all potassium acetate solutions were higher by up to 2 % than reference values presented in (Melinder, 1998; Melinder, 2007; Melinder, 2010). Note that the reference values for dynamic viscosity are based on both pure solutions and commercial products that may influence the quality of reference values. Moreover, no experimental data for pure potassium acetate were found. Thus, this study provides more accurate data for pure solutions of potassium acetate at different concentrations.

Fig. 74 and 75 present result of the thermal conductivity and specific heat capacity results. As seen, the obtained results for different potassium acetate solutions were in very good agreement reference values found in (Melinder, 1998; Melinder, 2007; Melinder; 2010). The specific heat capacity experimental results were higher between 1 and 8 % than reference values. Note that the specific heat capacity curve is changing with increasing concentrations in a similar way as it happens for other type solutions such as alcohols, glycols or salts. Moreover, similar results were obtained for different solutions of potassium formate, alcohols and glycols.



Fig.72 Density results.

Fig.73 Dynamic viscosity results.



Investigation of the most important thermophysical properties of mixtures of potassium acetate, potassium formate, propylene glycol and ethylene glycol was completed. The results showed some deviation with reference data that are mostly based on commercial products with different additives for specific heat capacity and thermal conductivity in some cases. Therefore, it is planned in future to publish more data as journal article. Moreover, these data may contribute to the improvement of tables for pure mixtures and provide data for specific concentrations that were not published before.

Objective 6: Improving the existing commercial products on the market

One of the objectives of the project was to continue to improve existing ethyl alcohol commercially available secondary fluids as well as to introduce the most suitable corrosion inhibitors. As reported, mixtures with up to 2 wt-% of propyl alcohol give the best thermophysical properties compared to pure ethyl alcohol - water. The obtained results showed that the chemical nature and concentration of different denaturing agents with ethyl alcohol can affect the thermophysical properties. Furthermore, samples of propyl alcohol (PA) and n-butyl alcohol (BA) showed higher specific thermal capacity and thermal conductivity than pure ethyl alcohol (EA) and ethyl alcohol based mixtures with ketones and methanol. Ethyl alcohol with the additives commonly used in Sweden give the best properties, ie. highest heat transfer (up to 10%) and lowest pressure drop (up to 2.7 %) among the various additives tested while products with higher concentrations of denaturants gave the worst results in terms of lower heat transfer and higher pressure drop than a pure ethyl alcohol water based solution. Ground source heat pumps in other European countries and the United States could achieve a better performance by switching from denaturing agents in the form of ketones and methyl alcohol to the above mentioned mixtures. This project helped to adjust the concentration of propyl alcohol (7-9 wt-%) and 2 wt-% n-butyl alcohol in a Swedish commercial product to exact 8 wt-% propyl alcohol and 2 wt-% nbutyl alcohol.

Another important goal was to investigate different types of adsorption and traditional (oxide forming) corrosion inhibitors compatible with ethyl alcohol based secondary fluids. Results showed that some corrosion inhibitors significantly affect properties such as freezing point, thermal conductivity and specific heat capacity. These studies helped to understand a link between molecule structure and concentration of various inorganic and organic corrosion inhibitors as well as helping one of project partners to create a commercial alcohol product with benzotriazole as a corrosion inhibitor.

The tests were conducted for different synthetic paraffins to analyse how composition, fractionation (seperation) methods and molecular weight can affect the thermophysical properties of the final product. It was found that the molecular weight significantly can affect the thermal properties and short chained iso-paraffins are the most suitable for low temperature applications. Further tests helped to select the most promising iso-paraffins blends for different applications and three commercial iso-paraffin based products were launched on the Swedish market by one of the industrial partners.

The results showed that different types of cation (e.g lithium, sodium, ammonium, cesium) can affect properties in different ways and more research is needed to find future salt based secondary fluids. Among all the investigated alternative formate and acetate salts, cesium formate and ammonium formate solutions showed the best performance at low temperatures by providing the lowest viscosity in case of cesium formate and low viscosity, high specific heat capacity and thermal conductivity in case of ammonium formate. Cesium acetate proved to be a good and cheaper alternative to cesium formate and maintained its good properties with high density and low viscosity but about 16% lower heat transfer than cesium formate. In addition, cesium formate was found to be least corrosive among all formate and acetate salts tested. These results gave a deeper knowledge to producers and

result in further development of their products and well new types of blends of different salts. Potassium acetate is not the only salt that can give lower corrosion rates and cesium formate and cesium acetate as well as sodium formate should be considered as well. The results showed some deviation with reference data that are mostly based on commercial products with different additives. Thus, new data may contribute to the improvement of tables for pure mixtures of potassium formate, potassium acetate, propylene glycol and ethylene glycol.

Conclusions

Summing up, the goals of this project were to validate properties of alternative ethyl alcohol and propyl alcohol blends, propose the most suitable corrosion inhibitors compatible with ethyl alcohol based secondary fluids. Moreover, this project had a strong focus on investigating the effect of different corrosion inhibitors on thermophysical properties and heat transfer. Additionally, numerous synthetic isoparaffins and organic formate and acetate salts have been investigated. Finally, the measurements that were not completed during Effsys+ project were completed as promised.

This project helped manufacturers to improve their commercial ethyl alcohol based products on Swedish market by providing the thermophysical properties of actual secondary fluids with denaturing agents. Results were published during numerous conferences and started a new discussion in other European countries as well as in USA to modify their regulations regarding the type and concentrations of denaturing agents in order to obtain better thermal performance of ground source heat pumps and other indirect refrigeration systems. Moreover, the goal of launching the first ethyl alcohol based product with compatible corrosion inhibitor not only in Sweden but also on European market was achieved.

Furthermore, these results proved that additives such as corrosion inhibitors actually have a big impact on thermophysical properties even if added in small concentrations. This study is the first to indicate that especially adsorption corrosion inhibitors affect the least the thermophysical properties when added in small concentrations as well as provide an excellent corrosion protection for many different metal alloys simultaneously. Therefore, adsorption corrosion inhibitors are highly recommended for commercial secondary based fluids. Unfortunately, more environmentally friendly sugar based corrosion inhibitors like sodium gluconate appear to have a significant effect on thermal conductivity (14% lower thermal conductivity) and is not recommended at all.

The tests conducted for different synthetic paraffins showed that composition, fractionation methods and molecular weight can affect the thermophysical properties of the final product. It was found that the molecular weight can significantly affect the thermal properties and short chained iso-paraffins are the most suitable for low temperature applications. Further tests helped to select the most promising iso-paraffin blends for different applications and the first three commercial iso-paraffin based products for very wide temperature applications were launched on the Swedish market.

Additionally, the results showed that different types of cation (e.g lithium, sodium, ammonium, cesium) can affect properties in different ways and more research

is needed to find future salt based secondary fluids. Among all the investigated alternative formate and acetate salts, cesium formate and ammonium formate solutions showed the best performance at low temperatures by providing the lowest viscosity in case of cesium formate and low viscosity, high specific heat capacity and thermal conductivity in case of ammonium formate. Cesium acetate proved to be a good and cheaper alternative to cesium formate, which maintained its good properties with high density and low viscosity but about 16% lower heat transfer than cesium formate. In addition, cesium formate was found to be least corrosive among all formate and acetate salts tested. This study gives a new benchmark to create better blends of different salts that will give better performance and result in lower corrosion character.

Investigation of the most important thermophysical properties of mixtures of potassium acetate, potassium formate, propylene glycol and ethylene glycol was completed. The results showed some deviation with reference data that are mostly based on commercial products with different additives for specific heat capacity and thermal conductivity in some cases. Moreover, these data may contribute to the improvement of tables for pure mixtures and provide data for specific concentrations not published before.

Future work

The F-gas Regulation has set a clear goal for the entire refrigeration industry to reduce the amount of GWP fluorinated greenhouse gases. Natural refrigerants with very low GWP values such as carbon dioxide, propane and ammonia have excellent properties and the only disadvantages are flammability and toxicity in case of ammonia. In order to increase the use of these refrigerants, and to reduce climate impact, it is important to find environmentally friendly and energy efficient secondary fluids for indirect systems with low pumping power and good heat transfer properties. Therefore, it is recommended to validate properties of alternative formate and acetate salts and their mixtures by measuring their basic thermophysical properties. This knowledge can be beneficial for both manufacturers, who can improve their products, and for customers as a basis for the design of indirect refrigeration systems and their components. In addition, stronger emphasis is placed on properties such as environmental friendliness and low fire hazard. Different additives should be investigated to raise the flash point of the ethyl alcohol based secondary fluids. Pine tree oil is already used in Canada as the denaturing agent for ethyl alcohol based products, but the thermophysical properties are unknown. At low concentrations, pine tree oil should have relatively little impact on thermophysical properties, a shorter degradation time during leakage and even higher flash points. This additive could be used both as denaturation product and to raise the flash point for various applications. Alfa-terpineols may also be added to increase the flash point to above 40 °C. Some studies confirm that an addition of alpha-terpineol to a pure mixture of 99% by weight ethyl alcohol (flash point about 13 °C) increases the flash point to about 63 °C. Different terpineols can be obtained as a by-product of pine tree oil and other plants and they prove to be compatible with other denaturing products such as propyl alcohol, n-butyl alcohol and ketones.

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