Project acronym:	**GeoHex**		
Project title:	Advanced material for cost-efficient and enhanced heat exchange performance for geothermal application		
Activity:	LC-CS3-RES-1-2019-2020 Developing the next generation of renewable energy technologies		
Call:	H2020-LC-CS3-2019-RES-TwoStages		
Funding Scheme:	INEA	**Grant Agreement No:**	851917
WP1	**Requirement analysis and project mapping**		

D1.5 – Thermophysical characterisation of ORC working fluid

Due date:	29/02/2020	
Actual Submission Date:	25/02/2020	
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Dissemination Level[1]**:**	PU	
Nature:	Report and data table	
Status of this version:		**Submitted**
		For Review by Coordinator
	X	**Submitted**
Version:	V1	
Abstract	As part of task 1.4, the deliverable reports on the characterization of ORC working fluid in terms of specific heat capacity, density, critical temperature, pressure, thermal conductivity, surface tension, etc.	

REVISION HISTORY

Version	Date	Main Authors/Contributors	Description of changes

This project has received funding from the European Union's Horizon 2020 Research and Innovation programme under grant agreement No. 851917

[1] Dissemination level security:

PU – Public (e.g. on website, for publication etc.) / **PP** – Restricted to other programme participants (incl. Commission services) /

RE – Restricted to a group specified by the consortium (incl. Commission services) / **CO** – confidential, only for members of the consortium (incl. Commission services)

This project has received funding from the European Union's Horizon 2020 program Grant Agreement No 851917. This publication reflects the views only of the author(s), and the Commission cannot be held responsible for any use which may be made of the information contained therein.

Document: Thermophysical properties of ORC fluids

Version:

Date: 25 February 2020

CONTENTS

1. EXECUTIVE SUMMARY

The overall objective of the GeoHex project is to develop advanced material with antiscaling and anticorrosion properties for cost-efficient and enhanced heat exchanger (HX) performance for geothermal applications. GeoHex excellence lies in the concept of developing HX materials addressing both the improvements in the antiscaling and anticorrosion properties, as well as, the heat transfer performance of the HX material, which will lead to smaller, more efficient and cheaper systems.

For phase change heat transfer case, most of the activities are focused on water and only limited research has been performed with low surface energy fluids, such as organic Rankine cycle (ORC) working fluids, this being one of the objectives of the GeoHex project. As a part of WP1, T1.4, was to make an overview of ORC fluid thermophysical characteristics of geothermal interest.

In this report the thermophysical characterization of most common ORC working fluids has been summarized at a reference temperature (T_r 298.15K) and reference pressure (P_r 0.1 MPa) together with sources of equations of state (EoS) available in the literature for calculations the thermophysical properties of ORC fluids as a function of temperature and pressure. In total 43 ORC fluids were included in the summary that can be used at low to high temperature (80 to 350°C) related to geothermal applications.

The thermophysical properties of the ORC fluids at variable conditions may be obtained from the CoolProp library [67] (http://www.coolprop.org/). CoolProp is a European open source thermophysical property library containing 110 pure and pseudo-pure fluids as well as properties of 40 incompressible fluids and humid air. The thermodynamic properties of the fluids in CoolProp are all based on Helmholtz-energy explicit EoS that are the preferred form for describing thermophysical properties of ORC fluids.

2. OBJECTIVES MET

The deliverable contributes towards the following work package objectives:

- Identify performance characteristics and operational limitations of SOA heat exchangers for geothermal application
- Identify the opportunities of GeoHex in geothermal sector and map GeoHex project activities

3. KEY THERMOPHYSICAL PROPERTIES OF INTEREST

3.1 Overview

The thermophysical properties of interest for ORC fluids include critical temperature and pressure, maximum operational temperature and pressure, mass specific constant pressure specific heat, fluid density, thermal conductivity, surface tension, enthalpy of vaporization, viscosity and boiling point. The respective symbols and units are listed in Table 1.

Wet and Dry fluids – Fluids with a negative or positive slope on a temperature-entropy curve, respectively. Dry fluids are superheated after isentropic expansion and therefore there is no risk of liquid droplets at the turbine outlet. Therefore, dry fluids are more appropriate in ORC systems.

Critical temperature and pressure – The pressure and temperature values that denote the critical end point on a phase equilibrium curve between the liquid and vapor phase of the fluids. Beyond these values phase boundaries disappear.

Maximum operational temperature and pressure – Practical limitations on maximum operational temperature and pressure. Near the critical point small changes in temperature can cause a large change in pressure. Therefore, it is practical to set a limit to the working fluid conditions. Here the maximum temperature for wet fluids is set to 10°C lower than the critical temperature as Delgado-Torres and Garcia-Rodeiguez [58] did. For Dry fluids we use the method Rayegan and Tao [56] used where they limit the mass fraction of the liquid to 1% across the turbine.

Mass specific constant pressure specific heat - The heat needed to raise the temperature of a unit mass of the working fluid by a unit degree under the same pressure conditions.

Density - The mass per volume of the fluid.

Thermal conductivity – The measure of the fluids ability to conduct heat. Heat transfers faster in fluids with high thermal conductivity than in fluids with low thermal conductivity.

Surface tension – The tension of a liquid surface due to uneven molecular forces of attraction on molecules at or near the surface.

Enthalpy of vaporization - The heat required to transform a quantity of a fluid from a liquid to a vapor phase under the reference pressure.

Viscosity - The measure of the resistance of a fluid to deformation under shear stress.

Boiling point - The temperature at which the liquid and vapor can coexist in equilibrium at the reference pressure.

Reference temperature – Set to 298.15K in this report.

Reference pressure – Set to 0.1 MPa in this report.

***Table 1**: Symbols for thermophysical properties.*

Symbol	Description	Unit
Fluid type	Wet or dry	
T_c	Critical temperature	K
P_c	Critical pressure	MPa
T^{max}	Maximum operational temperature	K
P^{max}	Maximum operational pressure	MPa
C_p	Mass specific constant pressure specific heat	J/kg/K
ρ	Density	kg/m^3
k	Thermal conductivity	W/m/K
γ	Surface tension	mN/m
ΔH^{vap}	Enthalpy of vaporization	kJ/kg
μ	Viscosity	mPa·s
BP	Boiling point	K
T_r	Reference temperature, 298.15K	K
P_r	Reference pressure, 0.1 MPa	MPa

3.2 Available databases and EoS for ORC fluids

A number of libraries exists for ORC fluids to calculate thermophysical properties with different capabilities. These include:

- REFPROP 9.1 [59]
- EES [60]
- FLUIDCAL [61]
- ZITTAU [62]
- FPROPS [63]
- HelmholtzMedia [64]

Of these REFPROP is the most used. REFPROP is a product of the United States National Institutes of Standards and Technology (NIST). It has the most fluids in its library, 127, followed by EES with 88, FLUIDCAL with 70, FPROPS with 36, Zittau with 34 and HelmholtzMedia with 9. Of these FPROPS and Helmholtz Media are open source [67].

The thermodynamic properties of the fluids in this report are all collected from the CoolProp library [67], (http://www.coolprop.org/). CoolProp is a European open source thermophysical property library containing 110 pure and pseudo-pure fluids as well as properties of 40 incompressible fluids and humid air. The library is written in C++ with wrappers available for most of the programming languages. The thermodynamic properties of the fluids in CoolProp are all based on Helmholtz-energy explicit equations of state (EoS). In this formulation, the total non-dimensionalised Helmoltz energy α is given as the sum of the residual α^r and the ideal-gas α^0:

$$\alpha = \alpha_r + \alpha^0$$

With this formulation all other thermodynamic properties can be derived from analytic derivatives of the α^r and α^0 terms. As an example, the pressure, p, can be obtained from:

$$Z = \frac{p}{\rho RT} = 1 + \delta\left(\frac{\partial \alpha^r}{\partial \delta}\right)_\tau$$

were Z is the is the compressibility factor, p is the pressure [kPa], ρ is the density [kg/m^3], R is the mass specific gas constant [kJ/kg·K], T is the temperature [K], δ is the reduced density given by δ=ρ/ ρ_{red}, and the reciprocal reduced temperature τ, is given by τ=T_{red}/T. For all the fluids studied in this report, except R134A, the reducing density is the critical density and the reducing temperature is the critical temperature. For R134A the reducing parameters are determined with the fitting process. The enthalpy in kJ/kg is obtained from:

$$\frac{h}{RT} = \tau\left[\left(\frac{\partial \alpha^0}{\partial \tau}\right)_\delta + \left(\frac{\partial \alpha^r}{\partial \tau}\right)_\delta\right] + \delta\left(\frac{\partial \alpha^r}{\partial \delta}\right)_\tau + 1$$

Other thermodynamic parameters such as entropy, speed of sound, specific heats, derivatives and more can be obtained analytically[67]. Detailed information about the derivatives and thermodynamic properties can be found in Lemmon et al [65] and Span [66]. Temperature and density are the independent variables in the explicit Helmholtz energy equations of state. Span et al [68] describe how to handle input state variables of temperature/pressure, pressure/density, pressure/enthalpy and pressure/entropy.

A wider range of methods are used in CoolProp to determine the transport properties, viscosity, thermal conductivity and surface tension. For many of the fluids a precise correlation has been developed but the lack of experimental data inhibits accurate correlations and therefore predictive or empirical methods are used. For these reasons fluid specific correlations for viscosity and thermal conductivity are only provided for 36 of the fluids in CoolProp. An extended corresponding state method can be used for those fluids that do not have fluid specific correlations for viscosity and thermal conductivity[67].

The surface tension has been evaluated from Mulero et al. [55]. The correlations of the surface tension of the fluids are:

$$\sigma = \sum_i a_i \left(1 - \frac{T}{T_c}\right)^{n_i}$$

where σ is the surface tension, T_c is the critical temperature and a_i and n_i are correlation constants. The mean absolute percentage difference in this correlation for all the fluids is less than 6% and for most of the fluids this difference is less than 3%.

3.3 Summary of thermophysical properties of ORC fluids

Here a selection of 43 common ORC fluids and their thermophysical properties at either 25°C, 0.1 MPa or both as appropriate is presented (reference temperature and pressure) (Table 2). The list is intended to give an overview of potentially available ORC fluids for geothermal application within the temperature range 80 to 350°C.

The effect of these thermophysical properties as a function of temperature and pressure can be obtained through the EoS of individual fluids, and formulations describing the temperature and pressure effects on thermal conductivity (k), surface tension (γ) and viscosity (μ). The sources of these information for individual ORC fluids is given in Table 3. The EoS properties can be calculated as a function of temperature and pressure with the aid of the CoolProp library [67], (http://www.coolprop.org/).

***Table 2**: Thermophysical properties of the ORC fluids*.

ORC fluid	Chemical formula	Fluid type	T_c [K]	P_c [MPa]	T^{max}[57] [K]	P^{max}[56] [MPa]	ΔH_{vap} [P_r] [kJ/kg]	BP [P_r] [K]	C_p [T_r,P_r] [J/kg/K]	ρ [T_r,P_r] [kg/m^3]	k [T_r,P_r] [W/m/K]	γ [T_r] [mN/m]	μ [T_r,P_r] [mPa·s]
Acetone	C_3H_6O	wet	508.1	4.7	486	3.379	501	329	2143	786		22.7	
Benzene	C_6H_6	dry	562.02	4.91	546.50	4.067	394	353	1735	874	0.141	28.2	0.602
Butane	C_4H_{10}	dry	425.13	3.8	410.51	3.013	386	273	1732	2.45	0.017	11.9	0.007
Butene	C_4H_8	dry	419.29	4.01	399.16	2.808	392	267	1561	2.36			
Perfluorobutane	C_4F_{10}	dry	386.33	2.32	380.29	2.057							
Perfluoropentane	C_5F_{12}	dry	420.56	2.05	417.36	1.803						9.35	
Cis-butene	C_4H_8	dry	435.8	4.23	413.61	3.035	414	277	1492	2.37			
Cyclohexane	C_6H_{12}	dry	553.60	4.08	547.7	3.665	356	354	1859	774		24.42	0.891
Cyclopropane(HC-270)	C_3H_6	wet	398.30	5.58	388				1357	1.75			
Decane	$C_{10}H_{22}$	dry	617.70	2.1		1.896	276	447	2193	727	0.129	23.39	0.848
Difluoromethane(R32)	CH_2F_2	dry	351	5.78	340								
Dodecane	$C_{12}H_{26}$	dry	658.1	1.82		1.723	256	489	2212	746	0.135	24.93	1.359
Ethane	C_2H_6	wet	305.33	4.87	295.33		489	185	1757	1.24	0.021	0.48	0.009
Heptane	C_7H_{16}	dry	540.13	2.74	534.71	2.41	317	372	2240	680	0.122	19.73	0.390
Hexane	C_6H_{14}	dry	507.9	3.03	499	2.68	335	342	2273	655	0.120	17.88	0.298
Isobutene	C_4H_8	dry	418.09	4.01	399.20	2.877	392	266	1629	2.36			
Isobutane	C_4H_{10}	dry	407.81	3.63	393.47	2.89	365	261	1692	2.44	0.017	10.00	0.007
Isohexane	C_6H_{14}	dry	497.70	3.04	490.03	2.682	323	333	2235	649		16.87	
Isopentane	C_5H_{12}	dry	460.40	3.37	451.02	2.887	343	301	2274	615	0.102	14.45	0.194
Neopentane	C_5H_{12}	dry	433.74	3.2	425.42	2.788	316	283	1715	3.06			
Nonane	C_9H_{20}	dry	594.6	2.28		2.059	289	424	2208	714	0.127	22.38	0.654
Octane	C_8H_{18}	dry	569.32	2.5		2.2	301	399	2228	699	0.125	21.17	0.512
Pentane	C_5H_{12}	dry	469.70	3.37	459.97	2.865	358	309	2316	621	0.112	15.45	0.180
Propane	C_3H_8	wet	369.83	4.25	359.83		426	231	1685	1.83	0.018	7.02	0.008
Propene(R-1270)	C_3H_6	wet	365.57	4.66	355.57		439	226	1551	1.75	0.017	6.96	0.009
Propyne	C_3H_4	wet	402.38	5.63	392.38				1551	1.67			
R-116	C_2F_6	wet	293.03	3.05	283.03		117	195	776	5.70	0.015		0.014
R-123	$C_2HCl_2F_3$	dry	456.83	3.66	439.20		170	301	1020	1464	0.076	15.19	0.418
R-124	C_2HClF_4	dry	395.43	3.62	375.93		166	261	742	5.73	0.013	9.66	0.013
R-134a	$C_2H_2F_4$	wet	374.21	4.06	364.21		217	247	742	5.73	0.013	8.03	0.012
R-152a	$C_2H_4F_2$	wet	386.41	4.52	376		330	249	1051	2.76	0.014	9.71	0.011
R-218	C_3F_8	dry	345.1	2.64		1.899	105	236	797	7.85	0.012	3.75	0.012
R-227ea	C_3HF_7	dry	376.0	3		2.352	132	257	813	7.15	0.013	7.04	0.012
R-23	CHF_3	wet	299.29	4.83	289.29		239	191	737	2.88	0.014		0.015
R-236ea	$C_3H_2F_6$	dry	412.44	3.5	405.84	2.955	165	279	867	6.43	0.014	12.00	0.011
R236fa	$C_3H_2F_6$	dry	398.1	3.2	381	2.288	159	272	838	6.42	0.013	9.59	0.011
R-245ca	$C_3H_3F_5$	dry	447.57	3.93	431.28	2.951	204	298	1379	1387		16.31	
R-245fa	$C_3H_3F_5$	dry	427.20	3.64	412.53	2.817	197	288	888	5.69	0.016	13.63	0.012
R-365mfc	$C_4H_5F_5$	dry	460.00	3.27	450.36	2.712	188	313	1377	1257		15.09	
R-41	CH_3F	wet	317.28	5.9	307.28		488	195	1118	1.40			
R-C318	C_4F_8	dry	388.38	2.78	379.69	2.314	117	267	791	8.43	0.012	8.18	0.011
Toluene	C_7H_8	dry	591.8	4.13	580.61	3.576	361	384	1701	862	0.130	27.91	0.552
Trans-butene	C_4H_8	dry	429	4.03	409	2.906	405	274	1610	2.37			

***Table 3**: Index list for the references for each ORC fluid.*

ORC fluid	EoS	k	γ	μ
Acetone	[1]		[55]	
Benzene	[2]	[3]	[55]	[4]
Butane	[5]	[6]	[55]	[7]
Butene	[8]			
Perfluorobutane				
Perfluoropentane			[55]	
Cis-butene	[8]			
Cyclohexane	[9]		[55]	[10]
Cyclopropane(HC-270)	[11]			
Decane	[1]	[12]	[55]	[13]
Difluoromethane(R32)				
Dodecane	[14]	[15]	[55]	[15]
Ethane	[16]	[17]	[55]	[17]
Heptane	[18]	[19]	[55]	[20]
Hexane	[21]	[22]	[55]	[23]
Isobutene	[8]			
Isobutane	[24]	[25]	[55]	[26]
Isohexane	[1]		[55]	
Isopentane	[1]	[27]	[55]	[28]
Neopentane	[1]			
Nonane	[1]	[12]	[55]	[13]
Octane	[29]	[12]	[55]	[13]
Pentane	[30]	[27]	[55]	[31]
Propane	[32]	[33]	[55]	[34]
Propene(R-1270)	[35]	[36]	[55]	[36]
Propyne	[11]			
R-116	[1]	[36]		[36]
R-123	[37]	[38]	[55]	[39]
R-124	[40]	[36]	[55]	[41]
R-134a	[42]	[43]	[55]	[36]
R-152a	[44]	[45]	[55]	[41]
R-218	[1]	[36]	[55]	[36]
R-227ea	[46]	[36]	[55]	[36]
R-23	[47]	[48]		[48]
R-236ea	[49]	[36]	[55]	[36]
R236fa	[50]	[36]	[55]	[36]
R-245ca	[51]		[55]	
R-245fa	[52]	[36]	[55]	[41]
R-365mfc	[46]		[55]	
R-41	[1]			
R-C318			[55]	
Toluene	[1]	[53]	[55]	[54]
Trans-butene	[8]			

4. CONCLUSIONS.

The data collated in this report will allow selection of appropriate fluids to meet varying requirements identified within the project (WP2-4). The published data will also be of value to researchers outside the project consortium.

The thermophysical characterization of most common ORC working fluids for geothermal application at 80-350°C are summarized (Table 2) that can be used for targeting potential ORC fluids at for a given temperature and pressure criteria. Following, a link to full EoS for detailed calculations of the thermophysical properties of the ORC fluids are listed and can be calculated in most cases using the CoolProp library [67] (http://www.coolprop.org/), a European open source thermophysical property database.

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