A REVIEW OF POTENTIAL WORKING FLUIDS FOR LOW TEMPERATURE ORGANIC RANKINE CYCLES IN WASTE HEAT RECOVERY

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ABSTRACT

The focus of this paper will be specific to working fluids for use in various technologies for waste heat recovery (WHR) of exhaust heat including internal combustion engines (ICE) and in the use of Organic Rankine Cycles (ORC). Several novel fluids have been developed (DR-2 or HFO-1336mzz(Z) and DR-12) which have a good potential fit for these low temperature heat recovery applications (up to 250ºC) and they have been characterized as having desirable working fluid properties such as good safety classification and environmental footprint. Additional properties from an ORC system, where mechanical systems are incorporated, are good thermal stability, chemical compatibility, material compatibility and thermodynamic performance. These systems must be reliable and therefore the interactions with the working fluids are paramount as design basis becomes an important attribute in the development of ORC components. The aforementioned HFO fluids will be assessed on the criteria mentioned to help identify their candidacy in using them in heat recovery technology platform, where interest is specifically ORC based. These novel HFO fluids provide a good alternative to existing working fluids currently under consideration with an added advantage of meeting low GWP regulations.

1. INTRODUCTION

The need to improve energy efficiency and fuel utilization efficiency has been a topic of discussion for the last couple of decades, the direction of integrating heat recovery systems in truck, marine, geothermal, biomass and waste heat from other various heat sources are progressively being adopted to help address this concern. In all of these applications, there are an array of potential different classes of working fluids, CFCs, HCFCs, PFCs, siloxanes, alcohols, hydrocarbons, ethers, amines, fluids mixtures, HCFOs and HFOs, which can be considered for use in ORCs and should be evaluated on a broad basis in order to identify the ideal working fluid for the desired system.

In recent years, an increased scrutiny has been placed on the environmental aspect of these fluids and regulatory pressures are driving global awareness of their impact on the environment. The ozone depletion potential (ODP) and greenhouse gas emissions (GHG) are of particular interest here and emphasis has been placed on choosing a working fluid which demonstrates an ability to meet these climate protection initiatives. When reviewing the various classes of working fluids listed above, certain characteristics will become unviable and as a result, CFCs and PFCs will not be evaluated due to their ODP and high GWP concerns, respectively. The ethers present another concern around reactivity and stability; the amines have been shown to have major toxicological effects, therefore these components were deemed to be outside the scope of good working fluids.

Within these classes of potential viable working fluids, a select few are provided to show their basic characteristics so a further discussion on relevant use in applications can be made more constructive. Additionally, the novel hydrofluoro-olefin (HFO) based fluids (DR-2 and DR-12) will be discussed as they have been developed specifically to address these concerns as well as having of other favorable characteristics such as being non-flammable and low toxicity concerns.

2. FLUID CHARACTERIZATION FOR LOW TEMPERATURE ORC

2.1 Simple Organic Rankine Cycles

The primary aim in identifying feasibility of working fluids for ORC system rests on conducting a thermodynamic analysis where the cycle configuration is an important variable. Determining the cycle performance is dependent on having precise evaporating and condensing temperatures combined with fluid properties (latent heat of vaporization, temperature, pressure, entropy, enthalpy and liquid and gas densities) and using these variables to determine expander output, required pumping power, net cycle efficiencies, mass flow rates and turbine size parameters for the fluids of interest. Without knowing exact system configurations, it is difficult to assess one fluid's benefits over another so temperature-entropy diagram and vapor pressure versus temperature curve will be provided for selected fluids as a general guideline. The properties shown in *Figures 1 through 3* were calculated by REFROP and CoolProp software, where each fluid and their respective EOS used are referenced in *Table 1*.

Table 1. EOS reference for Working Fluids using REFPROP and CoolProp

	program/ method	EOS reference:
HCFC-123 (R-123)	REFPROP	Younglove, B.A. and McLinden, M.O., "An International Standard Equation of State for the Thermodynamic Properties of Refrigerant 123 (2,2-Dichloro-1,1,1-trifluoroethane)," J. Phys. Chem. Ref. Data, 23:731-779, 1994.
HFC-134a (R-134a)	REFPROP	Tillner-Roth, R. and Baehr, H.D., "An international standard formulation of the thermodynamic properties of 1,1,1,2-tetrafluoroethane (HFC-134a) for temperatures from 170 K to 455 K at pressures up to 70 MPa," J. Phys. Chem. Ref. Data, 23:657-729, 1994.
HFC-245fa (R-245fa)	REFPROP	"Short Fundamental Equations of State for 20 Industrial Fluids," J. Chem. Eng. Data, 51:785-850, 2006.
DR-12	REFPROP	Peng-Robinson by Pavan Naicker
DR-2	REFPROP	Created at DuPont Based on Experimental Fit of PR-EOS - P. Naicker
SES36	CoolProp	Unpublished report: Monika Thol, Eric W. Lemmon, Roland Span, \"Equation of State for a Refrigerant Mixture of R365mfc (1,1,1,3,3-Pentafluorobutane) and Galden® HT 55 (Perfluoropolyether)\" https://github.com/ibell/coolprop/blob/master/CoolProp/pseudopurefluids/SES36.cpp
HCFO-1233zdE	REFPROP	"Thermodynamic Properties of Trans-1-chloro-3,3,3-trifluoropropene (R1233zd(E)): Vapor Pressure, p-rho-T Data, Speed of Sound Measurements
HMDSO	REFPROP	Multiparameter Equations of State for Selected Siloxanes, Fluid Phase Equilibria, 244:193-211, 2006.
Ethanol	REFPROP	A New Fundamental Equation for Ethanol, Master's Thesis, University of Idaho, 2011.
Toluene	REFPROP	Lemmon, E.W. and Span, R.,"Short Fundamental Equations of State for 20 Industrial Fluids,"J. Chem. Eng. Data, 51:785-850, 2006.
n-Pentane	REFPROP	Span, R. and Wagner, W."Equations of State for Technical Applications. II. Results for Nonpolar Fluids,"Int. J. Thermophys., 24(1):41-109, 2003.
	REFPROP:	Lemmon, E.W., Huber, M.L., McLinden, M.O. NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP, Version 9.1, National Institute of Standards and Technology, Standard Reference Data Program, Gaithersburg, 2013.
	CoolProp:	http://www.coolprop.org/citation.html

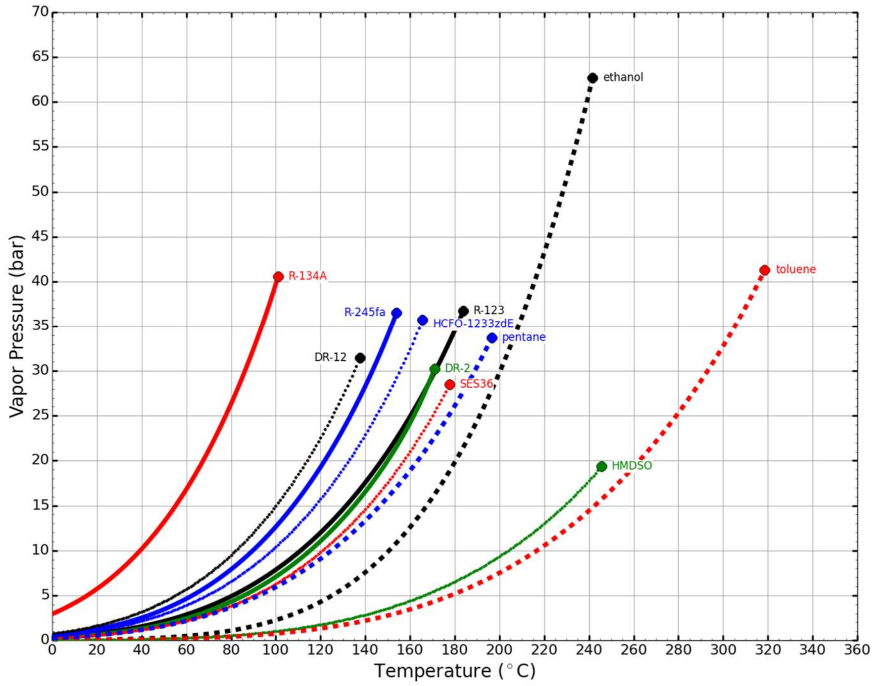


Figure 1. Vapor Pressure of Selected Working Fluids for Comparison

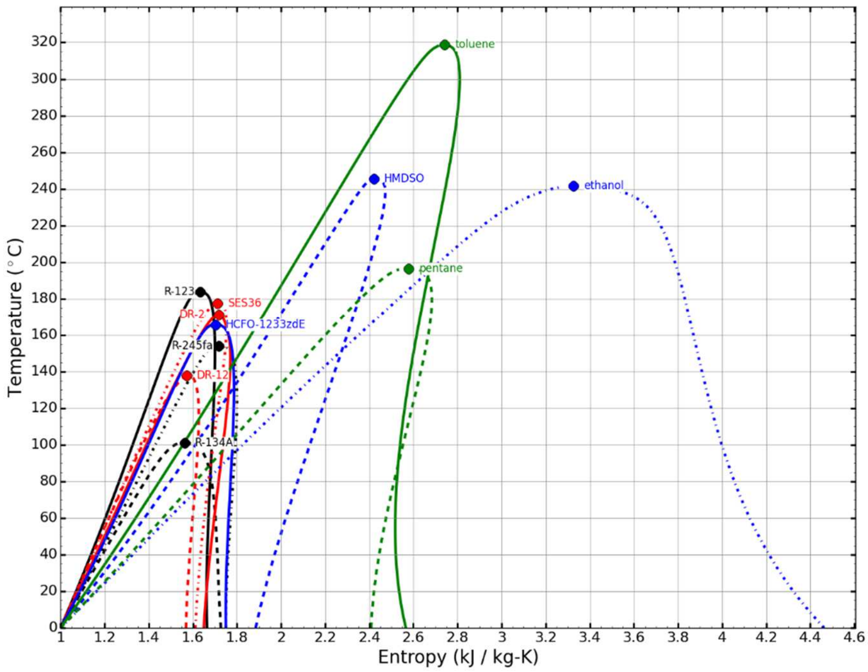


Figure 2. Temperature-Entropy Diagram for Selected Working Fluids for Comparison

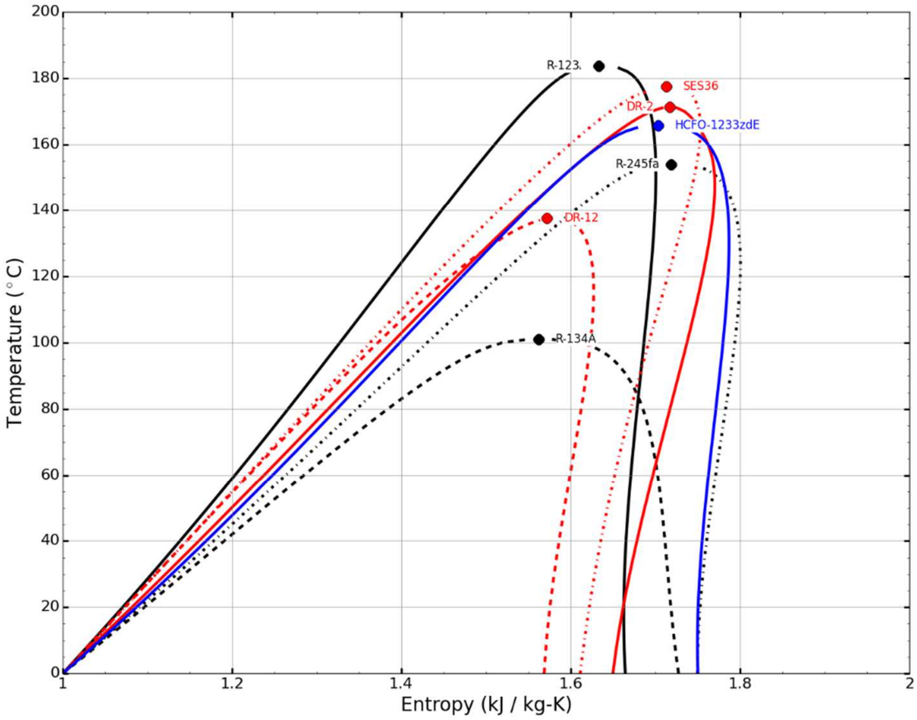


Figure 3. Enlarged Region of Temperature-Entropy diagram for Selected Working Fluids

Examples for Simple Organic Rankine Cycles systems are shown below and *Figure 5* illustrates heat being captured from the exhaust of internal combustion engine (Dupachy *et al*., 2009).

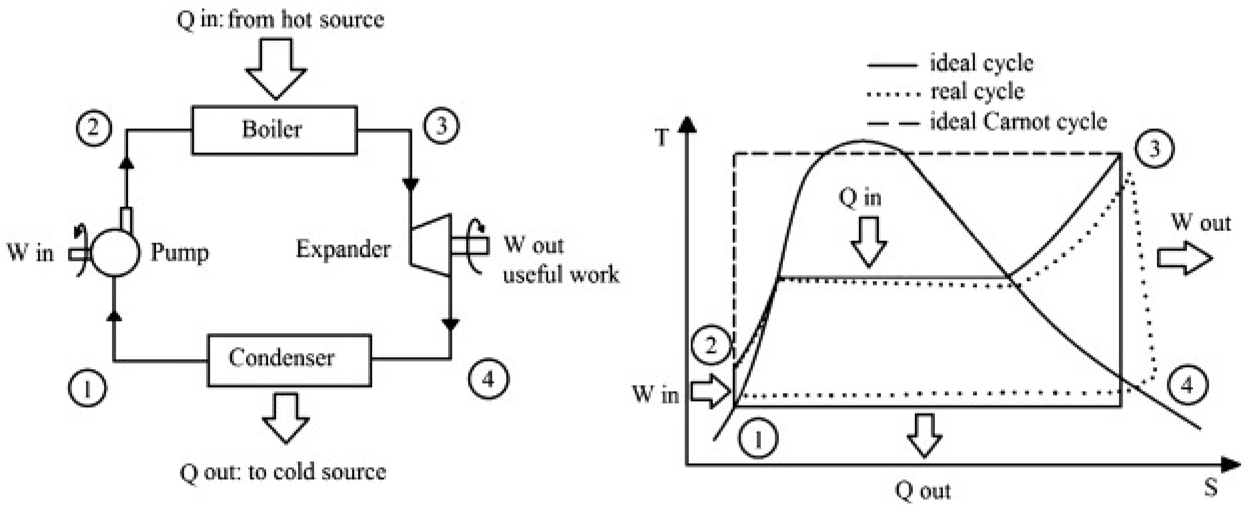


Figure 4. Rankine Cycle System

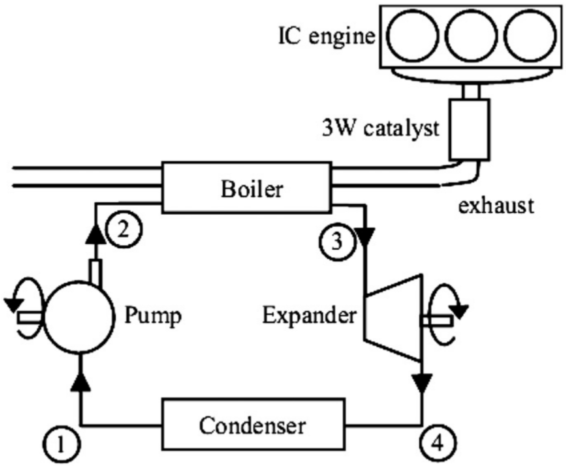


Figure 5. Layout of the waste heat recovery Rankine bottom cycle

Basic component selection for the expanders, pumps and heat exchangers is based on understanding the thermodynamics properties of the working fluids; however, there are other properties which can be overlooked which could be just as critical when selecting a fluid (safety, thermal stability, chemical and material compatibility, viscosity, etc.). These properties could influence reliability, the material construction – plastics, elastomers and metals as well as the robustness of the system where higher operating pressures and/or corrosion potential exists. From the refrigeration industry, many guidelines have been developed to address the safety management piece around the safe handling, storing and personnel exposure. Additional agencies such as NFPA, DOT, CFR, OSHA and TDG have placed many restrictions pertaining to the safe practice of toxic and flammable fluids and thus impose limitation which can affect a distribution and service facilities in terms of cost for electrical classification, breathing apparatuses and/or other infrastructure needs.

2.2 Working Fluids

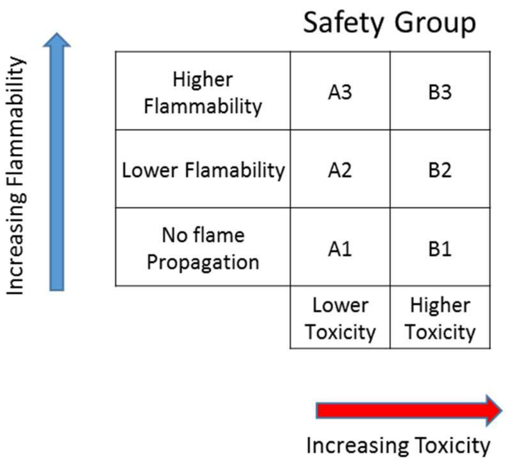
An effective way to screen out potential working fluid candidates can be an arduous task where emphasis of thermodynamic performance may be deemed as the most important element. Even though this is true, aspects such as flammability and toxicity affect the ability to safely work with the fluids in a given environment. Additionally, ODP and GWP are becoming a growing concerns as environmental restrictions and regulations may be imposed and ultimately negate the use of certain compounds (potential working fluids) as more friendly alternative fluids come into existence. In *Table 2* below, an overview of working fluids are provide to differentiate each based on physical properties, toxicity, flammability, GWP and ODP. Toxicity and flammability characterization for refrigerant fluids is provided in the last row, ratings specifically for HMDSO, ethanol and toluene are conducted by ASHRAE (2000, 2007, 2013) as they use represents a serious safety concern. *Table 3* highlights the general safety classification that is used to characterize working fluids. The category of A and B are used to distinguish the toxicity. The increasing number following the letter distinguishes the increasing flammability aspect of the fluid.

Table 2. Working fluid comparison of key thermodynamic, safety, health and environmental characteristics.

Properties	HCFC-123	HFC-134a	HFC-245fa	DR-12	DR-2	HCFO-1233zd(E)	SES36	n-Pentane	HMDSO(1)	Ethanol(2)	Toluene(3)
Normal Boiling Point, °C	27.8	-26.1	15.1	7.5	33.4	18.3	36.7	36.1	101	78.4	110.6
Critical Temperatures, °C	185	101.1	154	137.7	171.3	165.6	177.6	196.5	245.5	240.8	318.6
Critical Pressure, Mpa	3.67	4.06	3.65	3	2.9	3.57	2.85	3.36	1.94	6.15	4.13
Latent Heat @ 25 °C (KJ/Kg)	171.37	177.79	190.32	144.96	168.12	191.76	162.75	366.29	229.96	920.66	412.85
Specific Heat @ 0.1 Mpa 25°C (KJ/Kg-K)	1.02	1.43	1.32	1.09	1.19	1.24	1.08	2.32	1.91	2.44	1.7
Toxicity Class	See ASHRAE safety group rating								slightly	NA(7)	moderate toxic
Flammability Class(4)									serious flammable	severe flammability	serious flammability
Ozone Depletion Potential	0.02	0	0	0	0	0.0003		0		0	0
Global Warming Potential(5)	79	1300	858	32(6)	2	1	3710	5	ND(8)	1	3
safety group (ASHRAE)	B1	A1	B1	A1(6)	A1	A1	A1	A3	ND(8)	ND(8)	ND(8)

(1) Fisher Scientific, Hexamethildisiloxane, Material Safety Data Sheet, February 29,2008.
(2) NCP Alcohols, Ethanol, Material Safety Data Sheet, May 3, 2012.
(3) Honeywell, Toluene, Material Safety Data Sheet, December 21, 2005.
(4) ASTM (2004)
(5) Myhre et al. (2013)
(6) Expected value
(7) Not associated
(8) Not determined

Table 3. General Safety Group Classification



2.3 Thermal Stability

From *Table 2* above, an analysis can be made that the working fluids on the right side present concerns of flammability and of which, two have toxicity issues. A smaller subset of these fluids were screened for thermal stability in sealed tube tests to assess their suitability for higher temperature systems. Four of the fluids investigated, HFCF-123, HFC-245fa, DR-2, DR-12 and HCFO-1233zd(E), and subjected to 250°C for 1 and 7 days with metal coupons. An IC analysis for the anions F^- and Cl^- were conducted after the exposure conditions on the remaining fluids. Additional stability test of 14 days was carried out on HCFO-1233zd(E) and DR-2; results form HCFO-1233zd(E) were less favorable at 250°C, therefore a lower temperature study was performed at 200°C. As seen in the data in *Table 4*, results for HCFO-1233zd(E) at 200°C reflect significant degradation of the molecule as a function of time. DR-2 and DR-12 showed extremely favorable results. Interesting results were discovered regarding DR-12, where the fluoride ion was below detectable limits. The purity of DR-12 was only 98.1% and has no chlorines in its molecular structure; however, some trace chlorine containing species were present and very evident in the IC analysis as the Cl^- ions are seen at these elevated temperatures. These HFO fluids have an unsaturated (double bond) molecule and yet they do not demonstrate poorer thermal stability than saturated compounds. The notion that unsaturated compounds have less stability in a closed system at elevated temperatures is not necessarily correct a correct assumption. In a closed system, with all materials specified, only chemical and material compatibility tests with the exact system (including HFOs) can determine stability. Data presented in *Table 4* below incorporates some results previously presented by Kontomaris *et al.* (2013).

Table 4. Thermal Stability with IC Analysis Results

Fluid	Temperature (°C)	Duration	Coupon	IC Anion Results (PPM)	
				F-	Cl-
HCFO-1233zd-E	200	1 day	steel	8.23	61.5
HCFO-1233zd-E	200	7 days	steel	9.48	143.97
HCFO-1233zd-E	200	14 days	steel	34.28	554.18
HCFC-123	250	1 day	steel	328.43	496.44
HCFO-1233zd-E	250	1 day	steel	11.66	170.45
HFC-245fa	250	1 day	steel	3.6	< MDL
DR-12	250	1 day	steel	< MDL	18.28
DR-2	250	1 day	steel	0.6	11.3
HCFC-123	250	7 days	steel	2460.3	218.96
HCFO-1233zd-E	250	7 days	steel	1400.18	3854.26
HFC-245fa	250	7 days	steel	20	< MDL
DR-12	250	7 days	steel	< MDL	35.23
DR-2	250	7 days	steel	1.55	3.39
HCFO-1233zd-E	250	14 days	steel	2668.5	3194.7
DR-2	250	14 days	steel	1.83	2.02

2.4 Material Compatibility

An investigation was conducted on material compatibility for DR-2 where the study looked at 15 common materials in the presence of POE lubricant oil with DR-2 (Kontomaris, 2014); they were elevated to a temperature of 100°C for 14 days and their weight and hardness changes were measured at the conclusion of the experiment. Results display only a mild interaction between these plastics and elastomers and DR-2; they suggest that DR-2 would be suitable for use. It is recommend that further evaluations be conducted for material and chemical compatibility not only plastics and elastomers, but also covering various metals and lubricating typically found in a heat recovery system. This study is only a subset of current experiments from the lab. Future studies will be available where a selection of lubricant and recommendations will be incorporated as a function of temperature for DR-2 and DR-12.

Table 5. Weight Changes of Various Elastomers and Plastics with DR-2

DR-2 Compatibility with Plastics & Elastomers: (I)

Weight changes of polymeric specimens after exposure to
HFO-1336mzz-Z/POE Lubricant blends for 14 days at 100 °C

Material	Immediately after Exposure %	Twenty Four Hours after Exposure %
Neoprene	-0.55	-0.98
EPDM	2.39	0.84
Polyester Resin	10.04	4.94
Nylon Resin	-0.74	-0.79
Epoxy	0.66	0.56
Polyester PET	3.73	3.54
Polyester PBT	1.15	1.13
Polycarbonate	0.74	0.75
Polyimide	0.79	0.79
Teflon PTFE	3.05	2.72
Teflon FEP	3.29	3.09
Tefzel ETFE	6.25	5.61
Phenolic	-0.18	-0.31
PVC	0.68	0.70
PEEK	-0.06	0.01

Mild Interactions between HFO-1336mzz-Z and Many Plastics and Elastomers

Table 6. Hardness Changes of Various Elastomers and Plastics with DR-2

DR-2 Compatibility with Plastics & Elastomers: (II)

Hardness changes of polymeric specimens after exposure to
HFO-1336mzz-Z/POE Lubricant blends for 14 days at 100 °C

Material	Immediately after Exposure %	Twenty Four Hours after Exposure %
Neoprene	7.10	2.58
EPDM	2.56	0.64
Polyester Resin	-1.01	-0.51
Nylon Resin	-1.00	-2.00
Epoxy	-1.01	-3.54
Polyester PET	0.00	0.00
Polyester PBT	-1.00	-1.00
Polycarbonate	-1.00	0.00
Polyimide	0.00	0.00
Teflon PTFE	-0.50	0.00
Teflon FEP	0.00	-0.51
Tefzel ETFE	0.00	0.00
Phenolic	0.00	0.00
PVC	0.00	0.00
PEEK	0.00	0.00

Mild Interactions between HFO-1336mzz-Z and Many Plastics and Elastomers

3. CONCLUSION

The basis of this work was not to provide a deep analysis of ORC systems, but to focus on the viability and the selection process that comes with identifying good working fluid properties. The criteria to develop working fluids which perform under the high temperatures of heat recovery systems is essential as well as the need to have safe and environmental friendly alternatives to choose from. The ultimate goal from this study is to provide insight to existing entities like ASHRAE that review working fluids for the refrigerant industry, where all potential candidates are reviewed by a body of engineers and chemists for safety in use. It is conceivable that different environments may dictate that some safety concerns would represent less of an issue and they should be investigated based on their own merit. In general use, both flammability and toxicity are highlighted to pose significant risks and additional precautions are necessary to address their suitability for use. GWP and ODP represent two additional criteria which will influence working fluid selections in the future as regulations strive to find better alternatives as they affect the environment. Even though these influencers limit the choices of potential candidates, it does not mean that a significant loss of performance must be sacrificed to adhere to these values. The new HFO fluids offer comparable thermodynamic performance similar to fluids in their class and provide thermal stability as well. The DR-2 molecule with its low GWP and no ODP, has shown extremely good thermal stability at temperature up to 250^{o}C. These new class compounds, HFOs, have been shown to exhibit good overall characteristics for use in low and possible medium temperature ORC applications.

NOMENCLATURE

WHR	*waste heat recovery*
ORC	*organic Rankine cycle*
GHG	*greenhouse gases*
ICE	*internal combustion engine*
ODP	*ozone depletion potential*
GWP	*global warming potential*
EOS	*equation of state*
CFC	*chlorofluorocarbon*
HCFC	*hydrochlorofluorocarbon*
HFO	*hydrofluoro-olefins*
PFC	*perfluorocarbons*
HMDSO	*Hexamethyldisiloxane*
NFPA	*National Fire Protection Association*
DOT	*Department of Transportation*
CFR	*Code of Federal Regulations*
TDG	*Transportation of Dangerous Goods*
OSHA	*Occupational Safety and Health Administration*
ASHRAE	*American Society of Heating, Refrigeration and Air Conditioning Engineers*

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