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Regression comparison of organic working mediums for low grade heat recovery operating on Rankine cycle

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Abstract

A logistic-regression based classifier is developed here to predict the probability of any working fluid as a desirable candidate for ultra-low grade heat driven organic Rankine cycle. Global warming abilities, ozone depleting potentials as well as thermodynamic properties of the working medium are used to develop this generalized classifier. As a validation of the suggested classifier, more than 80 working fluids are screened, and regression analyses used to rate the most appropriate candidates. The preferable working mediums among those evaluated based on environmental impacts are HFCs. Considering environmental issues, safety concerns, and performance characteristics however, the preferable working fluids among those tested are HFC-245fa, followed by HFC-134a, HFC-227ea, HFC-236ea, HFC-236fa, HC-600, HC-600a, HC-601, and HC-601a.

Keywords: Working medium selection, Organic Rankine cycle, Low grade heat, Refrigerants

1. Introduction

Low grade thermal energy sources such as solar, geothermal, and industrial exhausts can be converted to electricity using simple systems such as Rankine cycles, or more complex ones such as Kalina cycles. The more complex cycles usually offer higher efficiencies, but at the cost of higher maintenance [1]. Because of the low operating temperature range, these cycles typically operate using organic mediums as working fluids. Of cycles operating on organic mediums, the most common is likely organic Rankine cycle (ORC), which has an added benefit of requiring only a single-stage expander, offering simpler and less costly design [2]. In addition to its simple cycle form, a few other variations of the Rankine cycle have also been proposed [3, 4]. More than 50 working mediums have been considered for thermodynamic cycles [5–10]. More rare mediums such as aromatic hydrocarbons [11] and mixtures of pure substances [12–17], the use of fluids such as CO_2 in the supercritical temperature range [18] have also been proposed as alternatives. Most of these comparisons are nonetheless conducted for defined operating conditions while some are for thermodynamic properties, or environmental benefits [8–10, 19–24]. A thorough review of ORCs has been conducted addressing design approaches and working medium selection [20, 25, 26]. To date, there is no methodology developed to compare working fluids across such variables, which would be applicable under all operating conditions, for all candidate fluids, and appropriate for low grade thermal energy recovery. This paper introduces a generalized screening methodology to compare and rank any working medium for

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low grade thermal energy recovery operating on a thermodynamic cycle, Rankine cycle in particular.

Beyond developing mathematical models which overwhelm the literature on the subject, as an emerging technology, design of the ORC still poses some challenges resulting from the need to efficiently capture low grade thermal energy, assure a robust design, achieve a reasonable cost reduction, etc. These issues have attracted some technical and economic analyses [27–29], as well as modifications to the design assemblage to improve performance or reduce cost by for example, using gerotor and scroll expanders [30], but without greatly increasing performance. In this paper, we focus on designing a comprehensive tool for refrigerant screening to make the most suitable selection, as a critical factor in improving system performance.

2. Organic Rankine Cycle

The majority of industrial waste thermal energy is rejected at moderate and low temperatures of less than about 260°C. More than half of the thermal energy recovery technologies are applicable to the high temperature range exceeding this value and up to 530°C. For ultra-low grade thermal energy recovery, assumed here as a range which falls below the boiling temperature of water, the need for a phase change of the working medium makes Organic Rankine Cycles (ORC) more desirable than water. For a given pressure, many organic mediums boil at significantly lower temperatures than that of water and condense in ambient conditions, which render them candidates thermodynamically to recover thermal energy from sources with lower temperature, [31]. The challenge is the choice of organic fluid which offers the highest efficiency and allows the highest utilization of the available thermal energy, and yet is acceptable based on other criteria such as the environment.

Pure working fluids such as HC-600 ($CH_3CH_2CH_2CH_3$) [25, 32], HFC- 245fa ($C_3H_3F_5$) [16, 33], HFC- 245ca ($C_3H_3F_5$) [8, 33], HCFC-123 ($C_2HF_3Cl_2$) [8, 34], and HC-600a as ORC working mediums have been studied widely [10, 13]. Fluid mixtures have also been proposed for ORC [13, 14, 35, 36] with varying environmental, physical and thermodynamic properties. But, no comprehensive tool encompassing the various relevant selection criteria such as Ozone Depleting Potential (ODP), Global Warming Potentials (GWP), and Thermophysical properties has been developed for the temperature range under consideration, prompting this current work.

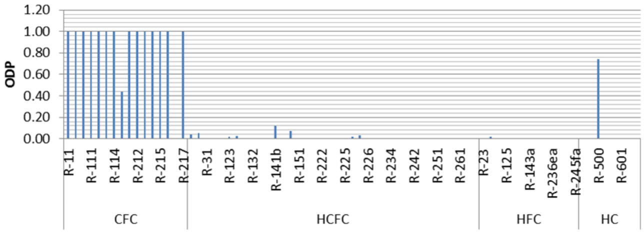

Figure 1: Ozone Depleting Potential for Common Refrigerant (adapted from [15])

3. Evaluation of Chlorofluorocarbons

Ozone Depleting and Global Warming Potentials:

ODP the relative ability of a refrigerant to destroy the stratosphere [37]. Figure 1 shows the ODPs of some common refrigerants including some future candidates. Furthermore, GWP compares the capacity of greenhouse gases to trap thermal energy in the atmosphere. GWP is calculated based on the energy absorbing ability of a greenhouse gas relative to that of carbon dioxide. For most greenhouse gases this ability declines over time. As a result, GWP is calculated over a range of life times, typically 20 years, 100 years, and 500 years to assess the impact of time. Some chlorofluorocarbons (CFCs) however have a long atmospheric lifetime with longer-lasting impact on GWP. Figure 2 shows the GWPs for some common refrigerants over a 100 year lifetime frame.

There is often a trade-off between system efficiency, i.e., suitable thermodynamic properties of the working medium on one side and GWP and ODP on the other; some of the most efficient refrigerants suitable for low grade thermal energy recovery are undesirable from the ODP, GWP, toxicity, etc. perspective. Figures 1 and 2 show that CFCs have high ODPs and GWPs. Most HCFCs have low ODPs (0.01–0.1) and GWPs. HFCs have very low ODPs but GWPs ranging from zero to very high. Among these R-123, (with atmospheric lifetime of 1.3 years) and R-152a (with atmospheric lifetime of 1.4 years)

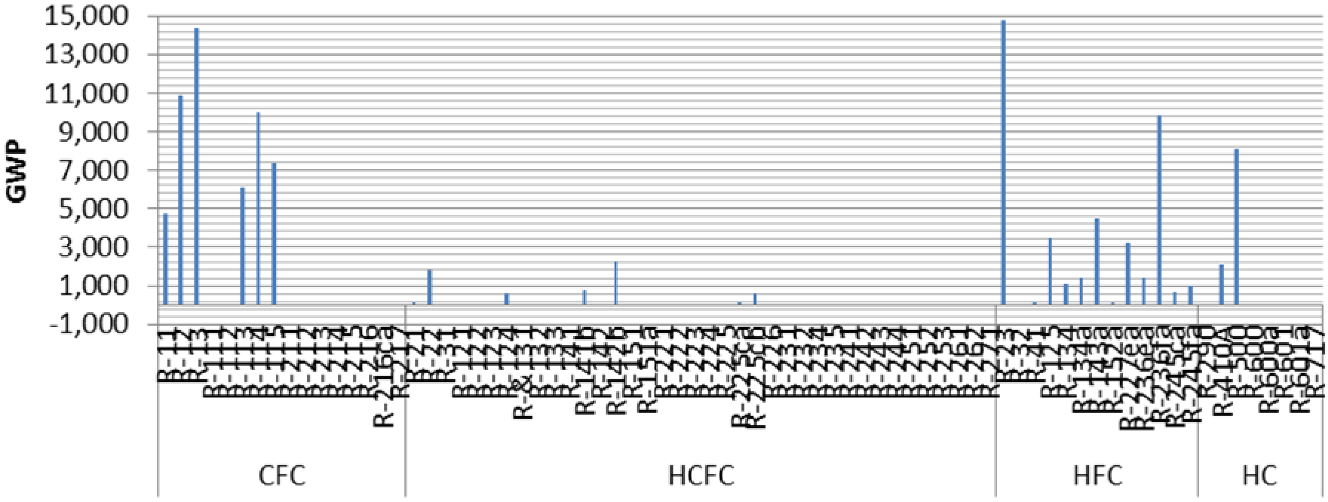

Figure 2: Global Warming Potential for Common Refrigerant (adapted from [15])

have both low ODP and GWP. However, R-123 is hazardous and also flammable under pressure, and R-152a is extremely flammable. None of the current refrigerants have all the desired criteria for an ideal refrigerant. Chemical and thermophysical analyses reveal conflicts in desired molecular makeup and properties which make the future discovery of a "perfect" refrigerant unlikely [38]. It would be useful to have a compartmentalized methodology for deliberate selection of a working medium from a list of the substances available and to maximize the performance of the working medium with the least environmental penalty and hazard risk.

Expansion gradient of Working Fluids:

The shape of the saturated vapor line in the temperature vs. entropy (T-s) diagram is a critical characteristic of the working fluid in an ORC. This characteristic has a great impact on the fluid applicability, performance, and design of the power generation system. Working fluids can be categorized as a wet fluid with negative slope (dT/dS), a dry fluid with positive slope (dT/dS), and an isentropic fluid with nearly vertical saturation line [22]. Because dT/dS leads to infinity for isentropic fluid, Liu et al. [26] used the inverse of the slope, $\xi\,(= dS/dT)$, to express the fluid type. Based on this expression, is $\xi < 0$, it is a wet fluid, $\xi > 0$ is a dry fluid, and $\xi \sim 0$ is an isentropic fluid. Table 1 shows the value of ξ for some of the working fluids.

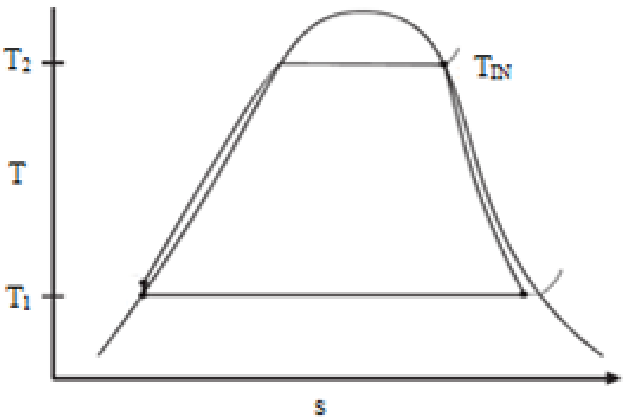

Figure 3: ORC cycle in T-s diagram

Dry and isentropic fluids are preferred for ORCs partly because these fluids do not condense during expansion, which protects the turbine blades from erosion. A negative slope of the saturated vapor line leads to droplets at the end of expansion requiring superheating to prevent turbine damage. In cases where the working fluid is too dry and leaves the turbine with substantial superheat, it may be rewarding to implement an internal heat exchanger. The superheated vapor cools down in the heat exchanger by transferring the thermal energy to the compressed liquid before entering the boiler, which will lead to higher cycle efficiency [22].

Table 1: Physical Properties of Selected Chlorofluorocarbon [39, 40]

ASHRAE Number	Saturation vapor slope, ξ (J/Kg K^2)	Critical Point	Boiling Ts at 1 atm	Molec. Weight, gr/mol	Vapor Cp, J/Kg K	Latent Heat, KJ/Kg
R-23	Wet, -6.49	25.6°C – 48.37 bar	-82.1°C	70	3884.02	89.69
R-32	Wet, -4.33	78.11°C – 57.83 bar	-51.7°C	52	2301.61	218.59
R-41	Wet, -7.20	44.25°C – 58.7 bar	-78.2°C	34	3384.66	270.04
R-116	Wet, -5.54	19.9°C – 30.4 bar	-78.2°C	138	4877.91	30.69
R-125	Wet, -1.08	66.18°C – 36.3 bar	- 48.45°C	120	1643.89	81.49
R-134a	Wet, -0.39	101°C – 40.6 bar	26.4°C	102.03	1211.51	155.42
R-143a	Wet, -1.49	72.73°C – 37.64 bar	-47.14°C	84	1913.97	124.81
R-152a	Wet, -1.14	113.5°C – 44.95 bar	-23.9°C	66.05	1456.02	249.67
R-218	Dry, 0.45	71.89°C – 26.8 bar	-36.4°C	188	1244.87	58.29
R-227ea	Dry, 0.76	101.74°C – 29.29 bar	20°C	170.03	1013	97.14
R-236ea	Dry, 0.76	139.22°C – 34.12 bar	6°C	152.04	973.69	142.98
R-236fa	Dry	125.55°C – 32 bar	-1.4°C	152	810	160
R-245ca	Dry, 0.60	174.42°C – 39.25 bar	28.2°C	134.05	1011.26	188.64
R-245fa	Isentropic, 0.19	154°C – 36.4 bar	14.6°C	134.05	980.9	177.08
R-290	Wet, -0.79	96.65°C – 42.5 bar	-41.89°C	44.097	2395.46	292.13
R-600	Dry, 1.03	152.05°C – 38 bar	-0.4°C	58.12	1965.59	336.82
R-600a	Dry, 1.03	135.05°C – 36.5 bar	-11.7°C	58.12	1981.42	303.44
R-601	Dry, 1.51	196°C – 33.6 bar	35.5°C	72.15	1824.12	349
R-717	Wet, - 10.48	132.4°C – 112.8 bar	-33.34°C	17.03	3730.71	1064.38

Density and Latent Heat:

Working fluids with high vapor density and high latent heat are preferable for ORC, [31]. A low vapor density leads to higher volume flow rate, and as a result high fluid velocity, which leads to higher pressure drop. Also, the size of the expander must be increased to absorb a higher volume flow rate. This has a significant impact on the cost of the system. A fluid with high latent heat absorbs more energy from the thermal energy source, therefore reduces the required flow rate and size of the equipment. Chen et al. derived an equation to compute the enthalpy change through the expansion (i.e. turbine work output), which is [26]:

$$\Delta h_{is} = C_p T_{IN}\left[1 - e^{\frac{L\left(\frac{1}{T_1}-\frac{1}{T_2}\right)}{c_p}}\right] \tag{1}$$

where Δh_{is} is enthalpy change in the expander, c_p is specific heat of the working fluid, T_{IN} is the turbine inlet temperature, e is the base of the natural logarithm, L is the latent heat, T_1 and T_2 are the saturation temperatures of two points on the vapor saturation line and $T_1 > T_2$. Based on Eq. (1), for a given temperature range, higher latent heat leads to higher work output. The T-s diagram of ORC cycle shown in Fig. 3 clearly illustrates this fact. With defined temperatures, the length of the horizontal line, which is proportional to the latent heat, defines the area formed by the cycle which is an expression of the work output.

Critical Point, Boiling Temperature, and Freezing Temperature:

Thermodynamic coordinates of refrigerants such as critical points, boiling temperature, as well as freezing temperature can be compared based on the operating conditions of ultra-low grade thermal energy ORC. For our purposes, thermal energy sources with 120°C and lower are considered ultra-low grade thermal energy. Also, the design condensation temperature is usually above 27°C in order to reject thermal energy to the ambient. As a result, working fluids with critical point far below 27°C such as R-14 (CF4) are excluded for difficulty of condensation. Other important thermodynamic properties to consider are boiling temperature, and freezing point.

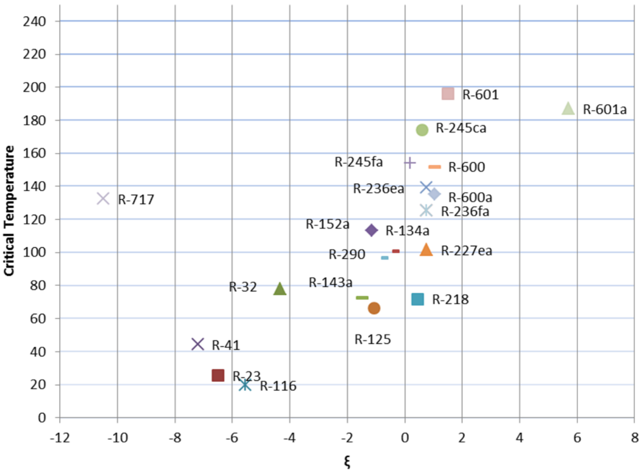

Figure 4: Distribution of screened working fluids in T-ξ diagram

Working fluids with a low normal boiling temperature below the cycle operating temperatures are not acceptable. The freezing point of the fluids should be below the lowest operating temperature in the cycle. Assuming a thermal energy source temperature of 80°C to 120°C and a thermal energy sink temperature between 10°C to 40°C, it is obvious that, R-21, R-22, R-23, R-32, R-41, R-116, R-124, R-125, R-142b, R-143a, R-152a, R-218, R-236ea, R-236fa, and R-290 can be eliminated because of their temperature ranges.

Thermophysical criteria:

A working fluid for ORC can be selected based on environmental impact, use-risks, thermodynamic characteristics, and physical properties. More than 80 working fluid candidates have been screened in this study, among which some of them have been phased out due to environmental concerns, or will be phased out soon. Generally CFCs which have high ODPs and GWPs and were set to be phased out in 1996 by the Montreal protocol are not acceptable for use as refrigerants, Figs 1 and 2. The use of HCFCs will be banned in 2030 in the United States. Therefore, R-21, R-22, R-123, R-124, R-141b, R-142b are not acceptable either. Currently HFCs which do not contain chlorine and do not damage the ozone layer are widely in use. Most HFCs are considered to be high GWP gases (Fig. 2) ranging from 154 for HFC-152a to 14,800 for HFC-23.

Table 2: Properties of Screened Working Fluids [39, 40]

ASHRAE Number	IUPAC Chemical Name	Semi-empirical ODP	Net GWP 100-yr
R-23	Trifluoromethane	0.00	14,800
R-32	Difluoromethane	0.02	
R-41	Fluoromethane	0.00	92
R-116	Hexafluoroethane	0.00	12,200
R-125	Pentafluoroethane	0.00	3,500
R-134a	1,1,1,2-Tetrafluoroethane	0.00	1,430
R-143a	1,1,1-Trifluoroethane	0.00	4,470
R-152a	1,1-Difluoroethane	0.00	124
R-218	Octafluoropropane	0.00	8,830
R-227ea	1,1,1,2,3,3,3-Heptafluoropropane	0.00	3,220
R-236ea	1,1,1,2,3,3-Hexafluoropropane	0.00	1,370
R-236fa	1,1,1,3,3,3-Hexafluoropropane	0.00	9,810
R-245ca	1,1,2,2,3-Pentafluoropropane	0.00	693
R-245fa	1,1,1,3,3-Pentafluoropropane	0.00	1,030
R-290	Propane	0.00	3
R-600	Butane	0.00	4
R-600a	Isobutane	0.00	4
R-601	Pentane	0.00	
R-601a	Isopentane	0.00	
R-717	Ammonia	0.00	0

Applying environmental impact as the first selection criterion limits our choice to 24 refrigerants from the pre-screened 80 working fluids, Tab. 2. The second criterion for the working fluid selection is thermo-physical properties of the working medium. Assuming a thermal energy source temperature range of 80°C to 120°C and a thermal energy sink temperature between 10°C to 40°C, none of the working fluids meet all the criteria discussed as ideal for ORC. Among the relevant thermophysical criteria, the critical temperature and the slope of saturation vapor line are important because they suggest the operating temperature range and limits of the thermodynamic cycle [39]. Figure 4 shows the critical temperature vs. ξ distribution of the screened working fluids.

Figure 4 suggests that the screened working fluids can be divided into four groups:

- Group 1: R-23, R-32, R-41, R-116, R-125, and R-143a are wet fluids with low critical temperatures and they usually require superheating. Among these fluids R-23 and R-116 have critical temperatures under 40°C, i.e., they require low condensation temperature near ambient conditions, which makes them less suitable for ORC. The condenser design for the rest of the fluids should not be a problem since their critical temperatures are above 40°C. Thus, R-32, R-41, R-125, and R-143a are promising candidates for supercritical ORC.

- Group 2: Fluids R-134a, R-218, R-227ea, R-236ea, R-236fa, R-245ca, R-245fa, and R-290 are isentropic fluids which makes them good candidates for ORC. Among these fluids R-236ea, R-236fa, R-245ca, and R-245fa have critical temperatures above 120°C, making them more fitting for us in ORC.

- Group 3: R-152a is a wet fluid with high critical temperature, and its use as ORC medium requires superheating.

- Group 4: Fluids R-600, R-600a, and R-601 are dry fluids which are good candidates for ORC without superheating requirements.

Based on these classifications refrigerants with suitable thermodynamic coordinates for ORC applications are HFC-134a, HFC-227ea, HFC-236ea, HFC-236fa, HFC-245fa, HC-600, HC-600a, HC-601, and HC-601a. Note that HFC-245ca is dropped from the list since it is flammable.

Next, we will use all the fluids listed in Tab. 1 and the preliminary conclusions arrived at above as a training data set to perform regression analysis and develop a hypothesized function which can be used to predict the suitability of a new refrigerant used in ORC for Ultra-Low grade thermal energy recovery.

4. Regression Analysis of Working Mediums Operating on ORC

Machine learning is a scientific approach to designing and developing algorithms that allow computers to predict a useful output for a new case based on the observed/training data set. A major focus in machine learning is to automatically learn to recognize complex patterns between observed data and make accurate prediction for a new/unseen scenario. In machine learning, regression analysis includes different techniques for analyzing and modeling a relationship between a dependent variable and one or more independent variables.

Linear Regression:

Linear regression is a method to model a linear relationship between a dependent variable, Y, and one or more explanatory variable, X (e.g. x_1, x_2, x_3, ...). In this method, observed data are modeled using linear predictor functions. A linear predictor function is a linear function of a set of unknown coefficient and explanatory variables, whose values are used to predict the outcome of the dependent variable. The unknown coefficients are estimated from the observed data.

Classification Problem:

Classification is the problem of identifying the set of categories to which a new observation belongs. The categories are defined based on the training set of the observed data whose categories are known. The individual observations are analyzed into a set of explanatory variables, or features. These explanatory

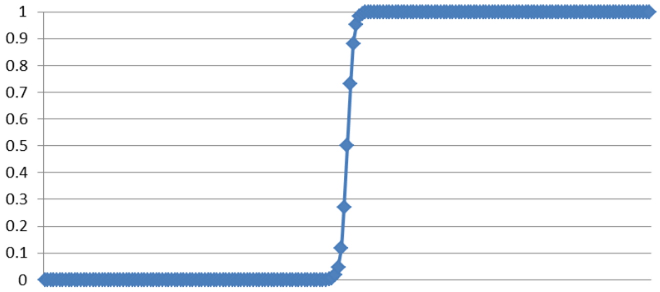

Figure 5: Logistic function

variables or features might be real-valued, integer-valued, or categorical. The algorithm that maps the input data to a category is known as a classifier. A large number of algorithms can be phrased in terms of linear function which is called linear classifier. Logistic Regression, Probit regression, and Support Vector Machine are examples of such algorithms.

Logistic Regression:

Logistic Regression is a type of analysis for classification problems, which is used for predicting outcome of a binary dependent variable based on one or more explanatory variables. The binary dependent variable is a type of variable that can take only two types of outcome, e.g. “Yes” vs. “No” or “Success” vs. “Failure”. Logistic regression attempts to model a function that predicts probability of Yes/Success of a given data based on the training set/observed data.

Logistic function, shown in Eq. (2) and Fig. 5, is used in logistic regression to model how probability of given data may be affected by one or more independent variables. Logistic function is useful because it can take an input from negative infinity to positive infinity and convert it to an output between 0 and 1.

The logistic function is:

$$f(x) = \frac{e^L}{e^L + 1} = \frac{1}{1 + e^{-L}}, \tag{2}$$

where $f(x)$ is the risk of having “Yes” or “1” as outcome, and the variable L is defined as

$L = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \ldots + \beta_k x_k$, where x_1, x_2, x_3,…, x_k are independent variables, and $\beta_1, \beta_2, \beta_3 \ldots \beta_k$ are called regression coefficients of x_1, x_2, $x_3 \ldots x_k$ respectively. Each of the regression coefficients describes the contribution size of the risk factors.

Logistic regression is based on a nonlinear function of a linear relation between the independent variables; compared to linear regression which is based on a linear function of the independent variables. That’s why logistic regression is considered to be a generalized linear model. Logistic regression has been used in this study since it is capable of describing the relationship between independent variables and a binary dependent/response variable, expressed as probability that takes only two values.

Data Preparation:

In this study we will use all the working fluids presented in Tab. 1 and the final results as our training set to model a relationship between five independent variables including Montreal protocol phase out year, ODP, net GWP in 100 years, type of fluid, and critical temperature, and a binary independent response with value 1 for being a good fit for low grade ORC and 0 for the opposite; x_1, x_2, …, x_5 are independent variables. As can be seen in Tabs 1 and 2 each independent variable has a different range of values. To make comparison possible and to remove the rather meaningless variation in the values of the continuous variables, the following categories for the values of each independent variable have been defined. These categories have no numerical meaning and there is no intrinsic ordering to them.

Montreal Protocol Phase out Year or x_1:

Class 1:	Has been phased out
Class 2:	Will be phased out in 2030
Class 3:	No restriction
Class 4:	unknown

Ozone Depleting Potential or x_2:

Class 1:	Fluid with ozone depleting potential of 0.2 and more
Class 2:	Fluid with ozone depleting less than 0.2
Class 3:	unknown ODP

Net GWP in 100 Year or x_3:

Class 1: Net GWP less than 10

Class 2: Net GWP between 10 and 100

Class 3: Net GWP between 100 and 1000

Class 4: Net GWP between 1000 and 10000

Class 5: Net GWP more than 10000

Class 6: unknown

Type of Fluids or x_4:

Class 1: Isentropic Fluids

Class 2: Dry Fluids

Class 3: Wet Fluids

Class 4: Unknown

Critical Temperature or x_5:

Class 1: Critical temperature below 40°F (4.44°C)

Class 2: Critical temperature between 40 and 80°F (4.44°C and 26.7°C)

Class 3: Critical temperature over 80°F (26.7°C)

Class 4: Critical temperature over 120°F (48.9°C)

Class 5: Unknown

4.1. Risk, Odds, and Log Odds

Risk is the potential that a chosen working fluid will lead to undesirable response of 0, which means that the fluid will not be a good choice for ORC. Risk for each value of independent variables can be calculated with Eq. (3).

$$Risk = \frac{\#\, of\ Bads + M \times \rho_{AVG}}{\#\, of\ Bads + \#\, of\ Goods + M} \tag{3}$$

where ρ_{AVG} is the population's average of Bad-rate and M is the smoothing factor. In this study we set the value of M at 50.

Odds is the ratio of the probability that a particular event will occur to the probability that it will not occur. Odds can be calculated in terms of risk and vice versa. For instance if the risk of an event is "P" the odds of that event can be calculated as $P/(1-P)$. The transformation from risk to odds is a monotonic transformation, meaning that the odds increase as the probability increases and vice versa. Risk ranges from 0 to 1 and odds range from 0 to positive infinity. The transformation from odds to log of odds is log transformation. This is another monotonic transformation which means that as the log odds, also called logit, increase so the odds increase and vice versa. One of the reasons for transforming risk to log odds is that it is usually difficult to model data that have a restricted value like risk between 0 and 1 compared to log of odds ranging from negative infinity to positive infinity.

Risk and log odds are used to transfer variables with categorical values (such as class I, class II, etc.) into variable into numerical values. The reason behind this is to be able to use categorical variables for mathematical calculations.

4.2. Logistic Regression and Log Odds

Logistic regression determines an equation that approximates the probability of Y (e.g. being a suitable fluid for ORC) occurring. When a binary response variable is modeled using logistic regression, it is assumed that the logit (log odds) transformation of the response variable has a linear relationship with the independent variables. Logistic regression models the logit transformed risk as a linear relationship with the independent variables. If Y is the binary outcome which takes the value of 0 for failure and 1 for success, and P is the risk of Y being 1, and $x_1, x_2, \ldots, x_5$ are independent variables, then the logistic regression of Y on $x_1, x_2, \ldots, x_5$ estimates coefficients of $\beta_0, \beta_1, \beta_3 \ldots \beta_5$ via maximum likelihood estimation.

$$\begin{gathered} L = Logit\,(P) = Log\,(odds) = Ln\left(\tfrac{P}{1-P}\right) = \\ \beta_0 + \beta_1 x_1 + \ldots + \beta_5 x_5 \end{gathered} \tag{4}$$

For a better understanding of this analysis—justification as to why log odds are used in this process—it can be assumed that there is only one independent variable, x_1. Therefore Eq. (4) can be simplified to Eq. (5).

$$L = Log\left(\frac{P}{1-P}\right) = \beta_0 + \beta_1 x_1 \tag{5}$$

Therefore logit, L, has a linear relationship to x_1. Let us take the log out of both sides of Eq. (5):

$$\frac{P}{1-P} = e^{\beta_0+\beta_1 x_1}$$

$$P = \frac{e^{\beta_0+\beta_1 x_1}}{1+e^{\beta_0+\beta_1 x_1}}$$

This equation is the same as Eq. (2). If log odds are linearly related to x_1, then the relation between P and x_1 is not linear, and has the form of an S-shaped curve shown in Fig. 5. The variable coefficients β_0, β_1, β_2, …, β_5 can be calculated through the maximum likelihood function of a binary output. The maximum likelihood function of a binomial model can be defined as

$$LD(P) = \prod_i \left[P^{Y_i} \times (1-P)^{1-Y_i}\right], \tag{6}$$

where LD is the likelihood of P and Y is the dependent variable, $Y = 1$ for success and $Y = 0$ for failure We need to find a P (i.e. β_0, β_1, β_2,…, β_5) that maximizes the likelihood function. It is equivalent to maximizing the logarithm of this function:

$$\begin{aligned} \log\left[LD(P)\right] &= \log\left(\textstyle\prod_i \left[P^{Y_i} \times (1-P)^{1-Y_i}\right]\right) \\ &= \textstyle\sum_i \left[\log\left(P^{Y_i} \times (1-P)^{1-Y_i}\right)\right] \\ &= \textstyle\sum_i \left[\log\left(P^{Y_i}\right) + \log(1-P)^{1-Y_i}\right] \end{aligned}$$

Therefore β_0, β_1, β_2, …, β_5 can be computed by maximizing Eq. (7).

$$\begin{gathered} \log\left[L(f(x))\right] = \\ \textstyle\sum_i \left[Y_i \times \log f(x) + (1-Y_i) \times \log(1-f(x))\right] \end{gathered} \tag{7}$$

5. Numerical Results

Tables 3 and 4 show the calculated risk, and log of odds for each value of independent variables in the proposed training set for some selected working fluids. The calculated values of log odds have been used in Microsoft Excel to compute the coefficients $\beta_0, \beta_1, \beta_2, \ldots, \beta_5$ using Eq. (7). The following values are the final computational results:

$\beta_0 = 0.99999485$
$\beta_1 = -0.99999923$
$\beta_2 = 0.93592602$
$\beta_3 = -0.49600496$
$\beta_4 = -0.94496621$
$\beta_5 = -0.59583844$

Table 5: Selected Model Output of the Proposed Training Set

Gas ID	Model Output	Y
R-23	0.00139215	0
R-32	0.00520977	0
R-32	0.00520977	0
R-116	0.00000337	0
R-125	0.01319707	0
R-134a	0.29007208	1
R-143a	0.01319707	0
R-152a	0.02600327	0
R-218	0.00067314	0
R-227ea	0.89498583	1
R-236ea	0.89498583	1
R-236fa	0.89498583	1
R-245ca	0.35768201	0
R-245fa	0.46032646	1
R-290	0.36327627	0
R-600	0.92248319	1
R-600a	0.92248319	1
R-601	0.76944694	1
R-601a	0.76944694	1
R-717	0.36327627	0

Thus, Eq. (4) can be shown as

$$\begin{gathered} L = 0.99999485 - 0.99999923\,x_1 + 0.93592602\,x_2 \\ -0.49600496\,x_3 - 0.94496621\,x_4 - 0.59583844\,x_5 \end{gathered}$$

Hence, $f(x)$ can be calculated as (Eq. 8):

$$\begin{gathered} f(x) = 1 \div \\ \left(1 + e^{-(0.99999485-0.99999923x_1+0.93592602x_2-0.49600496x_3-0.94496621x_4-0.59583844x_5)}\right) \end{gathered} \tag{8}$$

Now $f(x)$ for each gas can be calculated by inputting the values of each independent variable into Eq. (8). The calculated results are shown in Tab. 5.

Looking at the values of the model output shown in Tab. 5, it can be concluded that 0.45 is the marginal value. All gases with $f(x) < 0.45$ have the Y value of 0 which means they are not good fits for ORC (except for R-134a which has $f(x) < 0.45$ while its Y value is 1). All gases with $f(x) > 0.45$ have the Y value of

Table 3: Risk Values of the Proposed Training Set, selected results

Gas ID	x_1	x_2	x_3	x_4	x_5	Y
R-23	0.528221	0.8126616	0.997848	0.916448	0.997323	0
R-32	0.528221	0.8126616	0.952233	0.916448	0.998201	0
R-41	0.528221	0.8126616	0.994774	0.916448	0.998201	0
R-116	0.997848	0.8126616	0.997848	0.916448	0.997323	0
R-125	0.528221	0.8126616	0.750698	0.916448	0.998201	0
R-134a	0.528221	0.8126616	0.750698	0.916448	0.640997	1
R-143a	0.528221	0.8126616	0.750698	0.916448	0.998201	0
R-152a	0.528221	0.8126616	0.998645	0.916448	0.640997	0
R-218	0.997848	0.8126616	0.750698	0.305844	0.998201	0
R-227ea	0.528221	0.8126616	0.750698	0.305844	0.640997	1
R-236ea	0.528221	0.8126616	0.750698	0.305844	0.640997	1
R-236fa	0.528221	0.8126616	0.750698	0.305844	0.640997	1
R-245ca	0.528221	0.8126616	0.998645	0.305844	0.640997	0
R-245fa	0.528221	0.8126616	0.750698	0.834266	0.640997	1
R-290	0.528221	0.8126616	0.605691	0.916448	0.640997	0
R-600	0.528221	0.8126616	0.605691	0.305844	0.640997	1
R-600a	0.528221	0.8126616	0.605691	0.305844	0.640997	1
R-601	0.528221	0.8126616	0.952233	0.305844	0.640997	1
R-601a	0.528221	0.8126616	0.952233	0.305844	0.640997	1
R-717	0.528221	0.8126616	0.605691	0.916448	0.640997	0

Table 6: Order ranking of the proposed training set, sample results

Rank ID	GAS ID	Model Output
1	R-600	0.92248319
2	R-600a	0.92248319
3	R-227ea	0.89498583
4	R-236ea	0.89498583
5	R-236fa	0.89498583
6	R-601	0.76944694
7	R-601a	0.76944694
8	R-245fa	0.46032646
9	R-290	0.36327627
10	R-717	0.36327627

1 which means they are suitable working fluids for ORC. Moreover, the value of $f(x)$, which represents the probability of being a good candidate for ORC, provides a measure for rank ordering the fluids under study. The higher the value of $f(x)$, the higher the fluid's rank is in the overall screening. Based on this, the ranking of the screened working fluids and their scores are represented in Tab. 6.

6. Conclusion

Logistic regression is a useful tool to find a classifier (e.g. Eq. 8) that distinguishes the desirable working fluids for ORC from the undesirable ones with very high precision (1 error in 82 instances). Any new gas outside of the proposed training set should first be classified based on different categories defined for each independent variable. Then risk and log odds can be calculated for each independent variable. Then $f(x)$ can be calculated using the risk and odd logs. For a value of $f(x) > 0.45$ the value of response is equal to 1 which means that working fluid is a proper candidate for ORC. The methodology suggests that the top ten working mediums for ultra-low grade thermal energy recovery from among the tested cases are R-600, R-600a, R-227ea, R-236ea, R-236fa, R-601, R-601a, R-245fa, R-290, and R-717.

Table 4: Log odds Values of the Proposed Training Set

Gas ID	x_1	x_2	x_3	x_4	x_5	Y
R-23	0.113	1.4674	6.13917	2.39504	5.92039	0
R-32	0.113	1.4674	2.99248	2.39504	6.31857	0
R-41	0.113	1.4674	5.24878	2.39504	6.31857	0
R-116	6.13917	1.4674	6.13917	2.39504	5.92039	0
R-125	0.113	1.4674	1.10234	2.39504	6.31857	0
R-134a	0.113	1.4674	1.10234	2.39504	0.57969	1
R-143a	0.113	1.4674	1.10234	2.39504	6.31857	0
R-152a	0.113	1.4674	6.60259	2.39504	0.57969	0
R-218	6.13917	1.4674	1.10234	-0.8196	6.31857	0
R-227ea	0.113	1.4674	1.10234	-0.8196	0.57969	1
R-236ea	0.113	1.4674	1.10234	-0.8196	0.57969	1
R-236fa	0.113	1.4674	1.10234	-0.8196	0.57969	1
R-245ca	0.113	1.4674	6.60259	-0.8196	0.57969	0
R-245fa	0.113	1.4674	1.10234	1.61617	0.57969	1
R-290	0.113	1.4674	0.42924	2.39504	0.57969	0
R-600	0.113	1.4674	0.42924	-0.8196	0.57969	1
R-600a	0.113	1.4674	0.42924	-0.8196	0.57969	1
R-601	0.113	1.4674	2.99248	-0.8196	0.57969	1
R-601a	0.113	1.4674	2.99248	-0.8196	0.57969	1
R-717	0.113	1.4674	0.42924	2.39504	0.57969	0

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Nomenclature

$\beta_1, \beta_2, \beta_3 \ldots \beta_k$	Regression coefficients of x_1, x_2, $x_3 \ldots x_k$
$\prod_i$	Multiplication symbol of variable i
ρ	Population average of bad-rate
ξ	Inverse slope of dT/dS
AVG	Average
c_p	Specific Heat
e	The base of natural logarithm
$f(x)$	Logistic function

h	Enthalpy
in	Inlet
is	Isentropic
L	Latent heat
L	Sum of $\beta_0, \beta_1 x_1, \beta_2 x_2, \beta_3 x_3, \ldots, \beta_k x_k$
LD	Likelihood of P and Y
M	Smoothing factor
P	The risk of an event
S	Entropy
T	Temperature
x_1, x_2, x_3,…, x_k	Independent variables
Y	Dependent variable
CFC	Chlorofluorocarbons
GWP	Global Warming Potential
HFC	Hydrofluorocarbon
ODP	Ozone Depleting Potential
ORC	Organic Rankine Cycle
SVL	Saturation vapor line