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1 Uncertainty in the prediction of the thermophysical 2 behavior of new halogenated working fluids

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9 Abstract

10 Halogenated olefins can be an attractive alternative to working fluids that
11 are under consideration for phase-out. In order to evaluate the potential of
12 halogenated olefins as working fluids for organic Rankine cycle units with
13 a realistic perspective it is necessary to predict both their primary thermo-
14 physical properties and their associated uncertainties. In this work we eval-
15 uated the uncertainty of two predictive models, based on the classical group
16 contribution approach and on neural networks, for the critical temperature,
17 critical pressure, acentric factor, and ideal gas heat capacity of halogenated
18 substances. Based on this, guidelines for the most convenient model depend-
19 ing on the property and the fluid molecular structure were provided. The
20 non-linear propagation of the uncertainty through the Peng-Robinson equa-
21 tion of state for the simulation of an organic Rankine cycle unit were also
22 studied. The results suggest that the uncertainty of the predicted properties
23 is highly dependent on the molecular structure for the classical model. The
24 propagation of uncertainties in the simulation of an organic Rankine cycle
25 unit also depends on the saturation properties of the fluid.

26 *Keywords:* uncertainty propagation; thermophysical properties; halogenated
27 working fluids; Peng-Robinson equation of state; Monte Carlo simulation.

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Nomenclature

$c_{p,0}$	molar ideal gas heat capacity, $\text{Jmol}^{-1}\text{K}^{-1}$	ORC	organic Rankie cycle
T	temperature, K	PDF	probability distribution function
p	pressure, bar	PR-EoS	Peng-Robinson equation of state
h	molar enthalpy, Jmol^{-1}	<i>Greek letters</i>	
<i>Abbreviations</i>		ω	acentric factor
ANN	artificial neural network model	ρ	molar density, molm^{-3}
cEoS	cubic equation of state	σ	standard deviation
EoS	equation of state	<i>Subscripts</i>	
GCM	classical group contribution model	b	boiling
GWP	global warming potential over 100 years relative to CO_2	c	critical
HFC	hydrofluorocarbons	exp	experimental
HFO	hydrofluoroolefins	liq	saturated liquid
ODP	ozone depletion potential relative to CFC-11	pred	predicted
		vap	saturated vapor

1. Introduction

In the last few years environmental regulations have been a major driving force for the industry to seek novel working fluids, as many of the conventional fluids in use today will be soon phased out. Although the Montreal Protocol in 1989 [1] and the Kyoto Protocol in 1997 [2] already imposed restrictions on the use of some refrigerants, other regulations of regional coverage, such as the Regulation on Fluorinated Substances of the European Parliament (F-gas regulation)[3], impose now additional requirements and limitations. As a matter of fact, on 15th October 2016 a total of 197 countries agreed on the amendment of the F-gas regulation to the Montreal Protocol, thus extending its phase-out schedule for hydrofluorocarbons (HFCs) within the United Nations. This agreement will have a significant impact on the existing refrigeration units and organic Rankine cycle (ORC) power systems utilizing HFCs for their operation, increasing the efforts for the search of alternative fluids. However, the design of new working fluids poses a great challenge, and finding an optimum solution for a given application often faces trade-offs between cycle performance, and environmental and safety criteria.

Halogenated olefins (also called hydrofluoroolefins (HFOs)) offer good en-

46 vironmental characteristics (*i.e.*, low or zero ozone depletion potential (ODP)
 47 and low global warming potential (GWP)), which is why their potential as
 48 working fluids for ORC units and refrigeration cycles is proposed. With the
 49 aim of evaluating the prospects of new halogenated olefins, in our previous
 50 work [4] we developed two alternative models based on the group contri-
 51 bution approach, for the prediction of the critical temperature T_c , critical
 52 pressure p_c , acentric factor ω , normal boiling temperature T_b , and ideal gas
 53 heat capacity $c_{p,0}$ of organic compounds containing fluorine and/or chlorine,
 54 based on an extended database of properties. The models were based on
 55 a classical and a neural-network-based group contribution approaches. It
 56 was observed that the two developed models improved the predictions for all
 57 properties with respect to other group contribution methods and molecular
 58 structure models available in the literature. Moreover, it was observed that
 59 the model based on a neural network approach yielded lower deviations from
 60 the experimental data than the one following the classical approach of the
 61 group contribution method for all properties but for the acentric factor.

62 In order to apply these predictive models for the comprehensive evalua-
 63 tion of the potential of new halogenated working fluids in ORC power systems
 64 and refrigeration systems it is necessary to evaluate and compare the uncer-
 65 tainty of their predictions, and analyze how the uncertainty propagates when
 66 the predicted values are used as inputs in equations of state (EoS) to sim-
 67 ulate industrial processes. In this work, we distinguish between the terms
 68 *uncertainty* and *deviation*. *Uncertainty* is considered here to be the range
 69 of statistically possible outcomes of a property model, for example expressed
 70 with 95% confidence, or the standard deviation of a (normal) distribution
 71 representing these outcomes [5]. *Deviation* refers, here, to the relative or
 72 absolute difference between the predicted value of a model and the value of
 73 the corresponding experimental measurement of the property.

74 The influence of the uncertainty of predicted fluid properties on the study
 75 of their thermophysical behavior in different processes has been previously
 76 analyzed by other authors. For instance, Whiting [6] raised the importance
 77 of analyzing the impact of the uncertainty of physical property data and
 78 predictive models on the simulation results of several industrial separation
 79 processes. Hajipour and Satyro [7, 8] presented the propagation of the uncer-
 80 tainty of the critical properties and acentric factor of large chain hydrocar-
 81 bons through the Peng-Robinson EoS (PR-EoS) and developed a correlation
 82 for their prediction based on the experimental uncertainty of the available
 83 data. Bjorner et al. [9] analyzed the propagation of the uncertainty in

the parameters of cubic plus association equations of state. More recently, Shacham et al. [10] considered the experimental uncertainty of the physical properties of fluids to account for the worst case scenario of the design of a heat exchanger and tubular reactor. Also, Hukkerikar et al. [11] analyzed the sensitivity of process design to the uncertainties in a set of thermophysical properties for the case study of an extractive distillation process. In the domain of working fluids for ORC power systems, the propagation of property uncertainties to the model output has been suggested as a promising tool to compare the uncertainties in property prediction methods on the cycle level [12]. In this regard, Frutiger et al. [13] utilized a Monte Carlo method to propagate the uncertainty of the fluid-specific equations of state parameters to the cycle model output.

Nevertheless, a common problem when analyzing the uncertainty propagation of fluid properties in process design is the lack of uncertainty values for the predicted properties. Although the prediction uncertainty of several classical group contribution methods, such as Joback and Reid [14] and Marrero and Gani [15], is unknown, it is expected that longer repeating chains of molecular groups will have higher deviations, whereas shorter chained molecules with varying groups will have lower deviations. In order to overcome the lack of uncertainty values from these predictive models, Hukkerikar et al. [16] presented a method based on the Marrero and Gani [15] model with new contributions, additional properties, and reported uncertainties. However, as many groups that describe halogenated fluids are missing, the uncertainties are expected to be high for them if their contributions were estimated with the connectivity index method [17], which adds uncertainty to the prediction. Moreover, Frutiger et al. [18] presented recently a methodology for the uncertainty estimation of group contribution based property models, which provides every predicted data point along with its respective uncertainty range.

The aforementioned publications deal with the analysis of the impact of experimental or predicted property uncertainty on the design or simulation of different processes, and how these uncertainties are determined in the case of developed predictive models. In this work we aim to evaluate how the nature of the predictive model or the fluid molecular structure influence the expected uncertainty of predicted properties for halogenated organic fluids. Then the impact of the selection of the predictive models on the overall uncertainty of the results in the study of new halogenated substances in power cycle systems is analyzed. The necessary tools for the estimation of the uncertainty of new

halogenated fluids are provided enabling researchers in the field to assess the propagation of the uncertainty of the predictions in their simulation models. This work presents a number of novel contributions. First, an evaluation of the uncertainty of prediction models for the thermophysical properties of halogenated substances is provided. Second, the uncertainty of the predicted values obtained from models based on different approaches (group contribution methods and artificial neural networks) are compared, giving a first insight into what could be the advantages or disadvantages of using these models for different fluids and properties, in terms of the uncertainty of their predictions. Third, based on the results, a series of guidelines on the convenience of using specific models depending on the deviations of their predictions, the uncertainty, and the fluid molecular structure, are provided.

First, the paper introduces, in Section 2, the methods followed for the estimation of the uncertainty of the predicted properties, the propagation of the uncertainty through the PR-EoS, and the estimation of the uncertainty propagation on the case study of an ORC unit. Section 3 presents and compares the results obtained for each of the predictive methods and properties. Finally, the results are discussed in Section 4, including an analysis on the uncertainty improvement based on the availability of experimental data and a comparison with the expected uncertainties from other models. The main conclusions of this work are summarized in Section 6. An example of estimation of the uncertainty and additional material is provided in the Supporting Information (see section 5).

2. Methods

2.1. Prediction of thermophysical properties

The easiest method to predict the thermophysical behavior of a certain fluid is by using a cubic equation of state, where only the critical temperature T_c , critical pressure p_c , the acentric factor ω , and the ideal gas heat capacity $c_{p,0}$ are needed. The experimental values of these parameters can be easily accessed for a large number of substances through databases, or they can also be predicted if no experimental data are available. In this regard, the greatest challenge that arises when attempting to predict the thermophysical behavior of new working fluids is the lack of experimental data of their core properties. As a consequence, the development of models for predicting different properties of new fluids of interest is a topic of high interest for both researchers and industry.

158 In our previous work [4] we developed two models, based on a group con-
 159 tribution approach, to predict the critical temperature T_c , critical pressure
 160 p_c , acentric factor ω , and ideal gas heat capacity $c_{p,0}$ of halogenated organic
 161 substances:

- 162 1. The first model (from now on referred to as the GCM) followed the
 163 classical approach of the group contribution method, as described by
 164 Marrero and Gani [15],
- 165 2. The second model (from now on referred to as the ANN) combined the
 166 use of artificial neural networks with the group contribution approach.

167 The results indicated that the two developed methods were able to pre-
 168 dict the mentioned properties with lower deviations from the experimental
 169 values, than with other available molecular-based methods. Moreover, it was
 170 found that the model following the neural network approach (ANN) yielded
 171 lower absolute average relative deviations than the model following the clas-
 172 sical approach (GCM) for all the studied properties, except for the acentric
 173 factor. This success in improving the predictive performance was due to the
 174 reduction of the scope of the method to a specific fluid group, the use of an
 175 extensive database of experimental data, and the use of neural networks, in
 176 the case of the ANN.

177 However, it was unclear whether the improvement in the prediction ca-
 178 pacity of the ANN was accompanied by a reduction in the uncertainty of
 179 the prediction, and which of the two methods yielded a lower uncertainty in
 180 the prediction of the properties. Moreover, it is important to study how the
 181 uncertainty of the predicted values by using both models propagates through
 182 the use of cubic equations of state, in order to evaluate if initial differences
 183 on the uncertainty values are smoothed in the final simulation results.

184 2.2. Estimation of fluid behavior with cubic equations of state

185 As mentioned previously, the easiest way to predict the thermophysical
 186 behavior of fluids for which limited experimental data are available is by
 187 using cubic equations of state (cEoS). A cEoS is an equation of state that
 188 provides the pressure as a function of temperature and volume, being roots
 189 third order in volume (*i.e.*, there are three real and/or imaginary solutions
 190 for the volume for a specific temperature T and pressure p). The general
 191 form of a cEoS is given in Eq. 1 [19].

$$p = \frac{RT}{v - b} - \frac{a_c \alpha(T_R, \omega)}{(v + \Delta_1 b)(v + \Delta_2 b)} \quad (1)$$

Here a_c and b are the attraction and co-volume parameters, respectively, that are calculated with the critical temperature T_c , critical pressure p_c , and acentric factor ω of the fluid, and α (the so-called attraction term) is a function of the temperature, and/or the acentric factor. Δ_1 and Δ_2 are parameters whose values determine the type of cEoS.

The advantage of the use of cEoS is that reasonably accurate predictions can be expected if only the critical parameters, the acentric factor, and the ideal gas heat capacity of the fluid are known. Moreover, the computing time required by the calculation subroutines is, in many cases, significantly lower than that required by other equations of state (*e.g.*, the Helmholtz-free energy based EoS, which can offer a more accurate representation at the expense of more complexity and the requirement of fluid-specific parameters). The predictions of cEoS are more accurate in the vapor phase, and when the fluid is non-polar, but are known to fail in the estimation of the compressed liquid volume, and near the critical region. In this context, Brown [20] demonstrated that using cEoS is a reliable method to study the performance of new refrigerants in vapor compression systems, even in the absence of experimental data for the critical parameters and ideal gas heat capacity. The work showed that, when these parameters are known, relative deviations of less than 5% can be expected for the predicted properties with respect to those obtained from the Helmholtz-based equations of state of Refprop [21]. Liu et al. [22] observed similar deviations when using the PR-EoS to evaluate the potential of a set of HFO as working fluids of ORC power systems.

Nevertheless, the aforementioned studies only evaluated the predictive performance of the PR-EoS, without considering how the uncertainty of the critical parameters, acentric factor, or ideal gas heat capacity propagated in the predictions of the EoS. In this context, Frutiger et al. [12] recently analyzed the uncertainty propagation of these parameters in the Soave-Redlich-Kwong EoS, for the case of an ORC unit. Previously, Frutiger et al. [13] used the propagation of the experimental uncertainties of the critical parameters, acentric factor, and ideal gas heat capacity through the PR-EoS for the optimization of the working fluid selection in an ORC unit.

In this work we study the propagation of predicted property uncertainties for halogenated fluids on the PR-EoS (for which the values of Δ_1 and Δ_2 in Eq. 1 are $\Delta_1 = 1 + \sqrt{2}$ and $\Delta_2 = 1 - \sqrt{2}$, and the parameters a_c and b are defined as $a_c = 0.45724R^2T_c^2/p_c$ and $b = 0.07780RT_c/p_c$), since this is the most widely used cubic EoS.

2.3. Uncertainty analysis

In this section the methods used for the evaluation and propagation of the uncertainty are described. First, the availability of the experimental uncertainty in the property database is discussed. For the two considered models (GCM and ANN) the uncertainty of the predicted property values was estimated by using the bootstrap method, and the 95% confidence interval of the predicted properties is provided. Next, the propagation of these estimated uncertainties through the PR-EoS is explained, and the propagation of uncertainties on a case study of an ORC unit is presented. This method allows the comparison of the uncertainty generated by the GCM and the ANN, both at the level of the prediction and at the level of the cycle simulation. Figure 1 provides an overview of the method.

Figure 1: Schematic overview of the method for uncertainty analysis and propagation.

2.3.1. Uncertainty of experimental data

In our previous work [4] we collected an extensive dataset containing the experimental critical temperature, critical pressure, normal boiling temperature, acentric factor, and ideal gas heat capacity constants of up to 334 organic fluids containing fluorine and/or chlorine. In this set, only 75 fluids included information about their associated measuring uncertainty for

the critical temperature and critical pressure, and only 14 included information about the uncertainty for the acentric factor (corresponding to those data obtained from the database of the Project 801 of the Design Institute for Physical Property Data (DIPPR[®] 801) [23]). Regarding the ideal gas heat capacity, this database reports the constants of the Aly-Lee model for heat capacity [24] for 31 fluids. In this case the fitting errors for each of the constants are reported. This situation represents a drawback for the comprehensive evaluation of the uncertainty of the predictions of the models developed in Ref. [4], since the few experimental uncertainties available in the dataset cannot provide an insight of the overall quality of the data, nor the presence of outliers. Since the impact of including the few available experimental uncertainties in the analysis would be low, it was decided not to include them into the uncertainty propagation analysis. Instead, the experimental uncertainties are later compared with the calculated uncertainties from both models in section 4.

2.3.2. *Uncertainty of predicted data*

While most of the published models for the prediction of thermophysical properties lack an assessment of the uncertainty of their predictions, this practice is recommended, and should be standardized [25]. When, as in our case, the uncertainty of the experimental data used for the fitting of the predictive models is only partially available, the uncertainty analysis provides the estimated uncertainty of the fitted model, independently of the quality of the experimental data. Thus, the results must be seen as a measure of the quality of the fitting of the model, but should be compared with the available experimental uncertainties to assess the total expected uncertainty of the predicted property value.

The parameters fitted in group contribution methods correspond to the individual contributions of each functional group and, in some cases, function coefficients. In the case of the neural network based GCM, the number of fitted parameters is greater than the number of functional groups, and there is no direct relationship between them. The parameters of the group contribution based models developed in our previous work [4] were obtained by nonlinear least-squares regression of the predicted values of each property (for the GCM) and by the minimization of the mean of squared errors (for the ANN). In this optimization method, the residuals of the predicted values were minimized in order to determine the values of the parameters, as indicated in Eq. 2.

$$\theta^* = \operatorname{argmin} \left(\sum_i (y_i^{\text{exp}} - y_i^{\text{pred}})^2 \right) = \operatorname{argmin} \left(\sum_i (\epsilon_i)^2 \right) \quad (2)$$

Here, θ^* is the array of fitted parameters, and y_i^{exp} and y_i^{pred} are the experimental and predicted values of a specific property y for each fluid i in the dataset, and ϵ_i is the calculated error. The datasets used in this work correspond to those used in our previous work [4], which collected experimental data for halogenated substances from the database of the Project 801 of the Design Institute for Physical Property Data (DIPPR 801 [23]) of T_c , p_c , ω , and calculated values of $c_{p,0}$ from the Aly and Lee constants [24] at reduced temperatures of 0.6, 0.65, 0.7, 0.75, 0.8, 0.85, and 0.9. For each of the properties, the predicted value y_i^{pred} , predicted by the GCM and the ANN, was obtained as indicated in Eqs. 3 and 4, respectively:

$$f(y_i^{\text{pred}}) = \sum_j N_j C_j + \sum_k M_k D_k \quad (3)$$

$$f(y_i^{\text{pred}}) = f(w_{\text{ANN}}, b_{\text{ANN}}, N_j, M_k) \quad (4)$$

Here $f(y_i^{\text{pred}})$ is a function of the property to be predicted, and j , and k refer to the first, and second order groups defined in the GCM. N_j and M_k are the number of the j -th first order group, and the k -th second order group, respectively, present in the molecule, and C_j and D_k are the fitted contributions of the GCM to the first and second order groups, respectively. w_{ANN} and b_{ANN} refer to the fitted weights and biases of the artificial neural network of the ANN. The fitted neural networks were composed of one or two hidden layers, depending on the property. The number of neurons per layer, transfer function, groups decomposition, and the values of the fitted contributions, weights, and biases for each model and property can be consulted in Ref. [4].

Frutiger et al. [18] compared two different methods (i.e linear error propagation with parameter covariance matrices, and the bootstrap method) to evaluate the uncertainty of values predicted with group contribution models. The authors found that the bootstrap method was a valid alternative to the classical uncertainty analysis based on linear error propagation, especially when the residuals are not normally distributed and/or not independent. In order to check whether the prerequisites required for linear propagation were met in this work, a one-sample Kolmogorov Smirnov test [26] was used to

test the distribution of the residuals obtained for both models (GCM and ANN) and for each of the considered properties. The test yielded a positive result for the GCM for all properties and for the ANN for $c_{p,0}$, which means that for these cases the residuals do not follow a normal distribution. The result can be observed in Figure 2, where the normal probability plots of the residuals for each predictive model are represented. The linear correlation of the residuals for each predictive model and property was checked against the prediction values and input variables, and was found lower than 0.35 for all the cases except for the ANN for $c_{p,0}$ where a high correlation was observed.

Figure 2: Normal probability plots of the residuals of the predictive models GCM and ANN (in rows) for the properties T_c , p_c , ω , $c_{p,0}$ (in columns).

Because of the non-normal distribution of the residuals ϵ_i in the above-mentioned cases, the bootstrap method was selected to evaluate the uncertainty of the predictions in this work. The bootstrap method approximates the distribution of the residuals $\hat{F}$ by assuming that the residuals are uniformly distributed, $\hat{F} = \text{mass}_n^1$. With this distribution, a number n of synthetic datasets is generated, as indicated in Eq. 5. In this work, 100 synthetic datasets were generated for each of the studied properties and models (for more information on the choice of the number of samples, please refer to the Supporting Information).

$$y_i^* = y_i^{\text{pred}}(\theta) + \hat{\epsilon}_i, \hat{\epsilon}_i \in (\hat{F}) \quad (5)$$

Then, the model parameters θ^* are re-fitted for each of the generated datasets, and new predictions $y_i^{\text{pred},*}$ are obtained with these parameters. This results in a set of parameters and predictions from which the mean and standard deviation can be calculated by using inference statistics, as indicated in Eqs. 6 and 7

$$\mu_{\theta^*} = \frac{1}{n} \sum_{k=1}^n \theta^*(k) \quad (6)$$

$$\sigma_{\theta^*} = \sqrt{\frac{1}{n-1} \sum_{k=1}^n (\theta^*(k) - \mu_{\theta^*})^2} \quad (7)$$

Percentile inference statistics were also obtained from the resulting parameter estimation matrices from their empirical cumulative probability distributions, to allow the comparison of the uncertainty ranges of the properties predicted from different models.

2.3.3. Uncertainty prediction of new halogenated working fluids

While the analysis of uncertainties presented in sections 3.1 and 3.2 concerns the fluids included in the database used for the development of the models presented by Mondejar et al. [4], the main interest of this analysis is to provide a tool for the estimation of the uncertainty for the predictions of the critical temperature, critical pressure, acentric factor, and ideal gas heat capacity of new halogenated working fluids. The method used to predict the uncertainty of the property predictions of new fluids involves a reverse bootstrapping process, so that for each property and model, a number of samples of model parameters is generated based on their mean value and the estimated uncertainties as calculated in Eqs. 6 and 7, and by considering the specific probability distribution function (PDF) obtained from the Bootstrap method for each of the parameters (in order to avoid errors derived from the assumption of normal distribution for non-normal distributed parameters). The property value was obtained for each of the generated parameters and its uncertainty was obtained from the set of calculated values. The code of a function executing this method is provided in the Supporting Information (see Section 5).

2.3.4. Uncertainty propagation in the Peng-Robinson equation of state

When predicted values of the critical temperature T_c , critical pressure p_c , and acentric factor ω are used as inputs in a cEoS to estimate the thermophysical behavior of a fluid, and the ideal gas heat capacity $c_{p,0}$ is used to calculate its enthalpy and entropy, their associated uncertainties are propagated to the properties derived from the EoS. In order to evaluate the uncertainty of the thermophysical properties obtained from the PR-EoS, an

389 maximum pressure of the cycle (state 1), and then is evaporated with the
 390 energy from the heat source up to saturated or superheated vapor condi-
 391 tions (state 2). Afterwards the fluid flows through the expander (state 3)
 392 and enters the condenser to complete the cycle. The model has a standard
 393 configuration with no regeneration and without subcooling conditions (*i.e.*,
 394 the working fluid at the outlet of the condenser is saturated liquid). The net
 395 power output of the unit was obtained as:

$$W_{\text{net}} = \eta_{\text{gen}}(W_{\text{exp}} - W_{\text{pump}}) = \eta_{\text{gen}}m_{\text{ORC}}(\eta_t(h_2 - h_3) - (h_1 - h_0)/\eta_p) \quad (8)$$

396 where η_{gen} , η_t , and η_p are the efficiencies of the generator, the expander,
 397 and the pump, respectively; m_{ORC} is the working fluid mass flow rate, and
 398 h_i refers to the specific enthalpy on each of the states of the cycle, marked
 399 in Figure 3. The efficiency of the generator, and the isentropic efficiencies of
 400 the pump and expander were set to constant values equal to $\eta_{\text{gen}} = 0.975$,
 401 $\eta_p = 0.4$ and $\eta_t = 0.7$, respectively. The thermal efficiency of the cycle is
 402 obtained as $\eta_{\text{ORC}} = W_{\text{net}}/Q_{\text{in}}$, where Q_{in} is the heat transferred from the
 403 heat source to the working fluid in the evaporator.

404 For each of the predictive methods (*i.e.*, GCM and ANN) a set of 100
 405 samples of T_c , p_c , ω , and $c_{p,0}$ constants was generated by using the Latin
 406 hypercube sampling method for the Monte Carlo method. Then, a Monte
 407 Carlo simulation of the ORC unit was performed by considering the set of
 408 samples, and the distribution of the resulting net power output W_{net} and
 409 thermal efficiency η_{ORC} values was analyzed. The heat source of the ORC
 410 unit was assumed to be a hot stream of water at 358.85 K and the sink
 411 was considered as water at 291.55 K, resembling a hypothetical case where
 412 an ORC unit recovers the heat from the jacket cooling water of a ship's
 413 propulsion Diesel engine, using seawater as a sink. The process simulation
 414 parameters of the ORC unit were obtained for the halogenated olefins trans-
 415 1-chloro-3,3,3-trifluoropropene (R-1233zd(E)) and 2,3,3,3-tetrafluoropropene
 416 (R-1234yf), by following the optimization procedure described in the work
 417 of Andreasen et al. [29], for the maximization of the net power output. The
 418 values of these parameters are given in Table 1. Pressures losses in the unit
 419 piping and heat exchangers were neglected for simplicity.

Table 1: Process simulation parameters of the case study ORC unit, optimized for maximum net power output.

Parameter	Values	
Working fluid	R-1233zd(E)	R-1234yf
Source mass flow rate, kg s ⁻¹	35.9	35.9
Source temperature, K	358.9	358.9
Sink temperature, K	291.6	291.6
Boiler pressure, bar	3.7	16.4
Condensation temperature, K	307.2	307.2
Expander inlet superheat, K	5.0	12.3
Pump inlet subcooling, K	6.0	6.0

3. Results

3.1. Uncertainty analysis of the GCM and the ANN models

Figure 4 presents, for each of the analyzed properties, the relative deviation of the predicted values of the two considered models, from the experimental values. The error bars show the calculated uncertainty from the procedure described in section 2.3 for the GCM (figures on the left side) and the ANN (figures on the right side). As can be seen, the average relative deviation is slightly lower for all the properties when obtained from the ANN, with a significant decrease in the case of the ideal gas heat capacity. However, no significant difference can be seen in the uncertainty values between the methods, except for the ideal gas heat capacity where the uncertainty appears significantly lower for the ANN. For both methods, the relative uncertainties appear to decrease for higher values of the property (which is correlated with larger molecules), as expected. This is very clear in the case of the prediction of $c_{p,0}$ from the GCM, where there are higher uncertainty values at lower heat capacity values.

3.2. Uncertainty of EoS properties

3.2.1. Sensitivity of EoS to input properties

The uncertainty of the input magnitudes to the PR-EoS (*i.e.*, T_c , p_c , ω , and $c_{p,0}$) was propagated in a different way for each of them, and for different EoS properties, which means that their impact on the final uncertainty is not homogeneous. Figure 5 presents how an assumed uncertainty of 5 % on each of the input properties is propagated through the PR-EoS for different thermophysical properties of difluoromethane (R-32), at a temperature of $T=300$ K. This hypothetical and relatively high value is chosen for

Figure 4: Relative deviations of the predicted values of (a and b) the critical temperature, (c and d) critical pressure, (e and f) acentric factor, and (g and h) ideal gas heat capacity vs. the database values. Error bars show the uncertainties of the predicted values by using the GCM (figures on the left side) or the ANN (figures on the right side).

a better readability of the propagation results. For each input property, the bar represents the uncertainty of the calculated property when the indicated input variable has an uncertainty of 5 %, and null uncertainty is assumed for the rest of the input properties.

Figure 5: Impact of the uncertainties of the input variables (*i.e.*, T_c , p_c , ω , and $c_{p,0}$) on the overall uncertainty of p_{sat} , ρ_{liq} , ρ_{vap} , h_{liq} , and h_{vap} . For each of the listed properties χ , the bars represent its overall uncertainty $u(\chi)$ when a 5 % uncertainty is considered only on the corresponding input property at the bottom. Note the logarithmic scale on the y-axis. The enthalpy calculations correspond to a saturation temperature of 300 K.

As it can be seen, the uncertainty of the critical temperature affects the overall uncertainty more than any other input property. An uncertainty of 5 % in the critical temperature results in an uncertainty of more than 10 % for the calculated saturated pressure, and saturated vapor density and enthalpy. The uncertainty of the critical pressure has a similar impact on the saturation pressure, and saturated densities, resulting in an overall uncertainty of around 2 %, and less in the case of the saturated liquid enthalpies. The uncertainty in the acentric factor has a larger impact on the saturated enthalpies, similar to that of the ideal gas heat capacity, but still remains negligible compared to the impact of the uncertainty in the critical temperature. It is also observed that the impact of the ideal gas heat capacity uncertainty is greater for the saturated vapor enthalpy, which is expected, as the ideal enthalpy is larger than the residual enthalpy in the vapor calculation, whereas in the liquid calculation the residual term is dominant, and is affected by the uncertainties in the critical parameters.

These results indicate that the critical temperature is the key in order to reduce the uncertainty propagated through the PR-EoS, whereas reducing the uncertainty of the other properties will not have a similar impact on the total property uncertainty.

3.2.2. Examples of propagation in the PR-EoS

In order to illustrate how the uncertainty in the input properties is propagated through the use of the PR-EoS, two fluids were selected from the set to represent two cases with large and low estimated uncertainties for the considered properties (based on the values from the GCM). The selected fluids are 2,2-dichloropropane and propyl chloride, as they present large and low uncertainties, respectively (see uncertainty values in Figure 6). Figure 7 presents the propagation of the uncertainty of T_c , p_c , ω , and $c_{p,0}$ for 2,2-dichloropropane, by using the GCM and the ANN, through the PR-EoS for the calculation of the saturation pressure p_{sat} , saturated liquid and vapor densities (*i.e.*, ρ_{liq} , ρ_{vap}), and saturated liquid and vapor enthalpies (*i.e.*, h_{liq} , h_{vap}). Figure 8 presents the equivalent uncertainty propagation results for propyl chloride.

Figure 6: Estimated uncertainties of T_c , p_c , ω , and $c_{p,0}$ (at 350 K), for (a) 2,2-dichloropropane and (b) propyl chloride, using both models.

Figure 7: Example of propagation of the uncertainty of the estimated values of T_c , p_c , ω , and $c_{p,0}$, for 2,2-dichloropropane (represented in (a) [30]) by using the GCM and the ANN, through the PR-EoS for the calculation of: (b) the saturation pressure p_{sat} , (c, d) saturated liquid and vapor densities (*i.e.*, ρ_{liq} , ρ_{vap}), and (e, f) saturated liquid and vapor enthalpies (*i.e.*, h_{liq} , h_{vap}). Continuous lines represent the mean of the predicted property values for the 100 samples generated from the Monte Carlo simulation, while dashed lines represent their standard deviations. The predicted values of the critical temperature are: $T_{c,\text{GCM}} = 539.46 \text{ K}$ and $T_{c,\text{ANN}} = 540.98 \text{ K}$.

Figure 8: Example of propagation of the uncertainty of the estimated values of T_c , p_c , ω , and $c_{p,0}$, for propyl chloride (represented in (a) [30]) by using the GCM and the ANN, through the PR-EoS for the calculation of: (b) the saturation pressure p_{sat} , (c, d) saturated liquid and vapor densities (*i.e.*, ρ_{liq} , ρ_{vap}), (e, f) and saturated liquid and vapor enthalpies (*i.e.*, h_{liq} , h_{vap}). Continuous lines represent the mean of the predicted property values for the 100 samples generated from the Monte Carlo simulation, while dashed lines represent their standard deviations. The predicted values of the critical temperature are: $T_{c,\text{GCM}} = 522.25$ K and $T_{c,\text{ANN}} = 501.54$ K.

As it can be observed, the uncertainty limits for both models are comparatively larger for 2,2-dichloropropane than for propyl chloride, being the uncertainties predicted by the ANN the greatest in most of the cases. The first fluid, with molecular formula $\text{CH}_3 - \text{CCl}_2 - \text{CH}_3$, can be divided into the following first order groups (according to the groups in Ref. [4]): 2 groups CH_3 , and 1 group CCl_2 . As it can be seen in the correlation matrices represented in Figures 3 and 4 of the Supporting Information, the combination of the groups CH_3 and CCl_2 does not present a significantly strong correlation, however, the uncertainty associated with the functional group CCl_2 for both the predicted T_c and p_c is high due to the fact that the group was present in only one fluid in the dataset. Propyl chloride, with formula $\text{CH}_2\text{Cl} - \text{CH}_2 - \text{CH}_3$, can be divided into the following first order groups: 1 group CH_3 , 1 group CH_2 , and 1 group CH_2Cl . Although the correlation be-

494 tween the two first groups is strong, due to the simultaneous presence of both
 495 groups in many molecules, the correlation with the group CH_2Cl is low. This
 496 fact, together with the low uncertainties associated to the three groups for
 497 all properties (see Figure 2 in the Supporting Information), contribute to the
 498 low overall uncertainty of the properties for this molecule. It can be noted
 499 that there is no significant difference in magnitude for the saturated pressure
 500 and saturated densities between the GCM and the ANN. This is true even
 501 in the case of propyl chloride, which exhibits a significant difference in the
 502 uncertainty for the critical temperature, which was found to be one of the
 503 main contributors to the overall uncertainty. For this fluid, the main differ-
 504 ences observed come from the difference in the predicted values of the critical
 505 temperature and pressure (about 20 K and 1 bar, respectively), which impact
 506 the calculated saturated pressures and densities. The propagated values of
 507 the uncertainties for the vapor pressure are in line with those observed by
 508 Hajipour and Satyro [7] in their study of the propagation of uncertainties
 509 on thermodynamic models. In the case of the saturated enthalpies, it can
 510 be seen that the uncertainty ranges increase at higher temperatures, and the
 511 uncertainty range is larger in the case of the saturated vapor enthalpy.

512 3.3. Propagation of the uncertainty in a case study: organic Rankine cycle 513 unit

514 Figure 9 shows the values of the net power output and the thermal effi-
 515 ciency of the ORC unit when using R-1233zd(E) and R-1234yf as working
 516 fluids, calculated by using the predictions from both methods, with the es-
 517 timated uncertainty indicated by the error bars, and Refprop [21]. Two
 518 interesting observations can be made. First, the estimated uncertainty for
 519 the net power output and thermal efficiency are of the same order of magni-
 520 tude for both the GCM and the ANN for R-1233zd(E), although the ANN
 521 exhibits more uncertainty. However, the estimated value of the net power
 522 output by using the predicted properties by the ANN is closer to that ob-
 523 tained by using Refprop. This is due to the fact that, for this case, the
 524 GCM overestimates the T_c by almost 60 K, which has a major impact on the
 525 calculation of the cycle pressures. For this case, the estimated uncertainties
 526 for the T_c are 8 K and 36 K for the GCM and the ANN, respectively. Also,
 527 the uncertainties for p_c and ω are larger for the ANN, which would explain
 528 the larger uncertainty in the net power output when using the values from
 529 the ANN. Second, in the case of R-1234yf, the results of both the net power
 530 output and efficiency for the GCM and the ANN differ substantially from

531 those of Refprop. In this case, both models underestimate the T_c value by
 532 more than 10 K, which has a major impact on the calculation of the cycle
 533 pressures and net power output. The overall uncertainty obtained for the
 534 ANN is high and can be a consequence of the high uncertainty associated
 535 with the group $\text{CH}_2 = \text{C}$ of R-1234yf, for the p_c model (see Figure 2 in the
 536 Supporting Information). Although the uncertainty in the predicted T_c by
 537 the ANN is of similar magnitude to that of R-1233zd(E), in this case it has a
 538 major impact on the calculation of the saturation pressures due to the slope
 539 of the saturation line of R-1234yf, thus increasing the uncertainty of the net
 540 power output. These cases may demonstrate that the uncertainty of the
 541 predicted values of a fluid's thermophysical properties will have a different
 542 impact on the prediction of net power output of an ORC unit, depending
 543 also on the deviation of their prediction and on the saturation line slope for
 544 that fluid.

Figure 9: Comparison of the value and uncertainty of the prediction of W_{net} and η_{ORC} for a case using (a) R-1233zd(E) or (b) R-1234yf as the working fluid, for both the GCM and the ANN approaches. The values obtained by using Refprop are indicated as a reference.

545 4. Discussion

546 4.1. Comparative analysis of the uncertainty of the GCM and the ANN

547 As it was observed in section 3.1, no significant differences existed be-
 548 tween the estimated uncertainty values of both models, except for the ideal
 549 gas heat capacity. Figure 10 depicts the average value of the calculated un-
 550 certainties for each method and property, and the standard deviation of the
 551 uncertainties. This figure indicates that the variance of the uncertainty ob-
 552 tained from the ANN is always lower than that of the GCM. This means

553 that the uncertainty values obtained for the predictions of the GCM may be
 554 more sensitive to the functional groups forming the molecule, while the un-
 555 certainty of the ANN predictions will have similar values for different fluids.
 556 A possible reason for this can be that while the GCM parameters are more
 557 sensitive to the number of instances of the specific functional group in the
 558 fitting dataset, the ANN parameters are independent of this. This observa-
 559 tion is also demonstrated in Figure 2 of the Supporting Information. This
 560 figure presents the uncertainty values obtained for T_c , p_c , ω and $c_{p,0}$ when
 561 only each of the functional groups is considered as an input, with the aim to
 562 search for correlations between molecular structure and overall uncertainty
 563 value. As it can be seen, while the variation in the ANN values is mostly
 564 negligible for all properties, the uncertainties of the GCM values vary to a
 565 larger extent for each functional group.

Figure 10: Average and standard deviation of the calculated uncertainties for the whole fluid dataset, for each of the considered properties (*i.e.*, T_c , p_c , ω , and $c_{p,0}$), and for each prediction model (GCM and ANN).

566 4.2. Impact of the availability of experimental data on the propagated uncer- 567 tainty

568 Methods to predict thermophysical properties of fluids are of great utility
 569 in both industrial processes and research, but it is obvious that the high asso-
 570 ciated uncertainties of their calculated values can lead to inconclusive results
 571 when propagated in process simulations. Although the use of larger datasets
 572 for the fitting process of these methods can help reducing the uncertainty
 573 of the predictions, the uncertainty of the prediction cannot be less than the
 574 actual uncertainty of the available experimental data.

575 As mentioned in section 2.3.2, the uncertainty of the experimental data
 576 is not accounted for directly in the optimization of the group contribution or
 577 the neural network parameters. In some fitting procedures, not used here, the

578 uncertainty of the experimental data is used only as a weight for the fitting
 579 process, but this still can result in estimated uncertainties less than those of
 580 the experimental data. Here, we compare the estimated uncertainties of the
 581 properties for those fluids for which data of their experimental uncertainties
 582 is available. Figure 11 shows this comparison by representing the estimated
 583 uncertainties of both GCM and ANN for the fluids in the dataset for which
 584 the experimental uncertainties of the critical temperature, critical pressure,
 585 acentric factor, and ideal gas heat capacity were available (i.e. selected data
 586 from the Project 801 of the Design Institute for Physical Property Data
 587 (DIPPR® 801) [23]).

Figure 11: Comparison of the available experimental uncertainties with the predicted uncertainties from both models (GCM and ANN) for the same fluids. +: experimental uncertainty; Δ uncertainty obtained from the GCM; $\circ$ uncertainty obtained from the ANN. Note the logarithmic scale of the y-axis.

588 In the case of T_c , p_c and $c_{p,0}$ some of the experimental uncertainty val-
 589 ues are less than those obtained from the models. This may indicate an
 590 underestimation of the model for those specific fluids, that however, would
 591 not be solved by including the available experimental uncertainties in the
 592 fitting process, due to their low number. Finally, for the acentric factor ω ,
 593 the experimental uncertainties are well below those of the models, indicating
 594 a more realistic situation.

595 *4.3. Comparison with other predictive methods*

596 Although comparing the deviation of different predictive models for spe-
597 cific inputs is easy, doing the equivalent comparison for the uncertainty of
598 their predictions can be challenging. The main reason for this is that, as
599 pointed out by Frutiger et al. [18], the uncertainty of the model predictions
600 is rarely reported.

601 When it comes to the available predictive models for the properties and
602 fluid groups treated in this work, this problem is also encountered. For in-
603 stance, the models developed by Marrero and Gani [15], Constantinou et al.
604 [31], and Joback and Reid [14] for the prediction of the critical temperature
605 and critical pressure, acentric factor, and ideal gas heat capacity, respectively,
606 do not provide information about the uncertainty of the predictions or the
607 model parameters. Sobati et al. [32] provided the 95% confidence intervals
608 of the parameters of their models based on the quantitative structure prop-
609 erty relationship approach for the prediction of the critical temperature and
610 critical pressure of pure refrigerants.

611 In order to illustrate how the uncertainties estimated in this work compare
612 to the confidence intervals of the aforementioned model, Figure 12 presents
613 the calculated values for 2,2-dichloropropane (circles) and 1,2-dichloro-1,1,2,3,3,3-
614 hexafluoro-propane (squares). For the considered fluids, the uncertainties for
615 the critical pressure of the model of Sobati et al. [32] are similar to those of
616 the GCM and the ANN, being slightly lower from the highest critical pressure
617 value and slightly greater for the highest critical pressure value. In the case
618 of the critical temperature, the results suggest that the uncertainties of the
619 model of Sobati et al. [32] are greater than those of the ANN for both fluids,
620 and they are only exceeded by the GCM for the highest critical temperature
621 value.

Figure 12: Estimated values and uncertainties of (a) the critical temperature T_c and (b) critical pressure p_c for 2,2-dichloropropane (circles) and 1,2-dichloro-1,1,2,3,3,3-hexafluoropropane (squares).

4.4. Guidelines

Based on the obtained results, a series of guidelines can be provided with regards to the expected uncertainty of new halogenated working fluids. In this section we summarize these findings in the form of guidelines with respect to the preferred method in order to reduce the uncertainty in the estimation of the properties depending on the molecular structure of the fluid.

As previously mentioned, the uncertainty values obtained from the GCM tend to vary more with the molecular structure of the fluid, while the uncertainty values obtained from the ANN are more homogeneous. This indicates that, in terms of the uncertainty of the prediction, the ANN value is more robust to changes in the molecular structure, which is an advantage in cases where the GCM yields high uncertainties in the predictions.

In this regard, Figure 2 in the Supporting Information provides a good insight on which groups are expected to add higher uncertainty to the prediction depending on the property and the model. A good way to predict for which fluids the predictions of the GCM can have higher uncertainties is by observing this Figure, which represents the uncertainty of each property when the specific functional group is used as input for the models. In the case of the critical temperature, molecules containing the functional groups $\text{CH} = \text{C}$, CCl or CCl_2 are expected to yield larger uncertainties for the GCM. This can be motivated by the fact that these groups were underrepresented in the dataset used for the fitting of the GCM [4]. In the case of the critical pressure, only the functional group CH is expected to have greater uncertainty on the prediction from the GCM. For some of the groups, such as $\text{CH}_2 = \text{C}$ or CHF_2 , the prediction of the GCM is expected to have a signifi-

cantly lower uncertainty than that of the ANN. This can be motivated by a major presence of the mentioned group in the dataset used for the fitting of the models, or a lower degree of correlation of these groups with the rest of groups. In the case of the acentric factor, groups CH, CCl, and CH = C are expected to yield larger uncertainties for the GCM. Finally, for the ideal gas heat capacity, it may be observed that several functional groups are expected to give a higher uncertainty for the GCM, especially in the case of HCCIF.

Combining the predictive models for each property of a fluid depending on their expected relative deviations and uncertainty could help obtaining a prediction of its thermophysical behavior with low uncertainty.

5. Supporting information

The Supporting Information of this work contains the following material:

- An example of calculation of the uncertainty of the predicted values of T_c , p_c , ω , and $c_{p,0}$.
- The uncertainty results for each of the individual groups for the models.
- The correlation matrices of the groups in the fluid set.
- The estimated uncertainties associated to the functional groups for the GCM.

The Matlab code of the function developed for the estimation of the uncertainty of the critical temperature, critical pressure, acentric factor, and ideal gas heat capacity of halogenated fluids using the GCM and the ANN is provided in the institutional repository (doi.org/10.11583/DTU.7438607), together with the needed variables of the predictive models. The repository link contains the following functions and variables:

- `uncertainty_model.m`: obtains the estimated uncertainty for a specified model and property, as indicated in section 2.3.3. The input for its use is the array containing the number of groups for the fluid, except for the case of the ideal gas capacity, where the first element of the array will be the temperature in Kelvin. An example of use of this function can be found in Section 1 of the Supporting Information.

- 677 • `Tc_model.mat`: this is a structure that contains the array of experi-
678 mental values of T_c (`Tcexp`), the fluid groups (`groups`), the models'
679 parameters (`param_GCM`, `param_ANN`), the predictions of the GCM and
680 the ANN (`Tc_GCM`, `Tc_ANN`), their uncertainties (`u_GCM`, `u_ANN`), and
681 the PDF of both model parameters (`pdf_GCM`, `pdf_ANN`).
- 682 • `Pc_model.mat`: analogous to `Tc_model.mat`.
- 683 • `w_model.mat`: analogous to `Tc_model.mat`.
- 684 • `cp0_model.mat`: analogous to `Tc_model.mat`.
- 685 • `Tc_model.csv`, `Pc_model.csv`, `w_model.csv`, and `cp0_model.csv`: con-
686 tain the data of the .mat files in csv format.

687 6. Conclusions

688 In this work we estimated, analyzed, and compared the uncertainty of
689 the predictions of the critical temperature, critical pressure, acentric factor,
690 and ideal gas heat capacity of halogenated substances, by using two different
691 predictive models. The propagation of these uncertainties through the use of
692 the PR-EoS was studied, and a case study of an organic Rankine cycle unit
693 was used to illustrate the effect of the uncertainties in process simulation.
694 Based on the obtained results the following conclusions are drawn:

- 695 • On average, the estimated uncertainties of the critical temperature,
696 acentric factor and the ideal gas heat capacity are lower for the model
697 based on the ANN, while the uncertainties yielded by the GCM are
698 lower for most of the considered fluids for the critical pressure.
- 699 • The estimated uncertainties from the GCM depend considerably on the
700 molecular structure of the fluid, while the uncertainties yielded by the
701 ANN predictions are less sensitive in this respect. As a consequence, the
702 presence of some specific functional groups will add more uncertainty
703 to the predicted value by using the GCM, and for fluids where those
704 groups are present, the use of the ANN could be more recommendable.
- 705 • The GCM yields larger uncertainties on its predictions when the fluid
706 molecule contains functional groups such as CH and CCl_2 . In those
707 cases the ANN yields lower uncertainty values.

- 708 • The uncertainty in the critical temperature is the main contributor
709 to the overall uncertainty of properties calculated by using the Peng-
710 Robinson equation of state, with a high influence on the saturated
711 pressure and saturated liquid density and enthalpy.
- 712 • The propagation of the uncertainty of the critical parameters to the
713 overall uncertainty of the net power output of an organic Rankine cycle
714 unit is affected by different factors. Although the uncertainty of the
715 critical temperature is the main contributor to the overall uncertainty,
716 its combination with the uncertainty of the other parameters and the
717 saturation behavior of the fluid can influence its impact on the total
718 uncertainty.
- 719 • Although the uncertainty propagation in the prediction of the thermo-
720 physical properties of halogenated fluids has been exemplified on an
721 ORC application, it must be noted that new halogenated substances
722 are now being introduced as refrigerants in the automotive industry
723 and in heat pumps. Therefore, the research presented in this work
724 may be of interest, not only for the ORC technology, but also for the
725 refrigeration industry.

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