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Project Report

Experimental planning and verification of working fluids

WP 5

Deenesh K. Babi, Post-doc

July 2016

Scope and Objective

Computer-aided molecular design (CAMD) helps in the reduction of experiments for the selection/design of optimal working fluids. In reducing the number of experiments, solutions obtain by trial and error is replaced by solutions that are based on mixture-process properties.

In generating optimal working fluid candidates a database is required that can be simultaneously searched in order to differentiate and determine whether the generated candidates are existing or novel. Also, the next step upon selection of the candidates is performing experiments in order to test and verify the generated working fluids. If performed properly, the experimental step is solely verification. Experiments can either be performed virtually (in order to further reduce the number of required experiments) and/or physically.

Therefore the objective of this work was the development of a database of existing working fluids and their properties and the development of a design of experiments method for verifying the optimal working fluids generated from CAMD

Design of Experiments Method

A working fluid is a fluid that is used for the conversion of a primary energy source into useful work. A primary energy source, for example, is the combustion of natural gas to produce heat energy (NIST 2011). Examples of working fluids are water utilized in steam plants and, air and combustion products (gaseous) used in gas turbines (Invernizzi, 2013).

Properties of Working Fluids

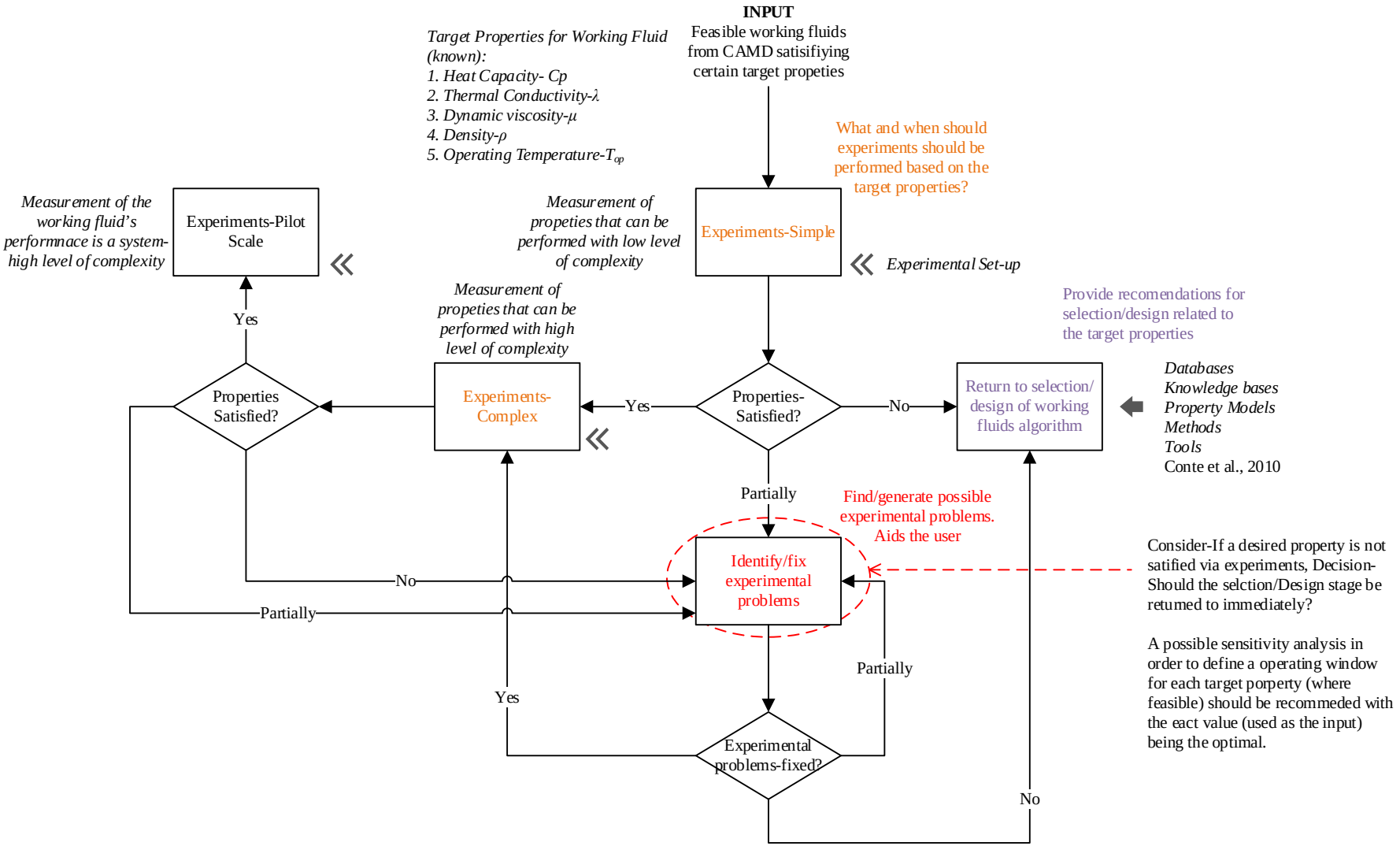
The properties of working fluids, according to Amaris et al. (2015) the thermos-physical properties of a working fluid are:

1. Critical Temperature- T_c
2. Critical Pressure- P_c
3. Boiling point- T_p
4. Heat capacity: Cp
5. Heat Transfer coefficient- h
6. Thermal conductivity- λ
7. Dynamic viscosity- μ
8. Density- ρ

Method Workflow & Summary

Conte et al. (2011) has proposed a general method for the design of experiments (DoE) related to the design of products. The method proposed by Conte et al. (2011) has been expanded for the development of a method for the DoE of working fluids. The proposed method has two versions, version 1 and version 2 and they are shown on Figure 1 followed by explanation of each version. The method consists of two main sections. In section 1 simple experiments are performed for measuring target properties that can measured with a low level of complexity and section 2 measurers properties with a high level of complexity. In version 1, single target property values are used in experiments-simple and experiments-complex. In version 2, the single property value is replaced by an operating window for each target property.

Work-flow-Operating Window of *target porperties* not considered
Version 1



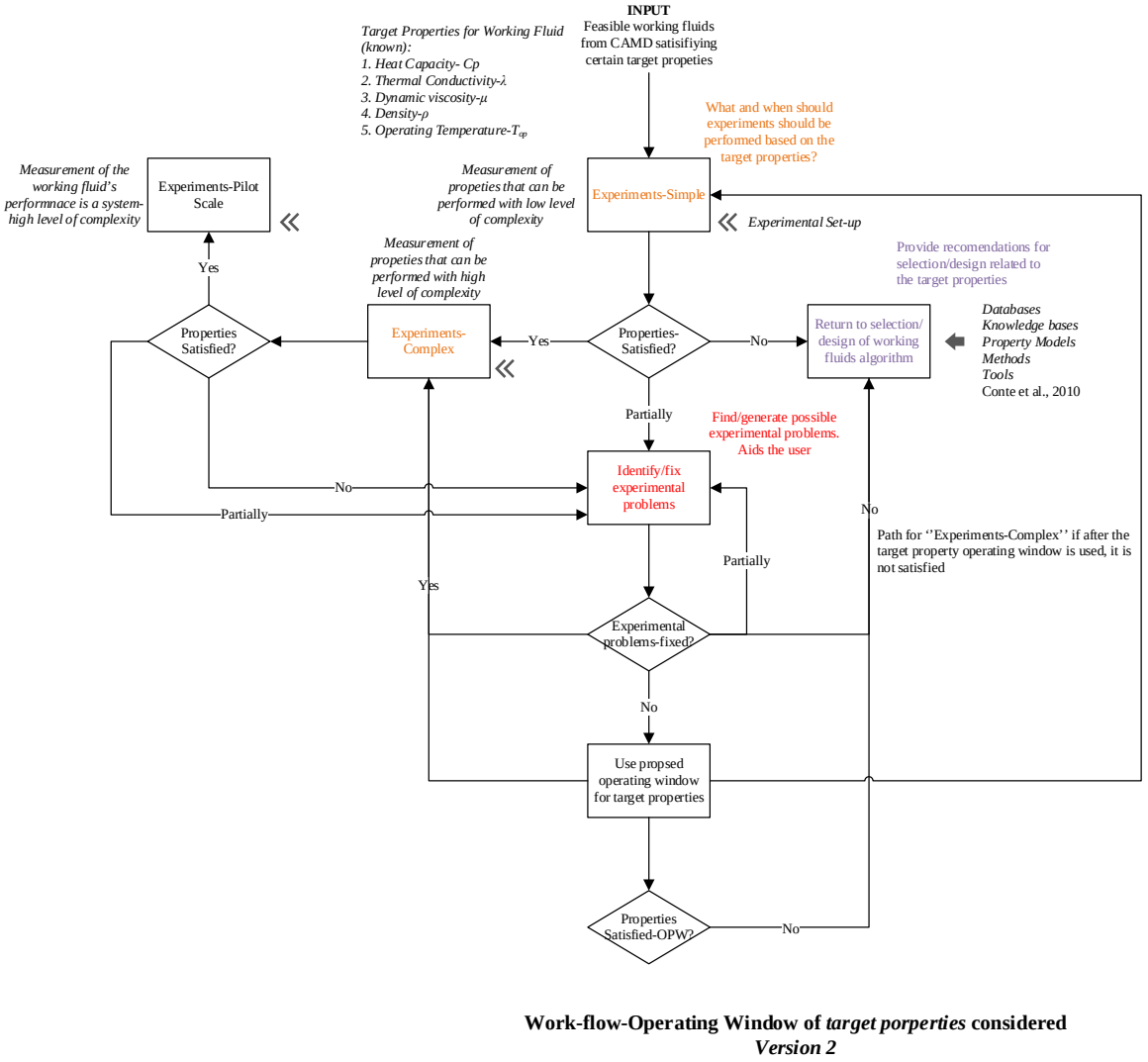


Figure 1: Proposed method for the design of experiments (DoEs) for working fluids

Version 1

Experiments-Simple (real experiments)

This is the starting point of the method. The inputs to the method are the proposed solvent candidates, design from computer aided molecular design (CAMD) and their target properties. In this step, simple experiments are performed in order to verify experimentally calculated target properties.

Properties Satisfied?

In this step, a decision is made whether the target properties for which experiments have been performed satisfies those calculated through CAMD. If the answer is 'yes', then proceed to the step 'Experiments-complex', otherwise for any other answer, proceed to the step 'identify/fix experimental problems'.

Identify/fix experimental problems

In this step, the type of experiment or problems related to the performing of the experiment for a certain target property may cause the wrong experimental validation. Therefore, these are identified and solutions proposed.

Experimental problems-fixed?

In this step, a decision is made whether the identified experimental problems have been fixed. If the answer is 'yes', then proceed to the step 'Experiments-complex', otherwise for any other answer, proceed to the step 'Return to selection/design of working fluid algorithm' in order to, select/design new working fluid candidates.

Experiments-complex

In this step, complex experiments are performed in order to, verify experimentally target properties that were not found in 'experiments-simple.

Properties- Satisfied?

In this step, a decision is made whether the target properties for which experiments have been performed satisfies those calculated through CAMD. If the answer is 'yes', then the next step will be to 'Experiments-Pilot Scale', otherwise for any other answer, proceed to the step 'identify/fix experimental problems'.

Experiments-Pilot Scale

In this step, once all the target properties have been satisfied via experiments, then, one can proceed to performing pilot scale experiments for the testing of the working fluid in the system that it will work, for example, organic Rankine cycle.

Version 2

In version 2 an operating window is used instead of a single value for the target property. In doing so, a new step is added, ‘use proposed operating window for target properties’.

Use proposed operating window for target properties

In this step, an operating window for the target properties are considered because there may be no problem with the experiments but that the finding of the exact value of the target property may not be possible.

Properties Satisfied-OPW?

In this step, a decision is made whether the target properties, using an operating window (OPW) for which experiments have been performed satisfies those calculated through CAMD. If the answer is ‘no’ then proceed to the step ‘Return to selection/design of working fluid algorithm’ in order to, select/design new working fluid candidates.

The steps, ‘Experiments-Simple’ and ‘Experiments-complex’ are related to experiments for, pure compounds and mixtures respectively. Figure 2 shows the sub-method for ‘Experiments-Simple’.

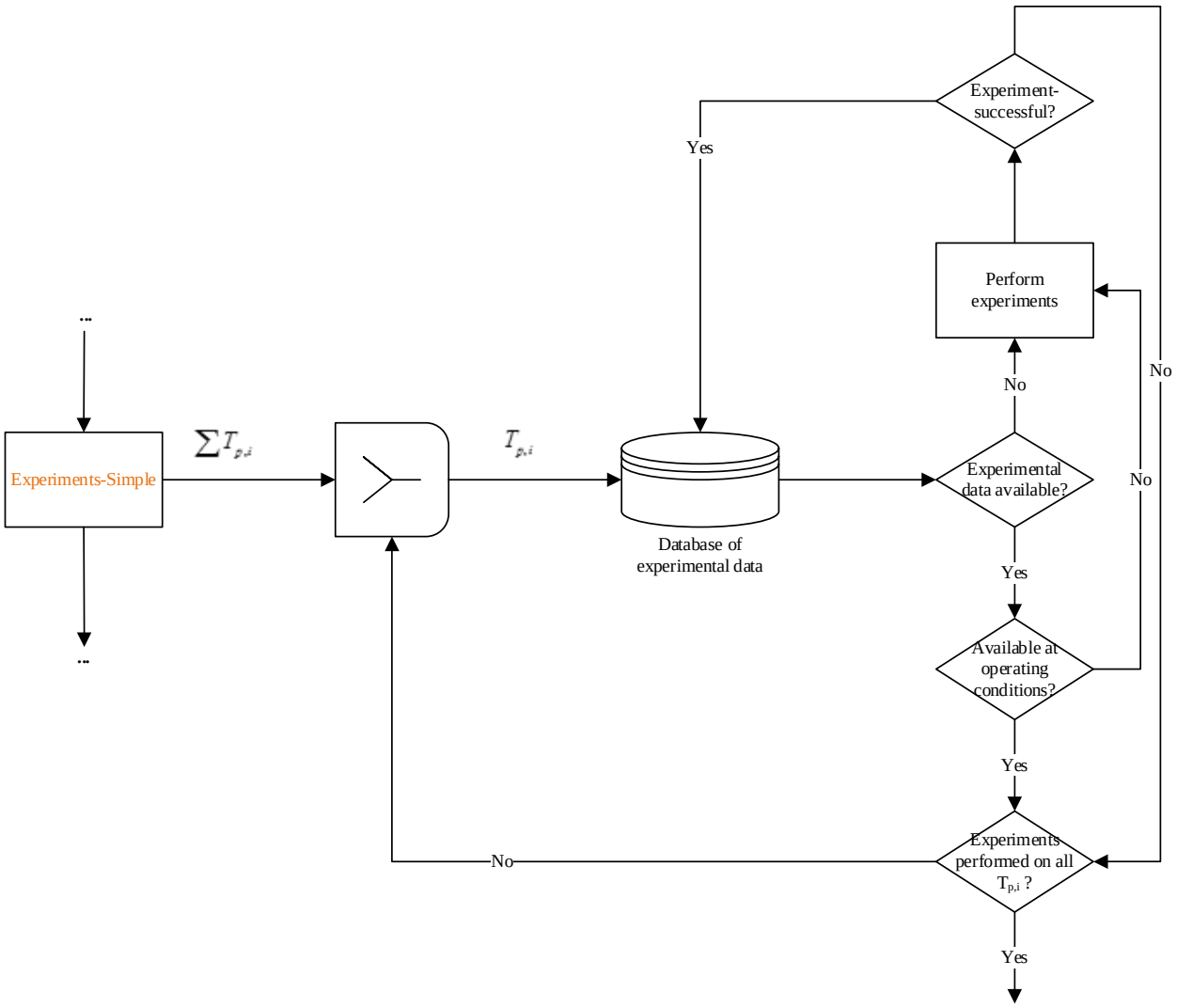


Figure 2: Sub-method associated with Experiments-Simple. *T-target, p-property, i-compound*

An explanation for the sub-method is as follows and uses and is related to the target properties (Tp,i).

Database of experimental data

In this step, a database of experimental data is developed. The database consists of experimental data that are available for a pure compound property. The database structure is based on an ontology.

Experimental data available?

In this step, a decision is made whether the experimental data is available, after a database check, for a given pure compound property. If the answer is ‘yes’, then no experiments for this property are to be performed at this point, then proceed to ‘Available at operating conditions?’, otherwise, proceed to ‘Perform experiments’.

Available at operating conditions?

In this step, a decision is made whether the available experimental data is available at the operating conditions at which the pure compound will be used. If the answer is ‘yes’, then proceed to ‘Experiments performed on all Tp,i ?’, otherwise proceed to ‘Perform experiments’.

Perform experiments

In this step, if experimental data is not available for a pure compound or not available at the operating conditions at which the pure compound will be used, then experiments are performed in order to, obtain the experimental data.

Experiment-successful?

In this step, a decision is made whether the experimental was successful. If the answer is ‘yes’ then proceed to the step ‘Database of experimental data’, otherwise proceed to step ‘Experiments performed on all Tp,i ?’.

Experiments performed on all Tp,i ?

In this step, a decision is made whether experimental data, from the performing of experiments, is available for the Tp,i’s considered. If the answer is ‘no’, then this step is repeated until all Tp,i’s have been investigated, otherwise, this sub-method is exited and the main workflow is re-entered.

Ontology for the Storing of Experimental Data

For storing and retrieving data, data ontology is required in order to easily retrieve and store data. The ontological structure for storing data is presented in Figure 3.

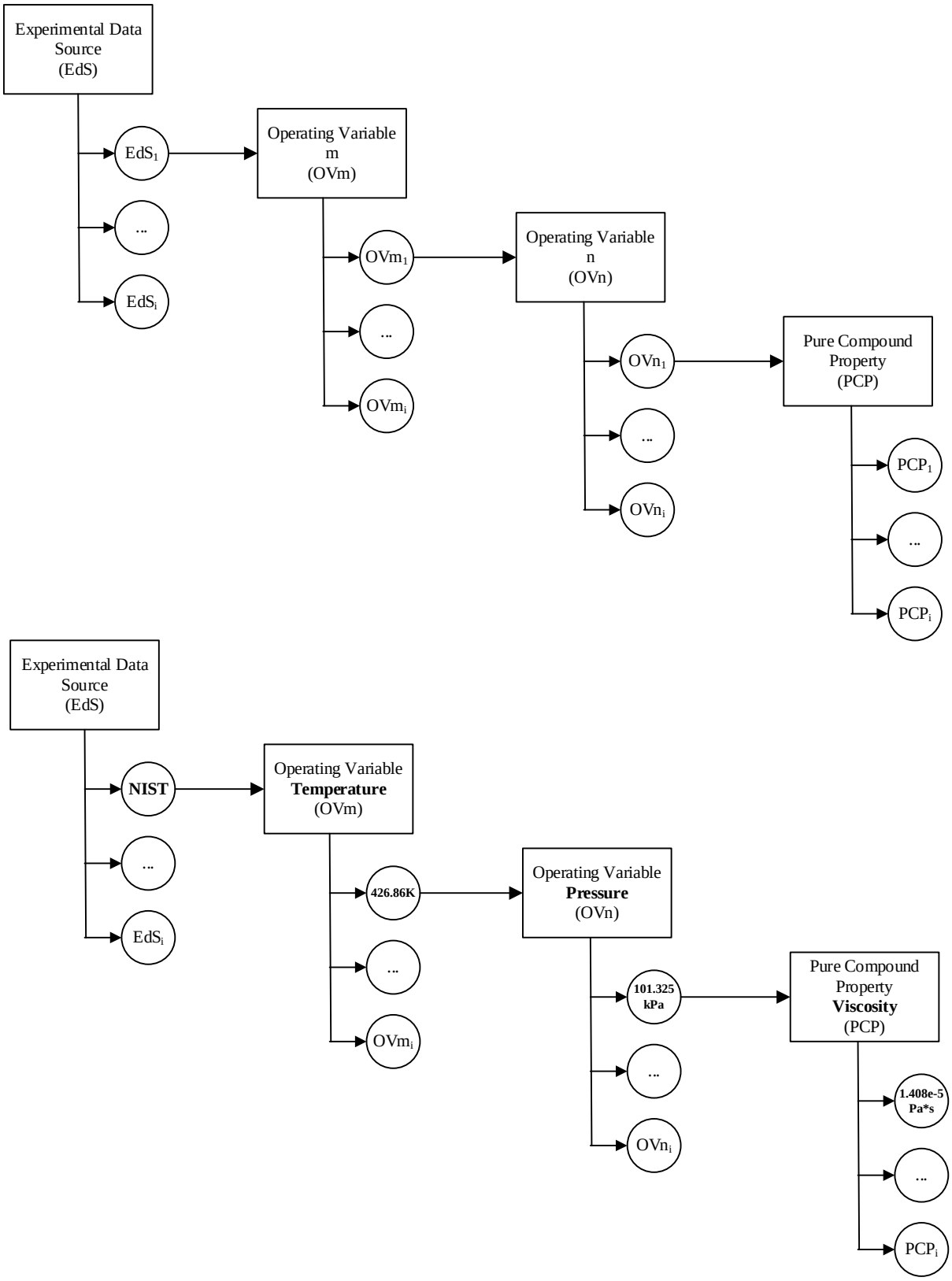


Figure 3: Ontological structure for storing pure compound experimental data

The ontological structure is explained as follows (Sing et al., 2010):

1. Each heading in the structure refers to different classes
2. The components of each class is an instance

This type of ontological structure is feasible and beneficial because of the following reasons:

1. It is generic
2. It can be extended to include further classes, when necessary, vertically. A vertical extension means that more rows of data are added.
3. It can be extended to include further instances, when necessary, horizontally. A horizontal expansion means that more columns of data are added

In Figure 3 an example is presented for the storing of experimental data for the viscosity of methanol. First, the source of data is identified, NIST. Second, the first operating variable for which this data is available is stored. Third, the second operating variable for which the data is available is stored. Fourth, the pure compound property experimental is stored.

The ontological structure for the database is presented in Figure 4.

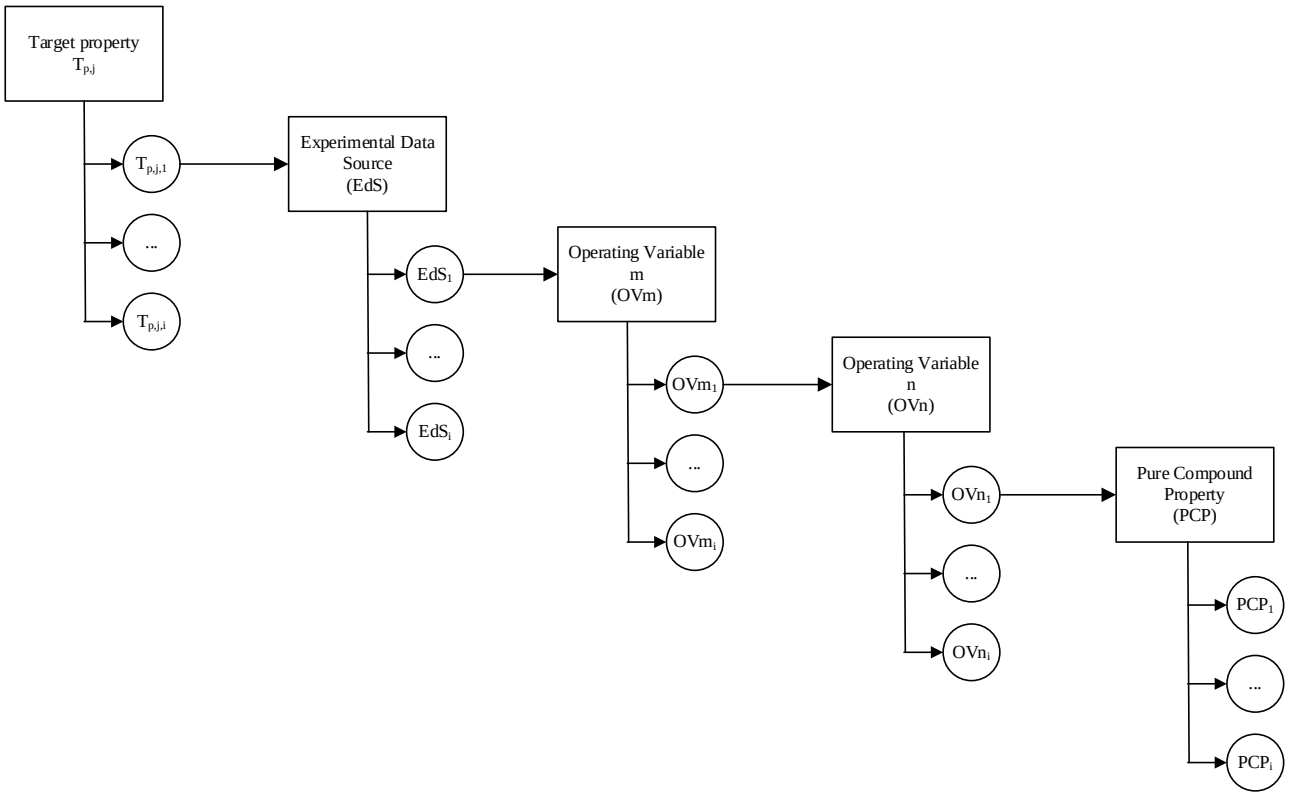


Figure 3: Ontological structure for the database of experimental data

Extension for Experiments-Simple: Virtual experiments

The sub-method for 'Experiments-Simple' is further developed in order to include model-based analysis. If experimental data are available, then models can be developed and validated, in order to accurately calculate the pure compound properties instead of performing experiments (Conte et al., 2011). Figure 4 shows the updated sub-method that was presented in Figure 2.

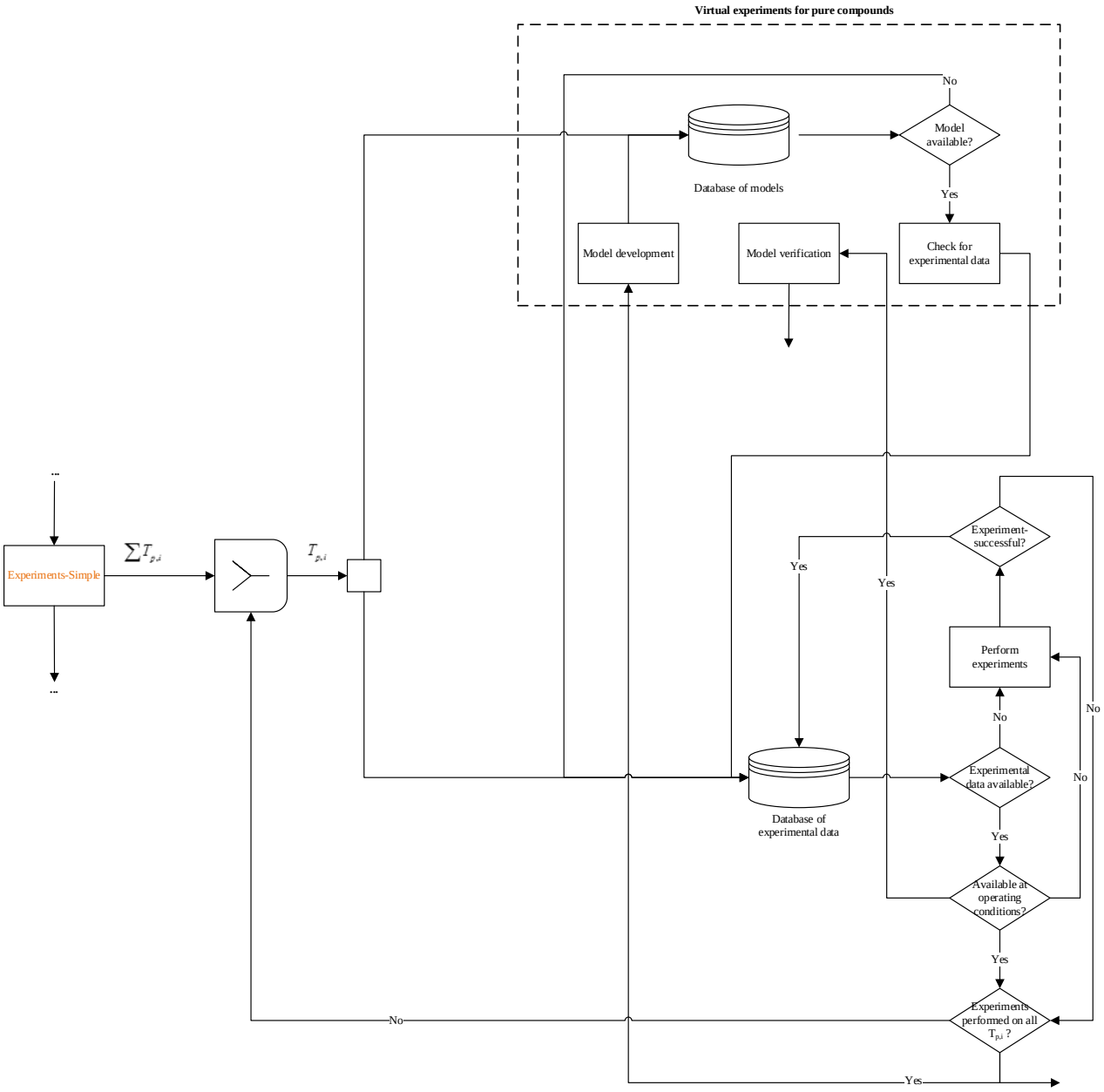


Figure 4: Sub-method (updated) associated with Experiments Simple

An explanation for the updated sub-method is as follows:

Database of models

One can chose either to perform experiments of perform virtual experiments, that is, the property is calculated using a model. If one choses to perform experiments, this has already been explained for the figure in Figure 2. If one choses to calculate the pure compound property, then a data base of models, that is, a model library, is searched in order to retrieve an existing model.

Model available?

In this step, a decision is made whether the model is available, after a database check, for calculating a given pure compound property. If the answer is ‘yes’, then proceed to ‘Check for experimental data’, otherwise, proceed to ‘Database of experimental data’.

Check for experimental data

In this step, a database search is performed in order to, retrieve experimental data to be used in the ‘Model verification’ step.

Model verification

In this step, the model is verified using the retrieved experimental data. If the model is verified for a given pure compound property, then for subsequent calculation of this property, the model is used. This saves on time and material usage for real experiments.

Model development

In this step, for the experiments performed for certain pure compound properties, the user has the option for model development that is beneficial for model re-use, for minimizing the number of experiments to be performed for future scenarios. If a model can accurately calculate a pure compound property then real experiments are not necessary. This can be termed as the performing of virtual experiments.

Ontology for the Storing Model Data

The ontological structure for storing the model data is presented in Figure 5.

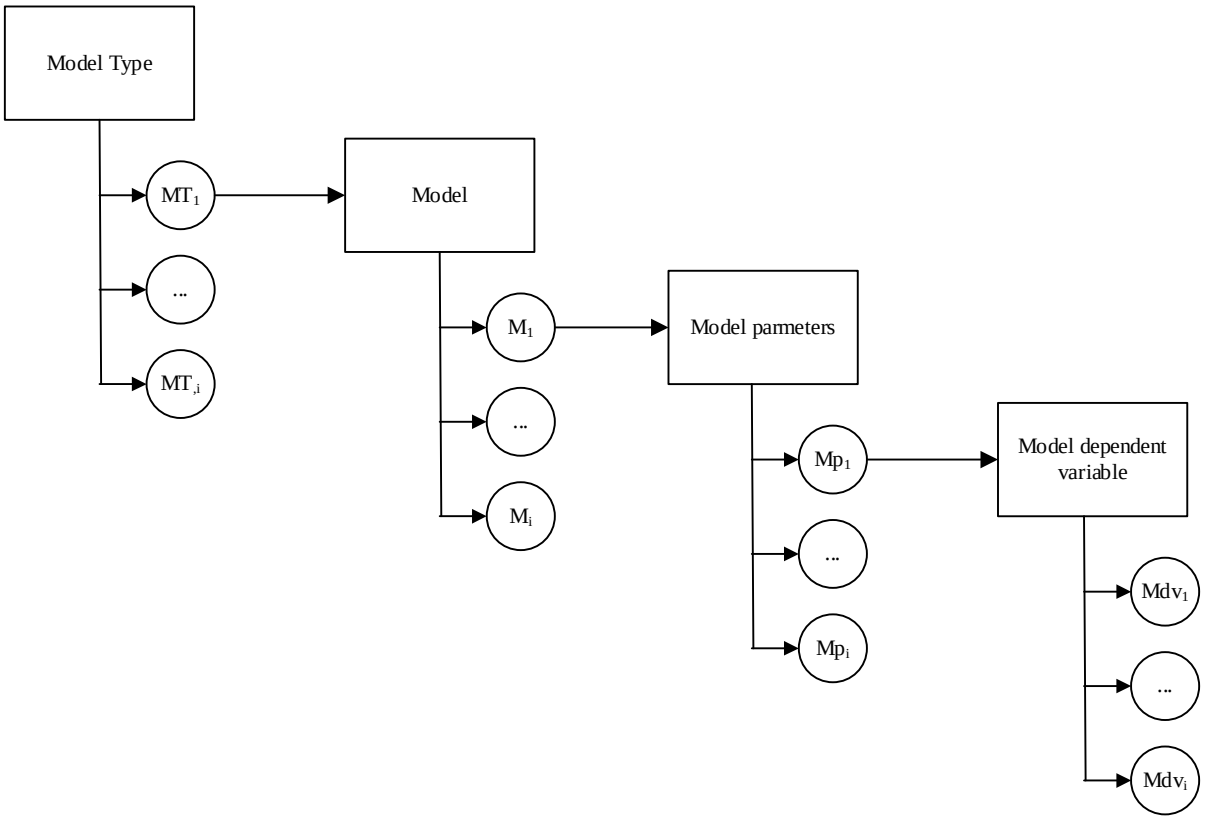


Figure 5: Ontological structure for storing model information

Method Step by Step Explanation

In this section the method is explained step-by-step for application. The steps of the method are presented in Figure 4 and Figure 5 and an excerpt of the database is presented in Table 1 and Table 2.

Step 1- Database Check

Objective: To search in the database of working fluids in order to determine whether the proposed working fluids (pure compounds or mixtures) from applying a CAMD method are available

Step 1.1- Order the proposed working fluids in terms of pure compound working fluids and mixtures of working fluids using the following proposed format

American Society of Heating, Air-Conditioning & Refrigerating Engineers (ASHRAE) Number	Chemical Name

Step 1.2- Select the thermo-physical property for which a model/experimental data (for model development and/or testing) is to be retrieved/obtained and check if information on this property is available in the database for a desired operating condition, for example, temperature

Step 1.3- Search within the database of working fluids using either the ASHRAE or Chemical name and retrieve the property model/data

Step 1.4- If the compound is not available in the database then proceed to step 2

Step 1.5- If the property is available but not at the desired operation condition or if the property is not available in the database for a compound in the database then proceed to step 2

Step 1.6- Repeat step 1.1 to step 1.5 for all considered target properties

Step 2- Experiments: Simple

Objective: To perform simple experiments in order to, verify experimentally a target property.

Step 2.1- For the selected target property defined in step 1, search the database of experimental data in order to check if experimental data for the property is available

Step 2.2- If experimental data is available, then check if the experimental data is available at the desired operating condition(s)

Step 2.3- If experimental data is available but not at the desired operating window or if no experimental data is available then perform the relevant experiments for measuring the target property. If experimental data and/or model are available at the operating window then perform virtual experimental

Step 2.4- Retrieve the experimental data from the performed experiments and update the database of experimental data

Step 3-Return to Selection/Design of Working Fluids

Objective: Return to the CAMD method for selection/design of other working fluid candidates

Step 3.1- If none of the properties of some of the working fluid candidates are satisfied, then remove them from the these working fluids from the list of possible candidates proposed by the CAMD method

Step 3.2- If none of the properties of the working fluid candidates are satisfied from application of step 2, then return to the CAMD method and re-generate another feasible set of candidates else enter step 4 if some of the properties are satisfied partially else, enter step 6 if all the properties are satisfied

Step 4- Identify/fix experimental problems

Objective: To identify experimental problems associated with performing experiments for verification to the selected target properties in step 1

Step 4.1- Identify experimental problems associated with performing the experiment for the verification of a target property

Step 4.2- Propose an alternative task to be performed in order to minimize/remove the experimental problem and return to step 2

Step 4.3- Repeat step 4.1 to step 4.2 for those properties of the working fluid candidates that have not been satisfied. If some of the experimental problems are fixed re-apply step 4.1 to step 4.2 else, if some of or none of the experimental problems cannot be fixed enter step 5 else, if all of the experimental problems are fixed enter step 6. Note: If the all or some of the properties cannot be removed from application of this step, then the problem may not be because of the experiments performed

Step 5- Use proposed operating window of Target Properties

Objective: To provide an operating window for the target property for which possible experiments can be performed

Step 5.1- Select an operating window for a target property and apply step 2

Step 5.2- If all of the target properties cannot be fulfilled for some working fluid candidates then remove these working fluids from the list of possible candidates proposed by the CAMD method

Step 5.3- If none of the target properties cannot be fulfilled all of the working fluid candidates then return to the CAMD method and re-generate another feasible set of candidates

Step 5.4- If all of the target properties are satisfied for a set of the candidate working fluids then proceed to step 6

Step 6- Experiments: Complex

Objective: To perform complex experiments in order to, verify experimentally a target property.

Step 6.1- Apply step 2.1 to step 2.4 but replace ‘’simple’’ with complex

Step 6.2- If some of or none of the properties of the working fluid candidates are satisfied from application of step 6.1, then enter step 3

Step 6.3- If some of or none of the properties of the working fluid candidates are satisfied from application of step 6.2 then remove these working fluids from the list of possible candidates proposed by the CAMD method (*This can be argued because maybe the experiments are just too difficult*)

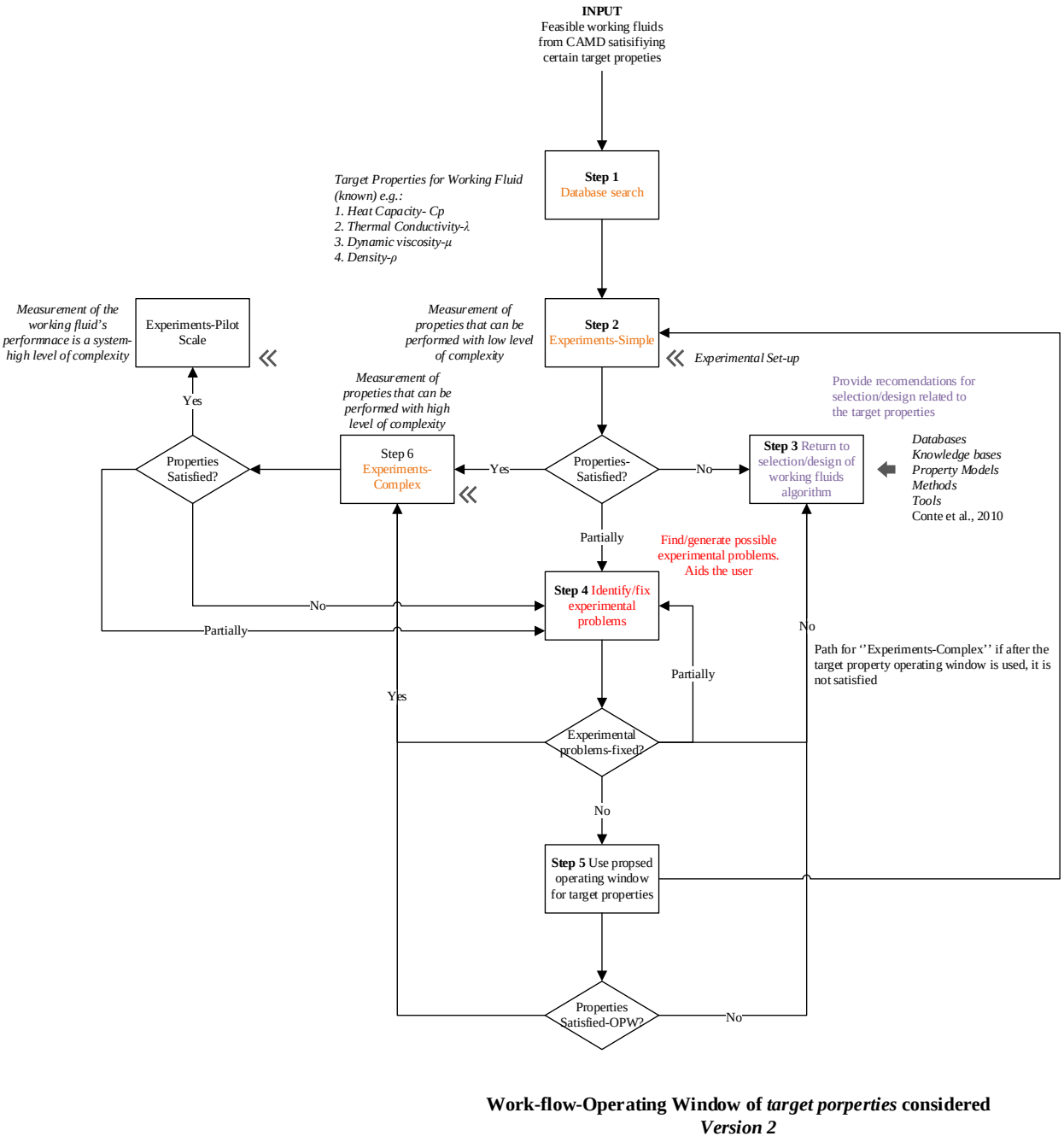


Figure 4: Proposed method for the design of experiments (DoEs) for working fluids

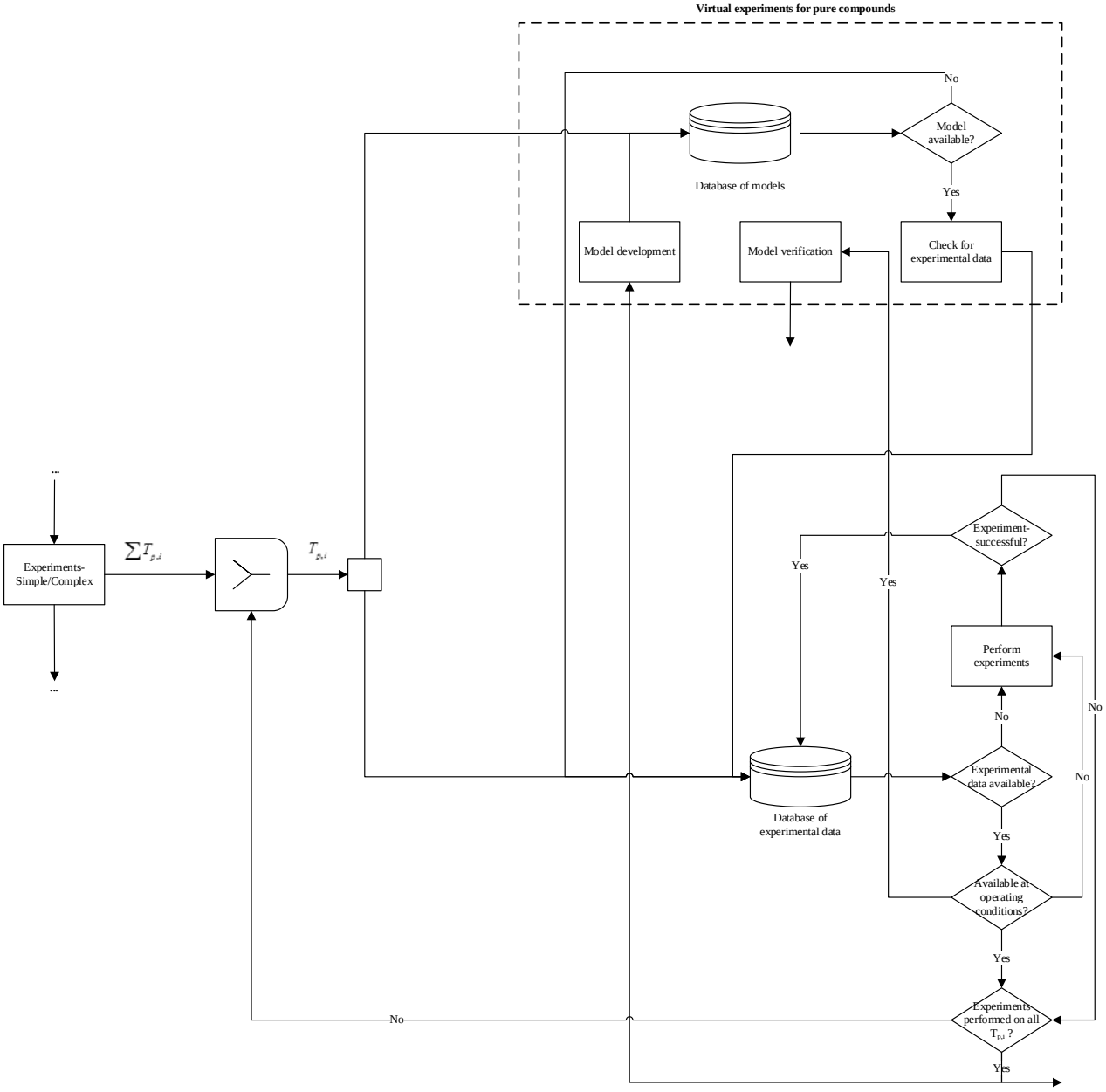


Figure 5: Sub-method associated with Experiments: Simplex/Complex

Table 1: Properties of working fluids available in the database

Property	Symbol	Description	Units	Available In the Database
Thermodynamic	ρ	Density	kg/m3	Y
Thermodynamic	Hv	Latent heat of vaporization	kJ/mol	Y
Thermodynamic	Cp	Liquid heat capacity	kJ/mol-K	Y
Thermodynamic	μ	Viscosity	Pa s	Y
Thermodynamic	λ	Thermal conductivity	W/m-K	Y
Thermodynamic	Tm	Melting point temperature	K	Y
Thermodynamic	Tc	Crictical temperature	K	Y
Environmental impacts	ODP	Ozone depletion potential		N
Environmental impacts	GWP	Global warming potential		N
Safety	LC50 (toxicity)	Lethal Concentration	mol/L	Y
Safety	LD50 (toxicity)	Lethal dose	mol/kg	Y
Safety	Flash point (measure for flammability)	K		Y
Process	η	Efficiency	%	N
Process	Pmax	Maximum operating pressure	bar	N
Process	Pc	Critical pressure	bar	Y
Process	mf	Mass flowrate	kg/hr	N

Table 2: Excerpt of the working fluids database

		Thermodynamic/Physical properties							Safety		Process
		ρ (kmol/m3). Correlation: A/B^(1+(1-T/C)^D)									
ASHRAE No.	**Name**	**A**	**B**	**C**	**D**	**Min T**	**Max T**	**Latent heat Hv (kJ/kg)**	**LC50 FM (mol/L)**	**LD50 (mol/kg)**	**Pc (Mpa)**
R-21	Dichlorofluoromethane	1.3746	0.27023	451.58	0.28651	138.15	451.58	216.17		1.7	5.18
R-22	Chlorodifluoromethane	1.5963	0.26566	369.3	0.28449	115.73	369.3	158.46		1.63	4.99
R-23a	Trifluoromethane	1.934	0.25946	299.3	0.27897	117.97	299.3	89.69	3.35	2.39	4.83
R-32	Difluoromethane	2.0463	0.24839	351.6	0.29221	137	351.6	218.59		4.15	5.78
R-41a	Fluoromethane	2.1854	0.24725	317.42	0.27558	131.35	317.42	270.04	2.37	1.88	5.9
R-116a	Hexafluoroethane	1.1916	0.26671	292.8	0.29865	173.1	292.8	30.69	3.47	4.86	3.05
R-123	2,2-Dichloro-1,1,1-trifluoroethane	0.98168	0.27049	456.86	0.28282	195	456.86	161.82	3.4	3.8	3.66
R-124	2-Chloro-1,1,1,2-tetrafluoroethane							132.97			3.62
R-125	Pentafluoroethane							81.49			3.62
R-134a	1,1,1,2-Tetrafluoroethane	1.2735	0.25854	374.3	0.2739	172.15	374.3	155.42		5.61	4.06
R-141b	1,1-Dichloro-1-fluoroethane							215.13			4.21
R-142b	1-Chloro-1,1-difluoroethane	1.041	0.24537	410.2	0.298	142.35	410.2	185.69		2.14	4.06
R-143a	1,1,1-Trifluoroethane	1.3867	0.27068	346.25	0.25079	161.82	346.25	124.81	2.93	3.35	3.76
R-152a	1,1-Difluoroethane							249.67			4.52
R-170a	Ethane	1.9122	0.27937	305.32	0.29187	90.35	305.32	223.43			4.87
R-218	Octafluoropropane	0.9089	0.2724	345.05	0.2817	125.46	345.05	58.29	3.59	1.86	2.64
R-227ea	1,1,1,2,3,3,3-Heptafluoropropane							97.14			3
R-236ea	1,1,1,2,3,3-Hexafluoropropane							142.98			3.5
R-245ca	1,1,2,2,3-Pentafluoropropane							188.64			3.93
R-245fa	1,1,1,3,3-Pentafluoropropane							177.08			3.64
HC-270	Cyclopropane	1.7244	0.28073	397.91	0.29437	145.59	397.91	366.18	2.46	2.1	5.58
R-290	Propane	1.3757	0.27453	369.83	0.29359	85.47	369.83	292.13	2.68	1.88	4.25
R-C318	Octafluorocyclobutane	0.79648	0.2612	388.37	0.27585	232.96	388.37	93.95			2.78
R-3-1-10	Decafluorobutane	0.66283	0.26303	386.35	0.25572	144.95	386.35	77.95	3.72	5.25	2.32
FC-4-1-12	Dodecafluoropentane							86.11			2.05
R-600	Butane	1.0677	0.27188	425.12	0.28688	134.86	425.12	336.82	2.97	1.93	3.8
R-600a	Isobutane	1.0463	0.27294	408.14	0.27301	113.54	408.14	303.44	2.58	1.88	3.63
R-601	Pentane	0.84947	0.26726	469.7	0.27789	143.42	469.7	349	3.25	1.97	3.37
R-717	Ammonia							1064.38			11.33
R-718	Water	5.459	0.30542	647.13	0.081	273.16	333.15	2391.79			22.06

R-744a	Carbon dioxide	2.768	0.26212	304.21	0.2908	216.58	304.21	167.53			7.38
R-1270	Propene	1.4094	0.26465	365.57	0.295	87.89	365.57	284.34	3.54	1.99	4.66
	Propyne	1.6086	0.26448	402.39	0.279	170.45	402.39	431.61	3.04	1.99	5.63
	Benzene	1.0162	0.2655	562.16	0.28212	278.68	562.16	418.22	3.11	2.2	4.89
	Toluene	0.8488	0.26655	591.8	0.2878	178.18	591.8	399.52	3.43	2.16	4.13

Note: a The critical temperature of the fluid is below 320 K, and the data is given based on 290 K.

CAPEC Database

ProPred

Conclusion

A method has been developed and proposed for the design of experiments (DoE) for working fluids. In principle, the DoE is a verification step for measuring the calculated target properties and manages the complexity of performing experiments by decomposing the experimental sections into two, simple and complex.

The method also uses the idea of virtual experiments that further reduces the need for real experiments if models are available (and have been verified) at the operating window of the working fluid under investigation. The method shows that in the absence of data/models, real experiments can be performed that provides data for updating the database/models in a model library.

Data is being used/obtained in the method and therefore, already developed ontological structure is proposed for use in the method for storing and/or retrieving data with respect to verifying the generated (optimal) working fluid candidates.

The next step would be application of the method for the generated working fluids based on CAMD applied to, for example, the organic Rankine cycle. A possibility exists that real experiments will be reduced because of the use of virtual experiments since for organic compounds, verified, reliable property/mixture models have been developed for wide property operating windows (Marrero & Gani, 2001, Zhang et al., 2016).

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