

HIDROUFF DENSITY CALCULATOR: AN OPEN-SOURCE SOFTWARE FOR PREDICTING DENSITY OF COMPLEX MIXTURES USING PENG-ROBINSON EQUATION OF STATE (PREOS)

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ABSTRACT

Commercial softwares dedicated to providing thermodynamic properties of complex mixtures in general have high-cost licenses and high computational cost, which makes its use limited for undergraduate students in remote classes or research tasks. Therefore, an open-source software was developed in Python, called HidroUFF Density Calculator, that is dedicated to predicting the density of complex mixtures using Peng-Robinson Equation of State (PREOS) as a resolution mechanism. Density was chosen for being one of the most requested thermodynamic properties. The proposed software was compared to a benchmark (UniSim Design), and its results were exactly equal or distant in less than 0.32%.

KEYWORDS

Density Calculator, Peng-Robinson Equation of State, PREOS, Thermodynamics Properties, Open Source Software

1. INTRODUCTION

The density of a fluid is a primary physical property for a wide range of engineering projects and studies. With this parameter, it is possible to obtain the volume that a fluid occupies, the weight contained in tanks, the pump sizing required, and the type of flow (Loria et al., 2009). In International System of units (SI), density is expressed in kg/m³, usually, in the oil and gas industry, the API (American Petroleum Institute) degree (API) is used, which expresses the specific gravity of the oil from the ratio between its density and the density of water, both at 60°F (American Society for testing and Materials, 2019).

For many real cases in engineering, mainly in offshore petroleum engineering, it is difficult and expensive to determine the density of certain fluids in their ambient conditions. Mainly due to the high pressure at which fluids are submitted, reaching over 200 atm. Therefore, several works in the literature have been dedicated to studying the *equations of state* for real fluids, which consider the interaction (pairwise, in a matrix calculation) between all the components of the mixture, and the compressibility factor Z (Borges, 2009). Among the main authors of versions for the *equations of state* for real fluids, we highlight Van der Waals with his proposition that starts the theme (1873), Redlich-Kwong (1949), Modification of Soave in Redlich-Kwong (1972) and Peng-Robinson (1976), widely used for hydrocarbons.

Solving these equations is not simple. Any modification in the working condition requires the observation of parameters tabulated in handbooks, matrix calculation between the n components of the mixture, calculations of accessory terms and, finally, the solution of a cubic equation. Currently, several commercial software dedicated to engineering already provide calculations for determination of specific mass and other more complex thermodynamic properties.

UniSim Design is a commercial-licensed software developed by Honeywell corporation which calculates physical, transport, separation, and reaction kinetics properties (Honeywell, 2018). However, the use of these commercial software is difficult for students, universities, and small companies due to the high price for acquiring these software licenses. This difficulty affects the teaching-learning relationship that will form future professionals in oil and petrochemical companies. In this context, it is necessary to produce low-cost and easy-to-use software.

This paper proposes an open-source software for calculating the density of complex mixtures using the Peng-Robinson equation of state, namely HidroUFF Density Calculator. We compare the density values with this software against those values gathered from the UniSim software, in order to validate our methodology. This work also analyzes the impact of using the software in classes of engineering courses, by means of being intuitive, easy-to-use and low-cost.

2. METHODOLOGY AND SOFTWARE DESCRIPTION

HidroUFF Density Calculator is an open source software under the GNU General Public License (GPL). The main feature of this application is the calculation of the density of gas mixtures, through the resolution of Peng Robinson's cubic equation of state (Peng and Robinson, 1976). PREOS is represented by Equation 1 as well as its terms in Equations 2, 3, 4, 5 and 6, where Z is the compressibility factor of the mixture, R is the universal constant of perfect gasses, and T is the working temperature.

For each substance in the calculator database, it is necessary to include three intrinsic terms: critical pressure (P_c), critical temperature (T_c), reduced temperature (T_R), obtained by T/T_c , and acentric factor (ω). For each pair of substances it is necessary to include an interaction parameter (k_{ij}). All these four parameters are taken from the National Institute of Standards and Technology (NIST) Online Handbook (NIST, 2022).

$$Z^3 - (1 - B) \cdot Z^2 + (A + 2 \cdot B - 3 \cdot B^2) \cdot Z - (A \cdot B - B^2 - B^3) = 0 \quad (1)$$

$$A = \frac{a \cdot \alpha \cdot P}{R^2 \cdot T^2} \quad (2)$$

$$B = \frac{b \cdot P}{R \cdot T} \quad (3)$$

$$a = \frac{0.45724 \cdot R^2 \cdot T^2}{P_c} \quad (4)$$

$$b = \frac{0.07780 \cdot R \cdot T_c}{P_c} \quad (5)$$

$$\alpha = (1 + (0.37464 + 1.54226 \cdot \omega - 0.26992 \cdot \omega^2)(1 - \sqrt{T_R}))^2 \quad (6)$$

2.1 Software Architecture

The software was developed in the Python programming language, chosen due its intuitive syntax. It is in growing use in universities and small companies and provides responsive libraries for specific steps. The proposed software uses its well-known libraries SimPy (SymPy Dev Team, 2021) — a process-based discrete event simulation framework — and Matplotlib (Matplotlib Dev Team, 2022) — a framework for static, animated, and interactive visualizations of data. PyQt5 library (PyPi, 2022) is used for the graphical user interface (GUI) with help of the tool Qt Designer (Qt Company, 2022), for designing and building GUI.

Figure 1 demonstrates the software architecture of the calculator's packages and modules. The packages are represented by the tree-larger rectangles. In blue, the modules that were implemented by the density calculator, and in yellow, the external modules (libraries). In green, the diagram shows the two CSV (Comma Separated Values) files – a database – that store the properties of substances added to the calculator.

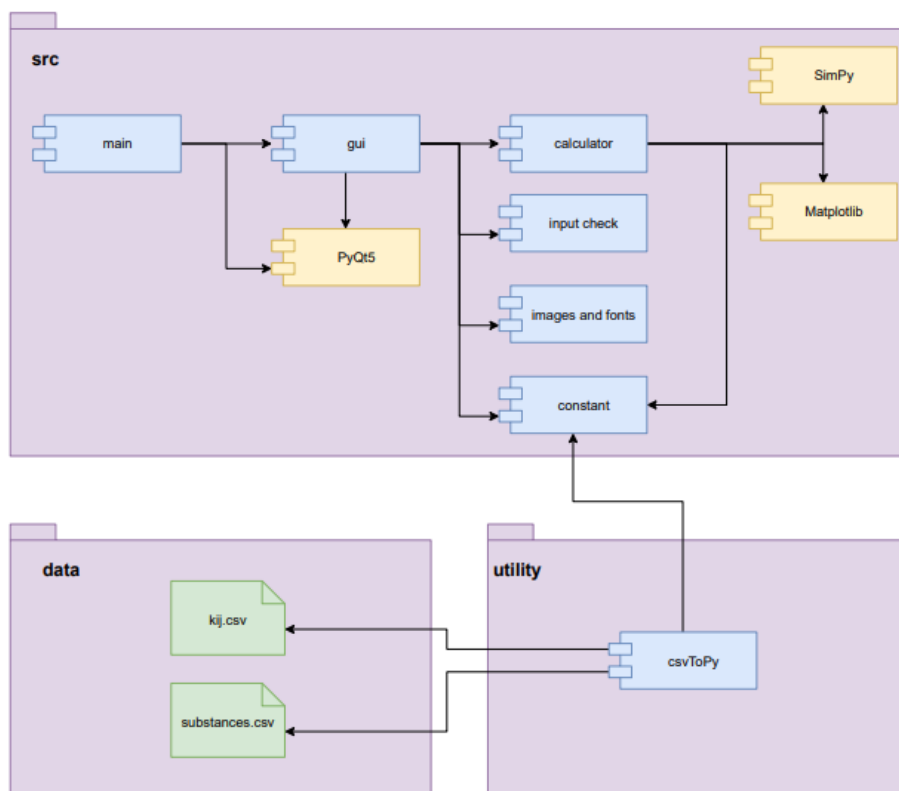


Figure 1. Software architecture representation

The src package stores the main code of the application and is composed of 6 modules: main, gui, calculator, constant, images and fonts and input check.

- **main:** this module used to launch the application through the PyQt5 and gui modules to build the graphical interface.

- **gui:** this module used for construction and user interaction with the graphical interface via PyQt5 and visual elements such as images and fonts. It is responsible for performing the data input, verifying them and passing them to the calculator module so that the necessary calculations are performed to display the result later.

- **calculator:** this module is responsible for performing density calculations by solving the PREOS equation and its terms defined in Equation 1. For this purpose, it receives the input data from the GUI module, that is informed by the user, and also the properties of the substances from the constant module. The SimPy module is used to help with density calculations and the Matplotlib module is used to generate the isotherm graphics.

- **constant:** this module contains the constants that store the values of the properties of substances that can be used by the program. This file is generated by the csvToPy utility from the files in data.

- **images and fonts:** this module stores the images and fonts used by the application in binary format.

- **input check:** this module contains the methods used to perform file and data input verification.

The data package stores input CSV files that contain the properties of the substances registered in the application, such as molar mass (g/mol), critical pressure (kPa), critical temperature (K) and acentric factor. Furthermore, it contains the values of the k_{ij} that represent the interaction parameters between each pair (i, j) of substances.

The utility package contains the utilities responsible for adding new substances to the application by transforming the files contained in data into a single file called constant.py in src for use by the application.

2.2 Software Functionalities

The diagram in Figure 2 demonstrates the flowchart (defined according to ANSI/ISO – American National Standards Institute/International Organization for Standardization) for the operations of the HidroUFF Density Calculator. Next paragraphs detail the workflow in this diagram.

When the software is initialized, the user can choose one of two options: 1) perform the calculation of density for a single pressure value (labeled *Yes*), or 2) for a range of pressure values (labeled *No*). According to this choice, the user must inform different input data. For both options, the user must specify the substances which compose the mixture, their respective molar fraction values and the temperature value with its scale degree (Fahrenheit, Celsius, or Kelvin). To inform the composition, the user clicks on the *Add* substance button, selects one of the available forms in the selection box, and enters the molar fraction value.

For option 1, the user may check *Single* choice. Then, the user types the pressure value, in atm. For option 2, the user must provide the initial and final pressure values and the steps between them. For this, the user needs to select the *Range* option and types these values, as exemplified in Figure 4b.

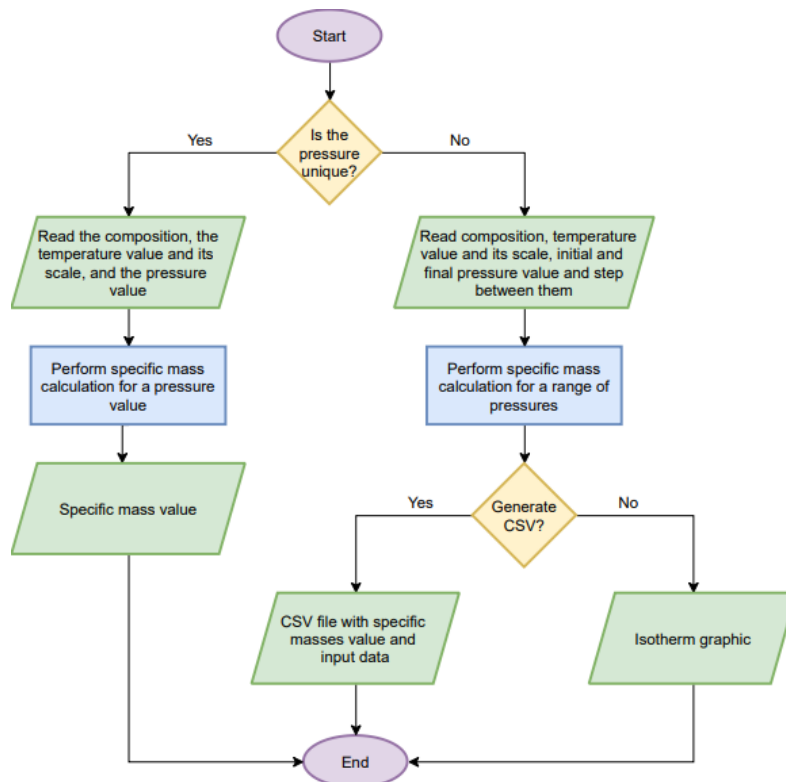


Figure 2. Software flowchart

For both options, the next step is to perform the density calculation using the PREOS (Equation 1). For option 1, the result of the density calculation is the specific mass and it is calculated only for the one pressure value. In this case, the workflow finishes here. For option 2, the user indicates the range of pressure values and the result is an isotherm graphic (density versus pressure). At this stage, in addition to data from the user interface, the software uses internal data that is stored in the constant module presented in Section 2.1. These data refer to the specific properties of the calculation for each substance.

After the density calculation, following the flowchart for option 2 in Figure 2, the user can choose to visualize the graphic in the tool by clicking on the button *Isotherm Graph*. This will generate and display an interactive graphic through the Matplotlib library, where the user can view, manipulate and save the graphic in various formats such as PNG, PDF, and SVG (see Figure 5 in Section 3). He/she also has the option to generate a CSV file by clicking on the button *Generate CSV*. Furthermore, the user can use his/her CSV file generated by the application as input and generate the isotherm graphic. This extra functionality is performed by clicking

the first circular button in the upper right corner of the calculator interface and choosing the desired CSV file (see Figure 3 in Section 3). Focus on the software maintainability, new substances can be easily added to the calculator. A developer can change the data inside the files in package data (see Section 2.1), namely `kij.csv` and `substances.csv`. Molar mass (g/mol), critical pressure (KPa), critical temperature (K), acentric factor, and k_{ij} parameters for the desired substances are the editable values in the CSV tables. The `csvToPy` utility converts the CSV files into a suitable format to the Python language. As this data is sensitive to the software, we decided to keep these modifications at a development level.

2.3 Software Validation

For software validation, a hypothetical mixture (Mix A), composed of methane (40%), ethane (30%), and carbon dioxide (30%), has its density computed with the HidroUFF Density Calculator and UniSim Honeywell. The goal is to evaluate the differences between the values obtained by both softwares. UniSim is a commercial software already established in the market, and it is considered our baseline.

Table 1 shows the comparison results between the HidroUFF Density Calculator and UniSim software for Mix A in an isothermal condition at 4°C, varying the pressure from 1 atm to 300 atm. Table 3 shows the comparison results between the HidroUFF Density Calculator and UniSim software for Mix A in an isobaric condition in 200 atm, varying the temperature from 1°C to 300°C. The deviation of both result values, in the last column, is the main result of both tables. They show that HidroUFF Calculator presents results extremely close to the baseline UniSim. The magnitudes of 0.004% to 0.32% are characterized as a regular deviation due to the range of the calculations (precision of the numbers), and it does not indicate problems in our calculation.

Table 1. Comparison between the specific mass values, in kg/m³, obtained by the HidroUFF Density Calculator and by the commercial UniSim software for Mix A in isothermal condition (4°C)

Pressure (atm)	HidroUFF Calc. (kg/m ³)	UniSim Honeywell (kg/m ³)	Relative Deviation (%)
1	1.27	1.27	0
10	13.34	13.33	0.080
50	91.57	91.73	-0.170
100	307.32	308.30	-0.320
200	464.12	464.30	-0.040
300	527.68	527.70	-0.004

To evaluate programming errors and non-conformities in the software, exhaustive unit tests were performed, modifying input parameters: number of components, components, compositions, temperature, and pressure. It was verified that the software does not present non-conformities, being the calculator ready for utilization by potential users in academia.

For a qualitative validation of the software, the calculator was initially available to a small group of university professors, graduate, and postgraduate students. So that they could give their opinion on corrections and opportunities for improvement. With the preliminary use by professors and students, it was possible to observe from the reports of these users that the software was considered relevant, intuitive, easy to use, with low computational cost, and advantageous for being free.

3. ILLUSTRATIVE EXAMPLES

Screenshots of the HidroUFF Density Calculator user interface is displayed in Figure 3. In this window there is a circular button in the lower left corner that is responsible for switching among the three available languages: Portuguese (Pt), English (En) and Spanish (Es). In the upper right corner there are three buttons: the first one allows the user to load from his computer a CSV file (explained in Section 2.2) generated by the application so that its graph is displayed on the screen; the second button displays a help screen with application usage instructions; and the third button displays a screen with application development information such as developers and current version. In some fields, there is a small circular button that presents a tool-tip with information on how to fill in the field. In addition, there is a button labeled Clear fields used to clear all fields filled in at any time.

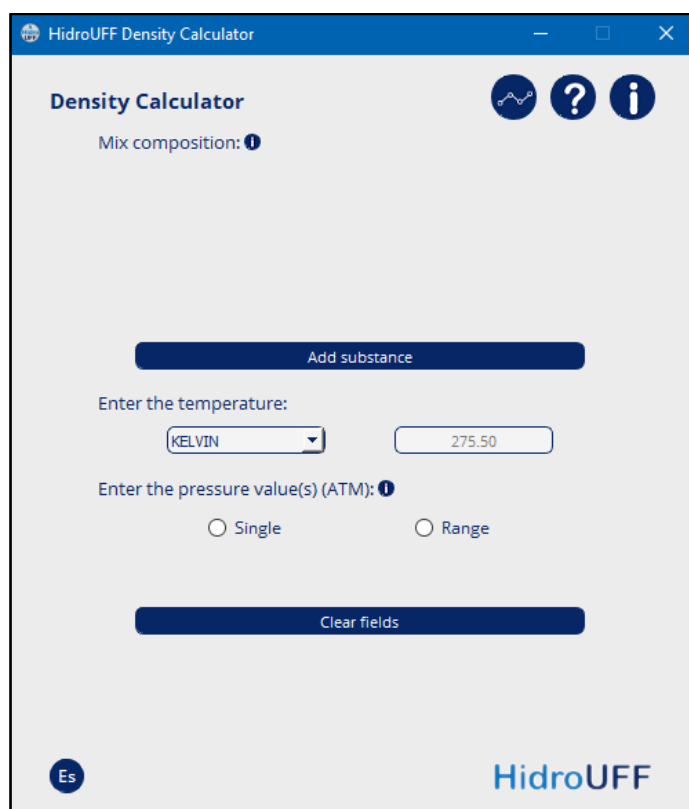


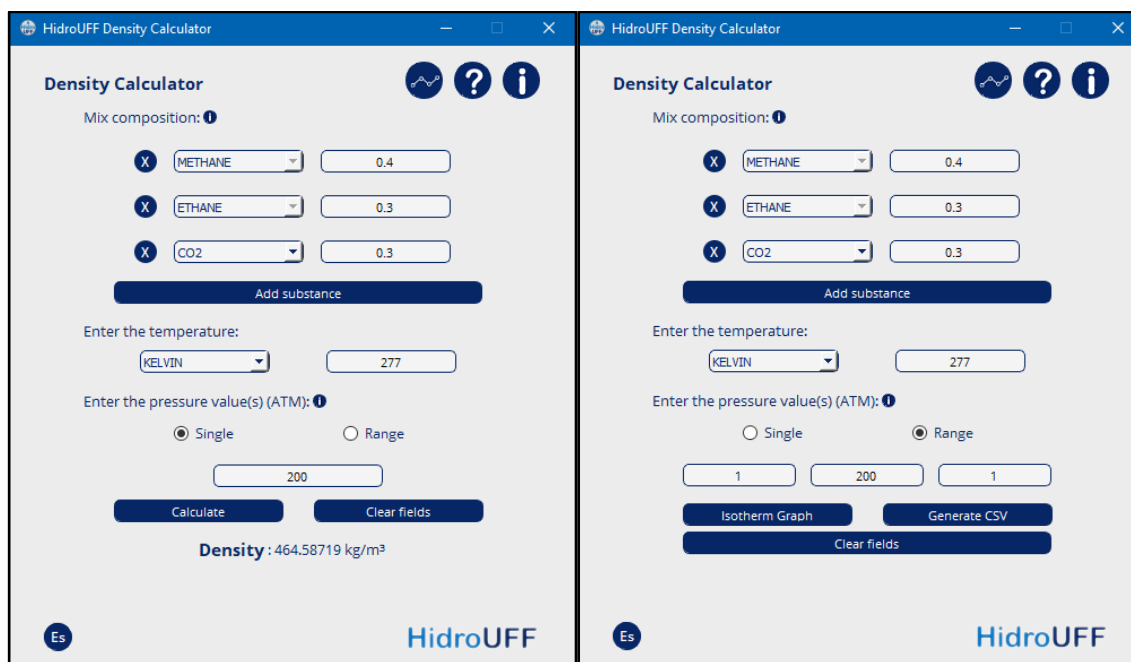
Figure 3. HidroUFF Density Calculator template

Still, in the main window of the software, the user can also add the chemical components, in the button *Add substance* and set the mixture composition. The temperature value and its scale (Fahrenheit, Celsius or Kelvin) is selected in the part labeled as “Enter the temperature”. For density in a single point, the user must select *Single* and the window proceeds to Figure 4a, for just filling the pressure field, in atm. The result of the density appears immediately below the button *Calculate* when it is clicked. For density in a pressure interval, the user must select *Range* and the window proceeds to Figure 4b. Then, the user should fill the three fields: initial, final value and the step between them. In this case, the user can choose as output a file in CSV format or an isotherm graph (see Figure 5). All those functionalities were described in Section 2.2.

4. IMPACT

The results of densities obtained with the proposed software were compared to those found in literature and in benchmark. The values obtained for different mixtures had approximated the same values with very low deviation, in the order of 0.004% to 0.32%.

HidroUFF Density Calculator had a significant impact on the local academic community and has potential to be used in other universities and small companies. In preliminary validation with academic users (professors, researchers, undergraduate and graduate students), it was possible to observe from users reports that the software was considered relevant, intuitive, easy to use, with low computational cost and advantageous to be free, and it offers a Portuguese language option.



(a) For a single pressure.

(b) In the form of an isotherm.

Figure 4. Demonstration of the two types of choice of presentation of results for the mixture A

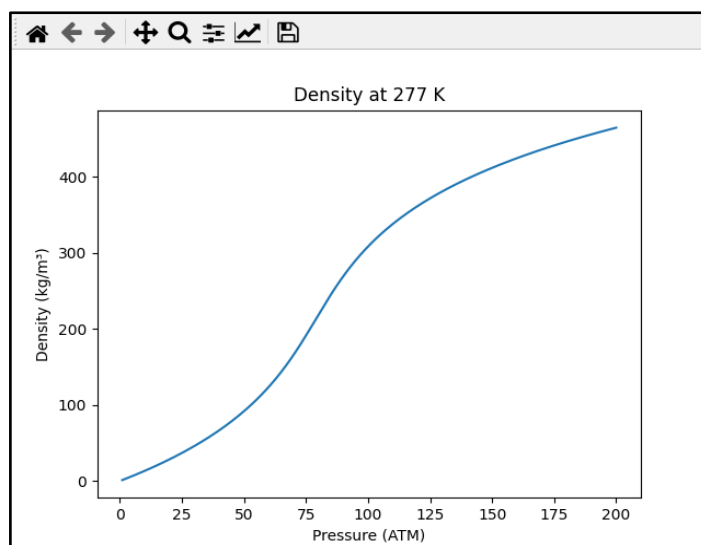


Figure 5. Isotherm (at 277 K) of the specific mass variation of the Mix A between 0 and 200 atm, in the software

The software, after its validation, was made publicly available (open source) in a GitHub repository and was published in the Zenodo platform repository (Sousa et al., 2021). The professors of petroleum engineering and chemical engineering undergraduate courses of Universidade Federal Fluminense (UFF) started to disseminate the tool to their students as an alternative to a commercial software. In a future stage, it is intended to quantitatively evaluate the students opinion about the calculator through online surveys.

The use of the calculator by the academic community is even more interesting for the university dynamics, since classes are being taught remotely due to the COVID-19 pandemic. This makes it increasingly necessary to use free, intuitive, low computational cost, and low-cost software that students can use on their personal computers during lessons or remote tasks. Another impact consists in increasing the operational and economic competitiveness of start-up and small companies, which now have accessible software, avoiding costs with licenses and computer improvements.

5. CONCLUSION

HidroUFF Density Calculator allows predicting the density of complex mixtures of multi-components both with a single point (temperature and pressure) and with an interval, generating an isotherm. In addition, chemical substances not yet provided in the software's database can be easily added by a user, *e.g.* a professor, by filling in substance information in a well-known format CSV.

The software was successfully validated front benchmarks and had a positive response to the target user group (professors, graduate and undergraduate students), highlighting qualities such as free access and low computational cost. Currently, the calculator is being used by our research group in tasks of some projects with industry, and for students as support in classes such as thermodynamics, fluid mechanics, and petroleum engineering. We believe the software can be adopted at other universities and small companies.

In the future, our team intends to produce other software calculators of properties derived from thermodynamics, such as calculation of flash, viscosity and surface tension of mixtures. In addition, a web-application version of the density calculator was developed following the same design and is currently available to the community on the laboratory's website.

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