Central European Journal of Energetic Materials
ISSN 1733-7178; e-ISSN 2353-1843

Cent. Eur. J. Energ. Mater. 2022, *19*(3): 295-310; DOI 10.22211/cejem/155004
Article is available in PDF-format, in colour, at:
https://ipo.lukasiewicz.gov.pl/wydawnictwa/cejem-woluminy/vol-19-nr-3/

Research paper

Research Output Software for Energetic Materials Based on Observational Modelling 2.2 (RoseBoom2.2©) – Update to Calculate the Specific Impulse, Detonation Velocity, Detonation Pressure and Density for CHNO Mixtures Using the Supersloth-function

In memory of Otto Wahler and Alexandra Wahler.

Thomas M. Klapötke*), **Sabrina Wahler**

Department of Chemistry, Energetic Materials Research, Ludwig-Maximilian University of Munich, 81377 Munich, Germany
** E-mail:* tmk@cup.uni-muenchen.de

ORCID information

Klapötke T.M.: https://orcid.org/0000-0003-3276-1157
Wahler S.: https://orcid.org/0000-0002-7515-0148

Abstract: RoseBoom2.2© can calculate parameters for CHNO mixtures, automatically minimizing user-input. In the present study, RoseBoom's© results were compared to 518 EXPLO5 calculations. The new version of RoseBoom© can calculate a variety of parameters for mixtures. The detonation pressure and detonation velocity, and the specific impulse were calculated using different methods. In the present study different approaches for calculating the average sum formula have been evaluated.

Keywords: calculations, EXPLO5, detonation parameters, specific impulse, RoseBoom, mixtures

1 Introduction

Current computer programs like EMDB or EXPLO5 for energetic materials all require time-consuming manual input of the sum formula, density and heat of formation [1, 2]named EXPLO5, is based on the chemical equilibrium, steady-state model of detonation. The program uses Becker-Kistiakowsky-Wilson's (BKW. The input for these programs for single molecules can be done fairly easy, even though the entry is still very prone to man-made mistakes and is time-consuming. The determination of the needed heat of formation and density require prior synthesis or time-consuming composite methods. Recent advances, directly addressing this problem and overcoming it, were made with the Software RoseBoom2.1© (Research Output Software for Energetic materials Based On Observational Modelling) licensed by RoseExplosive UG (in German: *haftungsbeschränkt*) [3]. This software combines empirical relationships for energetic materials published in different epochs of high-energy density materials (HEDMs) research. They have been revalidated for modern compounds on a dataset of over 480 compounds and merged in the user-friendly tool RoseBoom©, which allows quick and easy access to the performance parameters of HEDMs within experimental uncertainties [4, 5].

Often energetic materials will not exhibit the desired properties (*e.g.* oxygen balance, stability, mechanical properties) in a pure form, which is the reason why they are used in mixtures, to achieve a balance, with optimum performance (Figure 1).

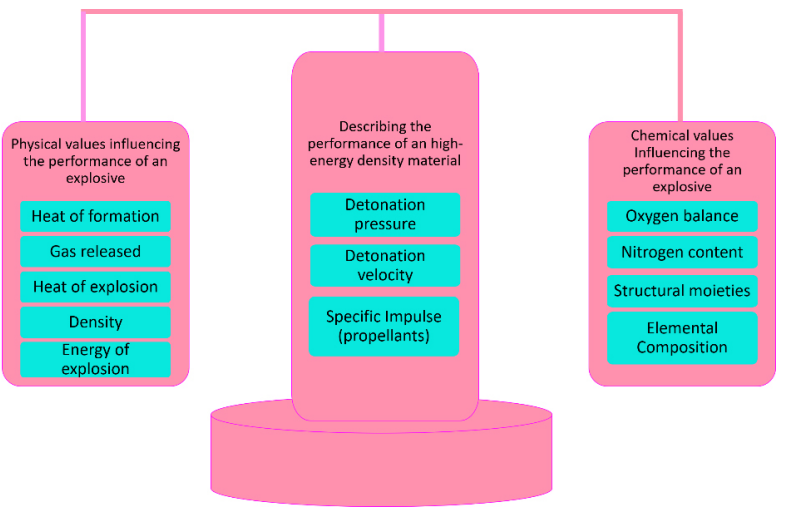


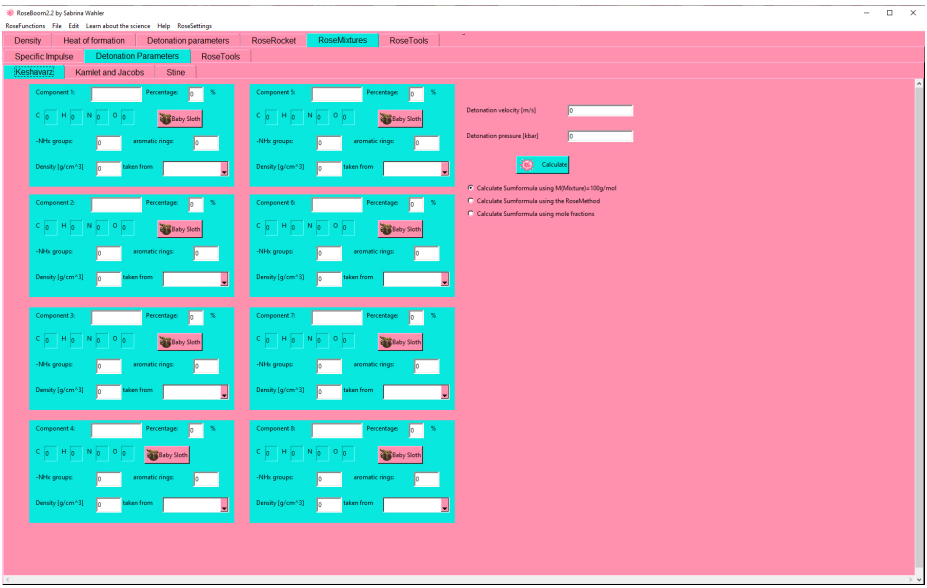
Figure 1. The physical and chemical values directly impacting the performance of energetic materials

The models implemented in RoseBoom2.2© however, have not been used in this recent study to predict the performance of energetic mixtures. These are even more time consuming for calculation in the current computer programs, because it requires the manual input of many different compounds instead of only one, and with programs like EXPLO5 [1]named EXPLO5, is based on the chemical equilibrium, steady-state model of detonation. The program uses Becker-Kistiakowsky-Wilson's (BKW the computational time increases to 2 min with multiple components. Furthermore, the results are obtained in individual ".txt" files, which do not allow for a quick scan by the user for the optimum mixture or for comparing different mixtures with each other. They have to be manually converted into tables. RoseBoom2.2© allows quick and easy calculation of up to eight component mixtures with a few clicks, allowing the user to quickly find the optimum balance, as illustrated in Figure 1, because the results are given in a CSV-file that can be opened with MS Excel™.

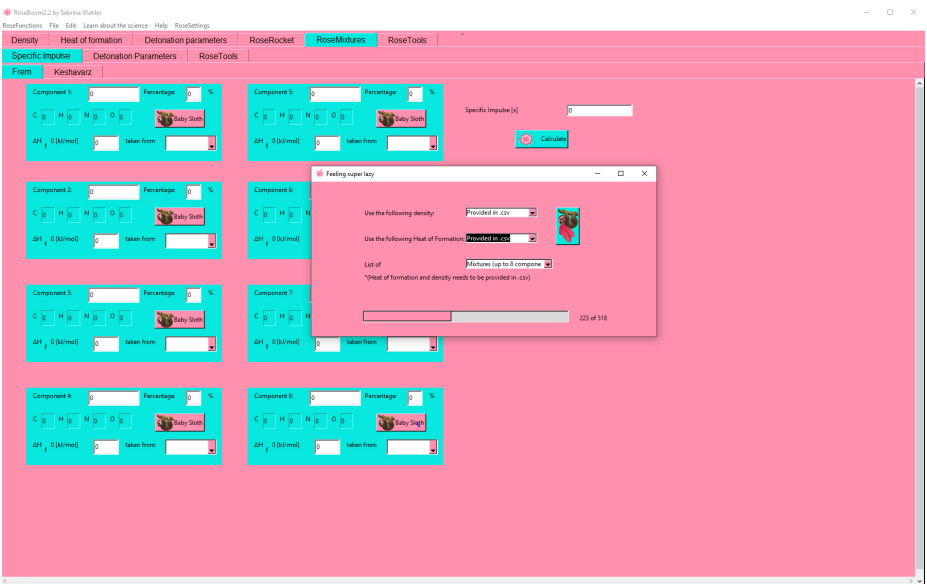
2 The Program

2.1 Basic information

RoseBoom2.2© contains different empirical models to predict the detonation parameters (*e.g.* detonation velocity and pressure). With RoseBoom2.2© it is possible to calculate named detonation parameters of mixtures using the models from Kamlet and Jacobs [6], Stine [7] and Keshavarz [8] and the specific impulse using the Frem [9] and the Keshavarz models [8]. The very user-friendly graphical user interface (Figure 2), allows the user to enter Simplified Molecular Input Line Entry Specification (SMILES) into the "Baby Sloth" – function, which automatically reads the required data for the component from the input (Figure 2).



(a)



(b)

Figure 2. The user-friendly interface of RoseBoom2.2© for calculating the performance of mixtures in the RoseMixture© Tab.

A new Supersloth© function is also available, which will read the information from a CSV file with an infinite number of mixtures (or single molecules) and run the calculations automatically, writing the output to another ".csv" file. The calculations presented in the results section of 518 mixtures, took three weeks computation time using EXPLO5; in RoseBoom2.2© theywere run three times, using different equivalent formulas, in under 10 min with the newly developed Supersloth© function. This automation is very useful, because mixtures require the manual input of several molecules, hence it is 5 times as time-consuming to run the calculation of a five-component mixture as it is to run the calculation of a single molecule.

2.2 Computational details

All calculations for the reference dataset were performed using EXPLO5 V6.05.04. The specific impulses were calculated at 7 MPa chamber pressure and 0.1 MPa ambient pressure. An issue was encounter when calculating the equivalent formula. For the example of a 65% ammonium dinitramide (AND, $H_4N_4O_4$) and 35% glicydyl azide polymer (GAP, $C_3H_5N_3O$) mixture, one would calculate it intuitively using Equations 1-4.

$$C = 0.65 \cdot 0 + 0.35 \cdot 3 = 1.05 \quad (1)$$

$$H = 0.65 \cdot 4 + 0.35 \cdot 5 = 4.35 \quad (2)$$

$$N = 0.65 \cdot 4 + 0.35 \cdot 3 = 3.35 \quad (3)$$

$$O = 0.65 \cdot 4 + 0.35 \cdot 1 = 2.95 \quad (4)$$

which leads to an equivalent formula of $C_{1.05}H_{4.35}N_{3.35}O_{2.95}$, but when checking with Frem's method [9] it is given as $C_{1.061}H_{3.863}N_{3.156}O_{2.449}$, and even more confusion is caused when calculating the same mixture inEXPLO5 [1] named EXPLO5, is based on the chemical equilibrium, steady-state model of detonation. The program uses Becker-Kistiakowsky-Wilson's (BKW, where the equivalent formula is indicated as $C_{1.208}H_{4.403}N_{3.597}O_{2.792}$. These differences are the result of Frem calculating the equivalent formula for mixtures with a fixed molar weight of 100 g/mol (Equations 5-8) and Sućeska's EXPLO5 [1] named EXPLO5, is based on the chemical equilibrium, steady-state model of detonation. The program uses Becker-Kistiakowsky-Wilson's (BKW using mole fractions (Equations 9 and 10).

$$C = 65 \cdot MW(ADN)^{-1} \cdot 0 + 35 \cdot MW(GAP)^{-1} \cdot 3 = 1.061 \quad (5)$$

$$H = 65 \cdot MW(ADN)^{-1} \cdot 4 + 35 \cdot MW(GAP)^{-1} \cdot 5 = 3.863 \quad (6)$$

$$N = 65 \cdot MW(ADN)^{-1} \cdot 4 + 35 \cdot MW(GAP)^{-1} \cdot 3 = 3.156 \quad (7)$$

$$O = 65 \cdot MW(ADN)^{-1} \cdot 4 + 35 \cdot MW(GAP)^{-1} \cdot 1 = 2.449 \quad (8)$$

(referred to as Method A)

$$C = (10 \cdot 65 \cdot MW(ADN)^{-1} \cdot 0 + 10 \cdot 35 \cdot MW(GAP)^{-1} \cdot 3) \cdot (10 \cdot 65 \cdot MW(ADN)^{-1} + 10 \cdot 35 \cdot MW(GAP)^{-1})^{-1} = 1.208 \quad (9)$$

$$H = (10 \cdot 65 \cdot MW(ADN)^{-1} \cdot 4 + 10 \cdot 35 \cdot MW(GAP)^{-1} \cdot 5) \cdot (10 \cdot 65 \cdot MW(ADN)^{-1} + 10 \cdot 35 \cdot MW(GAP)^{-1})^{-1} = 4.403 \quad (10)$$

$$N = (10 \cdot 65 \cdot MW(ADN)^{-1} \cdot 4 + 10 \cdot 35 \cdot MW(GAP)^{-1} \cdot 3) \cdot (10 \cdot 65 \cdot MW(ADN)^{-1} + 10 \cdot 35 \cdot MW(GAP)^{-1})^{-1} = 3.597 \quad (11)$$

$$O = (10 \cdot 65 \cdot MW(ADN)^{-1} \cdot 4 + 10 \cdot 35 \cdot MW(GAP)^{-1} \cdot 1) \cdot (10 \cdot 65 \cdot MW(ADN)^{-1} + 10 \cdot 35 \cdot MW(GAP)^{-1})^{-1} = 2.795 \quad (12)$$

(referred to as Method B)

It was of great interest to determine in which models the accuracy is influenced by how the average sum formula is calculated, and which equivalent sum-formula gives results closest to those from EXPLO5.

The different equivalent formulas however do not affect the average density of the energetic mixtures, which is needed to predict their performance parameters like the detonation pressure and velocity. One would intuitively multiply the densities with the corresponding amounts in the mixture, which gives the wrong results. It is necessary to consider the volume that each component will take up in a mixture (Figure 3).

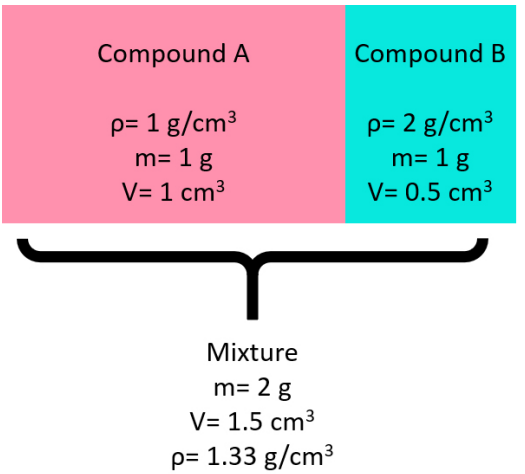


Figure 3. Graphical visualization of the problem that occurs when calculating the average densities of mixtures, with an example of two different compounds with densities of 1 and 2 g/cm³, respectively

1 g of a component weighing 2 g/cm³ will take up 0.5 cm³, while a component weighing 1 g/cm³ will take up 1 cm³ (Figure 3). Therefore a mixture of 2 g (1 g of each component) will have a volume of 1.5 cm³, which results in an average density of 1.33 g/cm³. This rule of three can be difficult for multi-component mixtures which have several ingredients, which is why it is very useful that it can be reduced in one single step with Equation 13.

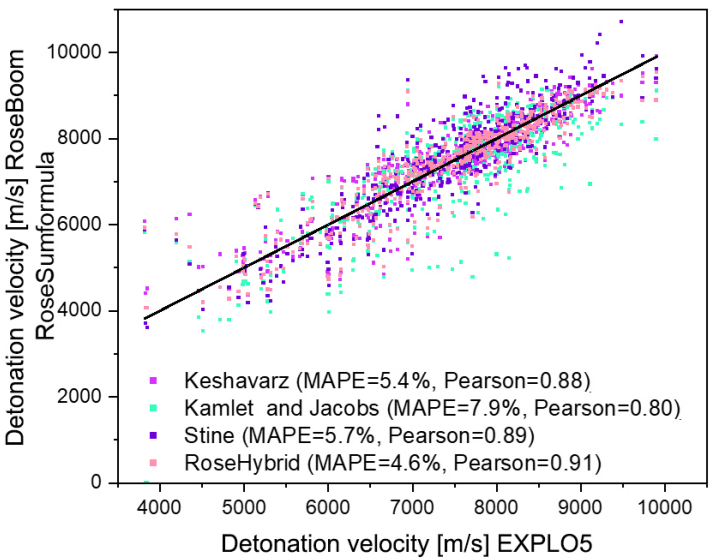
$$\rho(mixture) = \frac{1}{\sum_i^n X_i \cdot \rho_i^{-1}} \tag{13}$$

where is the amount of compound i and ρ_i is the corresponding density. Dividing one by the sum of the divisions of the amounts in the mixture,

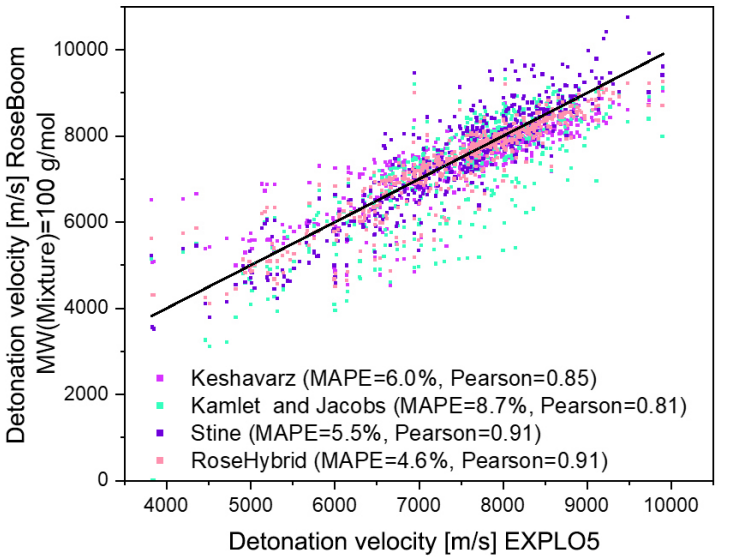
divided by the densities gives the average density of any mixture. This formula can be applied to mixtures with infinite amounts of components. Often energetic mixtures published in the literature contain 5 or more components in the calculation of the average densities, so the RoseDensity© formula makes it a lot easier and this is also implemented in RoseBoom2.2©.

3 Results

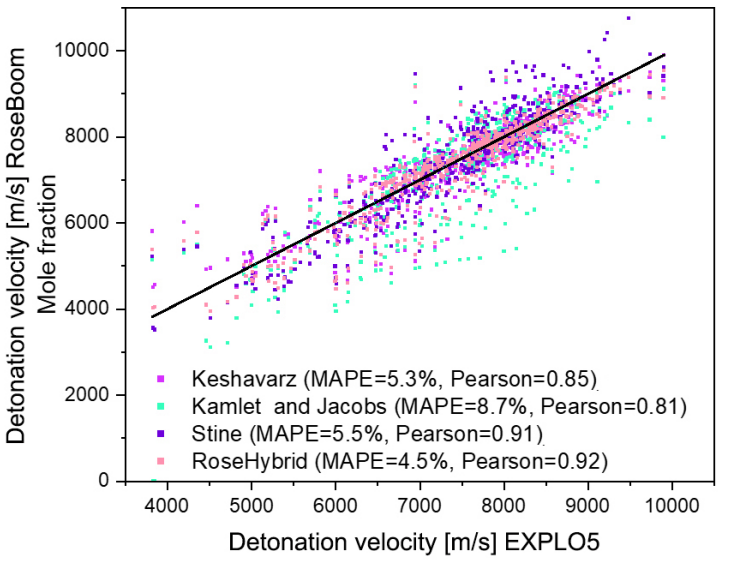
To validate the models implemented in RoseBoom2.2© a large homogenous test set was necessary. For this purpose 518 mixtures were calculated in EXPLO5 V6.05.04. These mixtures were then recalculated in RoseBoom2.2©. No studies have been published yet on a comparison of EXPLO5 values for mixtures, with experimental values. This is why, for detonation velocities, the benchmark for RoseBoom©'s predictions was 5%, because this is the deviation EXPLO5 values havefrom experimental values for pure compounds [1] named EXPLO5, is based on the chemical equilibrium, steady-state model of detonation. The program uses Becker-Kistiakowsky-Wilson's (BKW. The results of the performed calculations in RoseBoom2.2© are displayed in scattering plots in Figure 4.



(a)



(b)



(c)

Figure 4. Scattering plots of the detonation velocities of the 518 mixtures investigated in this study, with RoseBoom© values using different methods of determining the sum formula, plotted against the corresponding EXPLO5 values

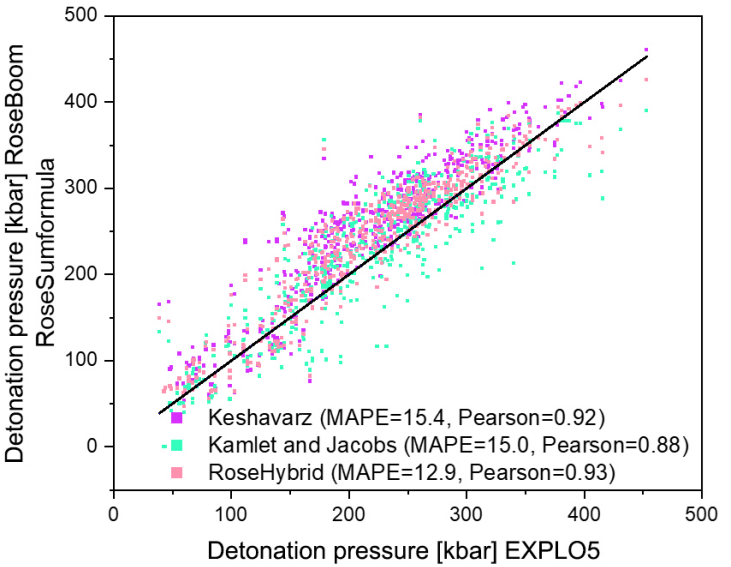
Taking a close look at the results, one can see that the benchmark of a mean absolute percentage error (MAPE) of5% is slightly better by 0.5% when using the RoseHybrid©-values using Method B for determining the sum formula. The Pearson coefficient is slightly higher for the equivalent formula with Methods A and B. Unlike the prediction of the detonation velocity for single molecules [4], the Keshavarz method out performs those of Kamlet and Jacobs, and Stine, for mixtures using Method B for the equivalent formula (Table 1).

Table 1. Ranking of the implemented methods using the different equivalent formulas

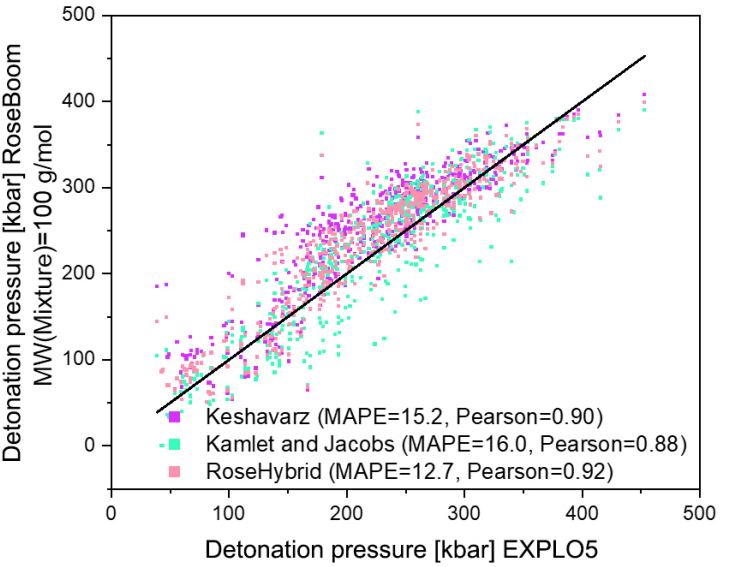
Method	Keshavarz	Stine	Kamlet and Jacobs	RoseHybrid
RoseSum formula	2	3	4	1
Method A	3	2		
Method B	2	3		

It is important to note, that it is indifferent to whether Stine's or Kamlet and Jacob's equations, Methods A or B, is used for the equivalent formula, because it is divided by the molar weight. Overall the results are satisfying, with a MAPE between 4.5-4.6% for all equivalent formulas using the RoseHybrid©-values, which is even better than the benchmark. Due to the much faster computing time and easier input, RoseBoom2.2© can be used not only to narrow down which mixtures should be further investigated, but also as an alternative to EXPLO5 to calculate the detonation velocities of mixtures.

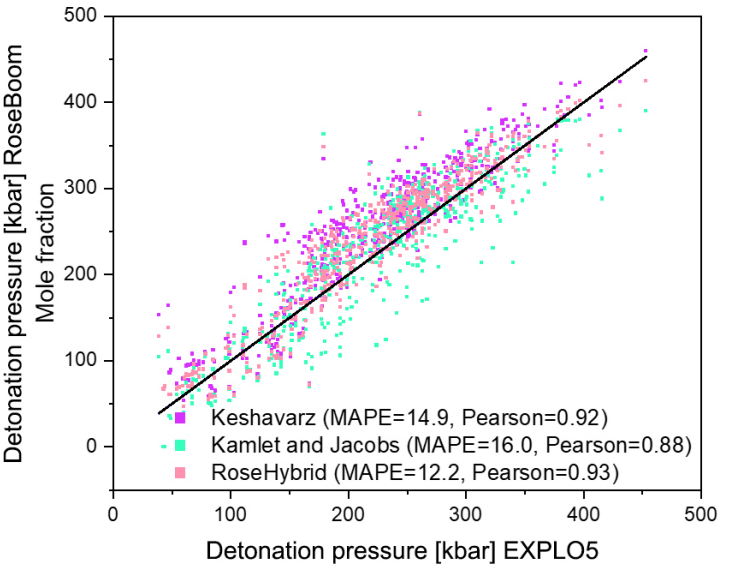
For detonation pressures, the benchmark for RoseBoom©'s predictions was 10%, because this is the deviation EXPLO5 values have from experimental values for pure compounds [1]named EXPLO5, is based on the chemical equilibrium, steady-state model of detonation. The program uses Becker-Kistiakowsky-Wilson's (BKW. The results of the performed calculations in RoseBoom2.2© are displayed as scattering plots in Figure 5.



(a)



(b)

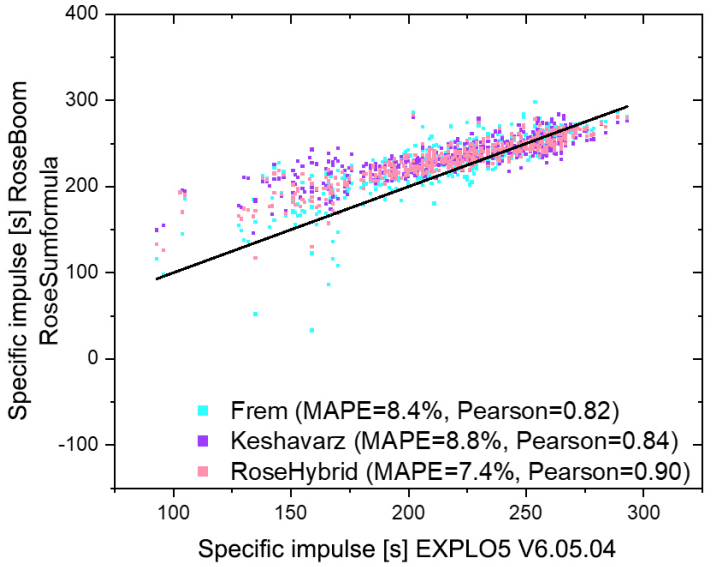


(c)

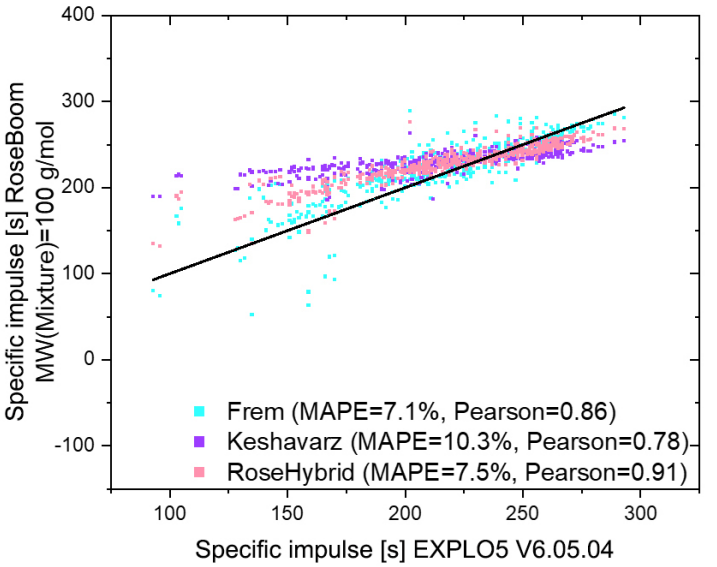
Figure 5. Scattering plots of the detonation pressures of the 518 mixtures investigated in this study, with RoseBoom© values using different methods of determining the sum formula, plotted against the corresponding EXPLO5 values

Once again, the RoseHybrid© - value showed the lowest MAPE values. Looking at the scattering plots in Figure 5, it is not difficult to tell that the Keshavarz method predicted the pressure as too high, and the Kamlet and Jacobs method too low, which is why the RoseHybrid©-value is the closest to the EXPLO5 values. Although the benchmark of 10% was slightly exceeded by 2.2% using the RoseHybrid©-value using Method B to calculate the equivalent formula, the predictions are still within a useful range. Future studies should investigate the accuracy of the models in RoseBoom© on a dataset of experimental values, for which one has to note that the different measurement techniques of detonation pressures can also deviate by up to 6% [10].

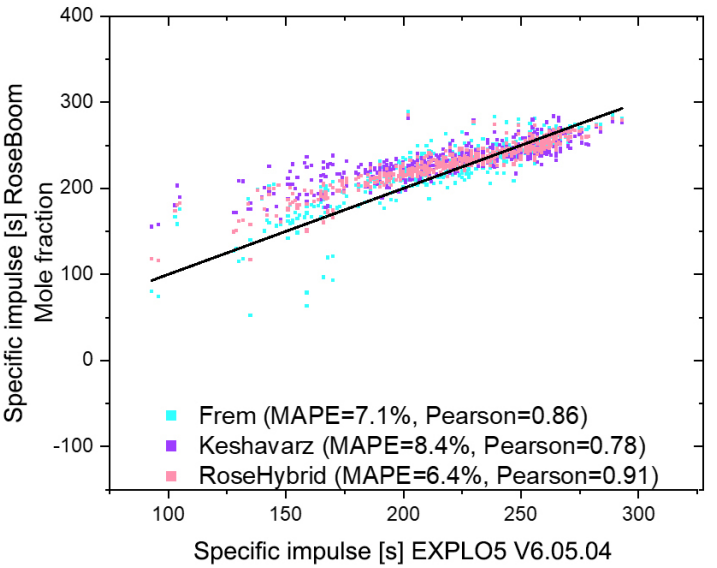
Calculating the specific impulse of energetic mixtures is also of great interest, because that is one of the key parameters for rocket propellants, for which mixtures of different materials are usually applied [11]. For the specific impulse, the goal was, as for the detonation pressure, to remain within 10% of the corresponding EXPLO5 values. The results of the performed calculations in RoseBoom2.2© are displayed as scattering plots in Figure 6.



(a)



(b)



(c)

Figure 6. Scattering plots of the specific impulses of the 518 mixtures investigated in this study, with RoseBoom© values using different methods of determining the sum formula, plotted against the corresponding EXPLO5 values

The benchmark for this value is outperformed by using the RoseHybrid©–value; with Method B for calculating the equivalent formula for the specific impulse, a MAPE of 6.4% was observed. Generally, one can say that the specific impulse, detonation velocity and pressure are best predicted using the RoseHybrid©–value with Method B. Therefore, these are the selections that should be made when calculating mixtures using RoseBoom2.2©. The Supersloth© functions allows precise computation of performance parameters for several thousand mixtures (and pure compounds) within experimental uncertainties, without much effort being required by the user.

4 The RoseFuture

- Future studies should investigate how the predicted performance parameters in RoseBoom2.2© compare to experimental values, now that it is proven that the predictions are within the uncertainties of EXPLO5 values. The prediction

of RoseBoom2.2© could be even more precise than the predictions made using EXPLO5. Furthermore, the software should be expanded for other elements, especially for aluminized mixtures.

- Another emerging research field, which could be categorized as mixtures are co-crystals of energetic materials. It would be interesting to investigate if RoseBoom© can predict the different parameters of co-crystals to allow for easier evaluation of their performance before synthesis [11, 12] salts of PA have been synthesised with 2,3-diaminotoluene (PIC:23DAT).

Acknowledgements

Valuable scientific discussions with Prof. Mohammed Keshavarz, Prof. Muhamed Suceska and Dr. Dany Frem are greatly acknowledged. The help they provided in explaining their work is much appreciated.

References

[1] Suceska, M. EXPLO5 – Computer Program for Calculation of Detonation Parameters. *Proc. 32nd Int. Annu. Conf. ICT*, Karlsruhe, Germany, **2001**, 110/1-13.

[2] Keshavarz, M.H.; Klapötke, T.M.; Sućeska, M. Energetic Materials Designing Bench (EMDB), Version 1.0. *Propellants Explos. Pyrotech.* **2017**, *42*(8): 854-856; DOI: 10.1002/prep.201700144.

[3] *Software for Energetic Materials and Custom Solutions.* Website: https://www.roseexplosive.com/ [accessed on 25.04.2022].

[4] Wahler, S.; Klapötke, T.M. Research Output Software for Energetic Materials Based on Observational Modelling 2.1 (RoseBoom2.1©). *Mater. Adv.* **2022**: 1-11; DOI: 10.1039/D2MA00502F.

[5] Wahler, S.; Klapötke, T.M. Research Output Software for Energetic Materials Based on Observational Modelling (RoseBoom2.0). *Proc. 24th New Trends Res. Energ. Mater. NTREM 2022*, Pardubice, Czech Republic, **2022**, 110-113.

[6] Kamlet, M.J.; Jacobs, S.J. Chemistry of Detonations. I. A Simple Method for Calculating Detonation Properties of CHNO Explosives. *J. Chem. Phys.* **1968**, *48*: 23-35; DOI: 10.1063/1.1667908.

[7] Stine, J.R. On Predicting Properties of Explosives – Detonation Velocity. *J. Energ. Mater.* **1990**, *8*: 41-73; DOI: 10.1080/07370659008017245.

[8] Keshavarz, M.H.; Pouretedal, H.R. Predicting Detonation Velocity of Ideal and Less Ideal Explosives *via* Specific Impulse. *Indian J. Eng. Mater. Sci.* **2004**, *11*: 429-432; ISSN: 0975-1017.

[9] Frem, D.J. A Reliable Method for Predicting the Specific Impulse of Chemical Propellants. *Aerosp. Technol. Manag.* **2018**, *10*: 1-21; DOI: 10.5028/jatm.v10.945.

[10] Pachman, J.; Künzel, M.; Němec, O.; Majzlík, J. A Comparison of Methods for

Detonation Pressure Measurement. *Shock Waves* **2018**, *28*: 217-225; DOI: 10.1007/s00193-017-0761-5.

[11] Klapötke, T.M. *Chemistry of High-Energy Materials.* DeGruyterW, Berlin/Boston, **2019**; ISBN: 9783110441390.

[12] Şen, N.; Nazir, H.; Atçeken, N.; Hope, K.S.; Acar, N.; Atakol, O. Synthesis, Characterisation and Energetic Performance of Insensitive Energetic Salts Formed Between Picric Acid and 2,3-Diaminotoluene, 2,4-Diaminotoluene. *J. Mol. Struct.* **2020**, *1205*, paper 127580; DOI: 10.1016/j.molstruc.2019.127580.

[13] Bozkuş, S.I.; Hope, K.S.; Yüksel, B.; Atçeken, N.; Nazır, H.; Atakol, O.; Şen, N. Characterization and Properties of a Novel Energetic Co-crystal Formed Between 2,4,6-Trinitrophenol and 9-Bromoanthracene. *J. Mol. Struct.* **2019**, *1192*: 145-153; DOI: 10.1016/j.molstruc.2019.04.109.

Received: August 24, 2022
Revised: September 28, 2022
First published online: September 30, 2022