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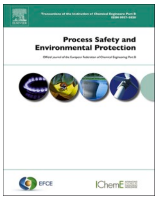

Flash point of binary and ternary monoterpene mixtures: Experimental and modeling

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ABSTRACT

The flash point (FP) of pure or mixtures of flammable substances is an important indicator in designing fire risk mitigation and prevention measures in the chemical and oil industry. Although FP data of fuel constituents and blends are often found in the literature, studies addressing other flammable mixtures, such as essential oils (EOs) and their constituents (terpenes and terpenoids), are scarce. EOs are aromatic, volatile liquid mixtures extracted from plant matrices that present diverse biological properties and find numerous applications in the food, pharmaceutical, cosmetic, and fragrance industries. In this work, experimental FP measurements of binary and ternary mixtures of four structurally diverse monoterpenes (carvone, eucalyptol, limonene, and linalool), widely found in different EO profiles, were carried out. Besides, the Liaw-UNIFAC model and the COSMO-RS model were used to calculate the FP data of the studied mixtures, resulting in global root-mean-square deviations (RMSD) of 2.0 K and 0.7 K, respectively. Both models deliver better predictions than the ideal approach (RMSD = 2.4 K) for the studied systems, demonstrating the importance of considering nonideal effects when estimating the FP data of terpene mixtures. These results provide essential information for accurate process safety and fire risk assessment in the EO industry.

1. Introduction

Apart from their potential environmental and health risks, organic solvents are typically the chemical industry's major fire and explosion sources (Crowl and Louvar, 2011). To identify and prevent such hazards, the knowledge of the safety-related properties of these compounds is essential. One of the most reliable indicators to characterize potential fire and explosion (F&E) hazards is the Flash Point (FP) (Crowl and Louvar, 2011; Liu and Liu, 2010), which represents the lowest temperature at which a liquid substance or mixture emits enough vapor to ignite in the presence of air (Yuan et al., 2021). Since a component's FP is lower than the corresponding boiling point (Tetteh et al., 1999), it does not apply to gases. Although at the FP the produced vapor is insufficient to go through combustion, it can burn temporarily, which makes this parameter an appropriate indicator of the inflammation possibility of a liquid when submitted to an ignition source as well as the rate of the flame speed after the ignition (Alibakhshi et al., 2017; Jalaei Salmani et al., 2018). To date, different experimental methodologies and predictive approaches have been proposed to obtain this important parameter (Liu and Liu, 2010; Phoon et al., 2014; Vidal et al., 2004). However, the reported flash point data present significant inconsistencies, even for ordinary substances, being the lowest value frequently considered in reference databases for safety purposes (Rowley et al., 2010).

Although the FP values of common pure compounds are often available in the open literature, there is a substantial lack of data for multicomponent mixtures (Cao et al., 2020; Di Benedetto et al., 2018a). The few existing studies usually address fuel constituents and their blends (Costa do Nascimento et al., 2021, 2020; Di Benedetto et al., 2018b; Huo et al., 2022, 2020; Jalaei Salmani et al., 2018; Vidal et al.,

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2006). Nonetheless, any liquid mixture that presents a FP at or below 93 ºC is considered a flammable liquid by the Occupational Safety and Health Administration (OSHA) (Occupational Safety & Health Administration OSHA, 2012; United States Department of Labor, 2012), and special safety measures are required for the storage, handling, and transportation of such materials (Occupational Safety & Health Administration OSHA, 2012). In the absence of these measures, any flammable substance can cause F&E incidents (Liaw and Yang, 2020). In this context, FP studies of mixtures containing flammable liquids other than traditional fuels are necessary to expand the current database and enable accurate risk assessments in additional fields of the chemical industry. An example of commercially important mixtures that often fall in the flammable liquid category and still present a poor FP database is the essential oils, which are complex liquid mixtures obtained from plants typically by solvent extraction and distillation processes (Sell, 2007; Sharmeen et al., 2021).

The major constituents of essential oils, terpenes, and their oxygenated derivatives, terpenoids, encompass more than 80,000 identified substances, corresponding to the most abundant and structurally diverse class of plant derivatives (Abbas et al., 2017; Christianson, 2017). Their large structural variety originates from their two five-carbon-based biosynthesis precursors, dimethylallyl diphosphate and isopentyl diphosphate, which can undergo different chemical reactions in natural organisms before achieving the final compound (Ajikumar et al., 2008; Christianson, 2017; Ninkuu et al., 2021). One of the most important subclasses of naturally occurring terpenes is constituted by monoterpenes and monoterpenoids, which are ten-carbon-based substances that correspond to about 90% of the components found in EO profiles (Tchimene et al., 2013; Zielińska-Błajet and Feder-Kubis, 2020). Apart from frequently exhibiting pleasant aromas (Sharmeen et al., 2021), monoterpenoids often present several biological and pharmacological activities (Perri et al., 2020; Tchimene et al., 2013), being the main ones responsible for the high commercial interest of EOs in the fragrance, cosmetic, food, and pharmaceutical industries (Aziz et al., 2018; Bhalla et al., 2013; Carvalho et al., 2016; Patel, 2015; Raut and Karuppayil, 2014; Sarkic and Stappen, 2018; Tongnuanchan and Benjakul, 2014; Zielińska-Błajet and Feder-Kubis, 2020). Moreover, some monoterpenes, such as α-pinene and (+)-limonene, have also been investigated as potential substituents to traditional solvents (e.g., dichloromethane, hexane) in the extraction of hydrophobic compounds from natural matrices (Boutekedjiret et al., 2014).

In the present work, experimental FP measurements of binary and ternary mixtures of four monoterpenoids (carvone, eucalyptol, limonene, and linalool), largely found in some EOs profiles, were carried out at different composition ranges following the ASTM D6450 closed cup procedure. Since monoterpenoids are the major components of most essential oils, their blends are commonly used to model these complex mixtures. It is worth mentioning that some of the terpenes mixtures studied in this work are the major representatives of real EOs, such as those obtained from caraway species (rich in carvone and limonene) (Bitterling et al., 2021; Laribi et al., 2013; Raal et al., 2012; Simic et al., 2008), mint and spearmint species (carvone + limonene and carvone + limonene + linalool) (Esmaeili et al., 2006; Hussain et al., 2010; Kokkini et al., 1995; Monfared et al., 2002; Şarer et al., 2011; Younis and Beshir, 2004), citrus species (limonene + linalool) (Arce and Soto, 2008; Arrout et al., 2021; Khalid et al., 2020; Koshima et al., 2015), and basil species (eucalyptol + linalool) (Marotti et al., 1996; Muráriková et al., 2017). Besides, the four selected monoterpenoids belong to different chemical families (i.e., hydrocarbon, ether, ketone, alcohol), and FP data are valuable for understanding the flammability behavior of mixtures containing such diverse compounds.

Although experimental FP data are preferable, those measurements are resource- and time-consuming for multicomponent mixtures where a wide compositional range analysis is needed (Cao et al., 2020; Phoon et al., 2014). An efficient alternative is the use of semi-predictive and predictive models to represent the FP behavior of mixtures. Several approaches have been proposed to estimate FP data of mixtures, including empirical, structural group contribution, quantitative structure-property relationship (QSPR), neural network, and quantum chemistry-based approaches (Banihashemi and Movagharnejad, 2018; Jalaei Salmani et al., 2018; Jiao et al., 2019; Nazari et al., 2019; Reinisch and Klamt, 2015; Torabian and Sobati, 2017). In this study, two well-established predictive approaches, the Liaw's model coupled with UNIFAC (Liaw et al., 2004, 2002; Liaw and Chiu, 2006; Liaw and Tsai, 2014) and the COSMO-RS model (Eckert and Klamt, 2002; Klamt, 1995; Klamt et al., 1998), were used to represent the FP data obtained for the binary and ternary mixtures, and the results were critically compared with the ideal FP curves.

2. Material and methods

2.1. Chemicals

All selected monoterpenes were used as received from the supplier and stored at room temperature. Their CAS number, chemical structure, source, purity, and boiling point are summarized in Table 1.

2.2. Mixture preparation

Binary and ternary mixtures of around 5 g with different compositions of the monoterpenes were gravimetrically prepared using an analytical scale (AX200, Shimadzu, precision of ± 1 mg) in Ambar flasks. The mixtures were submitted to slow agitation, followed by a settling period, to ensure the formation of homogenous phases.

2.3. Flash point measurements

The FP measurements were carried out by a Miniflash FLP/H Touch® analyzer (Grabner Instruments) following the ASTM D6450 standard closed cup procedure (ASTM D6450-05 (2010), *standard test method for flash point by continuously closed cup (CCCFP) tester*, 2010; Pichler, 2011), described in detail in our previous works (Costa do Nascimento et al., 2021; Dias et al., 2019; Henriques et al., 2020). In brief, this method is suitable for analyzing fuels, lube oils, solvents, and other liquids in a temperature range between 283.2 K and 523.2 K. To do so, 1 ml samples of the pure compound or mixture were transferred to a stainless-steel cup, and then placed into the test chamber. The measurements were performed under constant heating (5.5 ± 0.5 ºC min^{-1}) and continuous agitation. The obtained FPs were corrected to the atmospheric pressure at sea level (101.3 kPa) by the following expression (ASTM D6450-05 (2010), *standard test method for flash point by continuously closed cup (CCCFP) tester*, 2010):

$$\mathrm{FP}_{corrected} = \mathrm{FP}_{observed} + 0.25\cdot(101.3 - p) \tag{1}$$

where p is the ambient pressure (kPa) registered at the measurement.

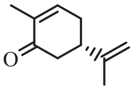
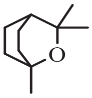
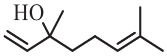
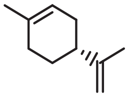
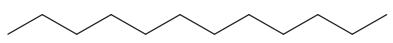
Each reported FP datapoint is the average of at least three independent measurements. To check the method's reliability, the FP of dodecane was periodically measured while the experiments were conducted.

2.4. Thermodynamic framework

2.4.1. Liaw-UNIFAC model

Although Le Chatelier's rule was proposed in 1891 based on empirical evidence, it does have a solid thermodynamic basis if one considers a few criteria, such as constant heat capacities, independent chemical species combustion kinetics, and no difference in adiabatic temperature rise between each chemical species involved (Mashuga and Crowl, 1999). As Liaw's model derives from Le Chatelier's rule, it should also obey these criteria. Moreover, the model only considers liquid phase nonideality, while the gas phase is assumed to behave ideally, describing

Table 1
CAS number, chemical structure, source, mass purity, and boiling point of dodecane and the monoterpenes addressed in this work.

Compound	CAS	Structure	Source	Purity (%)[a]	Boiling point (K)
L(—)-carvone	2244–16–8		Acros Organics	≥ 98	502.2 (Kobe et al., 1941)[b]
eucalyptol	470–82–6		Alfa Aesar	≥ 99	449.2 (Torcal et al., 2010)
(±)-linalool	78–70–6		Aldrich	≥ 97	471.8 (Lecat, 1928)
R-(+)-limonene	5989–27–5		Aldrich	≥ 97	450.8 (Steele et al., 2002)
dodecane	14073–97–3		Aldrich	≥ 99	489.4 (Perry and Thodos, 1952)

[a] The values correspond to the minimum mass purities granted by the manufacturer.
[b] No information regarding the major isomeric form.

the VLE through the modified Raoult's law (Liaw et al., 2004, 2002).

A frequently used vapor pressure-based compositional model for FP prediction is known as Liaw's model (Liaw and Chiu, 2006). It combines Le Chatelier's mixing rule for Low Flammability Limits (LFL) and the vapor-liquid equilibrium (VLE) isofugacity criteria in one equation:

$$\sum_{i=1}^{n}\frac{y_i}{LFL_i}=\sum_{i=1}^{n}\frac{x_i\gamma_i p_i^{sat}}{p_{i,FP_i}^{sat}}=1 \tag{2}$$

where y_i is the vapor phase composition of component i, x_i its mole fraction in the solution, γ_i its activity coefficient at the mixture's FP temperature, p_i^{sat} is the vapor pressure of i at the mixture's FP, and p_{i,FP_i}^{sat} is the vapor pressure of component i at its FP (pure compound). Vapor pressures p_i^{sat} and p_{i,FP_i}^{sat} were calculated from Antoine's equation, and the corresponding expression and parameters are listed in Table S1 (in the Supporting Information, SI) for each chemical species. Eq. (2) is non-linear due to the dependence of vapor pressures and activity coefficients on the temperature. The algorithm used in this work to solve this equation is described elsewhere (Costa do Nascimento et al., 2021).

Activity coefficients in Eq. (2) can be calculated from local composition excess Gibbs energy models. The Universal Functional-group Activity Coefficient model (UNIFAC) was selected, which calculates activity coefficients through a group contribution approach (Fredenslund et al., 1975). Therefore, UNIFAC has a predictive character compared to other semi-empirical local composition models.

2.4.2. COSMO-RS

The Conductor-like Screening Model for Real Solvents (COSMO-RS) (Eckert and Klamt, 2002; Klamt, 1995; Klamt et al., 1998) is a predictive model that allows the calculation of several thermophysical and equilibrium properties for pure components and mixtures. A comprehensive discussion of the COSMO-RS theory is available in the works reported by Klamt and co-authors (Eckert and Klamt, 2002; Klamt, 2005, 1995; Klamt et al., 1998). Briefly, the model combines quantum chemistry and statistical thermodynamics to compute the chemical potential of all the components in a mixture, requiring only information about the chemical structures of each compound (i.e., geometry, electronic energy, polarization charge density) (Klamt, 2016). To compute the FP data of mixtures using COSMO-RS, a modified version of the Liaw's mixing rule was applied (Reinisch and Klamt, 2015):

$$\frac{1}{\left(T^{flame}-FP_{Mix}\right)}\sum_{i}\frac{y_i\left(T^{flame}-FP_{,i}\right)}{p_{i,FP_i}^{sat}}=1 \tag{3}$$

where T^{flame} is the flame temperature, an adjustable parameter set equal to 1573 K (Reinisch and Klamt, 2015), FP_{Mix} is the mixture FP temperature, and FP_i is the FP temperature of pure component i. The FP data of pure compounds in the mixture can be inserted in Eq. (3) whenever available or estimated using the COSMO-RS theory (BIOVIA COSMOtherm, 2020, 2020).

In this work, the FP estimations of the terpene mixtures were carried out with the COSMOtherm software (version 21.0) (BIOVIA COSMOtherm, 2021; Eckert and Klamt, 2002) using the BP_TZVPD_FINE_21.ctd parametrization level. Additional details about the calculation procedure are available in the COSMOtherm reference manual (BIOVIA COSMOtherm, 2020, 2020). The.cosmo files containing the required information for each monoterpenoid were generated with the TmoleX software package (Steffen et al., 2010) using the COSMO-BP-TZVPD-FINE template. Following the methodology proposed by Reinisch and Klamt (2015), the required vapor pressures for the pure compounds were estimated using information extracted from the.cosmo files. To improve the accuracy of the FP predictions for the mixtures, the FP data measured in this work for the pure monoterpenes were considered in the COSMOtherm calculations.

2.5. Statistical analysis

The deviations between the experimental and predicted FPs for the terpene mixtures were assessed by calculating the root-mean-square deviation (RMSD):

$$\mathrm{RMSD}=\sqrt{\left[\frac{\sum_{j}\left(\mathrm{FP}_j^{\,exp}-\mathrm{FP}_j^{\,calc}\right)^2}{n}\right]} \tag{4}$$

where superscripts ″*exp*" and "*calc*" mean the experimental and calculated values, respectively, n is the total number of data points and j covers all the mixture datapoints.

3. Results and discussion

3.1. Pure compounds

The experimental FP obtained for L-(—)-carvone, eucalyptol, R-(+)-limonene, and linalool are compared to the literature data in Table 2.

The FP obtained in this work for dodecane (standard) strongly agrees with the data found in the literature (Costa do Nascimento et al., 2021; Henriques et al., 2020; Li et al., 2014; Luning Prak et al., 2017). Low coefficients of variation (< 0.2%) were obtained for all pure compounds, demonstrating the precision of the methodology. Regarding the

Table 2
Comparison of the experimental FPs measured in this work (at 101.3 ± 0.4 kPa) and found in the literature for the studied compounds.[a]

Compound	FP measured in this work (K)	FP from literature (K)
L(—)-carvone	371.1 ± 0.1	-
Eucalyptol	325.4 ± 0.5	322.2 (Buckeridge, 2010)[b]
(±)-Linalool	353.1 ± 0.1	344.3 (Api et al., 2015)[b]
R-(+)-limonene	327.4 ± 0.5	326.2 ± 1.9 (Henriques et al., 2020); 326.0 ± 0.5 (Donoso et al., 2022)[b]
Dodecane	354.5 ± 0.6	354.4 ± 0.1 (Henriques et al., 2020); 354.4 ± 0.4 (Costa do Nascimento et al., 2021); 354.2 (Li et al., 2014)[b]; 352.5 ± 2 K (Luning Prak et al., 2017)[c]

[a] Standard deviation is placed after the plus-minus sign.
[b] No information about the pressure conditions is reported.
[c] Experiments performed at 102 ± 1 kPa.

monoterpenes, the experimental FPs available in the literature are scarce, and most of the reported data were obtained using different methods from the ASTM D6450 procedure used in this work.

The FPs measured for the monoterpenes follow the same order as their normal boiling point: eucalyptol < R-(+)-limonene < linalool < L (—)-carvone. In the case of R-(+)-limonene, the FP measured in this work (327.4 ± 0.5 K) is consistent with the value reported by Henriques et al. (326.2 ± 1.9 K) (Henriques et al., 2020), who also applied the ASTM D6450 methodology. In addition, these FP values are considerably close to the value reported by Donoso et al. (Donoso et al., 2022) (326.0 ± 0.5 K), which was obtained using a different closed-cup-based procedure (EN ISO 2719).

For eucalyptol and linalool, the FP data measured in this work are less consistent with the values available in the literature (Api et al., 2015; Buckeridge, 2010), particularly for the latter, where a difference of 9 K in the FP values is observed. Nevertheless, the methodologies and the apparatus used to obtain the literature values were not reported. As discussed by Rowley and co-authors (Rowley et al., 2010), experimental FPs are deeply dependent on the apparatus and methodology, and differences up to 10 K are not uncommon when FP data are acquired under different circumstances. To the best of our knowledge, the FP of L (—)-carvone (371.1 ± 0.1 K) is reported here for the first time.

3.2. Binary mixtures

The experimental FPs of the five binary mixtures studied in this work (L-(—)-carvone + eucalyptol, L-(—)-carvone + R-(+)-limonene, L-(—)-carvone + linalool, eucalyptol + linalool, and R-(+)-limonene + linalool) are listed in Table S2. For each binary system, six mixtures with mole fractions in the range ($0.1 \leq x_i \leq 0.9$) were prepared and analyzed. Low coefficients of variation (CV), always inferior to 0.2%, were obtained. Moreover, the relative standard uncertainties on the sample concentrations were low ($u^r(x) = 0.003$), having a negligible influence on the obtained flash point data. The eucalyptol + R-(+)-limonene mixture was not studied due to the low difference between the FPs of the pure compounds (2 ± 1 K), which is lower (within the uncertainty limit) than the repeatability (1.9 K) of the ASTM D6450 standard closed cup procedure (Costa do Nascimento et al., 2021).

The experimental and predicted FPs using the Liaw-UNIFAC model and the COSMO-RS model are presented in Fig. 1. The ideal FP values, obtained considering $\gamma_i = 1$ in Eq. (2), were also included in Fig. 1 for

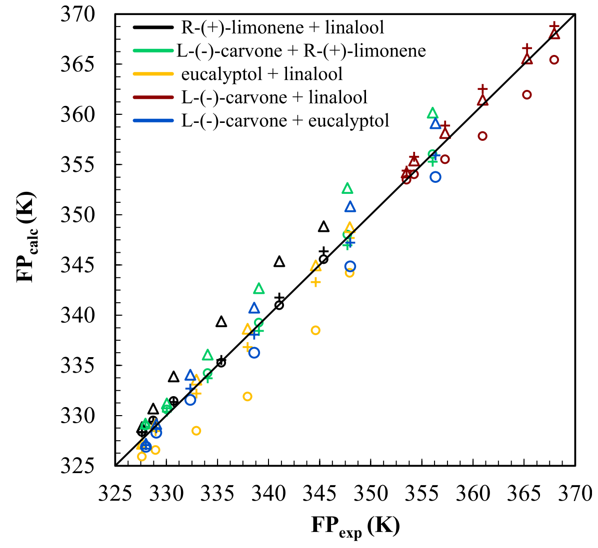


Fig. 1. Comparison between the experimental and the predicted FPs for the binary mixtures using the COSMO-RS model (+), the Liaw-UNIFAC model (○), and the ideal approach (Δ).

comparison purposes. The global RMSDs between the experimental and the predicted data with the ideal approach, the Liaw-UNIFAC model, and the COSMO-RS models were 1.9 K, 1.9 K, and 0.8 K, respectively. The data for each binary system are summarized in Table S3 of the SI. Besides, the activity coefficients obtained for the UNIFAC and COSMO-RS models at the FP conditions are depicted in Fig. S1 of SI.

For the Liaw-UNIFAC approach, the best results were obtained for the R-(+)-limonene + linalool and L-(—)-carvone + R-(+)-limonene systems (RMSD = 0.5 K), whereas the highest deviations are observed for eucalyptol + linalool (RMSD = 4.4 K). The COSMO-RS model delivers the worst estimations for L-(—)-carvone + linalool mixture (RMSD = 1.3 K), while lower deviations were achieved for all the other studied binary systems (0.6 K < RMSD < 0.9 K). The global performance of COSMO-RS is superior to Liaw-UNIFAC and the ideal approach to describe the FP of the binary mixtures when the FP data of pure monoterpenes are considered in the COSMO-RS calculations. Different from the Liaw-UNIFAC model, COSMO-RS presents a more predictive character; in COSMO-RS, other thermophysical properties rather than the FP of the pure compounds might be taken into consideration to improve the FP predictions of mixtures, such as the experimental vapor

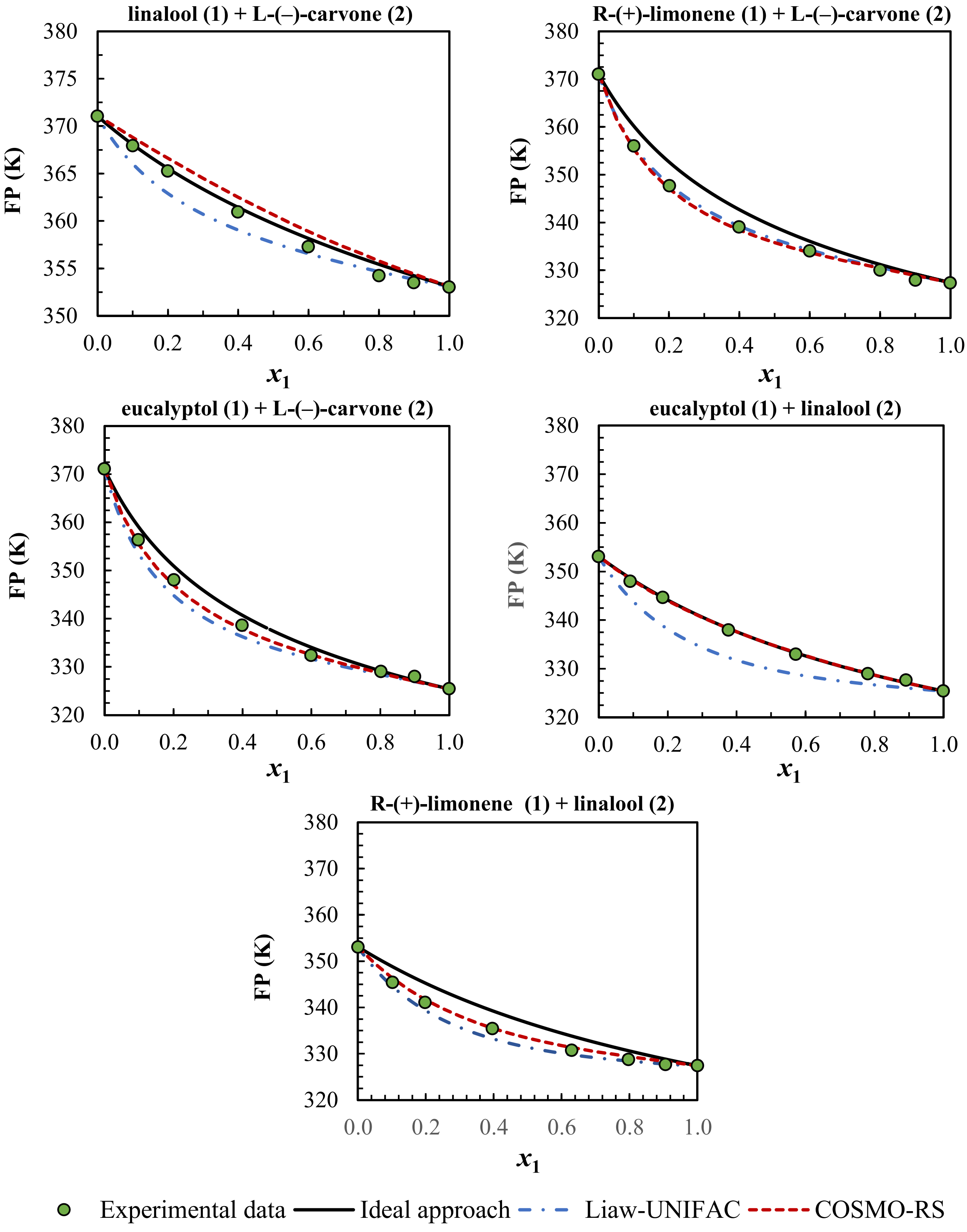


Fig. 2. Overview of the experimental and predicted FP profiles for the studied binary mixtures.

pressures or normal boiling points (BP). By considering only the BP of the pure compounds (listed in Table 1) to compute the COSMO-RS calculations, a global RMSD of 2.0 K for the binary mixtures was obtained, which is very similar to the value obtained with the Liaw-UNIFAC model (which requires the experimental FP of the pure compounds). Alternatively, considerably larger deviations were obtained with COSMO-RS when no experimental data were considered (global RMSD of 12.0 K). Nonetheless, the deviations obtained in this case for the predicted FPs of the binary mixtures are comparable to those found by Reinisch and Klamt (2015), where a global RMSD of 14.32 K was achieved for a large set of 1052 pure-substance FP data.

Apart from calculating specific FP data, the models can be applied to represent the FP profile in the whole composition range. The big picture is presented in Fig. 2, where component 1 corresponds to the one with the lower FP in the binary mixture. For all the analyzed mixtures, the FP decreases as the mole fraction of the lighter component increases, which is similar to the behavior registered before for other flammable liquid mixtures (Balasubramonian et al., 2015; Costa do Nascimento et al., 2021, 2020; Dias et al., 2019; Huo et al., 2020). Both COSMO-RS and Liaw-UNIFAC models capture the FP trend with the composition of the mixtures, offering an excellent qualitative description of the experimental data.

The FP curves illustrated in Fig. 2 reveal that most binary mixtures present experimental FPs lower than the ideal values, except for the eucalyptol + linalool, where a nearly ideal behavior is registered. The strongest deviations from the ideality occur for mixtures containing R-(+)-limonene and the oxygenated monoterpenes (i.e., carvone, linalool), where absolute differences up to 5 K are observed. Unlike the other monoterpenoids under study, R-(+)-limonene is a nonpolar hydrocarbon, and its presence in solutions with oxygenated compounds is likely to be governed by unfavorable interactions. This idea is supported by the activity coefficient values higher than the unity obtained at the FP conditions with UNIFAC and COSMO-RS, which indicate positive deviations from ideality for the R-(+)-limonene + oxygenated monoterpene mixtures.

Regarding linalool + L-(—)-carvone, COSMO-RS estimates negative deviations from ideality, while the UNIFAC model predicts the opposite behavior. In the case of the eucalyptol + L-(—)-carvone mixture, both COSMO-RS and UNIFAC predicts $\gamma_i > 1$ in most of the compositional range, but the values predicted by UNIFAC are higher than those obtained with COSMO-RS. For eucalyptol + linalool, UNIFAC also estimates positive deviations from ideality, while COSMO-RS deliver γ_i values close to the unity in the full compositional range. In fact, UNIFAC apparently overestimates the positive deviations from ideality (Fig. S1) for the three mixtures containing only oxygenated compounds (i.e., linalool + L-(—)-carvone, eucalyptol + L-(—)-carvone, and eucalyptol + linalool), which is likely the main reason for the larger deviations (RMSD ≥ 2.0) obtained with the Liaw-UNIFAC compared to the values achieved with COSMO-RS (0.6 ≤ RMSD ≤ 1.3), as Liaw's model can accurately predict the FP of many mixtures (Phoon et al., 2014), as long as the activity coefficient profile is well represented by the Gibbs Energy model chosen.

As shown in Fig. 2, the experimental FP profile of the eucalyptol + L-(—)-carvone mixture deviates more from the ideal behavior than the profiles obtained for the other two oxygenated monoterpene mixtures (linalool + eucalyptol and linalool + L-(—)-carvone). In the first case, eucalyptol (ether) and carvone (ketone) present hydrogen-bond donor groups, and repulsive interactions might arise when mixing these two compounds. On the other hand, linalool is an alcohol, and the hydroxyl group presents both hydrogen bond donor and hydrogen bond acceptor characters. Although favorable interactions are expected between linalool + eucalyptol or linalool and carvone due to the formation of hydrogen bonds, these interactions also occur among linalool molecules, which is a possible reason for the almost ideal FP behavior observed for these mixtures.

Although the ideal approach has been shown to adequately describe the FP behavior of some important binary systems for the oil industry, particularly those containing common fuel components such as hydrocarbons or fatty esters (Costa do Nascimento et al., 2020; Dias et al., 2019; Luning Prak et al., 2021), nonideal effects should be considered in mixtures composed by compounds with different polarities. The most concerning scenario occurs when the mixture exhibits lower FPs than the ideally predicted values since unknown stocking and handling risks arise. The limonene + linalool mixture and the limonene + carvone mixture, which are abundant in several citrus EOs (Arce and Soto, 2008; Arrout et al., 2021; Khalid et al., 2020; Koshima et al., 2015) and spearmint and caraway EOs (Bitterling et al., 2021; Hussain et al., 2010; Kokkini et al., 1995; Laribi et al., 2013; Monfared et al., 2002; Raal et al., 2012; Simic et al., 2008; Younis and Beshir, 2004), respectively, are practical examples of this situation, evidencing the importance of FP studies when assessing safety risks of flammable natural products.

3.3. *Ternary mixtures*

The experimental FPs of the four ternary mixtures studied in this work (L-(—)-carvone + eucalyptol + R-(+)-limonene, L-(—)-carvone + eucalyptol + linalool, eucalyptol + R-(+)-limonene + linalool, and eucalyptol + linalool + R-(+)-limonene) are presented in Table S4 of the SI. Like in the previous cases, low coefficient of variations (CV < 0.3%) and mole fraction uncertainties ($u^r(x) = 0.003$) were obtained. The COSMO-RS model, the Liaw-UNIFAC model and the ideal approach were applied to represent the experimental data, and the results are summarized in Fig. 3. The obtained RMSDs for each mixture are listed in Table S5.

The COSMO-RS model offers the best description of the experimental FP data, achieving a global RMSD of 0.6 K against a value of 2.1 K obtained with the Liaw-UNIFAC model. The two models present similar performances (RMSD = 0.6 K) only for the L(—)-carvone + eucalyptol + R-(+)-limonene. In contrast, the main differences were registered for the solutions with linalool, where COSMO-RS delivers RMSDs ≤ 0.7 K, while the Liaw-UNIFAC achieved RMSDs ≥ 2.0 K. Nevertheless, both models deliver better global FP estimations than the ideal approach (global RMSD of 2.5 K), evidencing the importance of considering nonideal effects to obtain high-quality FP estimations of mixtures of structurally different terpenes. From the four ternary solutions, L (—)-carvone + R-(+)-limonene + linalool presents the strongest deviations from the ideal behavior (RMSD = 3.7).

In general, the deviations obtained in this work with COSMO-RS and

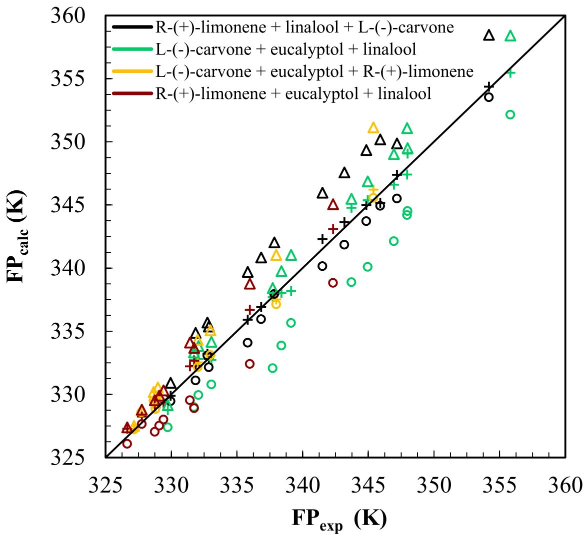


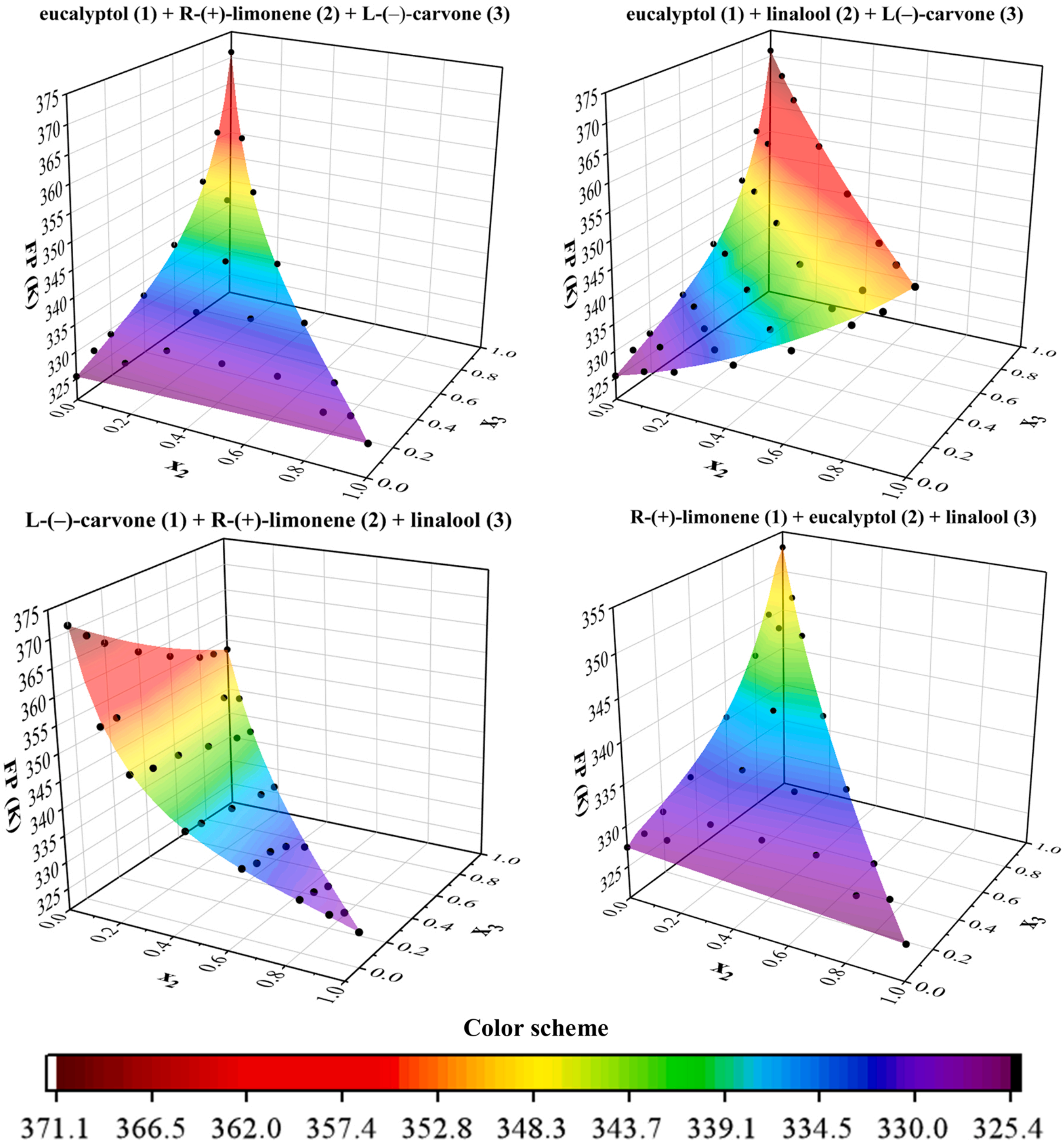
Fig. 3. Comparison between the experimental and the predicted flash points for the ternary mixtures using the COSMO-RS model (+), the Liaw-UNIFAC model (○), and the ideal approach (Δ).

the Liaw-UNIFAC model for the FP of the monoterpene ternary solutions are comparable to those found in the literature for other ternary mixtures (Costa do Nascimento et al., 2021, 2020; Lakzian and Liaw, 2021; Li et al., 2014; Liaw and Chiu, 2006; Liaw et al., 2011; Zarringhalam Moghaddam et al., 2012). To further explore the predictive potential of COSMO-RS and the Liaw model, those were used to represent the FP of the ternary mixtures in their whole composition range. The COSMO-RS results are exhibited in Fig. 4, where a colored map built from the model FP estimations is compared with the experimental data. Likewise, the FP profiles estimated with the Liaw-UNIFAC and the ideal approach are presented in Figs. S2 and S3, respectively.

Like in the binary solutions, adding more volatile compounds (e.g., eucalyptol and R-(+)-limonene) in the ternary mixtures generally decreases their FPs. This trend is well reproduced by the predictive models, though the Liaw-UNIFAC approach usually estimates higher FP values, while the ideal approach delivers mostly underestimated FPs. Nonetheless, the COSMO-RS' ability to accurately represent the FP values of binary mixtures (RMSD $\leq$ 1.3 K) and ternary terpene mixtures (RMSD $\leq$ 0.7 K) only by considering the experimental FP data of the individual components is notable, which is a great advantage over structurally-based or semi-empirical approaches that frequently require more thermophysical data, such as pure compound vapor pressures. In line with previous works that demonstrated COSMO-RS potential to represent other thermodynamic and equilibrium properties of mixtures containing monoterpenes (Teixeira et al., 2022; Vilas-Boas et al., 2022, 2021), the results found here suggest that COSMO-RS is also a reliable tool to represent FP data of mixtures widely found in different EO profiles. On the other hand, the Liaw-UNIFAC method has its merit once, globally, it delivers better FP predictions than the ideal approach for all the ternary mixtures studied in this work.

4. Conclusions

This work presents new FP data for four monoterpenes, five binary monoterpene mixtures and four monoterpene ternary mixtures largely found in different EO profiles, including citrus, basil, caraway, and


eucalyptol (1) + R-(+)-limonene (2) + L-(–)-carvone (3)

eucalyptol (1) + linalool (2) + L(–)-carvone (3)

L-(–)-carvone (1) + R-(+)-limonene (2) + linalool (3)

R-(+)-limonene (1) + eucalyptol (2) + linalool (3)

Fig. 4. Comparison between the experimental FPs (black spheres) and the colored maps built from the FP values predicted by COSMO-RS for the ternary mixtures.

spearmint species. Most of the pure substances and mixtures studied in this work present FPs data below 366.2 K (except pure L(—)-carvone), falling into the category of flammable liquids. The low coefficients of variation (<0.3%) confirm the excellent consistency of the results. In the case of the pure monoterpenes, the deviations between the experimental data measured in this work and those found in the literature are within the expected values for data obtained with different methodologies or apparatuses. Besides, the FPs of the monoterpenes follow the same order as their normal boiling point, with eucalyptol and L(—)-carvone presenting the lowest (325.4 K) and the highest (371.1 K) values, respectively. Regarding the mixtures studied, the addition of a less volatile compound always increases the FP. To the best of our knowledge, the FP data of L(—)-carvone and the monoterpene binary, and ternary mixtures have not been previously studied.

The COSMO-RS and the Liaw-UNIFAC were successfully employed to describe the FP data of mixtures addressed in this work. Regarding the binary solutions, COSMO-RS delivered RMSD values varying between 0.6 K and 1.3 K, whereas the Liaw-UNIFAC model achieved RMSDs between 0.5 K and 4.4 K. For the ternary mixtures, smaller RMSD ranges were obtained with COSMO-RS (0.4 K $\leq$ RMSD $\leq$ 0.7 K) and the Liaw-UNIFAC model (0.6 K $\leq$ RMSD $\leq$ 3.8 K). Both models could improve the description of the FP data compared to the ideal approach, with COSMO-RS delivering a global RMSD much lower than the value obtained with the ideal FPs, while the Liaw-UNIFAC model slightly reduces the global RMSD when compared to the ideal approach. Moreover, in most cases, the models can identify that the mixtures present lower FP values than those ideally predicted, which is an important asset when assessing the fire risk of nonideal flammable mixtures.

The FP behavior of essential oils is unclear due to the lack of available data in the literature. This manuscript partially fulfills this gap by supplying experimental FP data for different model EO mixtures and showing that addressed predictive models can accurately describe the experimental data. These results are valuable for assessing and reducing fire hazard risks related to storing and processing monoterpenes and essential oils. This work opens a call for future studies addressing the fire safety of essential oils, particularly investigating FP of surrogate or complex essential oil containing flammable compounds, such as those obtained from basil, eucalyptus, lavender, and mint species.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

List of the Antoine constants used in the FP calculations with the Liaw-UNIFAC model and ideal approach; Experimental FP data for the binary and ternary monoterpene mixtures; Activity coefficients of the monoterpenes in the binary mixtures calculated with the COSMO-RS and UNIFAC; List of RMSDs between the experimental and predicted FP values for the binary and ternary mixtures; Comparison of the experimental FP data with the colored maps built with the Liaw-UNIFAC model and the ideal approach. Supplementary data associated with this article can be found in the online version at doi:10.1016/j.psep.2023.02.088.

References

Abbas, F., Ke, Y., Yu, R., Yue, Y., Amanullah, S., Jahangir, M.M., Fan, Y., 2017. Volatile terpenoids: multiple functions, biosynthesis, modulation and manipulation by genetic engineering. Planta 246, 803–816.

Ajikumar, P.K., Tyo, K., Carlsen, S., Mucha, O., Phon, T.H., Stephanopoulos, G., 2008. Terpenoids: opportunities for biosynthesis of natural product drugs using engineered microorganisms. Mol. Pharm. 5, 167–190.

Alibakhshi, A., Mirshahvalad, H., Alibakhshi, S., 2017. Prediction of flash points of pure organic compounds: evaluation of the DIPPR database. Process Saf. Environ. Prot. 105, 127–133.

Api, A.M., Belsito, D., Bhatia, S.P., Bruze, M., Calow, P., Dagli, M.L., Dekant, W., Fryer, A. D., Kromidas, L., La Cava, S., Lalko, J.F., Lapczynski, A., Liebler, D.C., Miyachi, Y., Politano, V.T., Ritacco, G., Salvito, D., Shen, J., Schultz, T.W., Sipes, I.G., Wall, B., Wilcox, D.K., 2015. RIFM fragrance ingredient safety assessment, Linalool, CAS registry number 78-70-6. Food Chem. Toxicol. 82, S29–S38.

Arce, A., Soto, A., 2008. Citrus essential oils: extraction and deterpenation. Tree For. Sci. Biotechnol. 2, 1–9.

Arrout, A., El Ghallab, Y., Lefriyekh, M.R., Ait Haj Said, A., 2021. Citrus essential oils and main terpenes: chemical composition and good litholytic activity on gallstones. Vegetos 34, 600–605.

ASTM D6450-05, 2010. Standard Test Method for Flash Point by Continuously Closed Cup (CCCFP) Tester, 2010.

Aziz, Z.A.A., Ahmad, A., Setapar, S.H.M., Karakucuk, A., Azim, M.M., Lokhat, D., Rafatullah, M., Ganash, M., Kamal, M.A., Ashraf, G.M., 2018. Essential oils: extraction techniques, pharmaceutical and therapeutic potential - a review. Curr. Drug Metab. 19, 1100–1110.

Balasubramonian, S., Srivastav, R.K., Kumar, S., Sivakumar, D., Sampath, M., Kamachi Mudali, U., Natarajan, R., 2015. Flash point prediction for the binary mixture of phosphatic solvents and n-dodecane from UNIFAC group contribution model. J. Loss Prev. Process Ind. 33, 183–187.

Banihashemi, M., Movagharnejad, K., 2018. Use of group contribution method and intelligent algorithms to predict the flash temperature of binary mixtures. Process Saf. Environ. Prot. 117, 539–550.

Bhalla, Y., Gupta, V.K., Jaitak, V., 2013. Anticancer activity of essential oils: a review. J. Sci. Food Agric. 93, 3643–3653.

BIOVIA COSMOtherm 2020, 2020. Reference Manual.

BIOVIA COSMOtherm, 2021. Release 2021, Dassault Systèmes.

Bitterling, H., Lorenz, P., Vetter, W., Kammerer, D.R., Stintzing, F.C., 2021. Storage-related changes of terpene constituents in caraway (Carum carvi L.) under real-time storage conditions. Ind. Crop. Prod. 170, 113782.

Boutekedjiret, C., Vian, M.A., Chemat, F., 2014. Terpenes as green solvents for natural products extraction. Alternative Solvents for Natural Products Extraction, pp. 205–219.

Buckeridge, J.S., 2010. Some biological consequences of environmental change: a study using barnacles (Cirripedia: Balanomorpha) and gum trees (Angiospermae: Myrtaceae). Integr. Zool. 5, 122–131.

Cao, W., Pan, Y., Liu, Y., Jiang, J., 2020. A novel method for predicting the flash points of binary mixtures from molecular structures. Saf. Sci. 126, 104680.

Carvalho, I.T., Estevinho, B.N., Santos, L., 2016. Application of microencapsulated essential oils in cosmetic and personal healthcare products - a review. Int. J. Cosmet. Sci. 38, 109–119.

Christianson, D.W., 2017. Structural and chemical biology of terpenoid cyclases. Chem. Rev. 117, 11570–11648.

Costa do Nascimento, D., Dorighello Carareto, N.D., Marinho Barbosa Neto, A., Gerbaud, V., da Costa, M.C., 2020. Flash point prediction with UNIFAC type models of ethylic biodiesel and binary/ternary mixtures of FAEEs. Fuel 281, 118717.

Costa do Nascimento, D., Conti, D.C., Barbosa Neto, A.M., Costa, M.C., 2021. Flash point measurement and prediction of dodecane + ethanol + FAEE systems. Fuel 306, 121723.

Crowl, D.A., Louvar, J.F., 2011. Chemical Process Safety: Fundamentals with Applications, third ed. Prentice Hall PTR.

Di Benedetto, A., Sanchirico, R., Di Sarli, V., 2018a. Flash point of flammable binary mixtures: synergistic behavior. J. Loss Prev. Process Ind. 52, 1–6.

Di Benedetto, A., Sanchirico, R., Di Sarli, V., 2018b. Effect of pressure on the flash point of various fuels and their binary mixtures. Process Saf. Environ. Prot. 116, 615–620.

Dias, R.M., Aquino, R.T., Krähenbühl, M.A., Costa, M.C., 2019. Flash point of fatty acid methyl ester binary mixtures. J. Chem. Eng. Data 64, 3465–3472.

Donoso, D., Bolonio, D., Ballesteros, R., Lapuerta, M., Canoira, L., 2022. Hydrogenated orange oil: a waste derived drop-in biojet fuel. Renew. Energy 188, 1049–1058.

Eckert, F., Klamt, A., 2002. Fast solvent screening via quantum chemistry: COSMO-RS approach. AIChE J. 48, 369–385.

Esmaeili, A., Rustaiyan, A., Masoudi, S., Nadji, K., 2006. Composition of the essential oils of Mentha aquatica l. and nepeta meyeri benth. from Iran. J. Essent. Oil Res. 18, 263–265.

Fredenslund, A., Jones, R.L., Prausnitz, J.M., 1975. Group-contribution estimation of activity coefficients in nonideal liquid mixtures. AIChE J. 21, 1086–1099.

Henriques, J.D., de, O., Sosa, F.H.B., Dias, R.M., Martinez, P.F.M., da Costa, M.C., 2020. Flash point and excess molar volumes of binary mixtures containing d-limonene and alcohol compounds from propanol to dodecanol. J. Chem. Thermodyn. 150, 106224.

Huo, X., Lu, Q., Sun, X., Shen, X., 2020. Study on flash-point measurement and reduced prediction model for ternary extraction system. Process Saf. Environ. Prot. 138, 99–107.

Huo, X., Lu, Q., Wang, J., 2022. Liaw-UNIFAC flash point model for alcohols-kerosene/diesel fuel blends using average fuel structure. Process Saf. Environ. Prot. 160, 400–410.

Hussain, A.I., Anwar, F., Shahid, M., Ashraf, M., Przybylski, R., 2010. Chemical composition, and antioxidant and antimicrobial activities of essential oil of spearmint (Mentha spicata L.) from pakistan. J. Essent. Oil Res. 22, 78–84.

Jalaei Salmani, H., Lotfollahi, M.N., Mazloumi, S.H., 2018. A model for predicting flash point of alkane-alkane and water-alcohol mixtures by the cubic-plus-association equation of state. Process Saf. Environ. Prot. 119, 191–197.

Jiao, Z., Escobar-Hernandez, H.U., Parker, T., Wang, Q., 2019. Review of recent developments of quantitative structure-property relationship models on fire and explosion-related properties. Process Saf. Environ. Prot. 129, 280–290.

Khalid, K.A., Ahmed, A.M.A., El-Gohary, A.E., 2020. Effect of growing seasons on the leaf essential oil composition of Citrus species that are cultivated in Egypt. J. Essent. Oil Res. 32, 296–307.

Klamt, A., 1995. Conductor-like screening model for real solvents: a new approach to the quantitative calculation of solvation phenomena. J. Phys. Chem. 99, 2224–2235.

Klamt, A., 2016. COSMO-RS for aqueous solvation and interfaces. Fluid Phase Equilib. 407, 152–158.

Klamt, A., Jonas, V., Bürger, T., Lohrenz, J.C.W., 1998. Refinement and parametrization of COSMO-RS. J. Phys. Chem. A 102, 5074–5085.

Klamt, A., 2005. COSMO-RS: From Quantum Chemistry to Fluid Phase Thermodynamics and Drug Design, first ed. Computer Aided Chemical Engineering. Elsevier Science.

Kobe, K.A., Okabe, T.S., Ramstad, M.T., Huemmer, P.M., 1941. P-cymene studies. VI. Vapor pressure of p-cymene, some of its derivatives and related compounds. J. Am. Chem. Soc. 63, 3251–3252.

Kokkini, S., Karousou, R., Lanaras, T., 1995. Essential oils of spearmint (carvone-rich) plants from the island of Crete (Greece). Biochem. Syst. Ecol. 23, 425–430.

Koshima, C.C., Nakamoto, K.T., Aracava, K.K., Oliveira, A.L., Rodrigues, C.E.C., 2015. Fractionation of bergamot and lavandin crude essential oils by solvent extraction: phase equilibrium at 298.2 K. J. Chem. Eng. Data 60, 37–46.

Lakzian, K., Liaw, H., 2021. Flash point investigation of ternary mixtures of 1-butanol/2-pentanol + acetic acid + ethylbenzene. Process Saf. Environ. Prot. 154, 131–141.

Laribi, B., Kouki, K., Bettaieb, T., Mougou, A., Marzouk, B., 2013. Essential oils and fatty acids composition of Tunisian, German and Egyptian caraway (Carum carvi L.) seed ecotypes: a comparative study. Ind. Crop. Prod. 41, 312–318.

Lecat, M., 1928. Nouveaux azeotropes binaires: Huitième liste. Recl. Des. Trav. Chim. Des. Pays-Bas 47, 13–18.

Li, X., Duan, P.P., Sun, K.N., Yan, X., 2014. Prediction of the flash point of binary and ternary straight-chain alkane mixtures. Adv. Mater. Sci. Eng. 2014, 1–5.

Liaw, H., Gerbaud, V., Li, Y., 2011. Prediction of miscible mixtures flash-point from UNIFAC group contribution methods. Fluid Phase Equilib. 300, 70–82.

Liaw, H.-J., Chiu, Y.-Y., 2006. A general model for predicting the flash point of miscible mixtures. J. Hazard. Mater. 137, 38–46.

Liaw, H.-J., Tsai, T.-P., 2014. Flash-point estimation for binary partially miscible mixtures of flammable solvents by UNIFAC group contribution methods. Fluid Phase Equilib. 375, 275–285.

Liaw, H.-J., Yang, C.-A., 2020. Maximum flash point behavior of ternary mixtures with single and two maximum flash point binary constituents. Process Saf. Environ. Prot. 143, 293–303.

Liaw, H.-J., Lee, Y.-H., Tang, C.-L., Hsu, H.-H., Liu, J.-H., 2002. A mathematical model for predicting the flash point of binary solutions. J. Loss Prev. Process Ind. 15, 429–438.

Liaw, H.-J., Tang, C.-L., Lai, J.-S., 2004. A model for predicting the flash point of ternary flammable solutions of liquid. Combust. Flame 138, 308–319.

Liu, X., Liu, Z., 2010. Research progress on flash point prediction. J. Chem. Eng. Data 55, 2943–2950.

Luning Prak, D.J., Luning Prak, P.J., Cowart, J.S., Trulove, P.C., 2017. Densities and viscosities at 293.15–373.15 K, speeds of sound and bulk moduli at 293.15–333.15 K, surface tensions, and flash points of binary mixtures of n -hexadecane and alkylbenzenes at 0.1 MPa. J. Chem. Eng. Data 62, 1673–1688.

Luning Prak, D.J., Simms, G.R., Hamilton, M., Cowart, J.S., 2021. Impact of low flash point compounds (hydrocarbons containing eight carbon atoms) on the flash point of jet fuel and n-dodecane. Fuel 286.

Marotti, M., Piccaglia, R., Giovanelli, E., 1996. Differences in essential oil composition of basil (Ocimum basilicum L.) Italian cultivars related to morphological characteristics. J. Agric. Food Chem. 44, 3926–3929.

Mashuga, C.V., Crowl, D.A., 1999. Flammability zone prediction using calculated adiabatic flame temperatures. Process Saf. Prog. 18, 127–134.

Monfared, A., Nabid, M.R., Rustaiyan, A., 2002. Composition of a carvone chemotype of mentha longifolia (l.) huds. from Iran. J. Essent. Oil Res. 14, 51–52.

Muráriková, A., Ťažký, A., Neugebauerová, J., Planková, A., Jampílek, J., Mučaji, P., Mikuš, P., 2017. Characterization of essential oil composition in different basil species and pot cultures by a GC-MS method. Molecules 22, 1221.

Nazari, B., Keshavarz, M.H., Hassanzadeh, A., 2019. Reliable prediction of the flash point of organic compounds containing hazardous peroxide functional groups as compared to the best available methods. Process Saf. Environ. Prot. 132, 134–141.

Ninkuu, V., Zhang, L., Yan, J., Fu, Z., Yang, T., Zeng, H., 2021. Biochemistry of terpenes and recent advances in plant protection. Int. J. Mol. Sci. 22, 5710.

Occupational Safety & Health Administration [OSHA], 2012. Standards CFR 1910.106.

Patel, S., 2015. Plant essential oils and allied volatile fractions as multifunctional additives in meat and fish-based food products: a review. Food Addit. Contam. Part A Chem. Anal. Control Expo. Risk Assess. 32, 1049–1064.

Perri, F., Coricello, A., Adams, J.D., 2020. Monoterpenoids: the next frontier in the treatment of chronic pain? J. Multidiscip. Sci. 3, 195–214.

Perry, R.E., Thodos, G., 1952. Vapor pressures of the light normal saturated hydrocarbons. Ind. Eng. Chem. 44, 1649–1653.

Phoon, L.Y., Mustaffa, A.A., Hashim, H., Mat, R., 2014. A review of flash point prediction models for flammable liquid mixtures. Ind. Eng. Chem. Res. 53, 12553–12565.

Pichler, H., 2011. Advances in Flashpoint Testing: Economic Impact, American Laboratory.

Raal, A., Arak, E., Orav, A., 2012. The content and composition of the essential oil Found in Carum carvi L. commercial fruits obtained from different countries. J. Essent. Oil Res. 24, 53–59.

Raut, J.S., Karuppayil, S.M., 2014. A status review on the medicinal properties of essential oils. Ind. Crop. Prod. 62, 250–264.

Reinisch, J., Klamt, A., 2015. Predicting flash points of pure compounds and mixtures with COSMO-RS. Ind. Eng. Chem. Res. 54, 12974–12980.

Rowley, J.R., Freeman, D.K., Rowley, R.L., Oscarson, J.L., Giles, N.F., Wilding, W.V., 2010. Flash point: evaluation, experimentation and estimation. Int. J. Thermophys. 31, 875–887.

Şarer, E., Toprak, S.Y., Otlu, B., Durmaz, R., 2011. Composition and antimicrobial activity of the essential oil from Mentha spicata l. subsp. spicata. J. Essent. Oil Res. 23, 105–108.

Sarkic, A., Stappen, I., 2018. Essential oils and their single compounds in cosmetics - a critical review. Cosmetics 5, 1–21.

Sell, C.S., 2007. A Fragrant Introduction to Terpenoid Chemistry, first ed. The Royal Society of Chemistry. Royal Society of Chemistry, Cambridge.

Sharmeen, J.B., Mahomoodally, F.M., Zengin, G., Maggi, F., 2021. Essential oils as natural sources of fragrance compounds for cosmetics and cosmeceuticals. Molecules 26, 666.

Simic, A., Rančic, A., Sokovic, M.D., Ristic, M., Grujic-Jovanovic, S., Vukojevic, J., Marin, P.D., 2008. Essential oil composition of Cymbopogon winterianus. and Carum carvi. and their antimicrobial activities. Pharm. Biol. 46, 437–441.

Steele, W.V., Chirico, R.D., Cowell, A.B., Knipmeyer, S.E., Nguyen, A., 2002. Thermodynamic properties and ideal-gas enthalpies of formation for methyl benzoate, ethyl benzoate, (R)-(+)-limonene, tert-amyl methyl ether, trans-crotonaldehyde, and diethylene glycol. J. Chem. Eng. Data 47, 667–688.

Steffen, C., Thomas, K., Huniar, U., Hellweg, A., Rubner, O., Schroer, A., 2010. Software news and updates TmoleX — a graphical user interface for TURBOMOLE. J. Comput. Chem. 31, 2967–2970.

Tchimene, M.K., Okunji, C.O., Iwu, M.M., Kuete, V., 2013. Monoterpenes and related compounds from the medicinal plants of Africa. In: Kuete, V. (Ed.), Medicinal Plant Research in Africa. Elsevier, Nsukka, pp. 1–32.

Teixeira, G., Abranches, D.O., Silva, L.P., Vilas-Boas, S.M., Pinho, S.P., Ferreira, A.I.M.C. L., Santos, L.M.N.B.F., Ferreira, O., Coutinho, J.A.P., 2022. Liquefying flavonoids with terpenoids through deep eutectic solvent formation. Molecules 27, 2649.

Tetteh, J., Suzuki, T., Metcalfe, E., Howells, S., 1999. Quantitative structure−Property relationships for the estimation of boiling point and flash point using a radial basis function neural network. J. Chem. Inf. Comput. Sci. 39, 491–507.

Tongnuanchan, P., Benjakul, S., 2014. Essential oils: extraction, bioactivities, and their uses for food preservation. J. Food Sci. 79, 1231–1249.

Torabian, E., Sobati, M.A., 2017. New models for predicting the flash point of mixtures containing different alcohols. Process Saf. Environ. Prot. 111, 439–448.

Torcal, M., García-Abarrio, S., Pardo, J.I., Mainar, A.M., Urieta, J.S., 2010. P, p, T Measurements and isobaric vapor - liquid - equilibria of the 1,3,3-Trimethyl-2-oxa-bicycle[2,2,2]octane + Propan-1-ol mixture: Cubic and statistical associating fluid theory-based equation of state analysis. J. Chem. Eng. Data 55, 5932–5940.

United States Department of Labor, 2012. Occupational Safety & Health Administration [OSHA] [WWW Document]. URL: 〈https://www.osha.gov/〉 (Accessed 11 April 2022).

Vidal, M., Rogers, W.J., Holste, J.C., Mannan, M.S., 2004. A review of estimation methods for flash points and flammability limits. Process Saf. Prog. 23, 47–55.

Vidal, M., Rogers, W.J., Mannan, M.S., 2006. Prediction of minimum flash point behaviour for binary mixtures. Process Saf. Environ. Prot. 84, 1–9.

Vilas-Boas, S.M., Teixeira, G., Rosini, S., Martins, M.A.R., Gaschi, P.S., Coutinho, J.A.P., Ferreira, O., Pinho, S.P., 2021. Ionic liquids as entrainers for terpenes fractionation and other relevant separation problems. J. Mol. Liq. 323, 114647.

Vilas-Boas, S.M., da Costa, M.C., Coutinho, J.A.P., Ferreira, O., Pinho, S.P., 2022. Octanol–water partition coefficients and aqueous solubility data of monoterpenoids: Experimental, modeling, and environmental distribution. Ind. Eng. Chem. Res. 61, 3154–3167.

Younis, Y.M.H., Beshir, S.M., 2004. Carvone-rich essential oils from mentha longifolia (l.) huds. ssp. schimperi briq. and Mentha spicata L. Grown in Sudan. J. Essent. Oil Res. 16, 539–541.

Yuan, S., Ji, C., Han, H., Sun, Y., Mashuga, C.V., 2021. A review of aerosol flammability and explosion related incidents, standards, studies, and risk analysis. Process Saf. Environ. Prot. 146, 499–514.

Zarringhalam Moghaddam, A., Rafiei, A., Khalili, T., 2012. Assessing prediction models on calculating the flash point of organic acid, ketone and alcohol mixtures. Fluid Phase Equilib. 316, 117–121.

Zielińska-Błajet, M., Feder-Kubis, J., 2020. Monoterpenes and their derivatives—recent development in biological and medical applications. Int. J. Mol. Sci. 21, 1–38.