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Flash points measurements and prediction of biofuels and biofuel blends with aromatic fluids

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ABSTRACT

The flash point of biofuels and petroleum fuels is an essential safety-related property for fuel processing, transportation and storage. Hydroprocessed renewable diesel (HRD-76) and synthesized isoparaffin (SIP), two biofuel blend stocks, were blended with commercial petroleum aromatic fluids (aromatic 100, 150 and 200) to investigate the impacts of aromatics on biofuel flash point and to formulate blends with identical flash point characteristics as NATO F-76 marine diesel and JP-5 jet fuel. To overcome the complexity of the fuel blends, COSMO-RS ("conductor like screening model for realistic solvation") was employed to predict the flash point of these biofuel + aromatic systems. COSMO-RS calculated the flash point of alkanes and aromatics present in biofuel and petroleum fuels and the flash point of SIP + aromatics binary mixture systems. Based on the pure compound and binary mixture predictions, COSMO-RS calculations were expanded to develop surrogate mixtures for biofuels and aromatic fluids. The surrogates were in turn utilized to predict the flash point of biofuel blends with aromatics and to formulate blends with the same flash point as petroleum fuels. The COSMO-RS calculation also assisted the selection of aromatics suitable for blending with different biofuels.

1. Introduction

The flash point of fuel is defined as the lowest temperature at which the fuel gives off sufficient vapor needed to ignite with air in the presence of a spark [1]. As expected, the flash point of fuel is directly correlated with its vapor pressure; higher vapor pressure usually results in lower flash point. Thus, the flash point provides a measurement of both flammability and volatility [1]. In addition, the flash point is a critical factor for: evaluating the potential of fire and explosion, especially in the process of fuel production; storage and transportation; and identifying fuels that are highly hazardous. At present, ASTM standards include mainly two types of testing methods to measure flash points of liquid fuels: closed cup (e.g. ASTM D56 [2], D93 [3], D3278 [4],D3828 [5], D6450 [6], D7094 [7], and D7236 [8,9]), and open cup (e.g. D92 [9] and D1310 [10]). The closed cup setup is more extensively used and has been listed as a required test in ASTM and military specifications, e.g. ASTM D7566-Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons [11] and MIL-DTL-16884 N-Specification for NATO F-76 diesel. The closed cup flash point of liquids is usually several degrees lower than the open cup flash point [12].

With the increased concerns of global warming and energy security, a large variety of alternative fuels have been produced from renewable feedstocks. The chemical compositions of these renewable biofuels usually differ from the conventional petroleum-based fuels and, therefore, the physicochemical properties and combustion behaviors of these biofuels may also be different. Hydroprocessed renewable diesel (HRD-76) and synthesized isoparaffin (SIP), also known as direct sugar to hydrocarbon (DSH), have been produced in sufficient quantity for testing by the US Navy for sailing the "Great Green Fleet". HRD-76 is produced by hydroprocessing of vegetable oil and animal fat [13], while SIP is a sugarcane-based biofuel produced from fermentation and hydrotreatment. SIP can be used as blending stock for both diesel (e.g. marine diesel NATO F-76) and jet fuel (e.g. JP-5), whereas HRD-76 can only be used for blending with F-76. HRD-76 and SIP are primarily comprised of n- and branched alkanes and contain minimum aromatic and heteroatomic compounds, while fossil fuels usually contain 20–25% aromatics [14–17]. Aromatics are generally considered as unfavorable compounds for fuel, and fuel with high aromatic content often has poor stability and increased particulate matter and gaseous combustion emission [18–20]. The aromatics, however, are also indispensable components of fuel, which can provide sufficient material compatibility/seal swell and other "fit-for-purpose" (FFP) properties [20–26]. Owing to the lack of aromatics, HRD-76 and SIP cannot be used as 100% replacements for conventional marine diesel and jet fuel. Blending aromatics with HRD-76 or SIP, therefore, is considered as a pathway to formulate 100% replacement fuel.

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Generally, the aromatics in petroleum fuel are mainly mono- and diaromatics, which have lower flash points than alkanes [27]. The choice of aromatic and the amount blended with HRD-76 or SIP will determine the flash point and the potential of fire and explosion. The flash point for pure aromatics and alkanes are easy to measure and can be obtained from various sources [27,28]. It is, however, difficult to predict the flash point behaviors of blended fuels. Due to their multicomponent characteristics and the variation in composition, it can be costly to experimentally identify fuel blends with specific flash points. Although many methods have also been developed to predict the flash point of pure liquid hydrocarbons and binary or even ternary liquid mixtures [29–39], these methods usually require routinely measuring thermochemical properties (e.g. boiling point, vapor pressure) or developing quantitative structure – property relationships (QSPRs) based on large numbers of molecular descriptors and statistical regression methods, which are often restricted to a single compound class. These methods usually cannot be employed to predict the flash point of fuel blends that contain hundreds or even thousands of compounds.

Surrogates, therefore, are developed for fuel research and use a few simple components to formulate mixtures that can act as model systems. Surrogates can significantly simplify the modeling of physicochemical properties and combustion behavior of fuel blends. In this study, the flash points of HRD-76 or SIP biofuel blends with three commercial aromatic fluids (i.e. aromatic 100, 150 and 200) were measured using a closed-cup setup to investigate the impacts of aromatics on biofuel volatility and flammability. COSMO-RS method ("conductor like screening model for realistic solvation") [40] was employed to predict the closed-cup flash point of pure alkanes and aromatics and evaluated by comparing the predicted values with measured values. COSMO-RS was then used to predict the flash point of SIP and pure aromatic compounds in binary mixtures and to develop surrogates for HRD-76 and three aromatics fluids. These surrogates were used for predicting the flash point of multicomponent fuel blends of HRD-76 or SIP with commercial aromatic fluids.

2. Materials and methods

2.1. Materials

F-76, JP-5, SIP, and HRD-76 were provided by Naval Fuels and Lubricants Cross Functional Team at Patuxent River, Maryland, United States (PAX River). The SIP and HRD-76 fuel lots were synthesized by Amyris Biotechnologies and UOP, respectively. Aromatic 100, Aromatic 150, and Aromatic 200 were produced by ExxonMobil and purchased from Fisher Scientific. 1,2,4-trimethylbenzene (CAS Reg. No. 95-63-6, with mass fraction purity > 98), 1,3,5-trimethylbenzene (CAS Reg. No. 108–67-8, with mass fraction purity $> 98\%$), isobutylbenzene (CAS Reg. No. 538-93-2, with mass fraction purity $> 99\%$), p-cymene (CAS Reg. No. 99–87-6, with mass fraction purity $> 99\%$), and 4-*tert*-butyltoluene (CAS Reg. No. 98-51-1, with mass fraction purity $> 95\%$) were purchased from Sigma-Aldrich. All the chemicals were used as received, unless otherwise noted.

2.2. Flash point measurement

A Setaflash Series 8 closed cup flash point analyzer (model 82000-2 U) by Stanhope-Seta (Surrey, UK) was used to measure the flash point of fuel samples according to ASTM D3828 method (hot wire ignition) [5]. For each fuel blend sample, at least two measurements of flash point were made; one using temperature ramp mode and one more using flash/no flash mode to validate the data obtained. The ramp mode allows for automatic flash point testing through a range of temperatures until a flash occurs or the end of the temperature is reached, while the flash/no flash mode allows for a test at a specified temperature. The temperature range of the ramp mode is set for 30 °C and the starting temperature should be set 10–15 °C lower than the actual flash point.

2.3. COSMO-RS prediction

COSMO-RS is a quantum chemical model for predicting thermodynamic states and equilibria of pure liquids and liquid mixtures based on the combination of unimolecular quantum chemical calculations and a statistical thermodynamics approach. This method is a variant of dielectric continuum solvation methods [41] and the calculation "takes place" in a virtual conductor environment [40,42]. During the quantum chemical calculations, the molecule is converged to its energetically optimal state with respect to electron density, and then the molecular geometry is optimized.

The COSMO-RS based calculation consists of two main steps: (1) the quantum chemical calculation for a species of interest, which is available in several quantum chemistry program packages, such as Turbomole [43], DMOL3, and GAMESS-US; followed by (2) a statistical calculation, which is implemented in the COSMO*therm* program [44]. The quantum chemical calculations were performed using the COSMO solvation model in Turbomole (TmoleX 3.4) software, which approximates a dielectric continuum by a scaled conductor. The molecule is considered to be located in a cavity of a dielectric continuum and the cavity surface is discretized into finite elements, i.e. segments. The structure of the molecule is optimized first for the gas phase and then in the virtual condensed phase using DFT (density function theory) with an approximate treatment of the electronic Coulomb interaction between the segments used to represent the molecule [43]. After the structure is first optimized, a single energy calculation with a basis set of TZVP (triple zeta valence polarized) is implemented [45]. COSMO*therm* (X17) then uses the parameters generated by Turbomole, such as dielectric constant, number of points per atom in the cavity construction, number of segments per molecule, and distance threshold for elements of matrix, to calculate the thermochemical properties of the substances in the virtual liquid phase [42].

The COSMO*therm* calculation on the flash point of pure compounds and mixtures is based on a single molecular size descriptor, i.e. molecular surface area, which can be considered a physically plausible descriptor, as the heat of combustion and the number of combustibles increases with the size of the compounds [46]. For a pure compound, the flash point (T_{FP}) corresponds to a saturation pressure (P_{FP}^{sat}), which is the lower flammability limit (LFL) at the T_{FP}. The P_{FP}^{sat} of a pure liquid compound can be calculated from the pressure correction to chemical potential at T_{FP}.

$$P_{FP}^{sat} = \exp\left(-\frac{\mu_{gas} - \mu_0}{RT_{FP}}\right) \tag{1}$$

where μ_{gas} is the chemical potential of the ideal gas at T_{FP}, and μ_0 is the chemical potential in the pure liquid state.

The chemical potential for pure compounds in the gas phase is estimated by an empirical equation [47],

$$\mu_{gas} = E_{gas} - E_{COSMO} + \omega_{ring} n_{ring} + \eta_{gas} \tag{2}$$

where E_{gas} and E_{COSMO} are the quantum chemical total energies of the molecule in the gas phase and in the COSMO virtual conductor, respectively, ω_{ring} is an adjustable parameter, n_{ring} is the number of ring atoms in the molecule, and η_{gas} provides the link between the reference states of the system's free energy in the gas phase and in the liquid. The difference between E_{gas} and E_{COSMO} is the energy change by moving a molecule from the gas phase into a hypothetical solvent state. $\omega_{ring} n_{ring}$ reflects the vibrational energy changes when a ring is brought from the gas to a hypothetical solvent state, and η_{gas} reflects a general change in the vibrational energies when going from gas phase to the liquid state [47].

The chemical potential of the compound in the liquid state is a function of the screening charge density (SCD) [47],

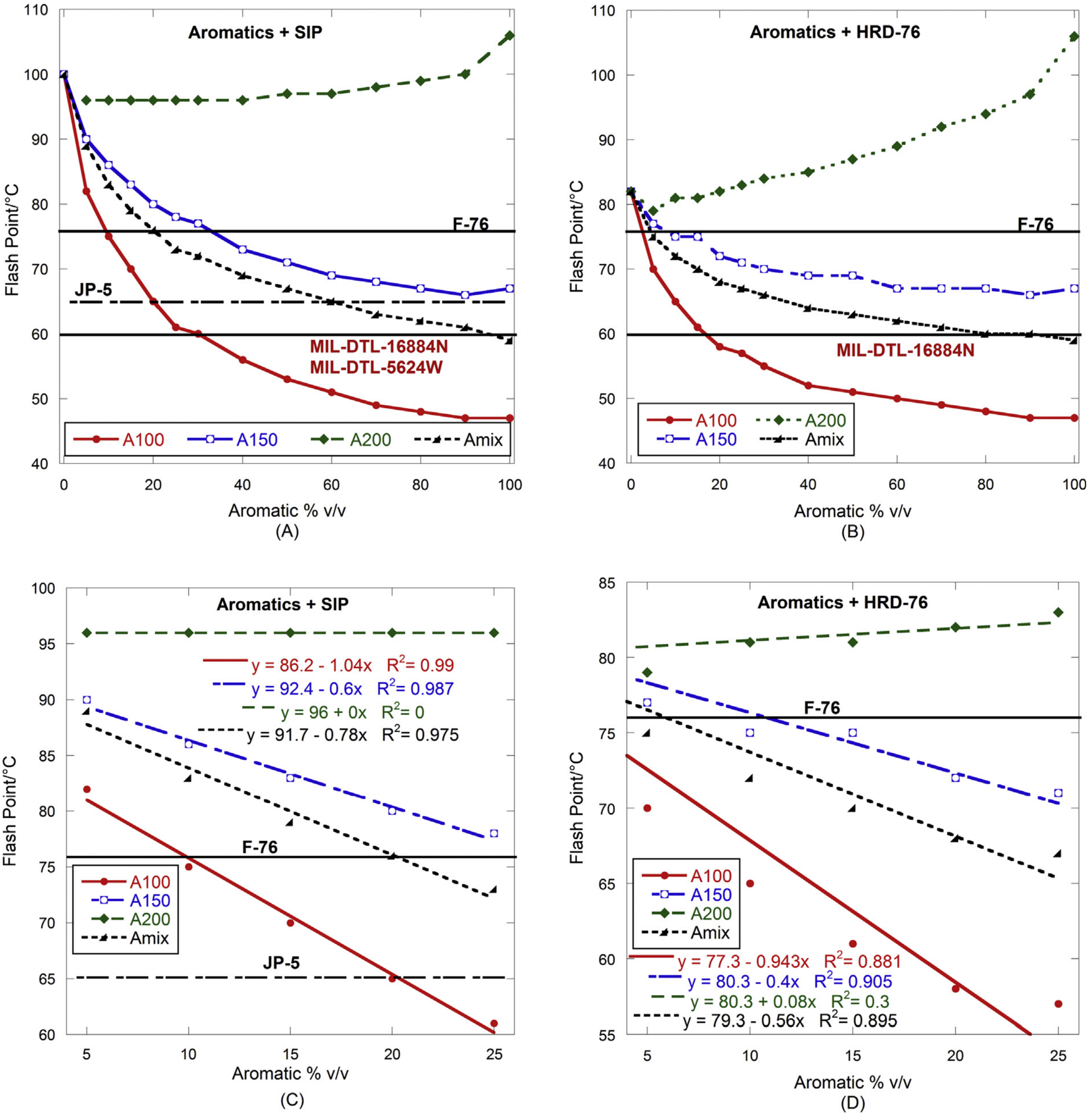

Fig. 1. Flash point of biofuel blends with aromatic fluids determined by ASTM D3828: (A) aromatic fluids + SIP blends with 0–100% v/v aromatics; (B) aromatic fluids + HRD-76 blends with 0–100% v/v aromatics; (C) aromatic fluids + SIP blends with 0–25% v/v aromatics; (D) aromatic fluids + HRD-76 blends with 0–25% v/v aromatics.

$$\mu_0(\sigma) = -\frac{RT}{\alpha_{\mathrm{eff}}}\ln\left[\int P_S(\sigma')\exp\left(\frac{\alpha_{\mathrm{eff}}}{RT}(\mu_0(\sigma') - e(\sigma,\sigma'))\right)d\sigma'\right] \tag{3}$$

$$e(\sigma,\sigma') = (E_{\mathrm{vdW}}(\sigma,\sigma') + E_{\mathrm{HB}}(\sigma,\sigma') + E_{\mathrm{MF}}(\sigma,\sigma'))/\alpha_{\mathrm{eff}} \tag{4}$$

where σ and σ' are the SCD of each segment of the acceptor and donor molecules (for pure compound, both present in the same molecule), respectively, a_{eff} is the effective contact area between two surface segments, μ_0 is a measure for the affinity of the compound to a surface polarity σ, and $p_0(\sigma)$ (the σ-profile of the compound) is the probability distribution of σ. E_{MF} is the specific interaction energy per unit area, which describes an electrostatic interaction arising from the contact of two different SCD, E_{HB} is hydrogen-bonding interaction energy caused by the contact of two polar surface segments of opposite polarity, and E_{vdW} describes the interaction energy between surface segments and depends only on the element type of the atoms that are involved in surface contact.

The calculation of pure compound flash point generally includes two-steps: (1) calculate $\mathrm{P}_{FP}^{\mathrm{sat}}$ based on a set of molecules for which experimental T_{FP} are available; (2) correlate experiment-based saturation pressures with the molecular surface area (α) of the molecules calculated by Turbomole, i.e. $\mathrm{P}_{FP}^{\mathrm{sat}}$ is estimated from a simple linear correlation:

$$\ln(\mathrm{P}_{FP}^{\mathrm{sat}}) = c_0 + c_1\ln(a) \tag{5}$$

where c_0 and c_1 are two generic fit parameters stored in the COSMO*therm* parameter file. To reduce the error of transforming the experimental T_{FP} to saturation pressures, the available experimental normal boiling points are utilized for the calibration of the COSMO*therm* vapor pressure [46]. The final set of the step (1) employed by COSMO*therm* contains 1056 molecules and their flash points, and the values obtained for c_0 and c_1 are 15.86 and −2.58, respectively [46].

In the case of mixtures, the T_{FP} is calculated according to the mixing rule developed by Liaw et al. [48–50]. T_{FP} is calculated based on

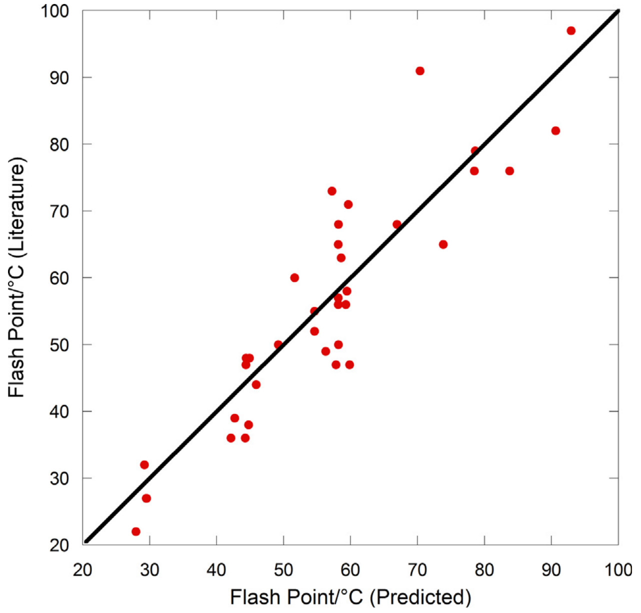

Fig. 2. Correlation of measured and predicted flash point of major aromatics existed in aromatic fluids.

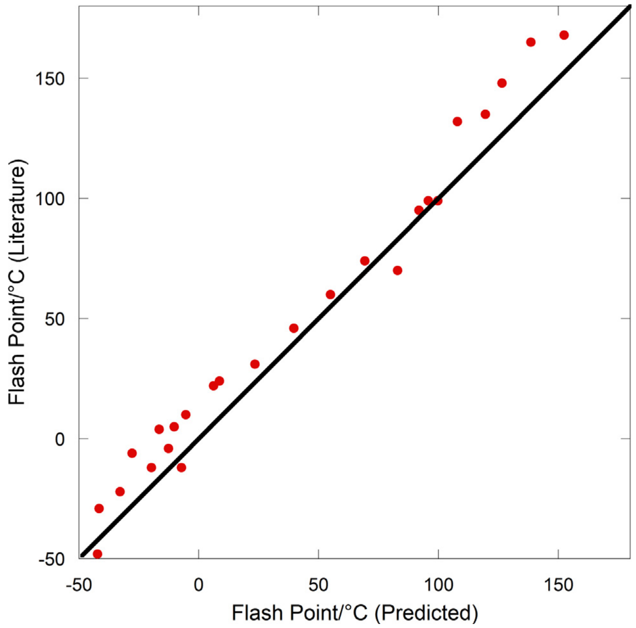

Fig. 3. Correlation of measured and predicted flash point of major n-alkanes existed in F-76 and JP-5.

variational minimization of the general flash point condition, at which the LFL is identical to P^{sat}_{FP} [44]. For miscible liquid mixtures , this condition becomes:

$$\frac{1}{T^{\text{flame}} - T_{\text{FPmix}}} \sum\nolimits_{i\neq k} \frac{x_i\gamma_i(T^{\text{flame}} - T_{\text{i, FP}})}{P^{\text{sat}}_{\text{i, FP}}} = 1 \tag{6}$$

where T^{flame} is the flame temperature [46], x_{i} is the mole fraction of compound i in the liquid phase, and $T_{\text{i,FP}}$ and $P_{\text{i,FP}}$ are the flash point and saturation pressure of compound i, respectively. The T^{flame} is assumed to be an adjustable parameter and is taken to be $T^{\text{flame}} = 1300$ °C by default [44]. The activity coefficient (γ_{i}) can be calculated by *COSMOtherm* based on the chemical potential of the mixture system [51].

3. Results and discussion

3.1. Aromatic fluids and biofuel blends

The fuel blends must meet all the military specification for F-76 and JP-5, i.e. MIL-DTL-16884N and MIL-DTL-5624W, respectively. Both specifications require the flash point of F-76 or JP-5 fuel blends > 60 °C. The flash point of F-76 and JP-5 samples determined in this study were 76 and 65 °C, respectively, which meet the corresponding military specifications and are lower than that of HRD-76 and SIP, 82 and 100 °C, respectively. The commercial aromatic fluids, i.e. Aromatic 100 (A100), Aromatic 150 (A150), and Aromatic 200 (A200), were selected for blending with HRD-76 and SIP to formulate fuels with flash points comparable to those of F-76 and JP-5. These three aromatic fluids are composed of mono- and di-aromatics with various alkyl substitutions. The primary components of A100 were found to be C3 (~83.6 %v/v) and C4 (~12.8% v/v) alkylated benzenes, whereas A200 mainly comprises naphthalene and alkylated naphthalenes (~84%) [20]. The composition of A150 is more complicated in comparison with A100 and A200 and has been reported as mainly C3 (~2.6%v/v), C4 (~62.2% v/v), C5 (~18.3% v/v), and C6 (~1.3% v/v) alkylated benzenes, C10- and C11-alkylated indans and tetralins (~7.3% v/v), and naphthalene (~6.7% v/v) [20]. The boiling temperature range of these three aromatic fluids is within the range of petroleum diesel F-76 [17]. The flash points of these three fluids are ranked: A100 (47 °C) < A150 (67 °C) < A200 (106 °C), and A100 is regarded as a light aromatic in comparison with A150 and A200.

The flash point of SIP or HRD-76 blends with A100, A150, A200, and a 1:1:1 v/v mixture of A100, A150 and A200 (Amix) were measured using a closed-cup setup (values listed in Table S1 and S2 in Supplementary Material) and shown in Fig. 1. Overall, the flash points of SIP and HRD-76 blends both decreased when blended with A100, A150, or Amix, whereas the impacts of A200 varied with biofuels. Fig. 1 (A) displayed the impacts of aromatic fluids on the flash point of SIP blends. No direct relationships were observed between the composition of aromatics fluids and the blend flash point. The flash point of SIP blends is identical to that of F-76 in ~9% v/v A100, ~20% v/v Amix, or ~33% v/v A150 mixtures, whereas ~20% v/v A100 or 60% v/v Amix would be needed for the flash point of the SIP blend to reach the value of JP-5. MIL-DTL-16884N for F-76 specifies that the minimum aromatic content of F-76 replacement fuel blends must be > 8.1 %w/w and the refined F-76 usually contains ~25% w/w aromatics [52], indicating that Amix could be a good blend stock for SIP to formulate an F-76 surrogate with a higher renewable content. MIL-DTL-5624W for JP-5, however, requires the aromatic content of JP-5 should be in the range of 8.0–25% wt, meaning that only A100 could possibly be selected for blending with SIP and utilized as 100% placement for JP-5. The flash point of A200 blends cannot reach the level of F-76 or JP-5 owing to the comparably low volatility of farnesane and naphthalenes. Although the flash point of SIP and A200 blends cannot reach the level of F-76 and JP-5, the SIP and A200 blend system exhibits the minimum flash-point behavior, i.e. the flash points of the blends over a wide composition range were lower than that recorded for the individual solution components. This special behavior is reportedly attributed to the highly positive deviation from the ideal solution behavior [50].

Similar flash point behaviors were observed in HRD-76 fuel blends (shown in Fig. 1(B)). The flash point of the HRD-76 fuel blend would be identical to F-76 using ~2% v/v A100, ~4% v/v Amix, or 7% v/v A150 mixtures, which is lower than the minimum required content of aromatics specified in MIL-DTL-16884N, i.e. 8.1% wt and much lower than the reported aromatic content of F-76, 25% wt [52]. The flash point of the HRD-76 blends would not meet the military specification when the content of A100 is > 17% v/v. Due to the formulation of A200, the flash points of its blends with HRD-76 are all higher than that of F-76. Although a linear relationship was not observed across the full composition range of the aromatic + biofuel blends, the biofuel blends

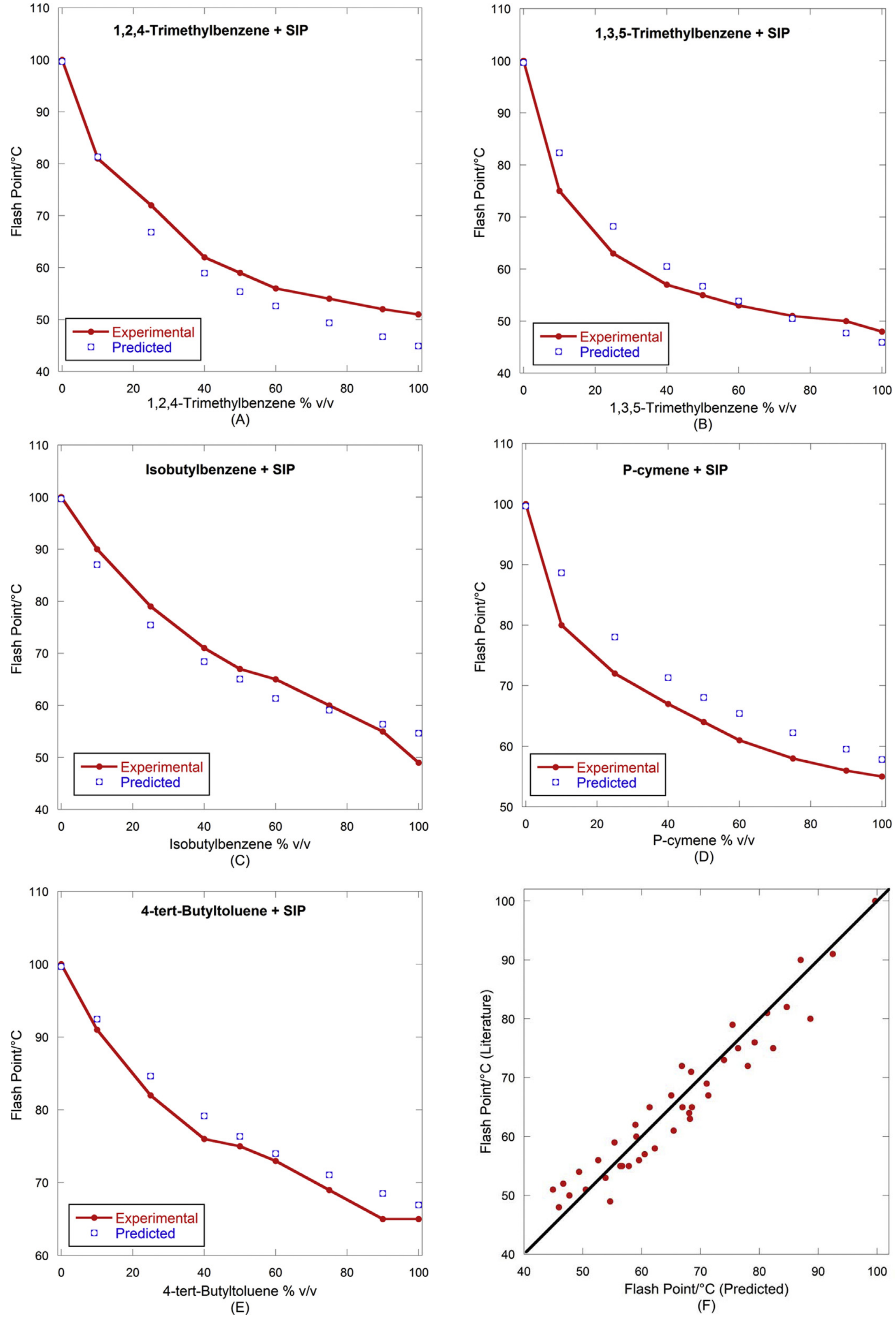

Fig. 4. Measured and predicted flash point of binary fuel mixtures: (A) 1,2,4-trimethylbenzene + SIP; (B) 1,3,5-trimethylbenzene + SIP; (C) isobutylbenzene + SIP; (D) p-cymene + SIP; (E) 4-tert-butyltoluene + SIP; (F) correlation of the measured and predicted values of (A)-(E) binary mixtures.

with A100, A150 and Amix decreases almost linearly with the increase of aromatic content in the range of 5–25% v/v (shown in Fig. 1 (C) and (D)). These linear relationships could be employed to estimate the flash point of biofuel blends within the range.

3.2. Pure aromatics and alkane prediction

Petroleum fuels usually contain hundreds, even thousands, of compounds, so it is difficult to formulate biofuel + aromatic blends that possess similar characteristics and require no modification to existing

Table 1
Experimental and predicted flash points (FP) of aromatics, fuels, and their surrogate mixtures.

Name	FP/°C (Exp)	Components	% v/v	FP/°C (Predicted)
Aromatic 100	47 ± 1	1,2,4-trimethylbenzene 4-ethyl-m-xylene	79.5 20.5	47.02
Aromatic 150	67 ± 1	4-ethyl-m-xylene 4-methylindane naphthalene	20.0 31.5 48.5	66.85
Aromatic 200	106 ± 2	naphthalene 2,6-dimenthlnaphthalene	1.0 99.0	105.93
1:1:1v/v Amix	60 ± 1	Based on the A100, A150, and A200		61.94
HRD-76	82 ± 1	pentadecane hexadecane heptadecane octadecane isooctane	10.8 8.9 46.3 32.5 1.5	81.89
SIP	100 ± 1	farnesane	100	99.69

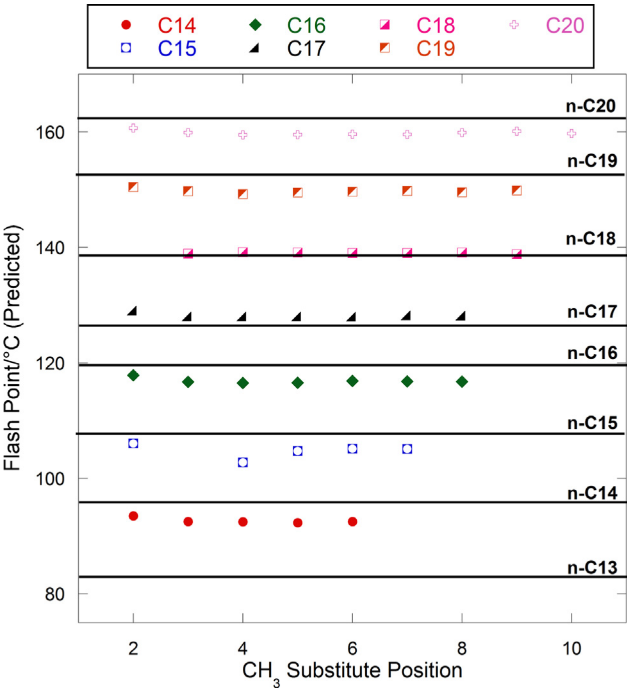

Fig. 5. Comparison of the calculated flash point between C14-C20 alkanes with mono-methyl substitution and n-alkanes.

equipment and fuel handling and transportation systems. Thus, it is important to develop models that can predict the properties of petroleum fuel, biofuel and aromatics. Alkanes and aromatics (mono- and di-aromatics) are the two major classes of chemicals in petroleum fuels. COSMO-RS was first employed to calculate the flash point of pure alkanes and aromatics existing in petroleum fuels, biofuels (i.e. HRD-76 and SIP) and aromatic fluids. 37 mono- and di-aromatic major components of A100, A150 and A200, and 25n- and branched C6-C19 alkanes present in F-76 and JP-5 were selected for calculation and the values obtained were compared with measured flash point determined using closed-cup systems (listed in Table S3). Fig. 2 showed the COSMO-RS predicted flash point of the 37 selected pure aromatics versus the measured values. The predicted values are in reasonable agreement with measured values, and the root-mean-square deviation (RMSE) for the prediction is 7.27 °C, which is lower than the RMSE based on the COSMO-RS prediction of 1056 chemicals (employed to build the software database), i.e. 14.32 °C [46]. Similar to aromatics, the predicted values of alkanes are also in agreement with measured values, with a RMSE of 13.99 °C (Fig. 3). The prediction results of aromatics are slightly better than that of alkanes, as the temperature range of the prediction is narrower in comparison with alkanes and a slightly larger dataset was selected for aromatics calculation. Interestingly, the RMSE for the combined calculation of aromatics and alkanes, i.e. 8.88 °C, is better than the RMSE reported for the COSMO-RS calculation of 1056 chemicals [46]. This may result from the absence of hetero-atoms (e.g. O, Cl) in the structure of hydrocarbons selected in this study.

3.3. Binary mixtures of SIP and pure aromatics

As COSMO-RS reasonably predicted the flash point of pure aromatics and alkanes present in petroleum fuels, it was also employed to calculate the flash point of alkane and aromatic binary mixtures. SIP was selected for investigating the impacts of various aromatics on biofuel flash point, as SIP is a single component fuel [17], and can be utilized as a drop-in replacement for both F-76 and JP-5. Five alkylated benzenes were selected and mixed with SIP across the composition range. The flash points of these five aromatics are in a range of 45–66 °C, all lower than the flash point of SIP, 100 °C. Fig. 4 compares the measured and predicted flash point of five SIP binary mixtures with alkylated benzenes. Overall, the flash point of the SIP-aromatic blends decreases with the increase of aromatic content, and the flash points of the binary mixtures were all higher than the flash point of the component with lower flash point. This may result from the weak interactions among the molecules, as SIP and alkylated aromatics are both non-polar with low dipole moment based on quantum chemical calculation using Spartan 14. The calculated flash points of the mixtures are all in reasonable agreement with measured values. The RMSEs for mixtures with 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, isobutylbenzene, p-cymene and 4-*tert*-butylbenzene are 4.06, 3.44, 2.99, 4.76, and 2.17 °C, respectively, and are lower than the RMSEs calculated for pure aromatics and alkanes, 7.27 °C and 14.37 °C, respectively. The RMSEs of mixtures with 1,2,4-trimethylbenzene and p-cymene are slightly higher than that of the other mixtures, but their data deviations are different. The calculated value of the SIP and 1,2,4-trimethylbenzene mixture is lower than the measured value, while the calculated flash point of the SIP and p-cymene mixture is slightly higher than the measured result. The under prediction of the SIP and 1,2,4-trimethylbenzene mixture system may result from the under prediction of the 1,2,4-trimethylbenzene, 51 °C(measured) vs. 44.91 (calculated). Interestingly, the maximum deviation of the SIP and p-cymene occurs for the 10%v/v blend and the deviation decreases with the increase of p-cymene mole fraction in the mixture.

The COSMO-RS calculation can also simplify the process for estimating the level of aromatics needed for blending with SIP to achieve a target flashpoint. Per COSMO-RS calculation, blends of 14% v/v 1,2,4-trimethylbenzene, 15%v/v 1,3,5-trimethylbenzene, 24% v/v isobutylbenzene, 29%v/v p-cymene, or 51% v/v 4-*tert*-butyltoluene with SIP would have flash points of 76 °C, identical to F-76. These SIP + aromatic binary mixtures were prepared accordingly to evaluate the accuracy of the prediction, and their flash points were found to be 73, 71, 65, 67, and 70 °C, respectively, all reasonably consistent with predicted values. For JP-5 replacement, the measured flash points of SIP binary blend with 28%v/v 1,2,4-trimethylbenzene, 30%v/v 1,3,5-trimethylbenzene, 50% v/v isobutylbenzene, or 62%v/v p-cymene were 64, 61, 56, and 59 °C, respectively, which is close to the flash point of JP-5, i.e. 65 °C. It is worth noting that the measured flash point of the SIP + isobutylbenzene surrogate mixtures for F-76 and JP-5 had the highest deviations from predicted values at 11 and 9 °C, respectively, although the RMSE for the whole blending range mixtures was only 2.99 °C.

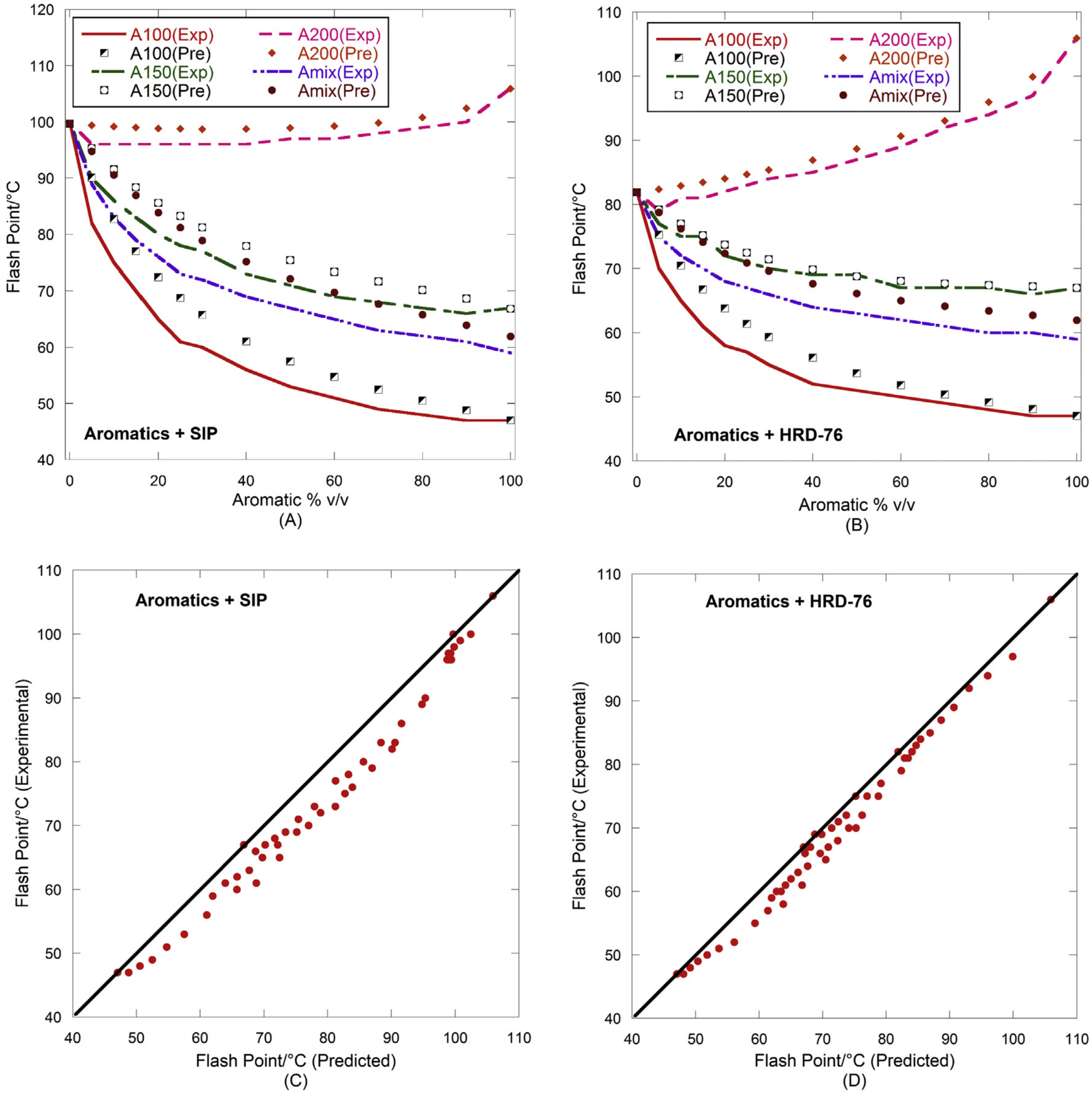

Fig. 6. Measured and predicted flash point of biofuel blends with aromatic fluids: (A) aromatic fluids + SIP blends; (B) aromatic fluids + HRD-76 blends; (C) correlation of the measured and predicted values of aromatic fluids + SIP blends; (C) correlation of the measured and predicted values of aromatic fluids + HRD-76 blends.

3.4. *Prediction of aromatic fluids and biofuel blends*

Surrogates are usually developed for fuels research, as the composition of conventional diesel and jet fuels are too complicated to model their physicochemical properties and combustion behavior. Surrogate mixtures of biofuels and the commercial aromatic fluids, developed based on their measured flash points, are listed in Table 1. The composition of the aromatic fluids A100, A150, and A200 were determined previously [17] and the chemicals selected for developing the aromatic fluid surrogates are aromatic compounds of high concentration in the corresponding aromatic fluids. For instance, 1,2,4-trimethylbenzene and 4-ethyl-m-xylene were selected to formulate the A100 surrogate, as C3 and C4 alkylated benzenes account for > 96% v/v of A100 and the concentration of 2,4-trimethylbenzene and 4-ethyl-m-xylene are the highest in C3 and C4 alkylated benzenes, respectively. The surrogate mixtures of the 1:1:1 v/v mix of A100, A150 and A200 were obtained based on the surrogate mixtures calculated for A100, A150 and A200 via COSMO-RS. The calculated flash point of the 1:1:1 mixture, 60.94 °C, is within the range of the measured value, 60 ± 1 °C.

As with aromatic fluids, the surrogate mixture for HRD-76 was also developed based on the estimated composition [16] of 11% v/v n-pentadecane, 9% v/v n-hexadecane, 22% v/v n-heptadecane, 25% v/v *iso*-heptadecane, 15% v/v n-octadecane, and 18% v/v *iso*-octadecane. The *iso*-heptadecane and *iso*-octadecane are mainly branched mono-methyl hexadecanes and heptadecanes, for which no flash point data are available owing to the difficulty of obtaining the pure compounds. COSMO-RS was employed to predict the flash point of C14-C20 alkanes with mono-methyl substitution (shown in Fig. 5). The calculated results were compared with the calculated flash point of n-alkanes to provide guidance on the surrogate formulation. Overall, the mono-branched alkanes with different substitution positions have similar flash points, and the values are < 3.2% different from the value of n-alkanes with the same carbon number. For mono-methylheptadecanes, the average flash point differences with n-C17 and n-C18 are 12.59 and 0.50 °C, respectively, indicating that n-octadecane can be used to represent the branched mono-methylheptadecanes when developing the surrogate for HRD-76. A similar trend was also observed in mono-methylhexadecanes, for which average flash point differences with n-C16 and n-C17 are 8.62 and 1.78 °C, respectively. The surrogate mixture, therefore, can be formulated as 11%v/v n-pentadecane, 9%v/v n-hexadecane, 47% v/v n-heptadecane, and 33% v/v n-octadecane. This surrogate, however, cannot represent the HRD-76 well, as the lower boiling point components that elute earlier in the chromatogram are not represented and these low boiling point components are usually associated with low flash point, which would highly affect the flash point of the surrogate, even at very low concentration. Prak et al. experimentally formulated an HRD-76 surrogate using a small amount of isooctane, ~2% wt [53]. Isooctane was also employed for developing the HRD-76 surrogate using COSMO-RS method, and by blending with 1.5%v/v isooctane with the aforementioned n-C15-C18 mixture. The flash point of the mixture, 81.89 °C, would be the same as that of HRD-76, 82 ± 1 °C. The major component of SIP is farnesane, and the calculated flash point of farnesane is identical to that of SIP, meaning farnesane can be used to represent SIP for calculation.

The flash points of biofuel and aromatic blends were calculated based on the developed surrogates and compared with the measured values in Fig. 6. Overall, the predicted values are in reasonable agreement with measured values, although the predicted values are all slightly higher than the measured values. For SIP blends, the RMSEs of the A100, A150, A200, and Amix systems are 5.38, 4.30, 2.43, and 5.80 °C, respectively, and the RMSE of all the SIP blends is 4.66 °C. The comparably high RMSEs for the SIP + Amix blend may result from the slightly higher number of compounds used for calculation. Interestingly, the RMSEs of HRD-76 + aromatic blends are all lower than the SIP + aromatic systems, although more compounds were employed to formulate the HRD-76 surrogate. The RMSEs for A100, A150, A200, and Amix mixture with HRD-76 are 3.71, 1.19, 1.93, and 3.44 °C, respectively, and the RMSE of the whole HRD-76 blends is 2.77 °C. It is worth noting that COSMO-RS successfully predicted the flash point of non-ideal multicomponent mixture systems, i.e. SIP + A200 blends, for which the flash points of the mixtures are all higher than the flash points of SIP and A200.

In summary, the COSMO-RS can be employed to assist the development of surrogates for diesel and jet fuel based on flash point. The surrogates can then be used to calculate the flash points of fuels at given blend ratios. COSMO-RS can save time and effort measuring the flash points of all possible fuel blends. The RMSE calculated by including all the fuel blends is 3.83 °C, meaning the calculated values are reasonably consistent with measured values.

4. Conclusion

The flash point of biofuels and their blends with aromatics were investigated experimentally and computationally. The biofuels SIP and HRD-76 were blended with commercial aromatic fluids (A100, A150, and A200) to experimentally study the impacts of aromatics on their flash point and to determine the blend percentages needed to match the flash points of F-76 or JP-5. COSMO-RS was utilized to calculate the flash point of pure compounds, binary mixtures, and complicated fuel blends, and to formulate surrogate mixtures.

Based on the experimental analysis and computational calculation, the following conclusions were drawn:

- A100 and Amix are suited for blending with SIP to match the flashpoints of F-76 and JP-5, respectively.
- None of the four aromatic fluids investigated were suitable for blending with HRD-76 to match the flash point and aromatic content (fuel specification) of F-76, however, an aromatic fluid mixture with a higher percentage of A200 could be an initial starting point for development.
- The calculated flash points were in reasonable agreement with measured values for pure alkanes and aromatics.
- COSMO-RS can be employed to calculate the flash point of SIP + aromatic binary mixtures.
- The predicted flash points of blends of HRD-76 and SIP with aromatics fluids were in reasonable consistency with measured values.
- COSMO-RS is an efficient technique in predicting the flash points of petroleum fuels and biofuels and in formulating fuel surrogates.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2018.12.105.

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