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Prediction of the flash points of multicomponent systems: applications to solvent blends, gasoline, diesel, biodiesels and jet fuels

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Abstract

Fuel reformulation and the development of alternative fuels are currently topics of great interest. For example, gasoline can be reformulated for a reduction of emitted toxic pollutants. However, fossil and bio fuels are of complex compositions, and reformulation can dramatically affect the physical, chemical and safety properties of the fuel. Tools that can predict these properties are then of particular importance. In this work, we propose a general approach to accurately predict the flash points of complex fuels such as gasoline, jet fuels, diesels, and biofuels. The predictive method is based on a combination of Catoire - Naudet model with a fully predictive activity coefficient model. Excellent predictions of the flash points of mixtures are obtained for a broad variety of systems, when the COSMO-SAC dsp thermodynamic model is used. It can be used to predict the flash points of mixtures of various types of fuels: ex-fossil, first, second and third generation biofuels and their mixtures. The new approach can take into account the addition of molecules to a complex fuel when experimental measurements are not available, whatever the reasons are. The theoretical predictions confirm the experimental observation that a small amount of volatile compound such as ethanol can dramatically reduce the flash point of multicomponent fuels.

Keywords: flash points, flammability, process safety, fuels, combustion, COSMO-SAC, COSMO-RS, vapor-liquid equilibrium

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1. Introduction

Fuel reformulation has been seeded by the consciousness of damages that their combustions can cause. Removing one or several components, or adding molecules, to reduce pollutants emissions and improve air quality or mitigate climate change, can modify many properties including safety parameters such as flammability limits, flash points and others. These safety data are needed for production, handling, transportation, storage and uses of the liquids. The flash point of a liquid is the lowest temperature at which the vapor in equilibrium with the liquid and mixed with an oxidizer, generally air at atmospheric pressure, may be ignited by a spark or a flame. The knowledge of this property is of crucial importance for car and plane fuels because standardization exists in term of flash points for any kind of fuels, among numerous other properties. For most fuel properties, the surrogate fuel approach is often preferred because fossil fuels are generally very complex mixtures containing up to several hundreds of components. A surrogate is a mixture devoted to the description of some of the properties of a real fuel: it consists of a mixture of few molecules belonging to the major chemical families present in the real fuel. In fact, the surrogate may be representative of the fuel for some combustion properties such as ignition delays, fundamental flame speeds and pollutant emissions but certainly not for properties related to accidental combustion. For safety purposes, only the consideration of the fuel itself makes sense, because the flash point temperature can dramatically change in the presence of a volatile and flammable molecule even present in very small amounts. Flash points can be measured generally relatively easily with appropriate apparatus according to standards, but the predictions of flash points allow the replacement of thousands of measurements for the design of *a priori* convenient alternative fuel blends. In some cases, experimental measurements are not feasible because of the toxicity of some components and in other cases it may be not feasible because hundreds or thousands

of measurements are needed. Furthermore, the accidental or unwished or unexpected addition of a small amount of a component into a fuel may lead to MFPB (Minimum Flash Point Behavior) and in such cases measurements are not generally available. Therefore, a flash point model that can predict the MFPB phenomenon is of great interest.

Predictive methods for flash points of complex multicomponent mixtures are still scarce in the literature. Most predictive approaches for flash point calculation of mixtures are based on Le Chatelier's rule [1-7]. One advantage of such an approach is the possibility to treat mixtures containing nonflammable compounds [3]. However, one drawback is the required knowledge of the flash point of each individual compound of the mixture. The flash point of the pure substance, if unknown experimentally, can be evaluated from a group contribution method [8] or from a QSPR approach [9] or some other approaches based on ab initio calculation [10]. Catoire and Naudet showed that flash points can be related to the boiling point and vaporization enthalpies of pure component and mixtures. They proposed an accurate phenomenological equation based on these thermodynamic properties [11].

The aim of this work is to propose a general method to accurately predict the flash points of any kind of fuels by considering their real compositions. The main advantage of the method compared to other models is that it does not require the experimental flash point of each individual component of the fuel, and it can be applied to any number of components in a fuel.

2. Predictions of flash points

2.1. Catoire and Naudet Model

It has been observed that flash points of pure compounds and mixtures are highly correlated with the thermodynamic properties and vapor-liquid equilibria of the systems. Indeed, the flash point temperature depends on the composition of the vapor phase in equilibrium with the liquid. It also depends on the vaporization enthalpy of the liquid since the heat of combustion must compensate the vaporization enthalpy. Catoire and Naudet [11] proposed a phenomenological expression to predict the flash point of pure compounds from the normal boiling point, the number of carbon atoms and the enthalpy of vaporization at 298.15K. This equation has been shown to be predictive for all chemical families and has been used for the search of erroneous flash points data reported in the literature and databases. Other equations are reported in the literature but they are generally not validated or validated for one or few chemical families and for pure compounds only. The predictive Catoire-Naudet (CN) model presented in [11] has been extended to mixtures made of up six flammable components by Catoire et al. [12, 13] and validated with binary and ternary mixtures. Here, we extend the CN model to mixtures containing hundreds of compounds. Let us consider a liquid mixture of n compounds and of composition vector x_i (mole fraction of component i). The flash point temperature (T_{FP}) of a liquid mixture at atmospheric pressure, is expressed in Kelvin as

$$T_{FP} = 1.477\, T_{b,mix}^{0.79686}\, \Delta H_{vap,mix}^{\;\;0.16845}\, n_{C,mix}^{-0.05948}, \qquad (1)$$

where $T_{b,mix}$ is boiling point (K) of the mixture at atmospheric pressure; $n_{C,mix}$ is average carbon number given by $n_{C,mix} = \sum_{i=1}^{n} y_i n_{C,i}$, where $n_{C,i}$ is the number of carbon atoms of molecule i; y_i is the mole fraction of component i in the vapor phase in equilibrium with the liquid phase at the mixture boiling point $T_{b,mix}$. $\Delta H_{vap,mix}$ is the vaporization enthalpy of the mixture expressed in kJ mol^{-1}, which is estimated from the Clausius-Clapeyron equation at T = 298.15K, as [12, 13]

$$\Delta H_{vap,mix} = \left(RT^2 \frac{\partial \ln P_{sat,mix}}{\partial T} \right)_{T=298.15K}, \qquad (2)$$

where R is the ideal gas constant, and $P_{sat,mix}$ the saturated pressure of the liquid mixture at T. Equation (2) is valid as long as the critical temperature of the mixture is over 298.15K. To determine $P_{sat,mix}$ and $T_{b,mix}$ one can use a predictive activity coefficient model for the liquid phase and assume that the vapor phase is an ideal gas mixture. Note that Eq. (1) is also valid for pure compounds. By assuming that the vapor phase is an ideal gas mixture, $P_{sat,mix}$ is

given by $P_{sat,mix} = \sum_{i=1}^{n} x_i \gamma_i P_{vap,i}$, where $\gamma_i$and $P_{vap,i}$ are the activity coefficient and the vapor pressure of component *i*, respectively. In Catoire and Naudet's original work [11], the $\gamma_i$were estimated by using the original UNIFAC method [14]. Three activity coefficient models are used in this study: the ideal solution model or Raoult's law ($\gamma_i = 1$ for all compounds),the original COSMO-SAC model [15, 16] and the COSMO-SAC dsp version [15, 16]. The main advantage of COSMO models compared to UNIFAC is that group contribution parameters in UNIFAC may be missing, while COSMO models are versatile approaches.

2.2. COSMO - SAC and COSMO-SAC dsp models

COSMO – like thermodynamic models are predictive activity coefficient models that use *ab initio* calculations as input data to characterize the molecules of the studied mixtures. The COSMO approach (COSMO-RS) was originally developed by Klamt [17-20]. Lin and Sandler [15] proposed the COSMO-SAC model as a modified version of COSMO-RS. Later, Hsieh et al. [16] introduced a dispersion term in the model and proposed the COSMO-SAC dsp model. In all these approaches, each molecule is characterized by its molecular volume, its surface and its sigma profile, which is the average charge distribution along the surface cavity surrounding the molecule. In the COSMO-SAC model of Lin and Sandler [15], only one sigma profile $p_i(\sigma_m)$ is considered for each molecule, and the activity coefficient of component *i* is expressed in terms of the sigma profile as

$$\ln \gamma_{i/S} = \sum_{\sigma_m} \frac{A_i p_i(\sigma_m)}{a_{eff}} [\ln \Gamma_S(\sigma_m) - \ln \Gamma_i(\sigma_m)] + \ln \gamma_{i/S}^{SG}, \quad (3)$$

where the summation is over all possible discrete charge densitiesσ_m, and a_{eff}= 7.5Å^2. $\gamma_{i/S}^{SG}$ is the Staverman-Guggenheim combinatorial contribution to the activity coefficient. The surface segment activity coefficients of component *i*, $\Gamma_i(\sigma_m)$, and of solution *S*, $\Gamma_S(\sigma_m)$ are determined by solving

$$\ln \Gamma_l(\sigma_m) = -\ln\left(\sum_{\sigma_n} p_l(\sigma_n)\, \Gamma_l(\sigma_n) \exp\left(\frac{-\Delta W(\sigma_m, \sigma_n)}{kT} \right) \right), \quad (4)$$

where the index *l* stands for all pure compound *l* and for solution *S*. $\Delta W(\sigma_m,\sigma_n)$ describes the interaction between two surface segments of charges σ_m and σ_n and is the sum of electrostatic and hydrogen bonding contributions. The reader is directed to Lin and Sandler's paper [15] for further details.

The COSMO-SAC-dsp model [16], which is rather similar to the COSMO-SAC 2010 version [21], as both models consider different sigma profiles for each molecule, in order to differentiate atoms that make hydrogen bonds from the others. In this case, the sigma profile is the sum of different contributions [16, 21]

$$p_i(\sigma) = p_i^{nhb}(\sigma) + p_i^{oh}(\sigma) + p_i^{ot}(\sigma) \ , \tag{5}$$

where $p_i^{oh}(\sigma)$ is the sigma profile that includes the segments on oxygen and hydrogen atoms on hydroxyl (OH) groups; $p_i^{ot}(\sigma)$ is the sigma profile involving oxygen (not on OH group) , N, and F atoms. $p_i^{nhb}(\sigma)$ contains all the other types of atoms. The main difference between COSMO-SAC 2010 and COSMO-SAC-dsp is the addition of a dispersion term in COSMO-SAC-dsp, which is based on atomic contributions and enables to correct some deficiencies of the COSMO-SAC 2010 model by introducing more universal parameters. This dispersion contribution is added to the excess Gibbs free energy and is based on a simple one-parameter Margules activity coefficient model. Further details can be found in the literature [16, 21]. The COSMO-SAC dsp model has been implemented into the Simulis thermodynamics simulation software within cooperation between the UCP lab of ENSTA ParisTech and Prosim.

3. Results and Discussion

3.1. Binary systems

We first apply the CN model combined with three different predictive activity coefficients models (Raoult's law, COSMO-SAC and COSMO-SAC dsp), to determine the flash point of binary mixtures of organic molecules. The absolute average deviations (in Kelvin) are reported in Table 1 for binary systems and comparisons between experiments and predictions are reported in Figs. 1 and 2a and 2b. As expected, large deviations can be found with

Raoult's law for highly non ideal systems, such as mixtures of polar (alcohols) and nonpolar (alkane) systems. This confirms that flash points are directly related to the thermodynamic properties and the phase behavior of mixtures, especially to the volatility of compounds. The COSMO-SAC and COSMO-SAC dsp models combined with the CN model, denoted as CN-COSMO-SAC and CN-COSMO-SAC dsp, respectively, both lead to accurate predictions of flash points. It is found that the COSMO-SAC dsp model gives better predictions compared to the original COSMO-SAC for binary systems: the average absolute deviation (AAD) obtained for a broad variety of binary systems is 2.7 for COSMO-SAC dsp, 3.3 for COSMO-SAC and 7.2 for the ideal solution model (Table 2). This was expected as the CN-COSMO-SAC dsp model is more recent and has more universal parameters (the dispersion term involves more universal parameters related to the types of atoms on the molecules). However, for some systems such as the methanol + trimethylpentane binary mixture, the COSMO-SAC dsp model overestimates the non-ideality of the solution, and the flash points are underpredicted: as shown in Fig. 3, the activity coefficients in the mixture methanol+trimethylpentane, predicted at 298.15K by COSMO-SAC dsp, are larger than those predicted by COSMO-SAC. For this binary mixture, a liquid-liquid immiscibility is predicted by the COSMO-SAC dsp model, which is not the case for the other models. The fully predictive CN-COSMO-SAC dsp model is particularly accurate for mixture of ethyl esters and ethanol, as shown in Fig 2, and the predictions are similar to those obtained by Carareto et al. [22], who adjusted NRTL parameters directly to the flash point data.

3.2. Multicomponent systems

Multicomponent systems under consideration here are fuels (ex-fossil, ex-biomass or both) but it can be extended to any kind of mixtures made of combustible components. Complex multicomponent mixtures are preferred. However, for such calculations detailed compositions are needed and these details are not always provided. One can present experimental studies about the effect of a given molecule added to a given biodiesel without reporting the details of the composition of the said biodiesel.

3.2.1. Gasoline

Gasoline is used as a car fuel for spark-ignition internal combustion engines. Its flash point is generally very low, generally around 233K, and it is always below 253K. The flashpoint depends on the composition which varies as the fuel is obtained from oil distillation. Guibet [23] reported the detailed composition of a US gasoline which contains 112 compounds and 11.6% in weight of the oxygenated molecule MTBE (Methyl Tertiary-Butyl Ether). The flash point for this fuel predicted by the CN-COSMO-SAC model is equal to 241.25K, which is consistent with the experimental data reported just above. Without MTBE the predicted flash point of the fuel is equal to 241.65K. The predicted flash point of pure MTBE is 241.2K, which is close to the experimental value of 241.15K reported in the MSDSs (Material Safety Data Sheets) of Sigma Aldrich. Another experimental value for pure MTBE , equal to 245.15K, was reported in the ICSCs (International Chemical Safety Cards). As a result, the presence of MTBE in the US gasoline does not affect significantly the flash point. The composition of this studied US gasoline is reported in the supplementary materials (Table A1). Using the same hydrocarbon composition of this fuel, we have predicted the influence of the amount of MTBE added to the full on the flash point. We also considered ethanol, ETBE (Ethyl Tertiary-Butyl Ether), TAEE (Tertiary amyl ethyl ether), and DIPE (diisopropylether) as alternative anti-knock agents. The CN-COSMO-SAC model predicts that an increase of MTBE concentration leads to a decrease of the flash point of the fuel. However, the inverse behavior is observed for all the other additives (Figure 4).

3.2.2. Jet fuels

Jet fuel is a type of aviation fuel, composed of hydrocarbons. Nine jet fuels are considered in this study (see Table 2): jets 1 to 6 are composed of ortho-xylene, trans-decahydronaphthalene, n-dodecane, n-hexadecane and n-octane, while jets 7 to 9 are composed n-decane, n-dodecane and n-tetradecane (see Table A2 in the supplementary materials). All thermodynamic models combined with the CN model lead to rather satisfactory and similar predictions, even the ideal solution model (Raoult's law). COSMO SAC and COSMO-SAC dsp are however a factor 2 better than Raoult's law. This shows that jet fuels behave almost as ideal solutions (activity coefficients close to 1). The most accurate predictions are obtained with the CN + COSMO-SAC model. The predicted flash points are very close to the experimental data (Table 2): the AAD is about 1°C with the CN-COSMO-SAC model. Furthermore, the low bias (less than 0.1°C) shows that the flash points are not systematically overpredicted or underpredicted.

3.2.3. Diesel fuels

Diesel fuels correspond to any liquid fuel used in diesel engines, which are compression-ignition internal combustion engines. Six mixtures representative of diesel fuels are taken into account here. The considered diesel fuels contain both alkanes and methyl esters (biofuels). Like for jet fuels, all three models give very similar predictions (Table 3), which are close to the experimental values. Again, diesel fuels behave as ideal solutions and the CN model combined with Raoult's law give rather good predictions of flash points. Better predictions are obtained with CN-COSMO-SAC and CN-COSMO-SAC dsp: both models give the same predictions of flash points because they provide rather similar activity coefficients for these systems. The compositions of the diesel fuels are reported in the supplementary materials (Table A4).

3.2.4. Biodiesels

Biodiesels are renewable fuels that can be manufactured from vegetable oils, animal fats, or recycled restaurant grease. They are used in diesel vehicles. Six biodiesel fuels are considered here. Their compositions are reported in the supplementary materials (Table A5). The properties of most components of biodiesels can be found in the DIPPR database [24] (simulis thermodynamics® software). For ethyl esters we readjusted the parameters of vapor pressure correlation to the available experimental data taken from the literature. These parameters are reported in the Supplementary materials (table A7). All models predict about the same values for flash points of a given biodiesel, as shown in Table 4. This is also to due to the fact that the components of biodiesels are very similar in nature, so biodiesels behave as ideal solutions. The deviation between the models and the experimental data are much larger compared to those obtained for the other fuels. Experimental data reported in Table 4 result from the average of numerous data from literature sources. Feedstock may be not all the time identical even if they were made with the same kind of oil by using the same process. This leads to very large experimental uncertainties for the measurements of the biodiesel flash points especially for mixtures #2, #3, #4 and #5 for which uncertainties of around 20 degrees are reported. Furthermore, the flash points of biodiesels are higher than the flash points of other

fuels, and it is well known that the experimental uncertainties (both absolute and relative) increase with the flash point value. Moreover, for the highest flash point reported, side reactions may be observed in the liquid phase. In that case, the vapor pressure above the liquid is not the one believed or predicted. However, despite the questionable quality of the fuels our predictions are generally within the experimental uncertainties (Table 4). It is remarkable that the best agreements are obtained for mixtures #1 and #6 for which the experimental uncertainties are the lowest.

It has been observed that a small presence of alcohol in biodiesels can dramatically decrease the flash point of the fuel [22, 25]. Boog et al. [25] also observed that the flash points of biodiesels in the presence of a given amount of methanol do not depend much on the origin of the oil (i.e. the methyl ester composition), while the flash points of biodiesels without methanol depend on the methyl ester distribution. We have predicted the flash point of biodiesel made from sunflower oil in the presence of methanol. Methanol is used in the esterification process and may contaminate the biodiesel obtained. The predictions have been compared with the experimental flash points measured by Boog et al. [25]. Note that the composition of the sunflower biodiesel used in Boog's studies was not reported. However, as shown by Bamboye and Hansen [26], the composition of biodiesel does not vary much as long as the origin of the oil (plant) is the same, although the biodiesel composition obviously varies with soil nature, weather conditions and plant species. We used biodiesel 6 composition as it is also a biodiesel made from sunflower oil. Such biodiesels mainly contain linoleate and oleate esters. The CN model combined with Raoult's law (CN-Raoult) gives rather poor predictions (see Fig. 5): this is due to the fact that mixtures of methanol + biodiesels are highly non-ideal solutions. Moreover, the presence of a very small of methanol gives rise to a dramatic drop of the flash point. The CN-COSMO-SAC dsp model is much closer to the experimental data: the CN-COSMO-SAC overestimates the data while the CN-COSMO-SAC dsp underpredicts them. The COSMO-SAC dsp tends to overestimate the non-ideality of the solution, as shown before for some binary mixtures, while the COSMO-SAC model underestimates the non-ideality. The CN-COSMO-SAC-dsp model is also particularly accurate for mixtures of ethyl esters and ethanol (Figs. 2c and 2d).

4. Conclusion

We have used the Catoire-Naudet (CN) model to predict flash points of multicomponent mixtures including gasoline, jet, diesel and biodiesel fuels. The CN model has been combined with several predictive thermodynamic models for mixtures. It is confirmed that the non-ideal behavior of the liquid mixture directly affects flash point temperatures: the use of COSMO-SAC and COSMO-SAC dsp predict models leads to much better predictions compared to Raoult's law, apart from mixtures of hydrocarbons that behave as ideal solutions.

The CN-COSMO-SAC dsp predictive model is in very good agreement with experimental flash points of biodiel + alcohol mixtures. The model can predict the experimental observation that a small content of alcohols (such as methanol) dramatically decreases the flash point of a fuel. Since the flash point is about the same for any kind of biodiesels mixed with a given amount of methanol or ethanol, it can be used to characterize the alcohol content. This behavior is well predicted by the CN-COSMO-SAC dsp model.

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Table 1. Absolute average deviations (AAD) between the predicted flash points of binary mixtures and experimental data. Comparison between three thermodynamic models combined with the CN approach: Raoult's law, COSMO-SAC [15] and COSMO-SAC dsp [16]. AAD stands for Average Absolute Deviation.

Binary mixture		Ref. data	Raoult'slaw	COSMO-SAC	COSMO-SAC dsp
Ethanol	ethyl decanoate	[22]	8.4	3.2	2.9
Ethanol	ethyldodecanoate	[22]	10.7	4.9	1.5
Ethanol	ethyltetradecanoate	[22]	11.2	4.7	1.4
Ethanol	ethylhexadecanoate	[22]	15.3	5.3	5.0
Ethanol	ethyloleate	[22]	13.2	8.1	3.3
Ethanol	ethyllinoleate	[22]	15.9	9.4	4.8
Ethanol	n-tetradecane	[6]	20.1	5.3	1.9
3-methyl-1-butanol	isopentylacetate	[27]	2.4	4.7	5.5
methanol	methylacetate	[5]	3.3	2.0	3.0
methanol	n-octane	[6]	7.7	3.2	7.4
methylacetate	methyl acrylate	[27]	5.8	5.6	5.7
n-heptane	ethylbenzene	[28]	3.7	2.0	1.9
n-heptane	m-xylene	[28]	1.4	0.8	0.9
n-heptane	o-xylene	[28]	1.5	1.2	1.4
methanol	2,2,4-trimethylpentane	[4]	10.4	2.3	3.6
n-octane	isopropanol	[27]	4.7	1.1	2.5
n-octane	2-butanol	[27]	4.5	1.2	0.5
n-octane	1-butanol	[27]	7.8	1.6	0.3
n-octane	ethanol	[27]	6.2	1.1	1.7
n-octane	n-heptane	[5]	1.8	1.8	1.8
tributyl phosphate	n-dodecane	[29]	6.3	4.0	3.9
Toluene	2,2,4-trimethylpentane	[4]	1.8	0.6	0.7
Acetone	n-decane	[6]	9.8	4.5	3.9
methanol	acetone	[4]	3.0	2.2	1.9
1-butanol	2-butanol	[30]	1.1	1.1	1.1
AAD over all binary mixtures/K			7.2	3.3	2.7

Table 2. Comparison between experimental [9] and predicted flash points (in Kelvin) for 9 jet fuels with Raoult's law and COSMO like models. The AAD (Average Absolute Deviation) and BIAS (Average Deviation) are also reported for all models. The compositions of jet fuels are reported in the supplementary materials (Tables A2 and A3).

Jet fuels	Experimental	Raoult'slaw	COSMO-SAC	COSMO-SAC dsp
# 1	326.0	325.2	322.9	322.6
# 2	322.5	325.3	322.2	321.8
# 3	294.5	295.1	294.3	294.3
# 4	313.0	317.7	316.7	316.6
# 5	312.5	314.4	312.1	312.0
# 6	304.5	306.7	304.8	304.7
# 7	338.5	337.9	338.1	338.1
# 8	330..0	330.6	330.7	330.7
# 9	345.0	344.9	345.3	345.3
BIAS		1.0	0.1	0.0
AAD		1.8	1.0	1.1

Table 3. Comparison between experimental [9] and predicted flash points (in Kelvin) for 6 diesel fuels with Raoult's law and COSMO models. The AAD (Average Absolute Deviation) and BIAS are also reported for all models. The compositions of these fuels are given in the supplementary materials (Table A4).

Diesel fuel	Experimental	Raoult's law	COSMO-SAC	COSMO-SAC dsp
# 1	337.0	338.9	339.1	339.1
# 2	346.5	349.0	349.0	349.0
# 3	329.0	330.9	331.1	331.1
# 4	358.5	354.8	355.1	355.1
# 5	350.5	359.5	358.3	358.3
# 6	345.5	347.2	347.5	347.5
BIAS		2.2	2.2	2.2
AAD		3.4	3.3	3.3

Table 4. Comparison between experimental [31] and predicted flash point (in Kelvin) for 6 biodiesel fuels with Raoult's law and COSMO models. The AAD (Average Absolute Deviation) and BIAS are also reported for all models. The compositions of these fuels are given in the supplementary materials (Table A5). #1 is made from coconut oil. #2 is made from Jatropha oil. #3 is made from palm oil. #4 is made from rapeseed oil. #5 is made from soybean oil. #6 is made from sunflower oil.

Biodiesel fuel	Experimental	Raoult's law	COSMO-SAC	COSMO-SAC dsp
# 1	386 ± 6	394.4	394.6	394.6
# 2	425 ± 20	446.8	446.7	446.7
# 3	436 ± 17	420.8	420.8	420.8
# 4	442 ± 16	425.3	425.4	425.4
# 5	432 ± 18	448.7	448.7	448.7
# 6	448 ± 9	449.7	449.8	449.8
BIAS		2.8	2.8	2.8
AAD		13.4	13.4	13.4

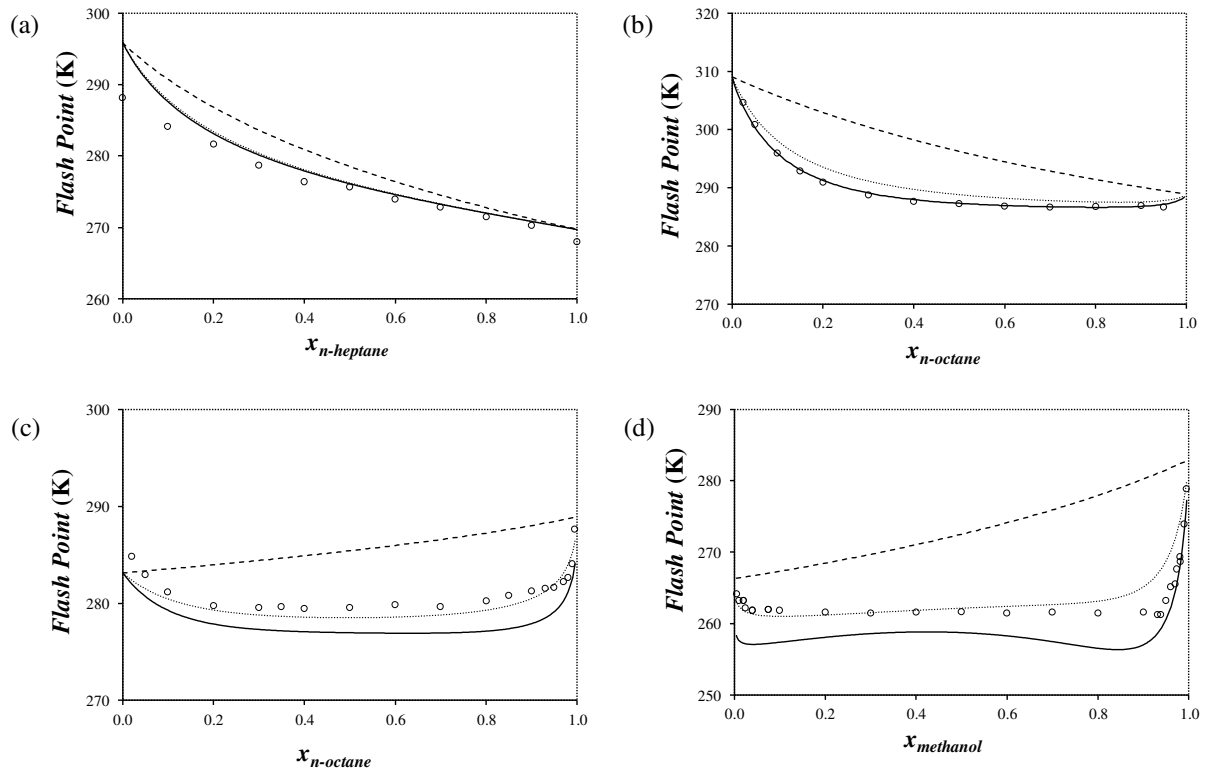


Figure 1. Flash points of binary mixtures (a) n-heptane+ethylbenzene; (b) n-octane + n-butanol; (c) n-octane+isopropanol; (d) methanol+trimethylpentane. Comparison between experimental data[27] (symbols) and the Catoire-Naudet model combined with Raoult's law (dashed curves), COSMO-SAC (dotted curves) and COSMO-SAC dsp (solid curves).

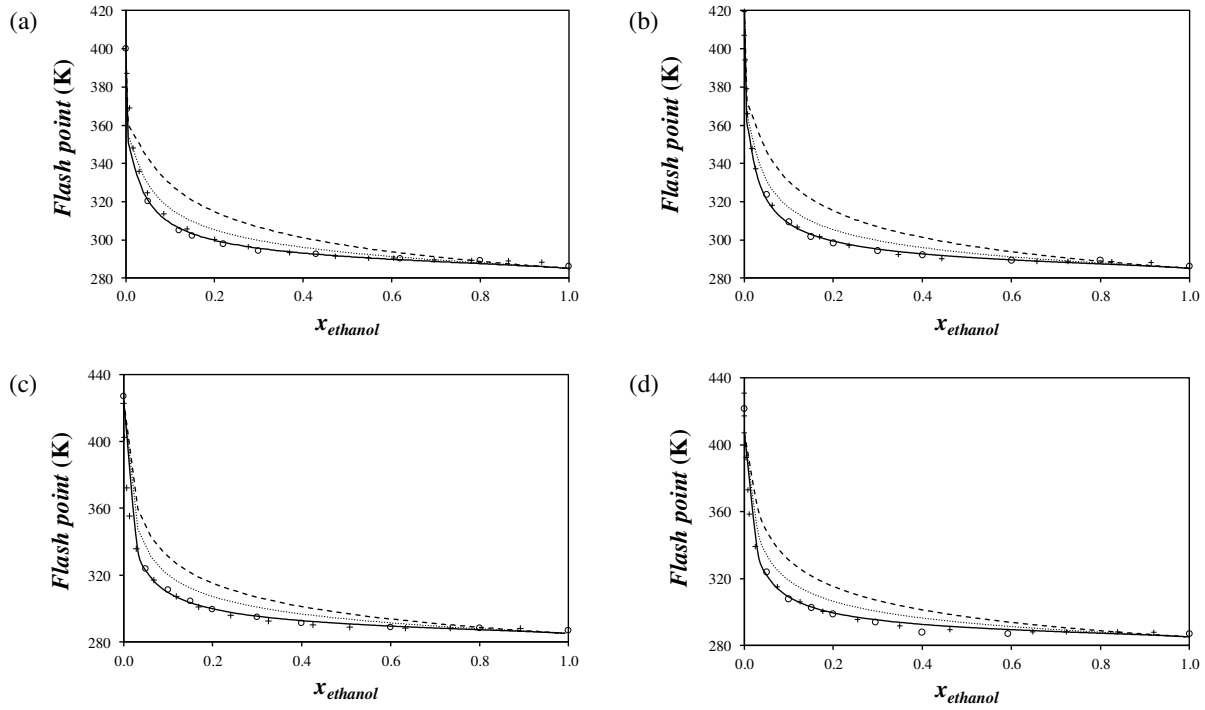


Figure 2. Flash points of ethanol + ethyl ester mixtures (a) ethanol + ethyl laurate (dodecanoate), (b) ethanol + ethyl myristate (tetradecanoate), (c) ethanol + ethyl oleate (technical grade), (d) ethanol + ethyl biodiesel made from palm oil. The compositions of the palm oil biodiesel and technical grade ethyl oleate are provided in the supplementary materials (Table A6). Comparison between experimental data [22] (circles) and the Catoire-Naudet model combined with Raoult's law (dashed curves), COSMO-SAC (dotted curves) and COSMO-SAC dsp (solid curves). The pluses (+) correspond to the model of Carareto et al. [22].

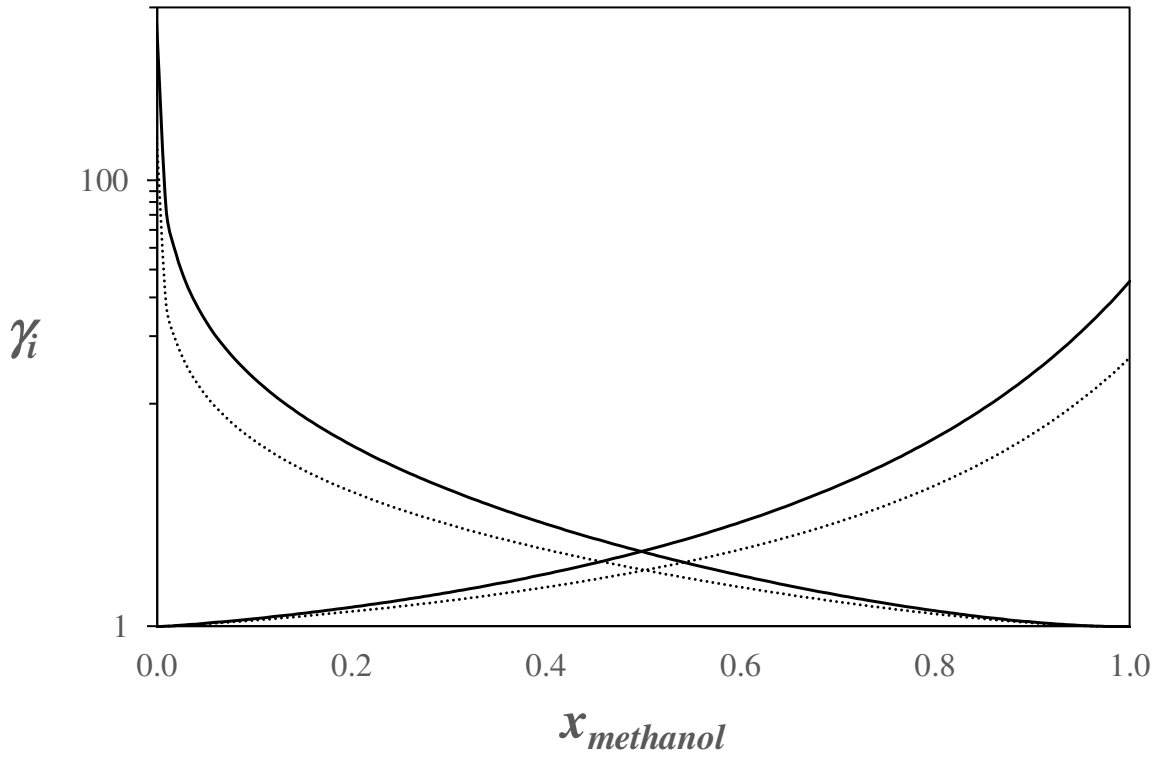


Figure 3. Activity coefficients of the compounds in the binary mixture methanol + 2,2,4 trimethylpentane, predicted at T=298.15K with the COSMO-SAC (dotted curves) and COSMO-SAC dsp (solid curves) models.

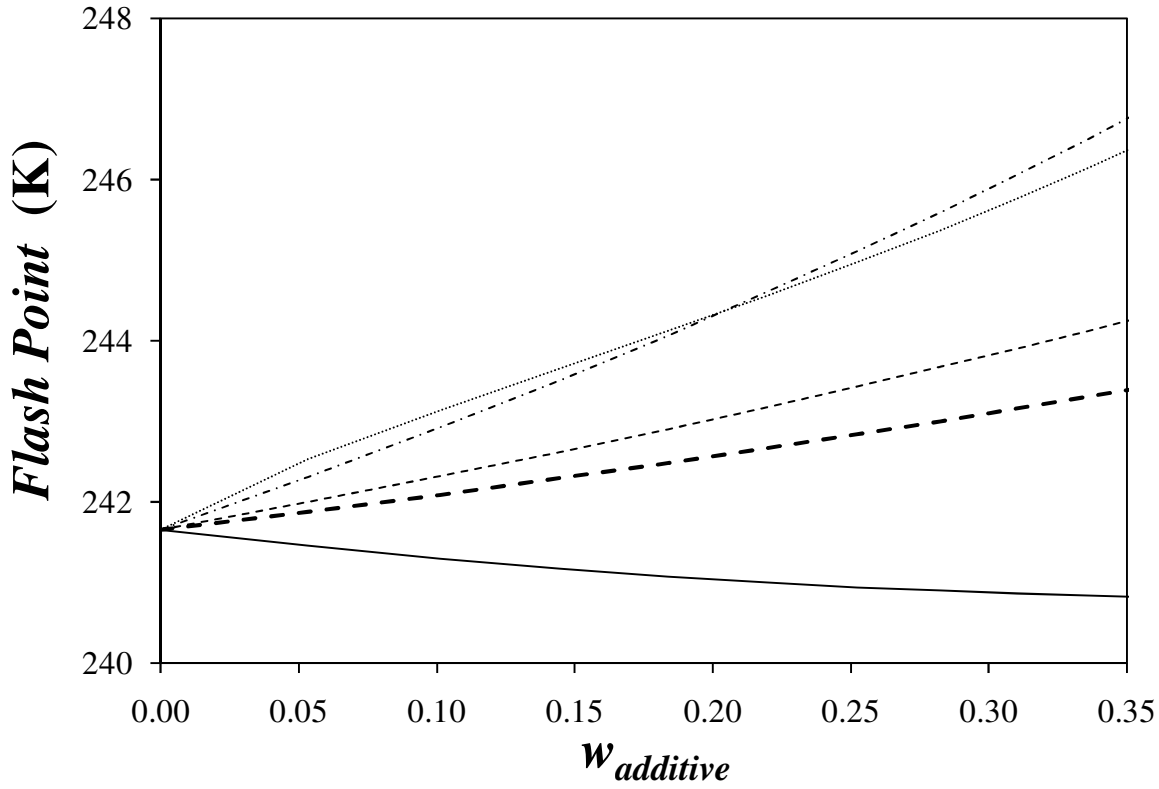


Figure 4. Effect of the composition (weight fraction) of various additives on the flash point of a US gasoline fuel (predictions with the CN-COSMO-SAC model). Solid line: MTBE; dotted line: ethanol; thin dashed line: ETBE; thick dashed line: DIPE; dash-dotted line: TAEE. The composition of the US gasoline fuel is provided in the suppTapez une équation ici.lementary materials (the case $w_{additive}$ =0 corresponds to the US fuel composition without MTBE).

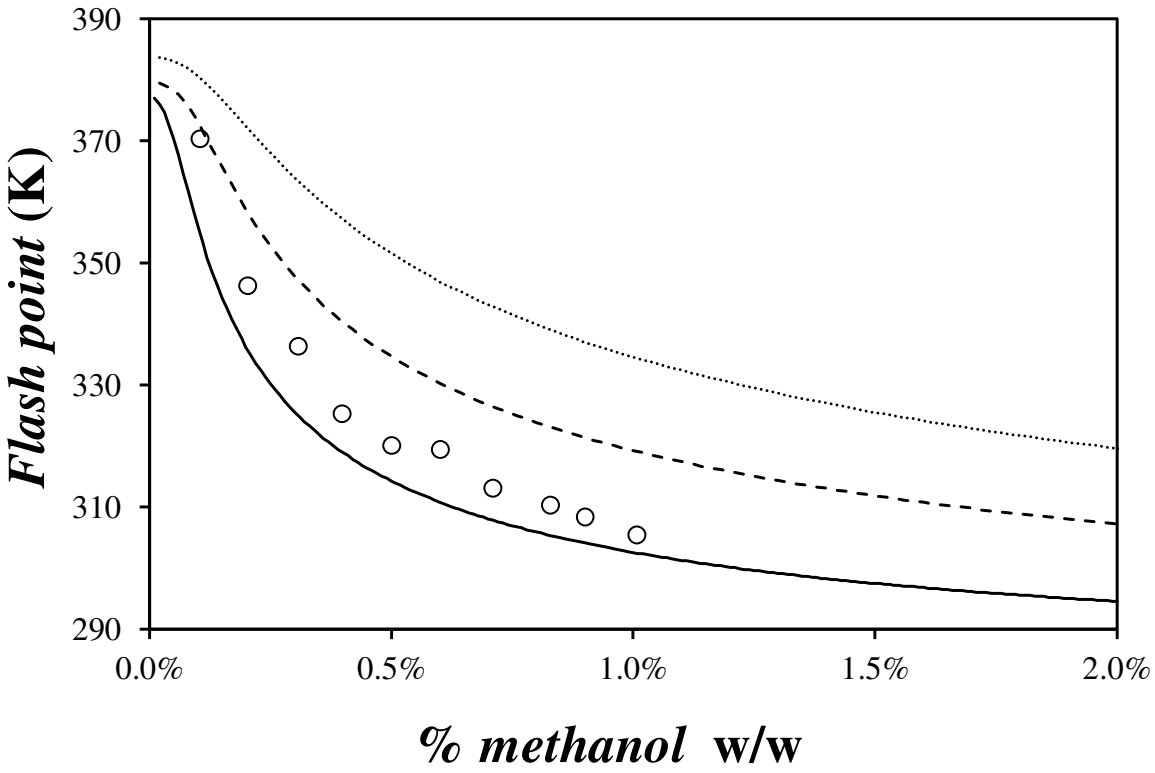
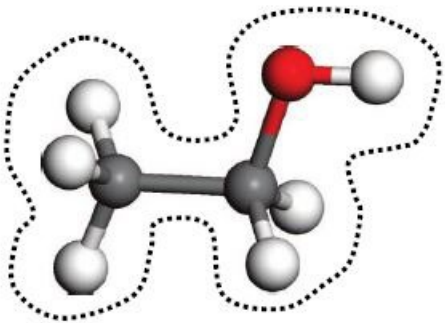


Figure 5. Predictions of the flash points of sunflower biodiesel+ methanol mixtures, with three models: CN-Raoult (dotted line), CN-COSMO-SAC (dashed line), and CN-COSMO-SAC dsp (solid line). The circles correspond to the experimental flash points of Boog et al. [25] and the lines were calculated by considering the composition of biodiesel 6 (biodiesel made from sunflower oil).

Prediction of Flash points of mixtures from ab intio calculation



COSMO Calculation

