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Prediction of the octane number: a Bayesian pseudo-component method

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Abstract

The energy transition leads to the development of unconventional liquid fuels. Unconventional liquid fuels are produced at a small scale so they are produced with a limited budget and they must be characterized at a cheap price. When liquid fuels are burned in piston engines, they are characterized by the Research Octane Number (RON) and the Motor Octane Number (MON). As the measurement of the RON and the MON is expensive, a cheaper alternative, like the pseudo-component method, is sought. Nevertheless, this method was only developed for the RON, it is not applicable for complex fuels with olefin and oxygenates, and its uncertainty has not been characterized. Moreover, it does not differentiate the isomers. For instance, the iso-paraffins

are considered as a blend of 2-methyl-alkane, 3-methyl-alkane, 2,2-dimethyl-alkane and 2,3-dimethyl-alkane in equal proportions. The authors address the limitations of the pseudo-component method using a Bayesian approach. The validity of the method is demonstrated for three gasoline blendstocks mixed with five oxygenated molecules: 1-propanol, 2-propanol, 1-butanol, 2-butanol and 2-methyl-1-propanol. As a result, the octane numbers are predicted within the theoretical uncertainty bounds and with less than 2% of error.

Introduction

The recent diversification of unconventional liquid fuels is favoured by four factors: the penetration of biomass,[1–3] the recycling of wastes,[4–8] new production technologies,[9–12] and the development of advanced combustion modes.[13–16] In the current paper, we focus on gasoline blendstocks mixed with oxygenated molecules. The oxygenated molecule can be composed of up to four carbon atoms and it can be produced via fermentation or gasification.[17]

Unconventional fuels show unusual properties that depends on the production process. The fuel properties vary from one production plant to another, so they must be monitored.

Among all the fuel properties, the research octane number (RON) and the motor octane number (MON) are fundamental. A minimal RON and MON are required to avoid knocking and to optimize the combustion efficiency. The RON and the MON test methods are expensive for a decentralized or small production plant as well as for a project in the design phase because they require a cooperative fuel research (CFR) engine, relatively costly products (n–heptane and iso–octane) and high level of qualification.[18,19] Nevertheless, unconventional fuels are produced at a small scale, so they are produced with a limited budget and they must be characterized at a cheap price. Moreover, the RON and the MON tests require 1L of material which may not be available for fuels in early research stage.

RON and MON measurements can be replaced by one of the many predicting methods available. They differ one another by the input quantities to run the model. The input quantities can either be chemical properties – nuclear magnetic resonance (NMR) data,[20,21] chemical fractions,[22,23] chromatographic data[24,25] – or physical properties – distillation curves,[23,26] ignition delay time.[16,27]

Among the different methods, the pseudocomponent (PC) method is based on the fractions of the hydrocarbon class (n-paraffin, iso-paraffin, naphthene, aromatic) and the distillation cut points. This method, was summarized by Riazi:[23] a PC is characterized by a boiling point which is equal to the mean average boiling point (MeABP) of a fuel. The method attributes a PC to each hydrocarbon class.

While the pseudo-component method relies on simple input quantities, it has several limitations.

- It does not cover fuels with olefin and oxygenated molecules so it cannot be applied to all of the unconventional fuels,[28–30] hence the method lacks generality.
- Its uncertainty has never been studied.
- It does not differentiate the isomers among each hydrocarbon class. For instance, the iso-paraffins are considered as a blend of 2-methyl-alkane, 3-methyl-alkane, 2,2-dimethyl-alkane and 2,3-dimethyl-alkane in equal proportions.
- It was only presented for the RON, so, no model exist to predict the MON with PCs.

To address these limitations, the current paper embeds an inductive probabilistic approach based on a Bayesian tuning. This kind of approach has already been used to relate bulk properties and the molecular composition.[31]

The pseudo-component method was used in recent publications. For instance, Nguyen et al.[32] proposed a model to predict the viscosity where n-alkane mixtures are represented by a single pseudo-component. Xu et al.[33] predicted binary-interaction parameters of cubic equation state for petroleum fluids represented by pseudo-components. Ramos-Pallares et al.[34] predicted the thermal conductivity of oils characterized into pseudocomponents. Liu et al.[8] extended the pseudocomponent representation to characterize the molecular information of pseudo-components. Bulk properties, including the octane numbers, were accurately estimated even if olefin constituted the fuel. Nevertheless, this method requires a deep characterization of the petroleum fraction as a pseudo-component is characterized every 20K. This requires the PIONA analysis of the petroleum product every 20K.

The aim of the current paper is to formulate a model applicable for gasoline blendstocks mixed with oxygenated molecules and which is able to predict the RON and the MON. The goal includes the characterization of the uncertainty.

After having described the new Bayesian PC method, the results are discussed and the conclusions are drawn in the last section.

Method

The method section starts with an overview of the original PC method. The original PC method summarized by Riazi attributes a PC to each hydrocarbon class.[23] A PC is characterized by a boiling point which is equal to the MeABP of a fuel. The MeABP depends on the distillation cut points:

$$\mathrm{MeABP} = \mathrm{VABP} - \Delta \mathrm{T_{Me}} \tag{1}$$

with the volume average boiling point (VABP):

$$\mathrm{VABP} = \frac{\mathrm{T_{10}} + \mathrm{T_{30}} + \mathrm{T_{50}} + \mathrm{T_{70}} + \mathrm{T_{90}}}{5}, \tag{2}$$

$\mathrm{T_{XX}}$ is the temperature at which xx% of the fuel is evaporated and the correction temperature is defined by:[23]

$$\ln(\Delta \mathrm{T_{Me}}) = -1.53181 - 0.0128(\mathrm{VABP} - 273.15)^{0.6667} + 3.646064\mathrm{SL}^{0.333} \tag{3}$$

with SL the 10–90 slope:

$$\mathrm{SL} = \frac{\mathrm{T_{90}} - \mathrm{T_{10}}}{80}. \tag{4}$$

An important assumption in the PC method is that the RON of each PC, $\mathrm{RON_{pc}}$, correlates with the MeABP of the fuel. The law between $\mathrm{RON_{pc}}$ and MeABP is based on the regression between the boiling point and the octane numbers of pure molecules. In the original PC method, the database of pure molecules does not take the isomer into account. Specifically, the aromatics are considered as n-alkylbenzenes, the naphthene as n-

alkylcyclopentanes and the iso-paraffins as the average between 2-methyl-alkanes, 3-methyl-alkanes, 2,2-dimethylalkanes and 2,3-dimethylalkanes. In the current study, we introduce a correcting factor that modifies the octane number of the PC according to the type of isomer. In the original PC method, a linear blending law by volume relates the RON of the fuel of interest with the RON of each PC:

$$\mathrm{RON}^{*}_{\mathrm{Riazi}} = \left[\mathbf{y_{Riazi}}\right]^{\intercal} \times \mathbf{RON_{pc}}, \tag{5}$$

where $\mathbf{y_{Riazi}}$ is the vector of the volume fractions of the PCs. These volume fractions are equal to the volume fractions of the hydrocarbon classes in the fuel and can be measured by gas chromatography (GC), comprehensive two-dimensional gas chromatography (GC × GC) or with a reformulyzer. Note that in the current paper, the letters in bold refer to vectors and matrices and "×" is the Cartesian product.

Table 1: Properties of the 45 BOB-Ox fuels used to train and to test the new method.

Property	Min	Mean	Max
30 Training fuels			
RON	85.8	91.7	99.2
MON	80.8	83.9	88.9
MeABP (°C)	79.3	89.9	101.5
Saturate (%)	57.3	66.0	74.0
Olefin (%)	2.1	4.6	7.8
Aromatic (%)	16.3	21.0	28.9
Oxygenate (%)	2.9	8.4	15.3
15 Test fuels			
RON	86.9	92.0	98.6
MON	81.0	84.0	88.6
MeABP (°C)	80.5	89.4	99.5
Saturate (%)	59.8	64.9	70.2
Olefin (%)	2.2	4.5	7.4
Aromatic (%)	17.0	20.7	27.4
Oxygenate (%)	7.8	9.9	11.6

Contrary to the one compiled by Riazi, the proposed method is developed for fuels with olefins and oxygenates. The study of Christensen et al.,[17] who highlighted the properties

of 77 fuels, offers a lot of experimental data to develop the method. Only 45 out of the 77 fuel are selected. This way of proceeding allows to obtain an equal representation of each oxygenated molecule, thus, achieving a more accurate model. Specifically, for these 45 fuels, three blendstocks for oxygenate blending (BOB) are mixed at three different proportions – at a low (3 to 4.1%), an intermediate (7.9 to 11.6%) and at a high volume fractions (10.6 to 15.3%) – with five oxygenated molecules – 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol. The 45 fuels are divided in a training set and in a test set. The training set is composed of the low and the high fractions (30 fuels) and the test set is composed of the intermediate fractions (15 fuels). Thus, the model is created with the framing fractions of oxygenates and validated with a fraction which is in between. The properties of the studied BOB-Ox fuels are reported in Table 1.

The method proposed here, based on Bayes' law, allows to assess the uncertainty, which was not possible with the original PC method. The original Equation 6 is modified with the expectancy of a correcting factor $\mathrm{E}(\mathbf{K})$ which is calculated applying Bayes' law. The correcting factor corrects the octane number of each PC according to the type of isomer in the corresponding hydrocarbon class. With the Bayesian PC method, an unbiased estimator of the octane number (ON) is proposed as:

$$\mathrm{ON}^{*} = [\mathbf{y}]^{\mathsf{T}} \times \left([\mathrm{E}(\mathbf{K}) \circ \mathbf{ON_{pc}}] \right) + \sigma^{*}, \tag{6}$$

with σ^{*} the random error, i.e. an unpredictable error due to the measurement method, and "$\circ$" the Hadamard product.

The modifications adopted to the original equation reported by Riazi[23] are described thereafter.

- $\mathbf{y}$ is the vector of the volume fractions of the four PCs (saturate, olefin, aromatic, oxygenate). Three hydrocarbon classes (n-paraffin, iso-paraffin, naphthene) are merged in a single hydrocarbon class (saturate) because the saturate class constitutes the

training data reported by Christensen et al..[17] Moreover, the olefin and the oxygenate hydrocarbon class are included.

- $\mathbf{ON_{pc}}$ is the vector composed of the octane numbers of the four PCs. The correlations between $\mathrm{ON_{pc}}$ and the MeABP are modified to include more isomers than in the original PC method:

$$\mathrm{ON_{pc}} = \mathbf{r}^{\intercal} \times \mathbf{T}, \tag{7}$$

with

$$\mathbf{T} = \begin{bmatrix} & 1 & \\ & \vdots & \\ \mathrm{MeABP} & & \end{bmatrix}. \tag{8}$$

The vector $\mathbf{r}$ is composed of the linear regression coefficients between the boiling points and the octane numbers of pure molecules from large databases.[17,23,35–38] These databases were completed by measuring the octane numbers of pentan–3–one and heptan–3–one. Relying on ketones as well as alcohol allowed us to propose a general methodology that can be applied to another type of fuel, for generating another model. $\mathbf{r}$ takes into account the evolution of the octane number depending on the boiling point. Nevertheless, the uncertainty on $\mathbf{r}$ does not need to be estimated to calculate the final uncertainty, according to Equation 12. The boiling points and the octane numbers are available in the Supporting Information and $\mathbf{r}$ is reported in Table 2.

- In equation 6, $\mathrm{E}(\mathbf{K})$ are the expectancies of the correcting factors $\mathbf{K}$ introduced by Bayes' law. The Bayesian method that calibrates the probability density functions (PDFs) of $\mathbf{K}$ is inspired by the work of Josephson et al.[39] With this method, we compute the estimated octane number with an initial guess and we compare the estimation to the measurement. The better is the match between the estimation and the measurement, the better is the initial guess. When the matching is satisfactory, the initial guess is set as being the right value for the parameters of the model. Below are summarized

Table 2: Coefficients (**r**) required for Equation 7. The coefficients were obtained with a linear regression between the octane number and the boiling points of pure molecules from the literature.[17,23,35–38] Additional octane number measurements were also lead for pentan–3–one and heptan–3–one (available in the Supporting Information).

	Saturate	Olefin	Aromatic	Oxygenate
		RON		
Intercept	103.07	112.89	142.14	108.80
Slope	-0.29143	-0.22733	-0.19927	-0.13568
		MON		
Intercept	9.4256	90.794	131.09	91.299
Slope	-0.24124	-0.12941	-0.19675	-0.08470

the calculation steps with a focus on how the work of Josephson et al. is adopted to the current study. The main concepts of the methodology used in the current paper are explained in depth in the paper of Josephson et al.[39]

According to Bayes' law, the conditional knowledge of the experimental octane number **ON** allows to estimate the correcting factor. When **ON** is known, the PDF of the correcting factor K_i, $f_{K_i|\mathbf{ON}}(K_i|\mathbf{ON})$, for the hydrocarbon class i is given by the following proportionality:

$$f_{K_i|\mathbf{ON}}(K_i|\mathbf{ON}) \propto f_{K_i}(K_i) f_{\mathbf{ON}|\mathbf{K}}(\mathbf{ON}|\mathbf{K}). \quad (9)$$

The prior PDF, $f_{K_i}(K_i)$, represents an initial knowledge of the correcting factor. The prior gives the distribution of K_i before any analysis is realized. The distribution of the PDF and the limits where K_i is studied must be defined. As K_i is unknown, we chose an uniform distribution to avoid any preferred choice in the studied range.[39] Thus, we chose a rectangular distribution so that the correcting factor K_i has equal probability across the studied range. Then, the limits where K_i is studied must be defined. As K_i is a priori unknown, the PDF called likelihood ($f_{\mathbf{ON}|\mathbf{K}}(\mathbf{ON}|\mathbf{K})$) informed us on how far the limits of K_i were from their true value. The likelihood depends on the values of the correcting factors. Thus, changing the limits of K_i changes the shape of the likelihood.

When K_i is defined in a wrong range, the value of likelihood tends towards zero. When the prior is defined in the right range, the likelihood tends towards a Gaussian shape because of Equations 10 and 11. Thus, we changed the limits of each K_i iteratively by trial-and-error until obtaining a well-defined Gaussian shape that correctly described the likelihood. We discretized each K_i simultaneously with a latin hypercube sampling (LHS) procedure and 20 000 samples to balance RAM memory and resolution when visualizing the likelihood.

The likelihood $f_{\mathbf{ON}|\mathbf{K}}(\mathbf{ON}|\mathbf{K})$ represents the probability to get the experimental octane numbers **ON** with the correcting factors **K**. Concretely, the probability of the likelihood is reduced when the octane number calculated with the chosen parameters does not correspond to experiments. The likelihood is given by the following equation which combines the probabilities $p\left(\mathrm{ON}|\mathrm{ON}^*(\mathbf{K})\right)$ for all the experimental ON:

$$f_{\mathbf{ON}|\mathbf{K}}(\mathbf{ON}|\mathbf{K}) = \prod^{n_{exp}} p\left(\mathrm{ON}|\mathrm{ON}^*(\mathbf{K})\right). \tag{10}$$

$p\left(\mathrm{ON}|\mathrm{ON}^*(\mathbf{K})\right)$ is the probability of the measured octane number when the estimated octane numbers are defined. The estimated octane numbers are randomly distributed because the parameters **K** were randomly sampled with a LHS procedure. Thus, the octane numbers estimated with the sampled **K** follow a Gaussian shape. This Gaussian is centred at a value equal to the measured octane number when the parameters **K** are correctly chosen.

$$p\left(\mathrm{ON}|\mathrm{ON}^*(\mathbf{K})\right) = \frac{1}{\sqrt{2\pi\sigma^2}}\exp\left(-\frac{\left(\mathrm{ON}-\mathrm{ON}^*(\mathbf{K})\right)^2}{2\,\sigma}\right) \tag{11}$$

Equation 11 gives the probability of getting a measured octane number relatively to its estimation. This probability depends on the Gaussian shape, i.e. on the variance σ. The estimation being intrinsically unbiased, this probability depends only on the precision of the experimental measurements. Consequently, the Gaussian shape, i.e. the variance σ, depends on the reproducibility of the ON measurement.

The reproducibility of the ON measurement was published in the ASTM D2699[18] (RON), ASTM D2700[19] (MON) and in The Precision of knock rating – 1936-1938[40] for RON equal to 50, 80, from 90 to 100, 101, 102, 103 and from 104 to 108 and for MON from 80 to 90 and from 102 to 103. The uncertainty has never been characterized in the other ranges so we adopted the worst uncertainty of the surroundings octane numbers. Moreover, we adopted the same reproducibility for low and high MON (below 80 and above 103) than the RON. The uncertainties are summarized in Table 3.

Table 3: Confidence interval of the experimental octane numbers (Reproducibility). The level of confidence of the measured octane number is given in the interval = ON ± half-width.

ON	Half-width	Confidence
	RON	
]0 - 50[	2	95
50	2	99.9
]50 - 90[	2	95
[90 - 100]	0.7	95
]100 - 101]	1	95
]101 - 102]	1.4	95
]102 - 103]	1.7	95
]103 - 104]	2	95
]104 - 120]	3.5	95
	MON	
]0 - 80[	2	95
[80 - 90]	0.9	95
]90 - 103]	2	95
]103 - 120]	3.5	95

The following procedure explains how to create a new model.

- Initialize the minimal and the maximal values of the correcting factors with a starting guess.

- Create samples for the correcting factors. We relied on 20000 samples generated via LHS.
- For each sample, calculate the octane number with Equation 6. The input parameters, namely the hydrocarbon class fractions and the MeABP are used.
- For each sample, calculate its probability with Equation 11. σ In Equation 11 is calculated with the reproducibility reported in Table 3. The objective parameters, namely, the experimental octane numbers are used.
- Calculate the likelihood with Equation 10.
- Plot the likelihood as a function of the sampled correcting factor to visualize the likelihood.
- Go back to the first step and change the minimal and maximal values of the correcting factor so that the plotted likelihood look like a Gaussian function.
- Once the likelihood looks like a Gaussian function, calculate the expectancy and the variance-covariance matrix of the correcting factors.

Example

This section shows how to compute the octane number once the model is created. As an example, we rely on the first fuel of the spreadsheet TestData provided in the supporting information. We show how to calculate the RON, the MON and their uncertainties. All the calculation steps of the current section are reported in the supporting information. The properties of this fuel are reported in the following table. The MeABP is first calculated with equation 1.

Then, the octane numbers of the pseudo-components are calculated with Equation 7 with the coefficients from Table 2. The result is reported in the following table.

Table 4: Properties of the fuel used as an example.

MeABP	80.46
Saturate (%)	66.1
Olefin (%)	7.3
Aromatic (%)	18.1
Oxygenate (%)	8.4

Table 5: Octane numbers of the pseudo-components.

	RON	MON
Saturate (%)	79.62	74.85
Olefin (%)	94.60	80.38
Aromatic (%)	126.11	115.26
Oxygenate (%)	97.90	84.48

Thereafter, the expectancy of correcting factors are applied. The expectancies of the correcting factors are reported on Figure 1 for the RON and figure 2 for the MON. The following table reports the result.

Table 6: Corrected octane numbers of the pseudo-components.

	RON	MON
Saturate (%)	89.97	90.56
Olefin (%)	-28.38	-45.82
Aromatic (%)	131.15	99.12
Oxygenate (%)	106.71	91.24

Finally, the corrected octane numbers are weighted by the hydrocarbon class fractions (in Table 4) of the fuel of interest to obtain the predicted octane number. The result and the measurement are reported in the following table.

Table 7: Estimated octane numbers compared with the measurements.

	RON	MON
Estimated	91.1	82.1
Measured	89.9	82.0

As showed by Equation 12, the uncertainty depends on the variance-covariance matrix and on the sensitivities. The variance-covariance matrix is reported in the supporting information while the sensitivities are governed by Equation 13.

Table 8: Sensitivities

	RON	MON
Saturate (%)	52.63	49.47
Olefin (%)	6.91	5.87
Aromatic (%)	22.83	20.86
Oxygenate (%)	8.22	7.10

Finally, the variance-covariance matrix and the sensitivities give the standard uncertainty, u. The expanded uncertainty at 95%, U, is obtained by multiplying u by 1.96.[41]

Table 9: Standard and expanded uncertainty at 95% of confidence interval

	RON	MON
u	0.80	0.82
U	1.57	1.60

Therefore, for the studied fuel, the RON and the MON are evaluated at 95% being equal to 91.10±1.57 and to 82.12±1.60, respectively.

Results and discussion

After having reported the values of the correcting factors, this section presents the precision of the method. Finally, it discusses the uncertainty and the sensitivity of the method.

Analysing the correcting factors enables us to understand the role of each hydrocarbon class while the covariances inform us about the interactions between the hydrocarbon classes. Figures 1 and 2 summarize the correcting factors **K** and their covariances for the RON and the MON models, respectively. The expectancies of the correcting factors, which are required in Equation 6 are also reported on Figures 1 and 2.

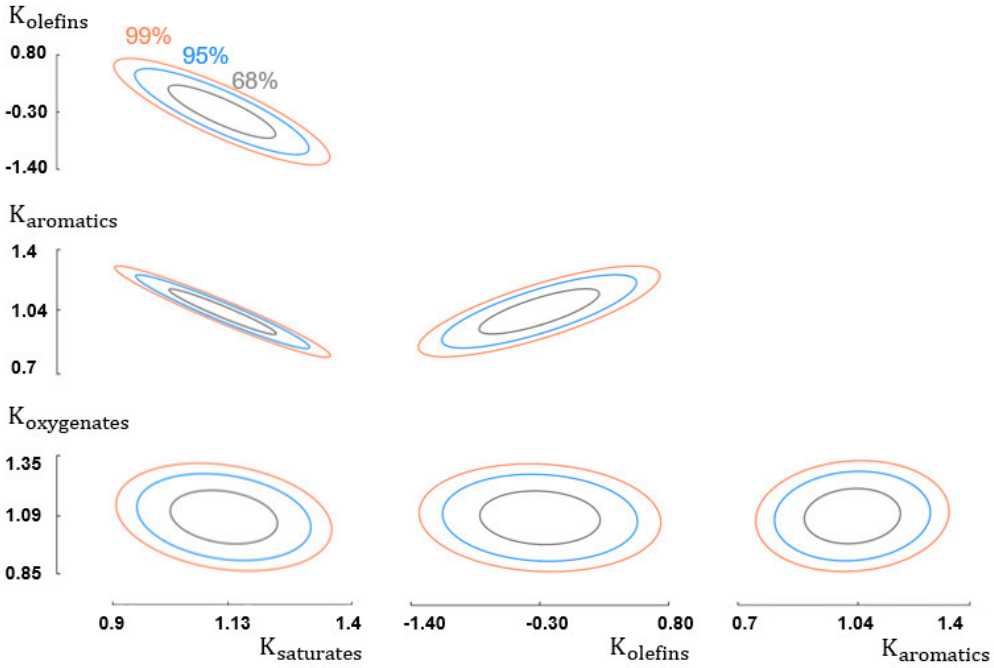


Figure 1: Visual representation of the symmetric variance-covariance matrix of the RON correcting factors. The three variance-covariance error ellipses represent the 99%, 95% and 68% confidence intervals. The ellipses represents the domains where the 20 000 samples of the correcting factors are defined. The directions of the ellipses shows how the correcting factors interact between each others. The variance-covariance matrix is reported in the supporting information.

The correcting factors of the saturates, the aromatics and the oxygenates is positive. For the olefins, it is either positive or negative. Therefore, the saturates, the aromatics and the oxygenates tend to increase the octane number of the mixture.

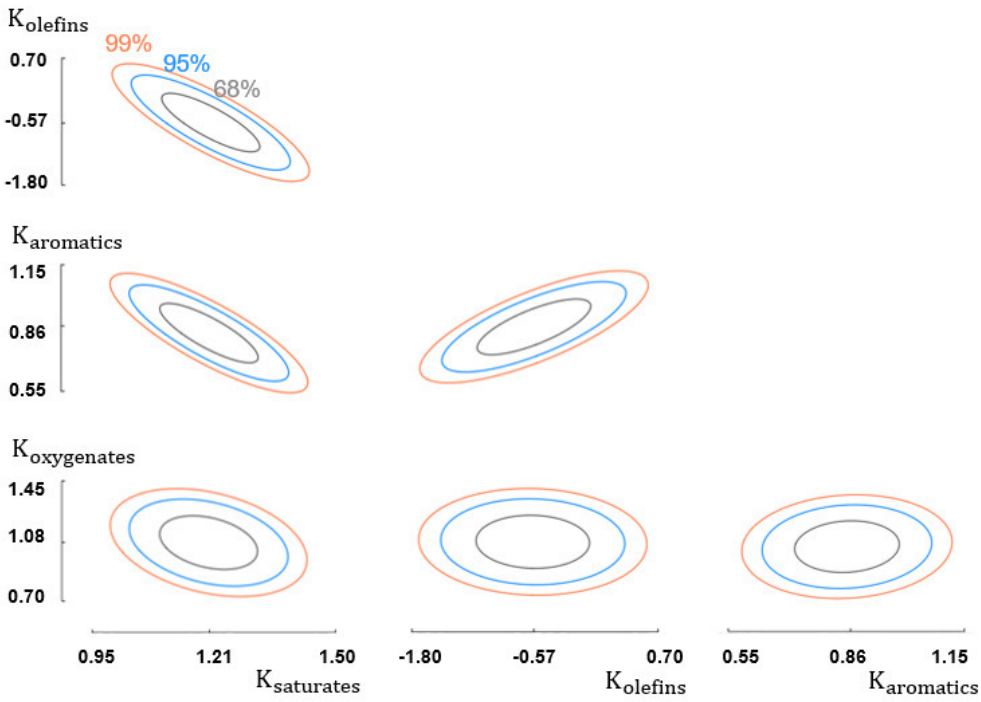


Figure 2: Visual representation of the symmetric variance-covariance matrix of the MON correcting factors. The three variance-covariance error ellipses represent the 99%, 95% and 68% confidence intervals. The ellipses represents the domains where the 20 000 samples of the correcting factors are defined. The directions of the ellipses show how the correcting factors interacts between each others. The variance-covariance matrix is reported in the supporting information.

The covariances inform us about the interactions between the hydrocarbon classes.

- The oxygenate class exhibits a negligible covariance, so, the oxygenates do not covariate with other classes.

- The saturate class has a negative covariance shared with all the other classes, so, the correcting factors decrease as far as the saturates are concerned. The saturate class counterweights the fuel octane numbers of the other classes. Thus, the saturate class controls the antagonist blending effect.[42]

- The covariance between the aromatic and the olefin classes is positive. Thus, an aromatic molecule mixed with an olefin tends to increase the octane numbers. Therefore, the aromatic class controls the synergistic blending effect.[42]

- The covariance between the aromatic and the saturate class is negative. Thus, the octane number decreases when aromatics and saturates are blended. Therefore, the antagonist blending effect prevails on the synergistic blending effect.

- The covariances are similar between the RON and the MON except for the covariance between the saturates and the aromatics. The dependency between the aromatics and the saturates is higher for the RON. This means that the RON decreases more than the MON when the correcting factor of the saturates increases.

According to Figures 3 and 4, the Bayesian pseudo-component method predicts accurately the octane number for the training and the test fuels, with less than 2% error for all the fuels and less than 1% for most of them. A small bias appears for the RON lower than 88.5. For these values, the RON is slightly over-predicted. The test fuels with a RON lower than 88.5 are the BOB fuels 1 and 2 mixed with 1–butanol. The RON of test fuel BOB 3 mixed with 1–butanol is also over-predicted. Thus, the octane numbers of fuels mixed with 1–butanol tend to be over-predicted. This can be explained by the low octane number of these mixtures, comparing with the other fuels.

On Figure 3, the new Bayesian PC method is compared with the one reported by Riazi. To lead the calculation, the saturate group was considered as iso-paraffins and the olefins and the oxygenates were neglected. Note that the original PC method would probably give better results without these assumptions. The new method gives better results than the original one.

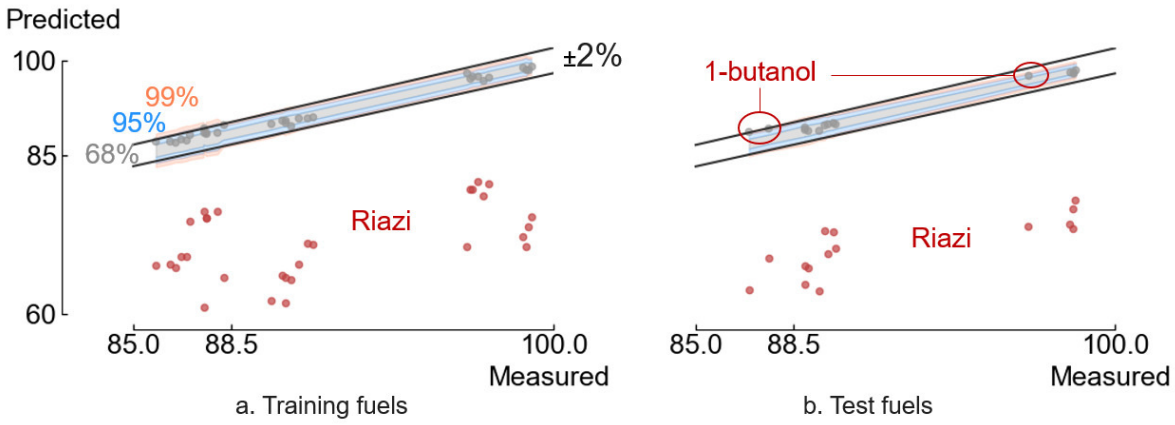


Figure 3: The new Bayesian pseudo-component method gives a very accurate RON prediction for the considered BOB-Ox subpopulation. The 68%, 95% and 99% theoretical confidence intervals are reported as well as a deviation of 2% from the observation. All the points are in accordance with the model uncertainty. The new method is more precise than the original PC method reported by Riazi.[23] Nevertheless, it should be pointed out that the original method was developed for narrow range fractions and for conventional gasoline or naphtas without oxygenates and olefinic compounds. This method may give good results with other fuels.

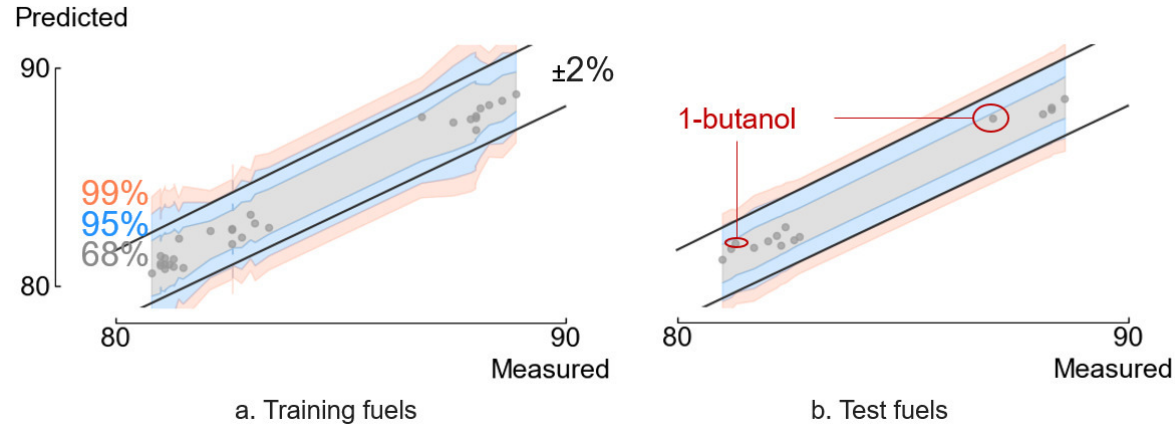


Figure 4: The Bayesian pseudo-component method gives a very accurate MON prediction for the considered BOB-Ox subpopulation. The 68%, 95% and 99% theoretical confidence intervals are reported as well as a deviation of 2% from the observation. All the points are in accordance with the model uncertainty.

Figures 3 and 4 report also the theoretical uncertainties with a confidence interval of 68%, 95% and 99%. All the experimental points fit within the theoretical uncertainty. This uncertainty was calculated with the following formula, from the book Evaluation of measurement data — Guide to the expression of uncertainty in measurement.[41]

$$u^2 = \mathrm{Var}(\sigma^*) = \sum_{i=1}^{n_{PC}} \left(s_i\right)^2 \mathrm{Var}\left(f_i\right) + 2 \sum_{i=1}^{n_{PC}-1} \sum_{j=i+1}^{n_{PC}} s_i s_j \mathrm{Cov}\left(f_i, f_j\right), \quad (12)$$

where $f_i = f_{K_i|\mathbf{ON}}\left(K_i|\mathbf{ON}\right)$ is the PDF of the ith pseudocomponent correcting factor and n_{PC} is the number of pseudo-components. The variance-covariance matrix is reported in the supporting information.

According to Equation 12, the sensitivities, s_i, indicate which variance of the correcting factor prevails on the combined uncertainty, u.

Owing to Equation 6, the sensitivity for each hydrocarbon class i is given by

$$s_i = \frac{\partial ON^*}{\partial E\left(K_i\right)} = y_i ON_{pc_i}. \quad (13)$$

The liquid volume fraction of the fuel hydrocarbon class, y_i, and the octane number of PC i, ON_{pc_i}, govern the sensitivity, s_i. The sensitivities and y_i depend linearly on each others. For instance, the sensitivity $s_{Saturates}$ is the highest because the saturate class constitutes the majority in BOB-Ox fuels (Figure 5). The sensitivity of the saturate group is the highest, so, according to Equation 12, the variance of the correcting factor of the saturates affects the combined uncertainty the most. The sensitivities are sorted in the following ascending order: olefin, oxygenate, aromatic, saturate. Additionally, the octane numbers of the PCs impact this linear trend (Equation 13). Specifically, the octane number of the aromatic pseudo-component is high, thus, it increases the sensitivities of the aromatic class (Figure 5). In opposite, the low octane numbers of the saturate class decreases the sensitivities of the saturate class.

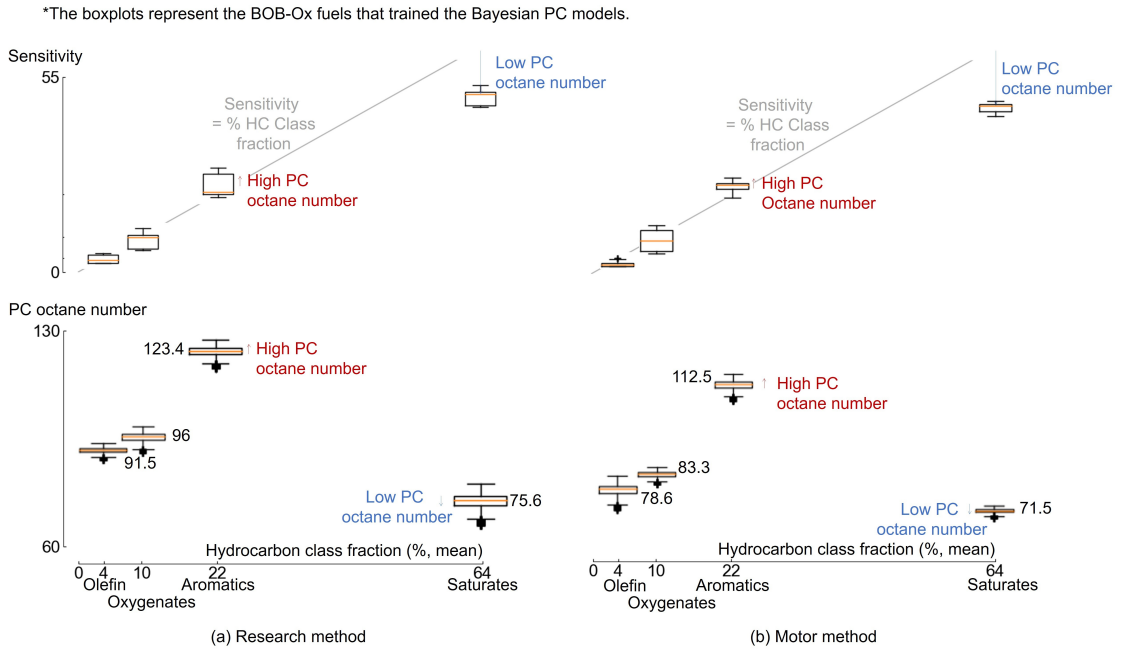


Figure 5: Estimated sensitivities according to the four correcting factors (attributed to Saturates S, Olefins O, Aromatics A and Oxygenates Ox). The estimated octane number is particularly sensitive to the saturate and to the aromatic correcting factors. This is a direct consequence of the higher concentrations of these species, and to the high octane number of the aromatics. The sensitivity is proportional to the hydrocarbon class fraction. This proportionality is impact by the low and the high octane numbers of the PCs.

Conclusion

The current study resulted in showing the power of Bayes' law to predict the octane numbers.

The method includes an uncertainty quantification and it incorporates the fuel complexity such as the hydrocarbon classes, including olefins and oxygenates, and the types of isomers. Moreover, relying on Bayes' law enabled us to draw the following conclusions for the studied fuels.

- The hydrocarbon class that has the higher impact on the uncertainty are sorted in the following ascending order: olefin, oxygenate, aromatic, saturate.
- All of the hydrocarbon classes tend to increase the fuel octane number, except the olefin class.

- The saturate and the aromatic hydrocarbon classes are associated with an antagonist and a synergistic blending effect,[42] respectively.

The model developed in the current paper is made to study gasoline blendstock for oxygenated blending mixed with 1–propanol, 2–propanol, 1–butanol, 2–butanol, or 2–methyl–1–propanol (BOB-Ox). The model requires the main hydrocarbon class fractions (Saturate, Olefin, Aromatic, Oxygenate) and the distillation cut points. It includes the olefin and oxygenate class fractions, so, it is promising for unconventional fuels.

The current model is not tailored for other fuels than BOB-Ox. However, an extension of the current model will be the subject of future research. The current description of the fuel by saturates, olefins, aromatics and oxygenated molecules would not be sufficient. This would lead to high variances, leading to high uncertainties. Thus, to extend the current method with additional fuels, the fuels must be described more precisely with the addition of the isomer groups rather than relying only on saturates, olefins, aromatics and oxygenated molecules.

Acknowledgement

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Supporting Information Available

The following files are available free of charge.

- SupportingInformation.xlsx:
  - The sheet called *TrainingData* contains the properties of the 30 fuel used to train the model.

- The sheet called *TestData* contains the properties of the 15 fuel used to test the model.
- The sheet called *PureONDatabase* contains the boiling points and the octane numbers used to calculate r which is useful in Equation 7.
- The sheet called *Practical example* contains the calculations to predict the octane numbers and their uncertainties of one fuel as an example. The fuel is the first fuel of the *TestData* sheet.
- *VarianceCovariance* contains variance-covariances matrices useful to calculate the uncertainty according to Equation 12.

References

(1) Sukiran, M. A.; Abnisa, F.; Daud, W. M. A. W.; Bakar, N. A.; Loh, S. K. A review of torrefaction of oil palm solid wastes for biofuel production. *Energy Conversion and Management* **2017**, *149*, 101 – 120.

(2) Pradhan, D.; Singh, R.; Bendu, H.; Mund, R. Pyrolysis of Mahua seed (Madhuca indica) – Production of biofuel and its characterization. *Energy Conversion and Management* **2016**, *108*, 529 – 538.

(3) Sanahuja-Parejo, O.; Veses, A.; Navarro, M.; López, J.; Murillo, R.; Callén, M.; García, T. Catalytic co-pyrolysis of grape seeds and waste tyres for the production of drop-in biofuels. *Energy Conversion and Management* **2018**, *171*, 1202 – 1212.

(4) Jody, B. J.; Daniels, E. J. *End-of-life vehicle recycling : state of the art of resource recovery from shredder residue.*; 2006.

(5) Achillas, C.; Vlachokostas, C.; Moussiopoulos, N.; Banias, G.; Kafetzopoulos, G.; Karagiannidis, A. Social acceptance for the development of a waste-to-energy plant in an urban area. *Resources, Conservation and Recycling* **2011**, *55*, 857 – 863.

(6) Ren, X.; Che, Y.; Yang, K.; Tao, Y. Risk perception and public acceptance toward a highly protested Waste-to-Energy facility. *Waste Management* **2016**, *48*, 528 – 539.

(7) Kumaravel, S.; Murugesan, A.; Kumaravel, A. Tyre pyrolysis oil as an alternative fuel for diesel engines – A review. *Renewable and Sustainable Energy Reviews* **2016**, *60*, 1678–1685.

(8) Liu, Y.; Ge, Y.; Xia, B.; Cui, C.; Jiang, X.; Skitmore, M. Enhancing public acceptance towards waste-to-energy incineration projects: Lessons learned from a case study in China. *Sustainable Cities and Society* **2019**, *48*, 101582.

(9) Jin, S. H.; Lee, H. W.; Ryu, C.; Jeon, J.-K.; Park, Y.-K. Catalytic fast pyrolysis of Geodae-Uksae 1 over zeolites. *Energy* **2015**, *81*, 41 – 46.

(10) Galadima, A.; Muraza, O. In situ fast pyrolysis of biomass with zeolite catalysts for bioaromatics/gasoline production: A review. *Energy Conversion and Management* **2015**, *105*, 338 – 354.

(11) Rockstroh, T.; Floweday, G.; Yates, A. Optimisation of synthetic gasoline blend recipes for use in modern charge boosted GDI engines. *Fuel* **2016**, *186*, 800 – 820.

(12) Fan, L.; Zhang, Y.; Liu, S.; Zhou, N.; Chen, P.; Liu, Y.; Wang, Y.; Peng, P.; Cheng, Y.; Addy, M.; Lei, H.; Ruan, R. Ex-situ catalytic upgrading of vapors from microwave-assisted pyrolysis of low-density polyethylene with MgO. *Energy Conversion and Management* **2017**, *149*, 432 – 441.

(13) Ahmed, A.; Goteng, G.; Shankar, V. S.; Al-Qurashi, K.; Roberts, W. L.; Sarathy, S. M. A computational methodology for formulating gasoline surrogate fuels with accurate physical and chemical kinetic properties. *Fuel* **2015**, *143*, 290 – 300.

(14) Badra, J.; Viollet, Y.; Elwardany, A.; Im, H. G.; Chang, J. Physical and chemical effects of low octane gasoline fuels on compression ignition combustion. *Applied Energy* **2016**, *183*, 1197 – 1208.

(15) Sarathy, S. M. et al. Compositional effects on the ignition of FACE gasolines. *Combustion and Flame* **2016**, *169*, 171 – 193.

(16) Naser, N.; Jaasim, M.; Atef, N.; Chung, S. H.; Im, H. G.; Sarathy, S. M. On the effects of fuel properties and injection timing in partially premixed compression ignition of low octane fuels. *Fuel* **2017**, *207*, 373 – 388.

(17) Christensen, E.; Yanowitz, J.; Ratcliff, M.; McCormick, R. L. Renewable Oxygenate Blending Effects on Gasoline Properties. *Energy & Fuels* **2011**, 4723–4733.

(18) ASTM International, ASTM D2699-15a, Standard Test Method for Research Octane Number of Spark-Ignition Engine Fuel. 2015.

(19) ASTM International, ASTM D2700-16a, Standard Test Method for Motor Octane Number of Spark-Ignition Engine Fuel. 2016.

(20) Kelly, J. J.; Barlow, C. H.; Jinguji, T. M.; Callis, J. B. Prediction of gasoline octane numbers from near-infrared spectral features in the range 660-1215 nm. *Analytical Chemistry* **1989**, *61*, 313–320.

(21) Abdul Jameel, A. G.; Van Oudenhoven, V.; Emwas, A.-H.; Sarathy, S. M. Predicting Octane Number Using Nuclear Magnetic Resonance Spectroscopy and Artificial Neural Networks. *Energy & Fuels* **2018**, *32*, 6309–6329.

(22) Pasadakis, N.; Gaganis, V.; Foteinopoulos, C. Octane number prediction for gasoline blends. *Fuel Processing Technology* **2006**, *87*, 505 – 509.

(23) Riazi, M. R. *Characterization and Properties of Petroleum Fractions*; ASTM International, 2005.

(24) de Paulo, J. M.; Barros, J. E.; Barbeira, P. J. A PLS regression model using flame spectroscopy emission for determination of octane numbers in gasoline. *Fuel* **2016**, *176*, 216 – 221.

(25) Lee, D.-M.; Lee, D.-H.; Hwang, I.-H. Gasoline Quality Assessment Using Fast Gas Chromatography and Partial Least-Squares Regression for the Detection of Adulterated Gasoline. *Energy & Fuels* **2018**, *32*, 10556–10562.

(26) Mendes, G.; Aleme, H. G.; Barbeira, P. J. Determination of octane numbers in gasoline by distillation curves and partial least squares regression. *Fuel* **2012**, *97*, 131 – 136.

(27) Badra, J. A.; Bokhumseen, N.; Mulla, N.; Sarathy, S. M.; Farooq, A.; Kalghatgi, G.; Gaillard, P. A methodology to relate octane numbers of binary and ternary n-heptane,

iso-octane and toluene mixtures with simulated ignition delay times. *Fuel* **2015**, *160*, 458 – 469.

(28) Lee, C.; Ahmed, A.; Nasir, E. F.; Badra, J.; Kalghatgi, G.; Sarathy, S. M.; Curran, H.; Farooq, A. Autoignition characteristics of oxygenated gasolines. *Combustion and Flame* **2017**, *186*, 114 – 128.

(29) Sarathy, S. M. et al. Compositional effects on the ignition of FACE gasolines. *Combustion and Flame* **2016**, *169*, 171–193.

(30) Tipler, S.; Mergulhão, C. S.; Vanhove, G.; Van Haute, Q.; Contino, F.; Coussement, A. Ignition Study of an Oxygenated and High-Alkene Light Petroleum Fraction Produced from Automotive Shredder Residues. *Energy & Fuels* **2019**, *33*, 5664–5672.

(31) Mei, H.; Wang, Z.; Huang, B. Molecular-Based Bayesian Regression Model of Petroleum Fractions. *Industrial and Engineering Chemistry Research* **2017**, *56*, 14865–14872.

(32) Nguyen, T. B.; Riesco, N.; Vesovic, V. Predicting the viscosity of n-alkane liquid mixtures based on molecular description. *Fuel* **2017**, *208*, 363–376.

(33) Xu, X.; Jaubert, J. N.; Privat, R.; Duchet-Suchaux, P.; Braña-Mulero, F. Predicting Binary-Interaction Parameters of Cubic Equations of State for Petroleum Fluids Containing Pseudo-components. *Industrial and Engineering Chemistry Research* **2015**, *54*, 2816–2824.

(34) Ramos-Pallares, F.; Schoeggl, F. F.; Taylor, S. D.; Yarranton, H. W. Prediction of thermal conductivity for characterized oils and their fractions using an expanded fluid based model. *Fuel* **2018**, *234*, 66–80.

(35) Aspen Technology Inc., *Aspen Physical Property System: Physical Property Methods*; 2013; pp 1–234.

(36) American Petroleum Institute, *Knocking Characteristics of Pure Hydrocarbons – Developed Under American Petroleum Institute Research Project 45*; American Society for Testing Materials, 1958.

(37) McCormick, R. L.; Fioroni, G.; Fouts, L.; Christensen, E.; Yanowitz, J.; Polikarpov, E.; Albrecht, K.; Gaspar, D. J.; Gladden, J.; George, A. Selection Criteria and Screening of Potential Biomass-Derived Streams as Fuel Blendstocks for Advanced Spark-Ignition Engines. *SAE International Journal of Fuels and Lubricants* **2017**, *10*, 2017–01–0868.

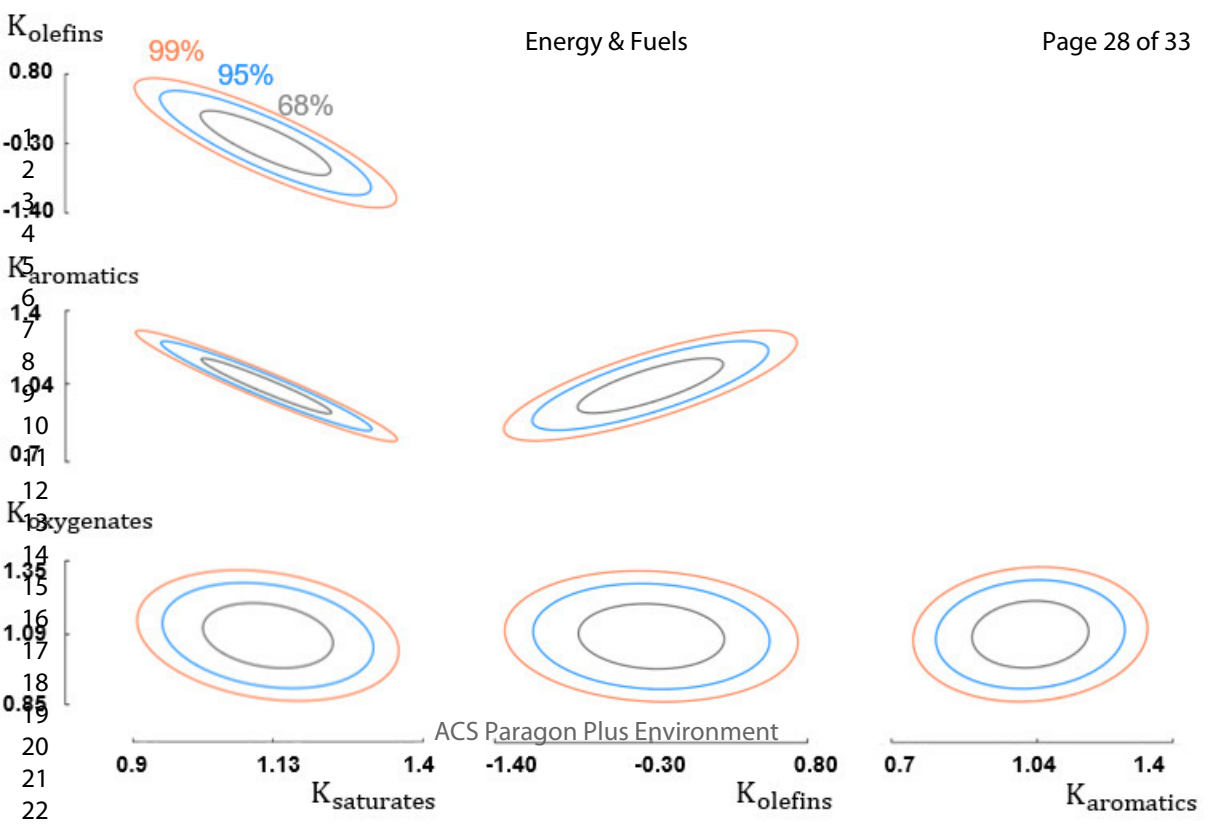
(38) Wallner, T.; Ickes, A.; Lawyer, K. Analytical Assessment of C2–C8 Alcohols as Spark-Ignition Engine Fuels. Proceedings of the FISITA 2012 World Automotive Congress. Berlin, Heidelberg, 2013; pp 15–26.

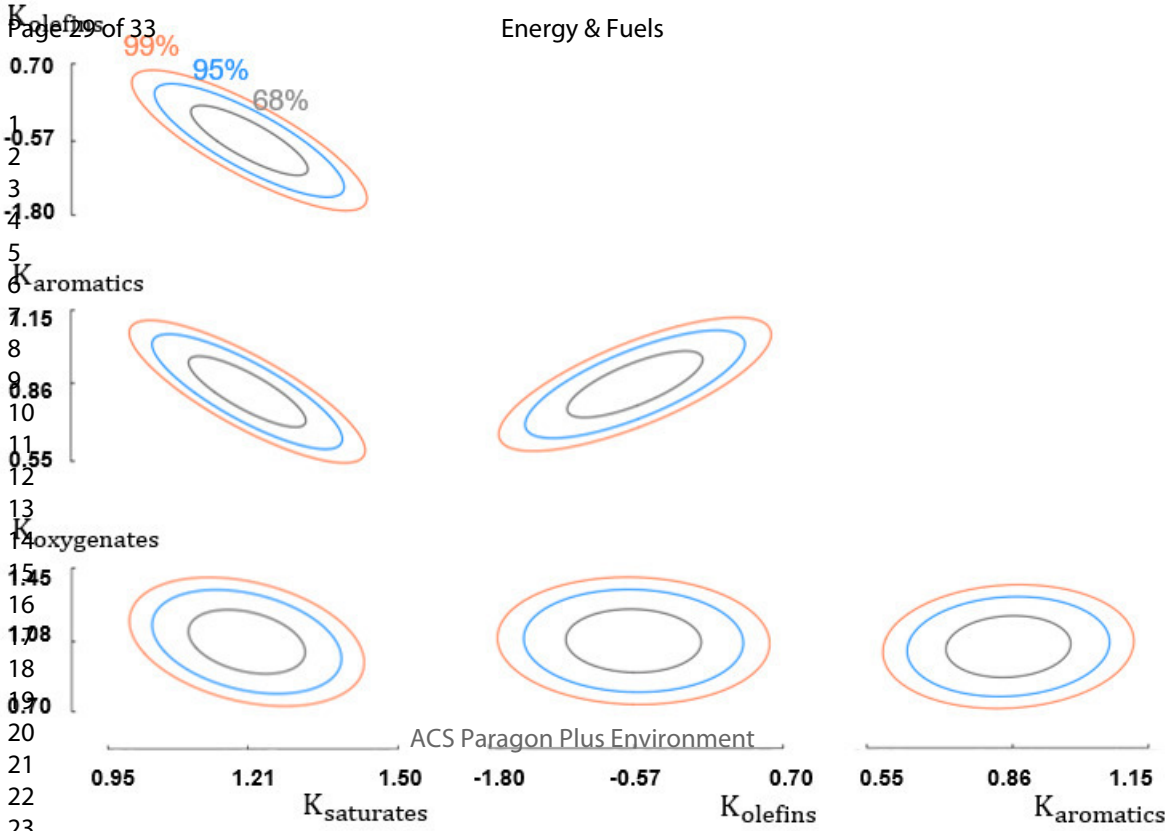
(39) Josephson, A. J.; Gaffin, N. D.; Smith, S. T.; Fletcher, T. H.; Lignell, D. O. Modeling Soot Oxidation and Gasification with Bayesian Statistics. *Energy and Fuels* **2017**, *31*, 11291–11303.

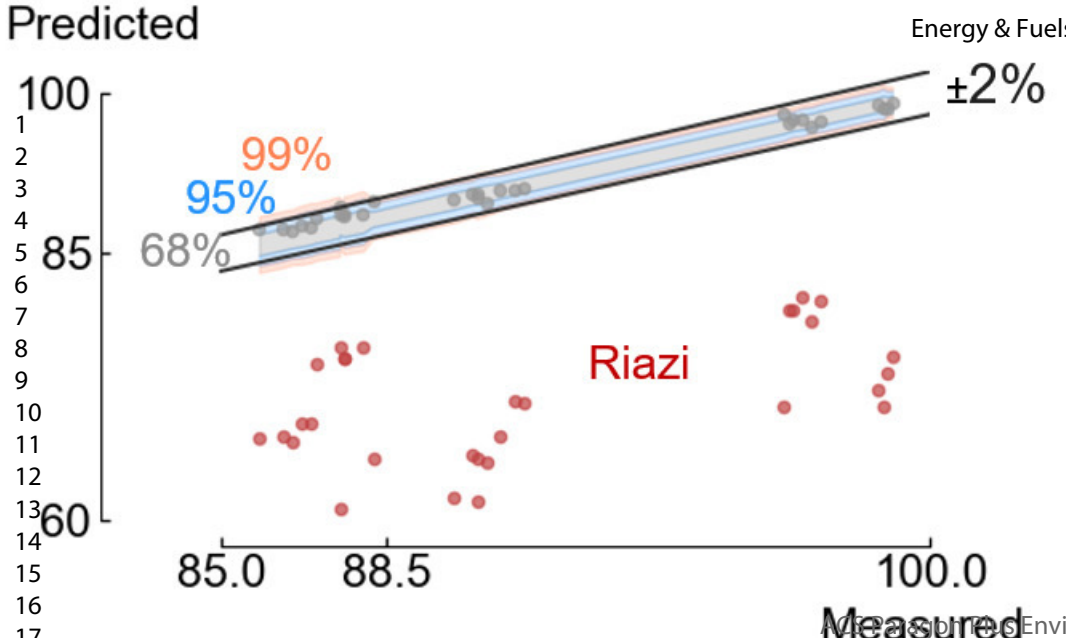
(40) Brooks, D. B.; Cleaton, R. B. The Precision of Knock Rating — 1936-1938: Report from Cooperative Fuel Research Committee. *SAE Transactions* **1939**, *34*, 449–456.

(41) Jcgm, Joint Committee For Guides In Metrology, *Evaluation of measurement data — Guide to the expression of uncertainty in measurement*; 2013; Vol. 50; p 134.

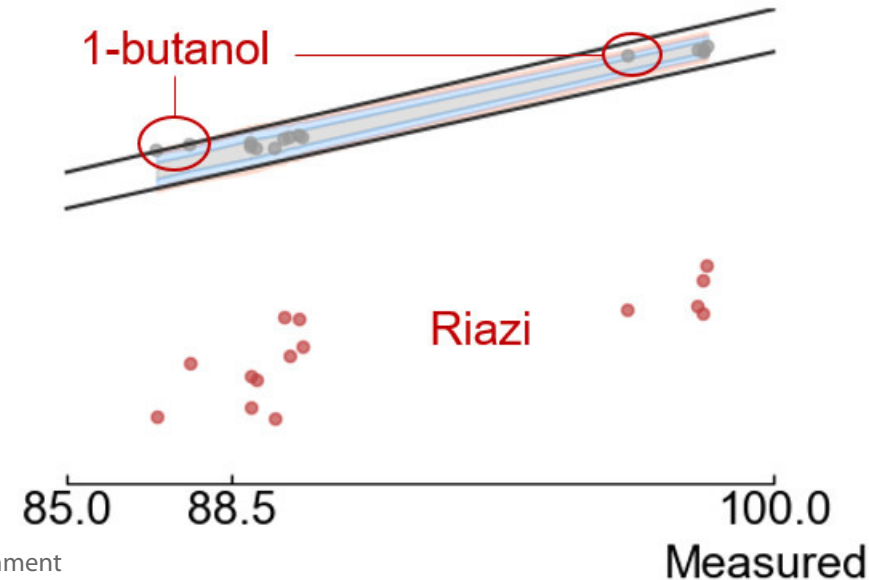
(42) Dauphin, R.; Obiols, J.; Serrano, D.; Fenard, Y.; Comandini, A.; Starck, L.; Vanhove, G.; Chaumeix, N. Using RON Synergistic Effects to Formulate Fuels for Better Fuel Economy and Lower CO2 Emissions. SAE Technical Paper. 2019.


K olefins
99%
95%
68%
0.80
-0.30
-1.40
K aromatics
1.4
1.04
0.7
K oxygenates
1.35
1.09
0.85
ACS Paragon Plus Environment
0.9
1.13
1.4
K saturates
-1.40
-0.30
0.80
K olefins
0.7
1.04
1.4
K aromatics


99%
95%
68%
0.70
-0.57
-1.80
K olefins
K aromatics
1.15
0.86
0.55
K oxygenates
1.45
1.08
0.70
ACS Paragon Plus Environment
0.95
1.21
1.50
-1.80
-0.57
0.70
0.55
0.86
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K saturates
K olefins
K aromatics

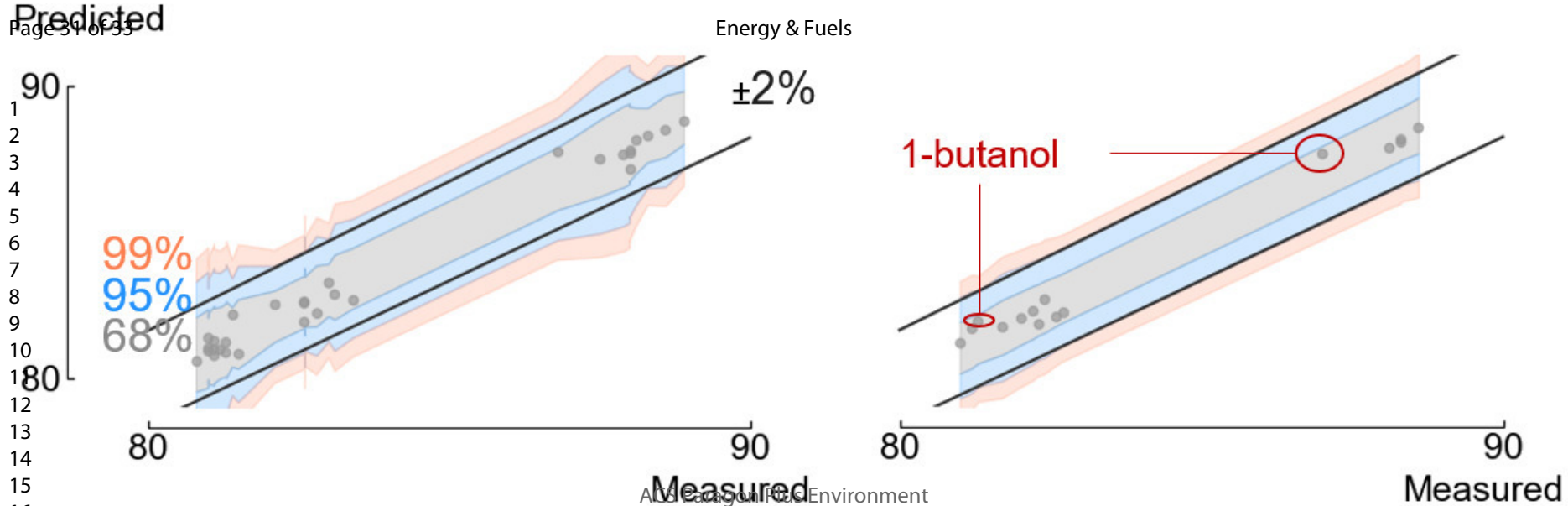


a. Training fuels



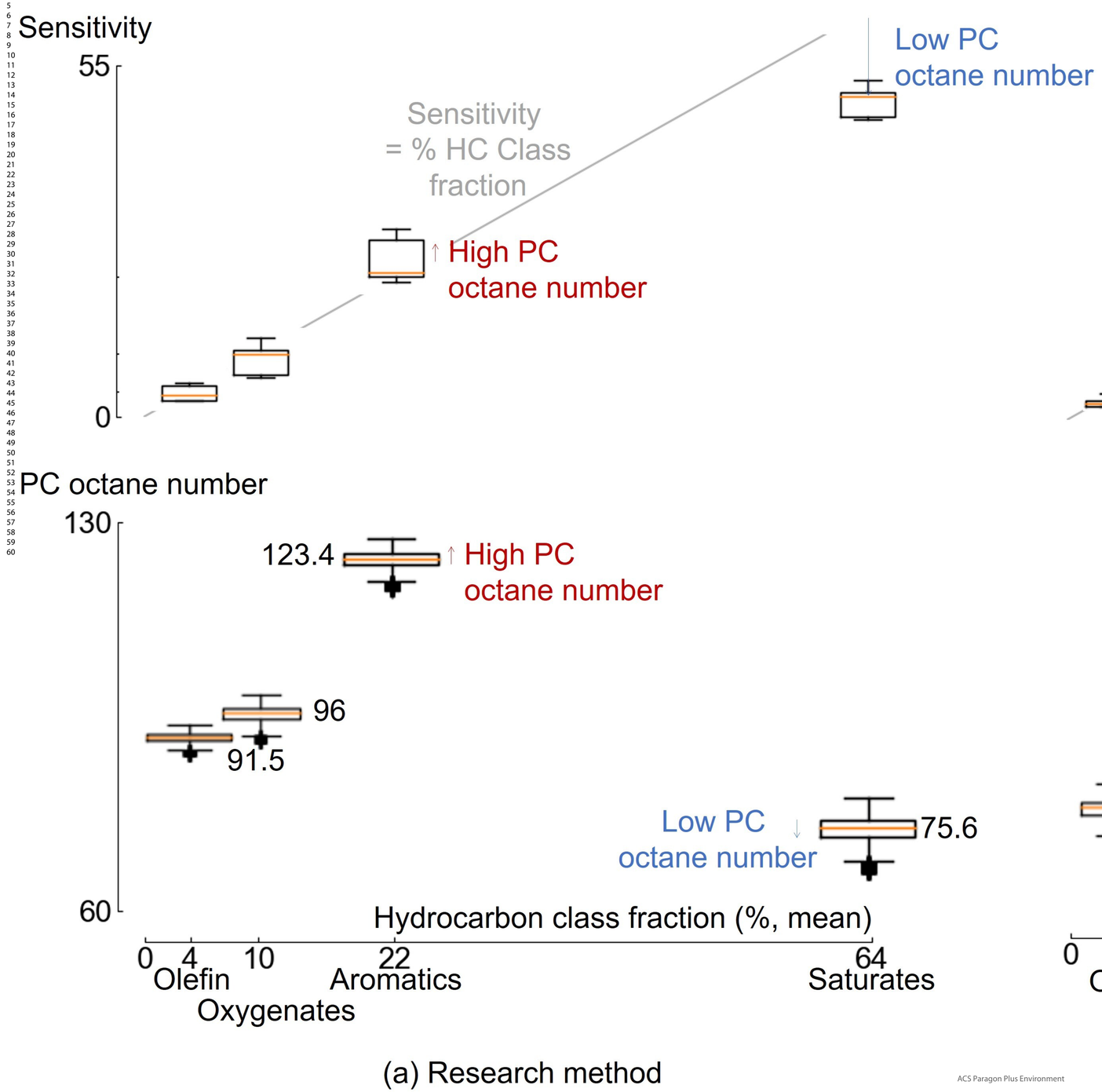
b. Test fuels

ACS Paragon Plus Environment

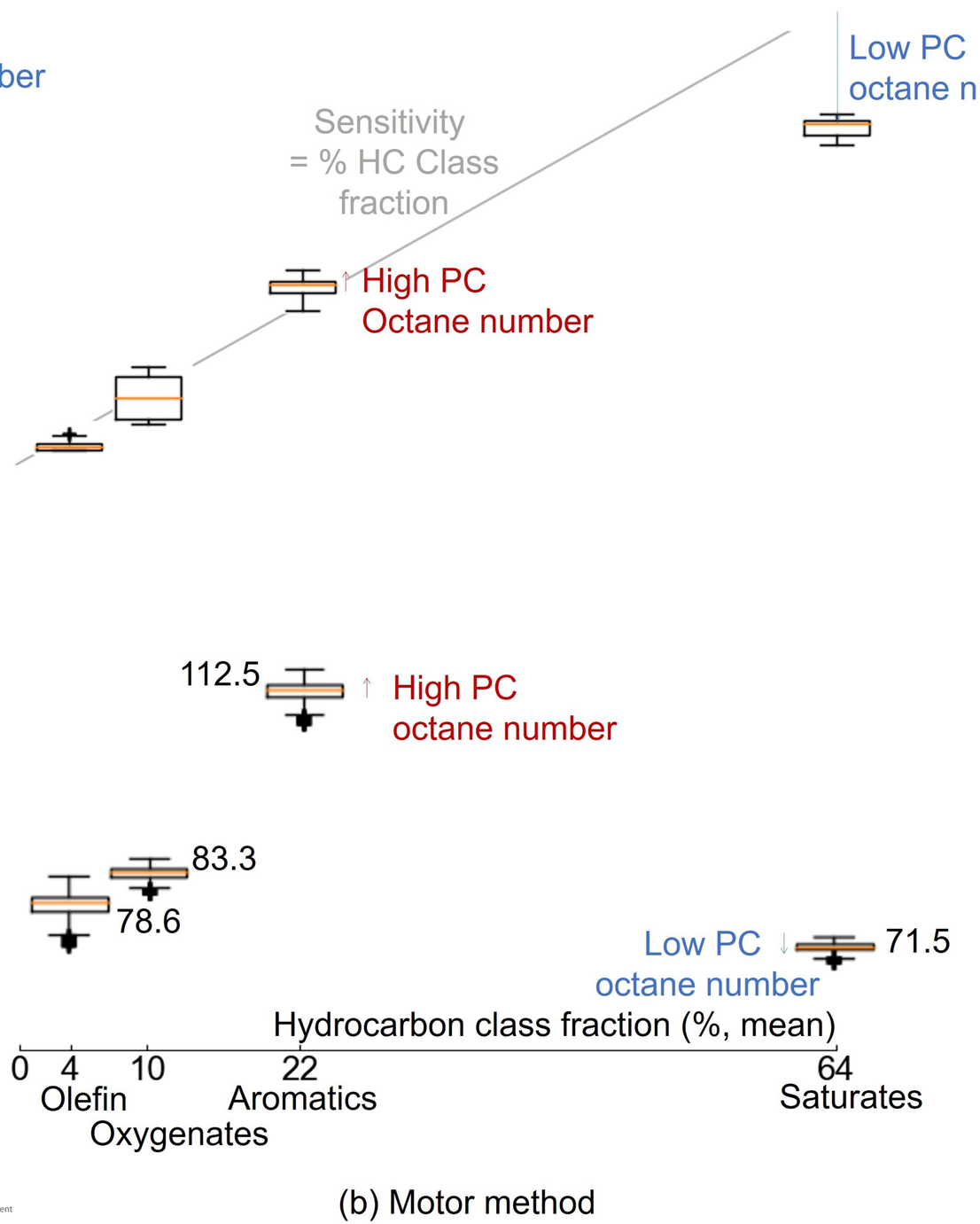


ACS Paragon Plus Environment

*The boxplots represent the BOB-Ox fuels that trained the Bayesian PC models.



(a) Research method



(b) Motor method



11x3mm (600 x 600 DPI)