Fast Determination of 2-Ethylhexyl Nitrate Diesel/Biodiesel Blends by Distillation Curves and Chemometrics

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ABSTRACT: A new method for the quantification of 2-EHN (2-ethylhexyl nitrate) was developed and validated. In order to speed up and simplify the chemical analysis of diesel samples throughout inspection procedures, we propose a single analytical method to determine 2-ethylhexyl nitrate by using the distillation curves routine assay used to evaluate the quality of diesel (ASTM D86). This test was allied with multivariate calibration based on PLS (partial least squares) regression. The results were comparable with reference methodology. Using distillation curves of commercial diesel samples results in a prediction of the cetane improver content with relative standard deviations lower than 12% for all fuel samples. Since this correlation was established using commercial samples, the new approach is immediately applicable in the petrochemical industry, which needs an adaptation to biodiesel/diesel blends.

1. INTRODUCTION

In order to improve the fuel properties of diesel, several kinds of chemicals such as nitrates, ether nitrates, or nitroso compounds are added. It has been checked that these chemical additives produce an increasing effect on the cetane number, which is associated with burning of fuel in the engine. Commonly, the additive most used is 2-ethylhexyl nitrate (EHN), due to the improvement in the combustion characteristics, shortening ignition delay and the start of combustion. The ignition delay period is counted from the injection start to the sharp rise of in-cylinder pressure. The ignition delay period of a diesel engine is mainly influenced by physical−chemical characteristics of the fuel. A fuel with a high cetane number has a short ignition delay and starts to burn soon after it is injected into an engine.[1] The time to vaporize the fuel and mix with the air content in cylinder and the time to react through free radical processes determine the ignition delay. Under normal conditions, if the ignition delay is excessively lengthy in the diesel engine, the outcome is unburned fuel, low power, and formation of particulates that increase engine noise and wear.[2]

Reported mechanisms include the decomposition of cetane improvers into free radicals and gas-phase catalysts such as NO_2. These generated species are involved in the fuel−air reaction. There are also reactions which inhibit free-radical scavengers found in the fuel.[3,4]

The fuel from petroleum distillation is obtained by mixing several fractions from the processing stages of crude oil. The ratio of these components in diesel is made so as to frame the normative specifications which enable good performance of the product, control toxic exhaust emissions, and minimize wear of engines and components.[5] Distillation is a physicochemical assay used to measure the volatility of the sample components of a complex liquid mixture. The boiling range gives information on the composition, the properties, and the behavior of the fuel during storage and use.[6] This assay is used to verify the right proportions of the light and heavy fractions of fuel in order to attain good performance. The assay results in a matrix with samples in rows and the temperature reached by recovering 10, 20, 30, 40, 50, 60, 70, 80, 85, 90, and 95% of initial fuel volume in columns, allowing the use of multivariate models.

The multivariate models associated with analytical techniques are an advantageous alternative to predict physicochemical parameters, because they are easy to apply, fast, low-cost, and useful for online determinations. Recent studies have shown the great potential of distillation curves, or a few specific points, for the analysis of different parameters of petroleum products,[7−12] specific gravity,[13] kinematic viscosity,[14] octane numbers,[15] cetane index,[16] flash point, ethanol content, and biodiesel content.[17] Bruno and co-workers demonstrated that different additive concentrations in fuel produce modifications in distillation curves.[18]

The worldwide output of this nitrated additive is approximated to be about 100 000 tons/year, a large-scale commodity. For a long time it has been regarded as not involving particular risks to human health. In spite of this, the substance shows no evidence of biodegradability in water,[19] is completely miscible in fat, and has potential for bioaccumulation and may form a film on water affecting the oxygen transfer.[71]

Decomposition products of the EHN form nitric oxides (NO and NO_2), giving as a result an additional source of NO_x.[73] Approximately the third part of the nitrogen in the cetane improver goes to the exhaust as NO_x in pure diesel combustion.[20] In diesel/biodiesel blends, owing to the lower cetane number (CN) of pure biodiesel (B100),[21] the addition of EHN is necessary to increase the CN. By considering that the percentage of biodiesel in the blends was increasing in recent years, the concentrations of EHN also did. Therefore, the determination of EHN in blends is very important in order to control the presence of this contaminant, which causes pollution of air and soils dangerous to life.[22]
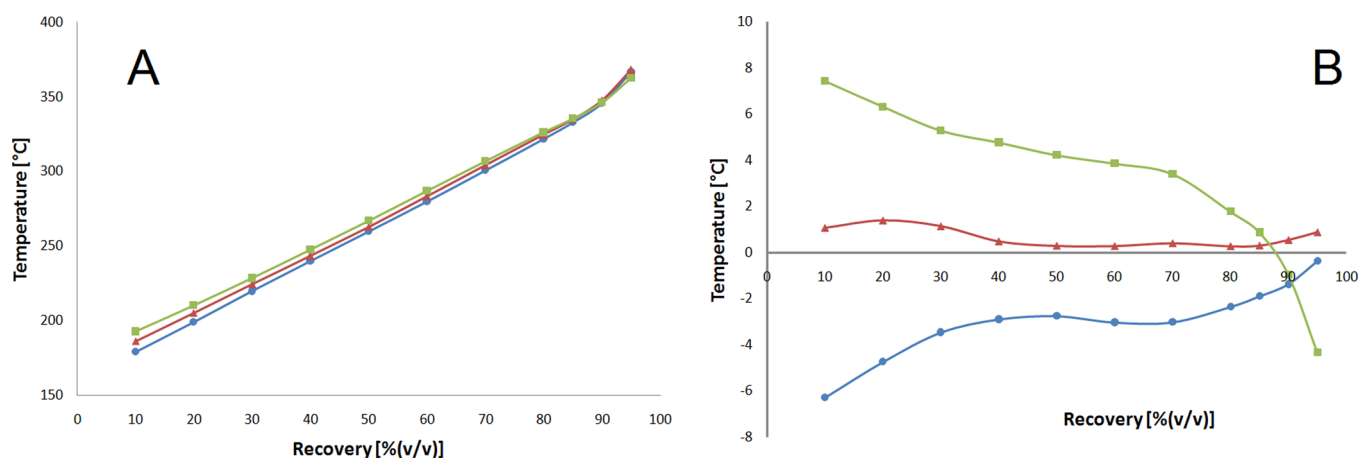
Figure 1. (A) Distillation curves data. (B) Behavior of mean centered distillation curves. (●) 0.03−0.12% EHN (v/v); (▲) 0.12−0.2% EHN (v/v); (■) 0.21−0.3% EHN (v/v).

The American Standard Test Method D4046 indicates the methodology to establish the alkyl nitrate quantity in fuel samples. The norm includes a wearisome liquid−liquid extraction by using organic solvents, a derivatization, and spectrophotometric measure. The procedure starts with a hydrolysis in nitric acid solution, and then reaction with 2,4-dimethylphenol. The reaction product is extracted by 2,2,4-trimethylpentane followed by addition of sodium hydroxide. The measure is done in a spectrophotometer at 452 nm. All these steps result in several methodology disadvantages, such as organic solvent consumption, large time expenditure, and relatively high values of relative standard deviations for repeatability and reproducibility. In the literature, there are some alternatives using headspace gas chromatographic/mass spectroscopy (GC/MS) assay,[23] chemiluminescence detection of a derived product,[24] or infrared spectrometry.[25] The developed GC/MS and infrared spectrometry methods, although they avoid the problems of the standardized method, require costly instruments not available in every laboratory and qualified operators.

The daily work of quality control in the automotive and petrochemistry industries seeks the development of new low cost and rapid methods for determining the cetane improver. Thus, the aim of this work is to propose a simple and rapid analytical method to predict the EHN concentration in blends through a chemometric model and the data obtained from the routine distillation curves.

2. EXPERIMENTAL SECTION

Commercial diesel samples were collected within the years 2010 and 2015, when the Argentinean fuel policy was changing, so the biodiesel content of the 120 diesel samples varies between 0 and 7% (v/v). In this country the biodiesel added to blend the petroleum diesel fuel is produced from soybean oil.

The samples were distilled with automatic ISL AD 86 5G according to ASTM D86. Distillation curves (distillation temperature vs the recovered volume) were recorded as a daily routine at the PETROBRAS laboratory (Bahía Blanca). This test is performed in all fuel laboratories, providing very important information to establish not only the quality of fuel but its price in the market. The distillation curves data are also useful for determining the cetane index (ASTM D4737).

In fuel laboratories, the EHN determination is not usually done as routine analysis because the ASTM Standard Method has a lot of steps which makes it complicated, as said above.

Therefore, the EHN contents in the 120 fuel samples were measured with the Eraspec Diesel Fuel Analysis from Eralytics Company of PETROBRAS (Bahía Blanca).[26] This instrument is a NIR/mid-FTIR interferometer which permits the determination of different parameters showing repeatability and reproducibility values comparable with the ASTM Method.

All distillation curves and EHN values were acquired in the same day that the samples left the refinery to go to gas stations. This information was registered in the daily fuel quality reports.

Construction of Chemometric Model. The multivariate analysis was carried out using the Kennard−Stone algorithm (KS)[27] for sample selection and partial least squares (PLS)[28] for calibration modeling.

From data of distillation curves and EHN contents obtained for the 120 samples, were separated into three sets: 60 for calibration, 30 for validation, and 30 for prediction.

The calibration set could be selected randomly from the whole set of 120 samples. Nevertheless, this procedure does not warrant the fair election of the set over the entire sampling range. To solve this problem, the KS algorithm ensures the representative choice of the prediction set and guarantees the predictive ability of the calculated model along the whole calibration range. The PLS model proposes data decomposition in score and loadings (latent variables) matrixes, and model relationships between sets of observed data. In order to choose the correct number of latent variables to model the distillation curve data, a so-called validation process, two strategies were used: "test set" and "cross-validation". In the "test set" process the calculation of the latent variables and scores were done using the calibration set of samples, and the validation was done predicting the validation set of samples. In the "cross-validation" process the calibration and validation sets were the same group of samples. In this work a "full cross-validation leave-one-out" was used; all calibration−validation samples were predicted by a model calculated with the remainder samples of the group.

Then, the 30 data of distillation curves selected as a prediction set were introduced into the calculated PLS models. Thus, the EHN concentrations can be obtained through the models. It is worth nothing that the 30 samples of the prediction set were not used in any step of the process to calculate the chemometric models.

The predicted values of EHN concentration were compared with those obtained experimentally with the Eraspec instrument.

3. RESULTS AND DISCUSSION

Figure 1A shows the distillation curves for different EHN concentration ranges. Three curves (an average curve of each range) were plotted in order to show the significant displacement of the curves, due to the presence of EHN. This effect can be best seen in Figure 1B, in which were plotted
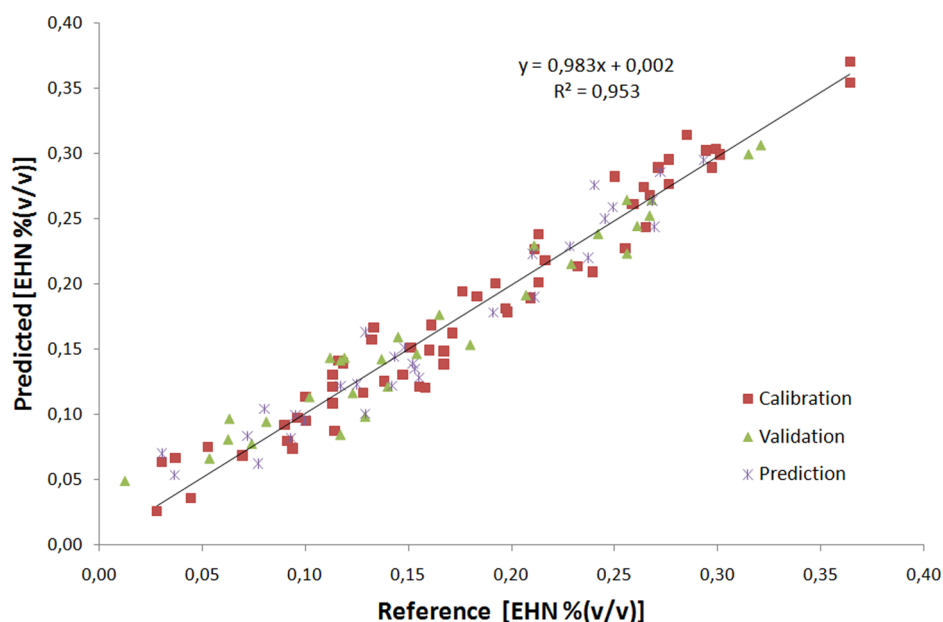
Figure 2. Cross-validation prediction versus reference value.

the mean centered curves (subtracting the mean temperature value of each recovery point).

The fuel additive presence retards the vaporization of lighter compounds; in the blend diesel fuel samples these components would be normally registered early in the distillation curve. An example of this effect is the concentration found of diethyl carbonate at 10, 20 and 30% (v/v) in the work of Bruno et al.[18] Another example of measuring an additive through a distillation curve comes from the measurement of molar concentration of tetraethyl lead in commercial aviation gasoline approaching the trace concentration level.[29]

Figure 2 presents a full cross-validation (leave-one-out) of the whole set of 120 samples, differentiating groups of samples used in calibration, validation and prediction sets. Each sample was predicted using four latent variable of a model calculated with the 119 remaining samples. In this plot of predicted vs reference values, is outlined as the KS algorithm separated the samples, and the linear behavior of the 120 samples.

The PLS modeling correlates the distillation curve data with the EHN content, giving the ability to predict additive concentrations in unknown fuel samples assaying only with the data obtained from the distillation curve test.

Table 1 presents the analytical figures of merit of the two strategies to validate the chemometric models, using a full cross-validation (CV) leave-one-out of 90 samples (calibration and validation sets founded with KS algorithm) and a test set validation (using calibration set of 60 samples and 30 samples of the validation set chosen by KS, too). Both ways of validation had comparable results, which can be shown with the relative error of prediction (%), which for CV is 13.18% and for the test set is 14.81%. However, as the number of samples used in the calibration step was higher for CV, the results were little better. This result may indicate that a larger set of samples for the calibration process could improve even better the prediction results. For all three calculated models, four latent variables were chosen. Also, Table 1 presents the prediction results for the external set of 30 samples which had not been used in the mathematical calculation of the chemometric models. This means that, once the statistical relationship

Table 1. Analytical Performance of PLS Models To Predict Different Sets of Samples

	all samples	validation set		prediction set	
	CV	CV	test set	CV	test set
samples	120	90	30	30	30
slope	0.9478	0.9489	0.8207	0.9654	0.9045
offset	0.0090	0.0089	0.0256	0.0059	0.0212
correlation	0.9730	0.9736	0.9720	0.9701	0.9717
R^2	0.9476	0.9490	0.9216	0.9404	0.9374
RMSE[a]	0.0186	0.0189	0.0200	0.0178	0.0200
SE[b]	0.0187	0.0190	0.0193	0.0183	0.0195
bias	0.00046	−0.00005	0.00599	0.00026	0.00572

[a]RMSE, root mean squared error [% EHN (v/v)]. [b]SE, standard error [% EHN (v/v)].

between distillation curve data and EHN content was obtained, the chemometric technique can be used from the results of the distillation curves, in order to calculate the concentration of the analyte.

The limit of quantification (LOQ) was defined as the lowest amount of an analyte in a sample that can be determined quantitatively with convenient precision and accuracy. It was calculated as LOQ = 10S, where S is the standard deviation of 20 prediction values for samples with 0% (v/v). The LOQ found for our methods is 0.0298% (v/v). The lower limit of detection (LOD) is the lowest quantity of a substance that can be distinguished from the absence of that substance. It was calculated as LOD = 3.28S. The LOD found for our methods is 0.0101% (v/v). The resultant LOD and LOQ are comparable with those found in the bibliography.[23−25]

The elliptical joint confidence region (EJCR) of the regression[30] of predicted versus nominal concentrations in the prediction set was studied for the two calibration models. The corresponding plots are shown in Figure 3. All confidence regions contain the ideal point of unit slope and zero intercept (indicating accuracy) at 95% confidence level, and the elliptical sizes obtained were comparable, suggesting that both chemometric methodologies shown similar predictive abilities.
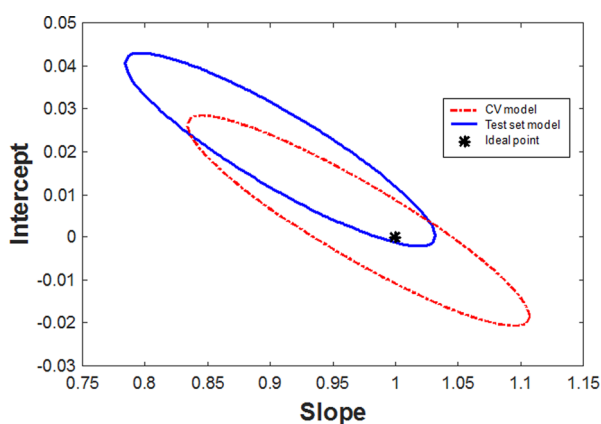
Figure 3. Elliptical joint regions (at 95% confidence level) for the slope and intercept of the regression of test set model (solid line) and CV model (dashed line) results. Black asterisk marks the theoretical (intercept = 0, slope = 1) point.

4. CONCLUSIONS

With the use of distillation curve data and multivariate calibration, the content of 2-ethylhexyl nitrate, which is an important additive to improve the cetane number, was predicted efficiently. The distillation curves were obtained following ASTM D86 specifications.

The proposed method reduces the time and costs of analysis since distillation assays are within the scope of laboratory analysis. The advantage of this quantification methodology is the use of data that is obligatorily acquired in daily routine analysis in every refinery. This new method avoids the need to perform another experimental analysis.

The ability to relate the changing composition with distillation curves is critical since many quality parameters could be estimated exploiting the data recorded in the ASTM D86 assay.

As the developed method is cheap and does not use any organic compound, it can be proposed as an alternative to the established standard method of EHN determination.

The refineries and petrochemical industries (where EHN has to be determined) could benefit from taking advantage of the present method. Commonly, adding biodiesel to diesel produces a decrease of the cetane number; thus, the improver is added. The new determining method could be helpful in adapting out-of-date laboratories to test biodiesel/diesel blends.

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Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Li, R.; Wang, Z.; Ni, P.; Zhao, Y.; Li, M.; Li, L. Effects of cetane number improvers on the performance of diesel engine fuelled with methanol/biodiesel blend. *Fuel* **2014**, *128*, 180−187.

(2) Burger, J. L.; Lovestead, T. M.; Gough, R. V.; Bruno, T. J. Characterization of the Effects of Cetane Number Improvers on Diesel Fuel Volatility by Use of the Advanced Distillation Curve Method. *Energy Fuels* **2014**, *28*, 2437−2445.

(3) Suppes, G. J.; Rui, Y.; Rome, C.; Chen, Z. Cetane-Improver analysis and impact of activation Energy on the Relative Performance of 2-Ethylhexyl Nitrate and Tetraethylene Glycol Dinitrate. *Ind. Eng. Chem. Res.* **1997**, *36*, 4397−4404.

(4) Clothier, P.; Aguda, B.; Moise, A.; Pritchard, H. How do dieselfuel improvers work? *Chem. Soc. Rev.* **1993**, *22*, 101−108.

(5) Albahri, T. A. Developing correlations for the properties of petroleum fuels and their fractions. *Fluid Phase Equilib.* **2012**, *315*, 113−125.

(6) *Standard Test for Distillation of Petroleum Products at Atmospheric Pressure*; ASTM D86; American Society for Testing and Materials: Washington, DC, 2010.

(7) de Oliveira, F. S.; Teixeira, L. S. G.; Araújo, M. C. U.; Korn, M. Screening analysis to detect adulterations in Brazilian gasoline samples using distillation curves. *Fuel* **2004**, *83*, 917−923.

(8) Bruno, T. J. Improvements in the measurement of distillation curves. Part 1: A composition-explicit approach. *Ind. Eng. Chem. Res.* **2006**, *45*, 4371−4380.

(9) Smith, B. L.; Bruno, T. J. Advanced distillation curve measurement with a model predictive temperature controller. *Int. J. Thermophys.* **2006**, *27*, 1419−1434.

(10) Aleme, H. G.; Costa, L. M.; Barbeira, P. J. S. Determination of gasoline origin by distillation curves and multivariate analysis. *Fuel* **2008**, *87*, 3664−3668.

(11) Burger, J.; Lovestead, T. M.; Windom, B. C.; Bruno, T. J. Characterization of renewable fuels and additives with the advanced distillation curve method. *Abstracts of Papers*, 242nd National Meeting of the American Chemical Society, Denver, CO, Aug 28−Sept 1, 2011; American Chemical Society: Washington, DC, 2011; p 145.

(12) Maheshwari, A. S.; Chellani, J. G. Correlations for pour point and cloud point of middle and heavy distillates using density and distillation temperatures. *Fuel* **2012**, *98*, 55−60.

(13) Aleme, H. G.; Costa, L. M.; Barbeira, P. J. S. Determination of ethanol and specific gravity in gasoline by distillation curves and multivariate analysis. *Talanta* **2009**, *78*, 1422−1428.

(14) Aleme, H. G.; Assunção, R. A.; Carvalho, M. M. O.; Berbeira, P. J. S. Determination of specific gravity and kinematic viscosity of diesel using distillation curves and multivariate calibration. *Fuel Process. Technol.* **2012**, *102*, 90−95.

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

(16) Aleme, H. G.; Barbeira, P. J. S. Determination of flash point and cetane index in diesel using distillation curves and multivariate calibration. *Fuel* **2012**, *102*, 129−134.

(17) Aleme, H. G.; Barbeira, P. J. S. Determination of biodiesel content in diesel using distillation curves and multivariate calibration. *Energy Fuels* **2012**, *26*, 5769−5774.

(18) Bruno, T. J.; Ott, L. S.; Lovestead, T. M.; Huber, M. L. The composition-explicit distillation curve technique: Relating chemical analysis and physical properties of complex fluids. *J. Chromatogr. A* **2010**, *1217*, 2703−2715.

(19) American Chemistry Council Petroleum Additives Panel. *High Production Volume: Challenge Program for Nitric Acid, 2-Ethylhexylester*; 2006.

(20) Ickes, A. M.; Bohac, S. V.; Assanis, D. N. Effect of 2-Ethylhexyl Nitrate Cetane Improver on NOx Emissions from Premixed Low-Temperature Diesel Combustion. *Energy Fuels* **2009**, *23*, 4943−4948.

(21) Nadai, D.; Simões, J. B.; Gatts, C. E. N.; Miranda, P. C. M. L. Inference of the biodiesel cetane number by multivariate techniques. *Fuel* **2013**, *105*, 325−330.

(22) Day, D. A.; Liu, S.; Russell, L. M.; Ziemann, P. J. Organonitrate group concentrations in submicron particles with high nitrate and organic fractions in coastal southern California. *Atmos. Environ.* **2010**, *44*, 1970−1979.

340 (23) Dvořák, B.; Bajerová, P.; Eisner, A.; Nykodýmová, O.; Ventura,
341 K. Determination of 2-ethylhexyl nitrate in diesel fuel. *J. Sep Sci.* **2011**,
342 *34*, 1664−1668.
343 (24) Wang, C. X.; Firor, R. *Analysis of Trace 2-Ethylhexyl Nitrate in*
344 *Diesel Using Chemiluminescence Detector*; Agilent Technologies,
345 Application Brief; 2010.
346 (25) Bajerová, P.; Bajer, T.; Adam, M.; Eisner, A.; Ventura, K. Fast
347 determination of 2-ethylhexyl nitrate in diesel oils by infrared
348 spectrometry. *Fuel* **2014**, *117*, 911−916.
349 (26) PAC [Internet], Advance Analytical Instrumentation for Lab
350 and Process Application. http://www.paclp.com/.
351 (27) Soares, S. F. C.; Gomes, A. A.; Galvão Filho, A. R.; Araujo, M.
352 C. U.; Galvão, R. K. H. The successive projections Algorithm. *TrAC,*
353 *Trends Anal. Chem.* **2013**, *42*, 84−98.
354 (28) Wold, S.; Sjöström, M.; Eriksson, L. PLS-regression: a basic tool
355 of chemometrics. *Chemom. Intell. Lab. Syst.* **2001**, *58*, 109−130.
356 (29) Lovestead, T. M.; Bruno, T. J. Application of the Advanced
357 Distillation Curve Method to the Aviation Fuel Avgas 100LL. *Energy*
358 *Fuels* **2009**, *23*, 2176−2183.
359 (30) Riu, J.; Rius, F. X. Method comparison using regression with
360 uncertainties in both axes. *TrAC, Trends Anal. Chem.* **1997**, *16*, 211−
361 216.