Study of simple detection of gasoline fuel contaminants contributing to increase Particulate Matter Emissions

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Abstract

The reduction of particulate emissions is one of the most important challenges facing the development of future gasoline engines. Several studies have demonstrated the impact of fuel chemical composition on the emissions of particulate matter, more particularly, the detrimental effect of high boiling point components such as heavy aromatics. Fuel contamination is likely to become a critical issue as new regulations such as Real Driving Emissions RDE involves the use of market fuel. The objective of this study is to investigate several experimental approaches to detect the presence of Diesel contamination in Gasoline which is likely to alter pollutant emissions. To achieve this, a fuel matrix composed of 12 fuels was built presenting diesel fuel in varying concentrations from 0.1 to 2% v/v. The fuel matrix was characterized using several original techniques developed in this study. These are Near Infrared spectroscopy (NIR) associated to Principal Component Analysis (PCA) and Partial Least Square (PLS) modelling, filtration. Their capacity to identify diesel fuel was compared to standard methods, such as, distillation, washed and unwashed gums, high boiling components by gas chromatography (EN16270 and VDA265). Furthermore, vehicle tests were conducted to evaluate the impact of Diesel contamination on tailpipe particle emissions on Worldwide harmonised Light vehicle Test Procedure WLTP. Vehicle test results suggest a significant impact of Diesel contamination on Particle emissions. A good detection of Diesel fuel (down to 0.5% v/v) is accomplished using filtration, NIR and high boiling components. Filtration and NIR have the added benefit of availability, ease of use and small test duration. This work highlights the critical impact of Diesel fuel contamination on pollutant emissions from future Gasoline engines. It proposes a novel practical approach of measuring Diesel contamination in market gasoline fuels.

1. Introduction

The rising concern about the impact of transport on global and local pollution have resulted in the tightening of pollutant and Greenhouse Gas (GHG) emissions standards in fulfillment of the objectives of Paris Agreement in addition to many other transnational policies on sustainability. More specifically, the emissions of particles from the combustion of fuels is raising an increasing interest from automotive and petroleum industries. These issues have triggered considerable efforts by several national and international agencies to establish limitations to the maximum emission levels of particles (e.g. particulate matter or PM; and particle number or PN). [1–3].

To achieve high fuel efficiency required for GHG abatement and low pollutants emission, new technologies have been introduced in spark ignition engines. The Gasoline Direct Injection (GDI) is one of the important development to enhance the control of fuel injection, reduce the fuel pumping losses and allow for a higher compression ratio and charge air cooling. However, direct injection strategy might be responsible for formation of fuel rich areas due to lower time available for fuel-air mixing. Besides, fuel impingement on the internal surfaces of the combustion chamber especially at cold start can favor fuel film formation. Under certain conditions, these might promote the formation of particles [4, 5].

Fuel composition and properties play also an important role in particle formation mechanism. The gasoline fuel volatility, more particularly, the presence of heavy fuel components was found to promote particles formation in GDI engines [6]. In fact, heavy fuel compounds with a high boiling point (150°C and above) were found to degrade fuel air mixing, thereby, promoting the formation of fuel rich areas or fuel films on combustion chamber walls. Furthermore, aromatics, especially high molecular weight monoaromatics and polycyclic aromatics (C_{9+}) are known to be soot precursors and thus

increase significantly particulate formation compared to light monoaromatics (C_7-C_8) [7, 8].

Additionally, market gasoline might contain minor contaminants resulting from fuel logistics which could impact engine proper functioning and pollutants formation. For example, a recent market survey conducted within this study have shown that Diesel contamination can occur in the market. Contamination at concentration as high as 1%v/v was not exceptional and may reach in extreme cases over 2%v/v.

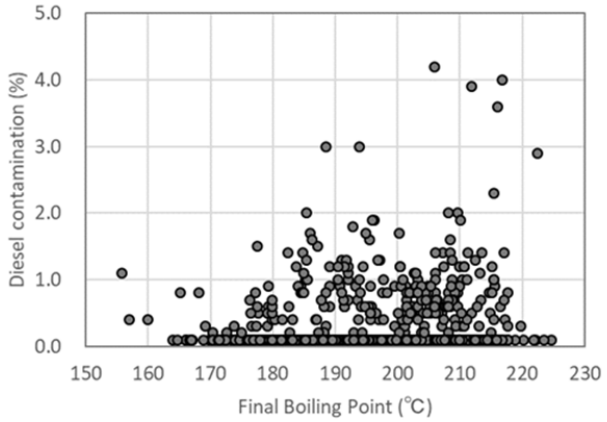

Figure 1: Correlation between Final Boiling Point (ISO 3405) and Diesel contamination (VDA 265) established in this study with European market gasoline fuels tested between 2016 and 2018.

Diesel fuel is used for road transportation such as in trucks, buses and light-duty vehicles. It is generally composed of C_9 to C_{25} hydrocarbons with various fractions of paraffins, naphthenes, aromatics in addition to alternative fuels (Fatty Acid Methyl Esters FAME as well as synthetic Diesel fuels) [9]. In addition, a variety of additives are used to improve diesel fuel properties such as lubricity, detergency and cold flow properties. Finally, diesel fuels may contain a wide range of heteroatomic compounds such as naturally occurring phenols, nitrogen and sulphur-containing species, organic acids and reactive olefins. As a result, gasoline contamination with Diesel fuel, certainly brings about new chemical components unknown to gasoline applications. The impact of these contaminants at trace concentration on engine performance, durability or pollutants emission is still poorly understood. Nevertheless, this contamination seems to escape detection by conventional EN228 analyses such as the distillation Final Boiling Point (FBP) as presented in Figure 1 which raises the question about what would be the most appropriate and practical way to measure it in the market.

The objective of this study is, first, to evaluate through vehicle tests the impact of Diesel contamination on tailpipe particle emissions on Worldwide harmonised Light vehicle Test Procedure WLTP. Second, to investigate several experimental approaches to detect the presence of Diesel fuel in Gasoline. To achieve this, a fuel matrix composed of 14 fuels was built presenting diesel fuel in varying concentrations from 0.1 to 2% v/v. The fuel matrix was characterized using several original techniques developed in this study. These are Near InfraRed spectroscopy (NIR) associated to Principal Component Analysis (PCA) and Partial Least Square (PLS) modelling, micro-filtration. Their capacity to identify diesel fuel was compared to standard methods, namely, distillation, washed and unwashed gums, high boiling components by gas chromatography.

2. Methodology

In order to evaluate the impact of Diesel fuel contamination on particulate matter emissions, a fuel matrix composed of 12 fuels was built presenting diesel fuel in varying concentrations from 0.1 to 2% v/v. The section 2.1 presents the fuel matrix developed. Vehicle test bench and WLTP testing methodology is presented in section 2.2. Finally, the different laboratory methods investigated to measure Gasoline contamination by Diesel fuel are presented in 2.3.

2.1. Selection of the fuel matrix

The fuel matrix selected is composed in total of 12 fuels. These include, three reference gasoline fuels (REF1, REF2 and REF3), two reference Diesel fuels (DF1 and DF2) and their blends.

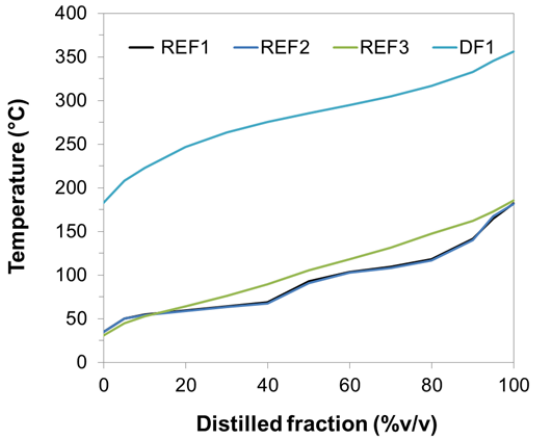

Figure 2: Distillation curve by ISO 3405 of reference gasoline fuels (REF1, REF2 and REF3) and of reference Diesel fuel (DF1)

Reference gasoline fuels: three reference gasoline fuels were evaluated. REF1 and REF2 are two E10 Gasoline fuels compliant with EN228 specification. Both are supplied by Total ACS with very similar characteristics. REF 3 is a E0 gasoline fuel. Figure 2 presents the distillation curve of the three gasoline fuels studied. Results show very similar curves of REF1 and REF2, whereas REF3 is slightly different. This difference may be associated to its different chemical composition as presented in Figure 3. Among main differences, one can underline the absence of ethanol in REF3 and the higher amount of unsaturated compounds (olefins and aromatics). More particularly, the presence of aromatics of a high molecular weight, that is to say, having 9 or more carbon atoms (C_{9+}) which represent about 15%wt in REF3 compared to 10%wt in REF1 and 11%wt in REF2.

Reference Diesel fuel: two diesel fuels were used in this study. First, DF1 is a European ultralow sulphur diesel fuel compliant with EN590 specification. DF1 contains 6.5%v/v of FAME and 25.3%v/v of total aromatics. Figure 2 presents its distillation curve that goes from 183-365°C which is above the distillation range of the three gasoline fuels studied. Note that DF2 is a B0 Diesel fuel. The analysis of this fuel was not available.

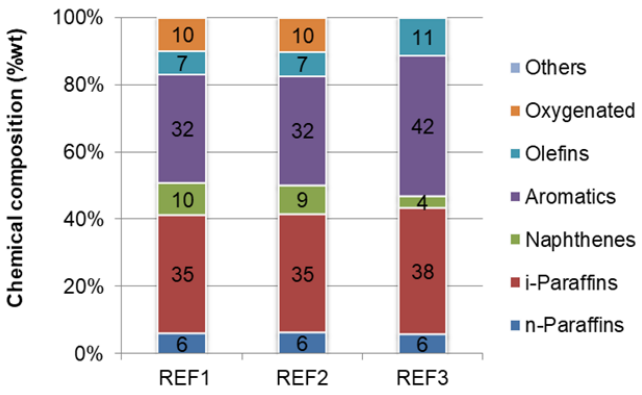

Figure 3: Global chemical composition of the Reference Gasoline Fuels. "Others" include HC with more than 15 carbon atoms and unknown molecules.

Gasoline – Diesel blends: DF1 was added to gasoline fuels REF1 at concentrations from 0.1 - 2%v/v, DF1 was added to REF2 at two concentrations: 1%v/v and 2%v/v. Finally, DF2 was added to REF 3 at two concentrations: 1%v/v and 2 %v/v. Table 1 summarises the fuel blends tested in this study.

Table 1: Fuel blends evaluated in this study. Symbols: & represents "Fuels series 1" and # represents "Fuels series 2" used for Vehicle experiments

Gasoline fuel	Diesel contamination rate (%v/v)				
	0.1	0.5	0.7	1	2
REF1	DF1				
REF2 &				DF1 &	
REF3 #				DF2 #	

2.2. Vehicles tests

This section presents the vehicle tests used to evaluate the impact of diesel fuel contamination as well as the driving cycle and particle measurement method. The validation was carried out using two fuel series composed of 3 fuels each and selected among the fuel matrix abovementioned:

- **Fuel series 1 (&)**: Fuels series 1 is composed of gasoline reference fuel REF2 and its blends with Diesel fuel (DF1) at two concentrations 1%v/v and 2%v/v. Fuel series 1 was tested on Vehicle A;

- **Fuel series 2 (#):** Fuels series 2 is composed of gasoline reference fuel REF3 and its blends with Diesel fuel (DF2) at two concentrations 1%v/v and 2%v/v. Fuel series 2 was tested on Vehicle B.

Table 2 presents a summary of the vehicles characteristics, the engine cycle and the fuels used for the validation. Two recent vehicles with Turbocharged Direct Injection compliant with Euro 6-b emissions levels, were selected to evaluate the fuel matrix. Vehicles were chosen to represent a share of market gasoline engines currently deployed. The vehicles were tested on the Worldwide harmonized Light vehicles Test Procedure (WLTP) with a start temperature of 23°C. Each fuel was tested 4 times to evaluate the uncertainty of the tests. The standardized Particle Number was acquired for each test.

Table 2: Main characteristic of the engines tests used. TWC designates "Three Way Catalyst", TDI designates "Turbocharged Direct Injection"

Fuels series	Fuel Series 1	Fuel Series 2
Vehicle model	A	B
Certification	Euro 6-b	
Engine	L4, 2.0L, TDI	
Aftertreatment system	TWC (aged >5000 km), without GPF	
Driving cycle	WLTC 4 phase	
Start temperature	23 °C	

2.3. Diesel contamination detection

To evaluate the fuel matrix and detect diesel contaminants, 7 laboratory methods were investigated. These can be classified into two categories:

- EN228 techniques: namely, Distillation (Final Boiling point), washed and unwashed gums;
- Alternative techniques, namely, high boiling components by 2 different standardized methods (EN16270, VDA265), Filterable contaminants and Near-IR spectroscopy.

The inventory of the methods evaluated is presented in Table 3. EN228 methods which are widely known standard methods [10, 11], this paragraph provides a summary description of the test methods and their use in this research work.

Table 3: Inventory of the laboratory tests used to characterize the gasoline fuel contaminations

Category	Lab Tests	Method
EN228	Distillation (Final Boiling Point)	ISO 3405
	Unwashed Gums – UWG	ISO 6246
	Washed Gums – WG	ISO 6246
Alternative techniques	High boiling components	VDA265
	High boiling components	EN16270
	NIR spectroscopy	IFPEN
	Filterable contaminants	IFPEN

2.3.1. High boiling components

In this study, two different methods are investigated to evaluate the high boiling components of gasoline fuel based on Gas Chromatography (GC): EN 16270 method and VDA 265 method. The comparison of Gas chromatography methods and their key characteristics is provided in Appendix 2 :.

High boilers by EN 16270

This method was proposed by the European Committee for Standardization (CEN) and aims at determining the content of high boiling components as well as FAME in gasoline using capillary gas chromatography associated to flame ionization detection. The detailed description of the method can be found elsewhere [12]. The non-polar column separates the fuel components according to their boiling points that are correlated with the retention times through calibration curves of known mixture of hydrocarbons covering a large variation of boiling temperatures as presented in Appendix 2 :. The amount of high boilers is defined by the sum of components eluted after 1-methylnaphthalene (included) and up to C_{32}. The application range of the method is also provided in Appendix 2. The repeatability and reproducibility of the results as provided in the standard are given by the following equations:

Repeatability “r”	Reproducibility “R”:
High boilers: 0,0393 + 0,0727 X FAME: 0,0222 + 0,0442 X	High boilers: 0,2884 + 0,0635 X FAME: 0,0731 + 0,1183 X

High boilers by VDA 265

This method allows to determine similarly to EN16270 High boiling components, FAME but also Diesel content. The detailed description of the method can be found elsewhere [13]. This method requires a calibration by a calibration function determined using mixture of Gasoline with Diesel fuel at three different concentrations and mixture with FAME at three different concentrations in addition to 1-methylnaphthalene and nC_{26} used to determine their retention time. The amount of high boilers is defined by the sum of components eluted after 1-methylnaphthalene (excluded) and up to nC_{26}. The repeatability “r” of the method provided in the standard is of 3% of peak area and the reproducibility “R” is of 10% and 5% of peak area on Total high boilers and FAME, respectively.

2.3.2. Near Infra-Red spectroscopy

Near Infra-Red (NIR) spectroscopy is an experimental technique used since several years to characterize oils and fuels. For gasoline fuel application, NIR was used to estimate key physical and chemical properties such as density, Reid vapour pressure, distillation, research and motor octane number and the chemical composition (aromatics, olefins, saturates and oxygenates). The availability and cost-effectiveness of the hardware needed for this method represent a key asset. This enables its use in field-portable fuel analysers in past works [14]. In this study, NIR spectra acquisition were performed using a MB3600 FT-NIR spectrometer from ABB presented in Figure 4, equipped with a DTGS detector, using a 2+/-0.02 mm cell. The spectra covered the range of 4000-12000 cm^{-1} at a spectral resolution of 4 cm^{-1}. Each spectrum was collected from an average of 100 scans. The measurements were carried out at 27.5°C with the help of a Pelletier cell.

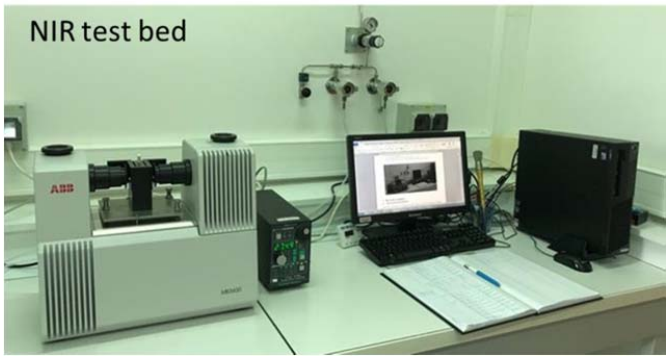

Figure 4: Near Infra-Red test bed at IFPEN

Principal Component Analysis

Principal Component Analysis (PCA) is a widely used technique in chemometrics. It was applied in this study to analyse NIR spectra. PCA is an unsupervised learning method meaning that the dataset has no target variable or no response value. PCA consists on analysing a database table of several dependent variables that correspond to wavenumbers of NIR spectra. Its goal is to extract the important information from the database table and to express this information as a set of new orthogonal variables called principal components (PC). PCA also represents the pattern of similarity of the observations and the variables by displaying them as points in maps. In this study, PCA was used to evaluate qualitatively the presence of Diesel contaminants.

Partial Least Square Modelling

Partial Least Square (PLS) modelling is a widely used technique in chemometrics. It is commonly utilized to model the relationship between spectral measurements such as NIR used in this study and a given property such as chemical composition or physico-chemical properties. The PLS process was carried out in two steps: calibration and validation. First, a PLS model is developed on the calibration database. Then, it is applied on a validation database. The latter contains samples that were not used in the model development (calibration database). The PLS model requires to fix only one parameter: the number of latent values (LV). The performance of the PLS model is then evaluated based on a number of statistical coefficients: the correlation coefficient R^2, the root mean squared

error of calibration (RMSEC), cross-validation (RMSECV) and prediction (RMSEP) calculated by the following equation.

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}(y_i - y'_i)^2}{n}}$$

Where yi represents the reference value of the property of interest and y'i the estimated value of the property. In this study, PLS was used to determine quantitatively the fraction of contaminants in an attempt to reduce the detection limit. The database dedicated to diesel contamination is presented in Appendix 3.

All the chemometric developments were performed with the PLS_Toolbox version 8.6 for Matlab version R2018b (Eigenvector Research Inc.,Wenatchee, WA, USA).

2.3.3. Filterable contaminants

Filtration methods are known for diesel and jet fuel applications. For example, to measure total contamination of diesel fuel, EN12662, uses a Glass fibre type filter with 0.7µm of mean pore size. The amount of total contamination is the mass of filtered residues after heptane washing. The European diesel fuel specification EN590 sets a limit of 24 mg/kg for Total Contamination. The protocol proposed by IFPEN aims at measuring the content of filterable contaminants (gums, particulates) present in gasoline fuel before and after contamination with Diesel. The working assumption is that these filterable contaminants are likely to be higher in Diesel that in gasoline due its heavier composition. Thus, the analysis might mirror the presence of Diesel contamination in gasoline. The protocol is composed of the following steps:

- **Sample preparation:** 100 mL ± 0.1 of fuel is introduced in a graduated flask.
- **Filtration:** the fuel is filtered through a filtration system from Merck (Fluids contamination kit) used for standard methods such as ASTM D2276 for aviation fuels. The filtration system, presented in Figure 5, is composed of a vacuum filtering flask, a chemical duty pump, a filter holder with stainless steel screen and filter forceps. Filters used in this study are Polyvinylidene fluoride PVDF filters having an average pore size of 0.45µm and 47 mm diameter. The filter is pre-weighed by the means of a XPR6UD5 balance from Mettler Toledo, having 0.5 µg precision (M1 in mg). After filtration, the filter is placed under extractor hood for 1 hour to allow for the degassing. The speed of aspiration of the hood is 0.5 m/s.
- **Drying:** The filter is dried in a heated oven at 50°C for 30 minutes. Then, it is left to rest for 30 minutes at ambient temperature.
- **Weighing:** The filter is weighed (M2 in mg) to determine the mass of Filterable contaminants according to the following equation Eq. 1

$Filterable\ Contaminants\ (mg/100mL) = M2 - M1$	Eq. 1

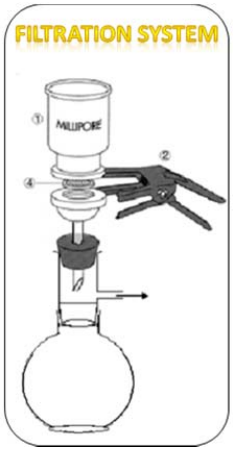

Figure 5: Experimental test apparatus for Filterable contaminants measurement by IFPEN protocol

Feasibility tests were carried out to validate the suitability of the PVDF filters with the protocol in terms of contact with the fuel and the drying process in the heated oven. No degradation of the filters and no loss of material was observed through visual inspection or through mass measurement. The repeatability error of the measurement is of 8%.

Note that this test differs significantly from gums measurement by ISO 6246. In one hand, Filterable contaminants are separated by filtration from the rest of fuel at ambient temperature. So only particulates with size higher than the filtration media are trapped. In the other hand, ISO 6246 separates gums by evaporating the fuel at a high temperature 160-165°C. So, high boiling components regardless of their size may remain in the beaker after the test. Besides, the use of high temperature and oxygen in ISO6246 may induce fuel thermo-oxidation, thereby, leading to possible formation of high molecular

weight oxidation products that were not initially present in the fuel. In summary, major differences exist between the two protocols, thus, no relationship should be expected between their results.

3. Results

First, the vehicle test results, are presented in section 3.1 especially PN measurement on WLTP. Second, the evaluation of laboratory techniques towards diesel detection is discussed in section 3.2.

3.1. PN measurement on WLTP

Vehicle tests were performed according to the methodology described in section 2. Results of PN emissions on WLTC were recorded for each fuel over 4 repeatability tests. The results were used to compute the average emissions as well as the measurement uncertainty.

Tests were performed using, in one hand, Fuels Series 1 composed of REF2 and its blends with Diesel fuel DF1 at 1% and 2%v/v, and in the other hand Fuel series 2 composed of REF3 and its blends with Diesel fuel DF2 at 1% and 2%v/v. A summary of the tested fuels can be found in Table 1.

Normalized PN emissions obtained using Fuels series 1 is presented in Figure 6. Results show an increase of PM emissions of about 5% with 1%v/v of Diesel contamination and of 25% with 2%v/v diesel contamination. In agreement with this trend, Figure 7 presents normalized PN emissions obtained using Fuels series 2. Results show an increase of PM emissions of about 12% with 1%v/v of Diesel contamination and nearly 20% with 2%v/v diesel contamination.

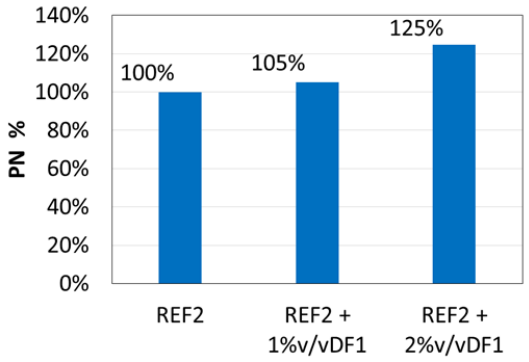

Figure 6: PN emission on Vehicle A evaluated over WLTC driving cycle (start temperature 23°C). Fuels series 1: REF2 gasoline fuel and REF2 contaminated with DF1 at two rates (1% v/v and 2%v/v).

Although there are differences between the two datasets, the results converge in both cases. Diesel contamination increases PN emissions on WLTC and this increase occurs at concentration as low as 1%v/v of Diesel in Gasoline. The average increase rate of PN is approximately 10% PN for 1%v/v of Diesel.

In summary, under the conditions evaluated in this study, diesel contamination increases particle number emissions. This increase occurs at concentration as low as 1%v/v. This impact raises a genuine need to detect qualitatively and quantitatively this contamination on real market use which is the topic of the second part of this study.

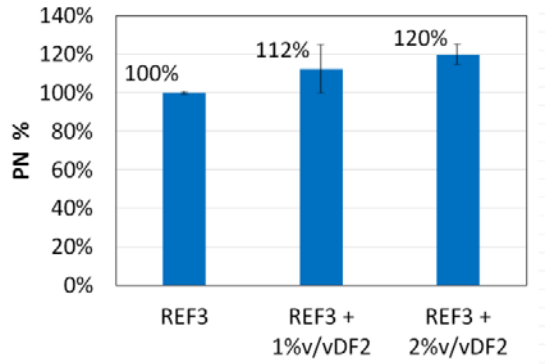

Figure 7: PN emission on Vehicle B evaluated over WLTC driving cycle (start temperature 23°C). Fuel Series 2 : REF3 gasoline fuel and REF3 contaminated with DF2 at two rates (1% v/v and 2%v/v).

3.2. Diesel contamination detection

The vehicle results suggest that Diesel contamination is likely to increase particle number emissions with concentration as low as 1%v/v in Gasoline fuel. Therefore, this section is dedicated to evaluate several standard and alternative laboratory analyses and their ability to detect qualitatively and quantitatively diesel contamination. A particular focus will be paid to techniques allowing to discriminate with high precision low diesel contamination (≥ 0.5%v/v).

3.2.1. Final Boiling point

Distillation curves were measured by ISO 3405 for the reference gasoline fuels as well as their blends with Diesel. A small variation especially of the high temperature profile of the distillation curve with the addition of diesel is observed. This can be explained by the boiling range of Diesel fuel generally higher than gasoline. For example, DF1 distillation range is from 183°C to 356°C which is above REF 1, REF2 having a FBP of 182°C, 181°C respectively. To represent the impact of Diesel on the end of the distillation curve, the Final Boiling Point FBP is presented as a function of Diesel fraction in Figure 8.

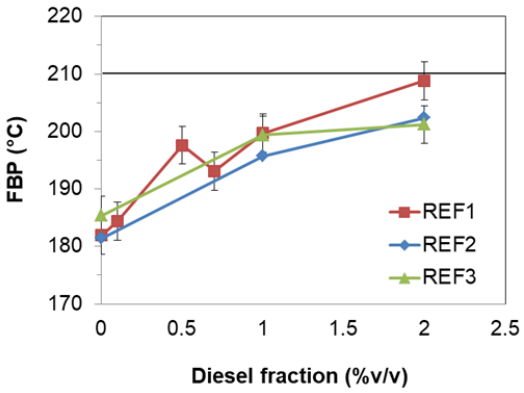

Figure 8: Impact of Diesel on distillation end point measured by ISO3405, automatic method

Results suggest that the addition of diesel modifies the end of the distillation curve for REF1 to 3. The addition of 0.5%v/v of Diesel enables a significant FBP difference compared to the raw gasoline fuel. In fact, contaminated fuels up to 2%v/v of Diesel remain within EN228 limits (FBP < 210°C) and could not be classified as outliers. In summary, in the tested conditions, distillation does not seem suitable to detect small amount of Diesel in gasoline for commercial use.

3.2.2. Gum by ISO6246

The measurement of unwashed gums (UWG) and washed gums (WG) was realized according to the standard method ISO 6246. The variation of UWG and WG as a function of Diesel contamination in Gasoline is discussed in this section.

Unwashed gums

Results of unwashed gums UWG function of Diesel, presented Figure 9.a, suggest an increase of the UWG with Diesel addition. However, different slopes are obtained. The addition of 1%v/v of Diesel to REF1 generates no UWG. However the addition of the same amount to REF2 generates higher level of UWG (6.5mg/100mL). This difference becomes even higher at 2%v/v with a factor of 15. Given that the same Diesel fuel DF1 was used in mixture with REF1 and REF2, the different slopes suggest possibly a different gum formation mechanism function of the gasoline or diesel / gasoline mixture. For REF3, the level of UWG is nearly zero without diesel. It does not change at 1%v/v Diesel (<0.5mg/100mL) and barely increases to 3mg/100mL with 2%v/v Diesel. The slope is slightly lower than REF1 which may be associated to differences in the reference gasoline/diesel or their mixture.

In summary, the results obtained suggest that the detection of Diesel is not always achievable at 1%v/v of Diesel. The detection limit of Diesel varies between 1 and 2%v/v according to the reference gasoline fuel and Diesel fuel. Thus UWG seem irrelevant to detect small Diesel contamination in gasoline.

Washed gums

The variation of washed gums WG with Diesel addition is presented in Figure 9.b. The amount of WG are on the overall much smaller than UWG with higher uncertainty which may be associated to the high solubility of gums that come from Diesel in heptane. This aspect

is rather expected according to previous literature works. Indeed, the washing step with heptane removes the non-volatile heptane soluble compounds such as some additives, carrier oils used with additives and diesel fuel [15].

The addition of Diesel generates a complex variation of the WG. For REF1, WG increase at 1%v/v, then tend to stabilize from 1 to 2%v/v considering the measurement uncertainty. The addition of Diesel to REF2 presents a similar trend up to 2%v/v. On the contrary, the addition of Diesel to *REF3* does not impact WG. This may be associated to the difference in both gasoline and diesel fuel used. For instance Diesel fuel added to REF3 contains no FAME whereas Diesel fuel added to REF1 and REF2 contains 6.5%v/v of FAME. Further work is needed to evaluate the impact of Diesel fuel variability on Washed Gums.

In summary, according to the present results, WG does not allow to detect diesel contamination at concentration as low as 1%v/v in all cases. Thus, this technique does not seem suitable to detect Diesel contamination in gasoline.

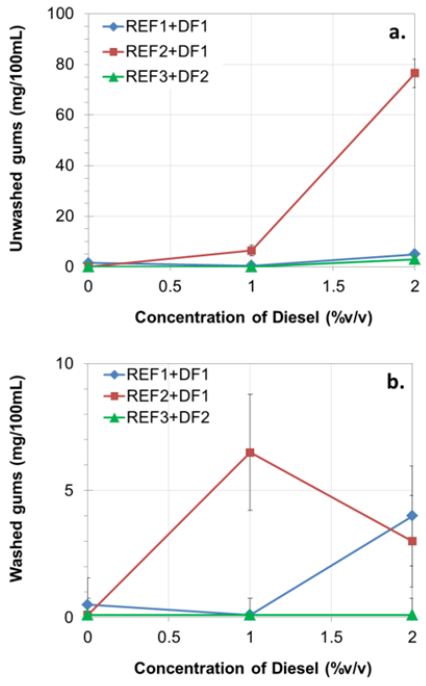

Figure 9: Variation of gums by ISO6246 with Diesel contamination in REF1, REF2 and REF3. A. Variation of Unwashed gums with no Limit in EN228. B. Variation of Washed gums. Limit in EN228: 5mg/100mL.

3.2.3. High boiling components

This section presents the analyses of high boiling components of gasoline fuel before and after diesel-contamination using two standard GC methods, namely, EN 16270 and VDA 265, described in section 0. EN16270 allows to measure high boiling components as well as FAME. VDA 265 measure in addition to these two the amount of diesel content.

EN16270

Figure 10.a presents the results of High boiling components variation with the addition of Diesel measured by EN16270. In general, the addition of Diesel induces a linear increase of the HB fraction. Note that HB without diesel is roughly the same for the three REF fuels (0.1%wt) considering the measurement uncertainty. Parity plot of diesel contamination and HB both in mass fraction presented in Appendix 5 shows a good agreement up to about 2%m/m. For higher contamination, the HB measurement underestimates slightly diesel contamination. This might be explained by the presence of light fractions of Diesel that are eluted before the cut-off point of the method (1-methylnaphthalene). These light fractions are not included in HB estimation.

It should be noted that high boiling components can be present both in uncontaminated gasoline as well as in Diesel, which, raises a question about their origin. A better knowledge of the variation of HB in uncontaminated gasoline fuels and diesel fuels is needed to better differentiate the normal variation from a variation related to diesel contamination.

The FAME content measured by EN16270 is presented in Figure 10.b. Results show that FAME increases with the addition of Diesel fuel (DF1) to REF1 and REF2. It can be recalled that DF1 contains 6.5%v/v of FAME. The variation slope is consistent with FAME content in DF1. However, FAME remains at zero with the addition of Diesel fuel (DF2) to REF 3. This trend is expected as DF2 does not contain FAME. Although FAME might seem a relevant indicator to monitor diesel presence in gasoline, it is not adapted to detect contamination by a FAME-free diesel (which is the case of REF3/DF2 blends). In addition, there might be an issue with Diesel

fuels containing low amount of FAME as the detection limit of the technique is 0.01%m/m.

In summary, the measurement of High Boilers (HB) in gasoline by EN16270 is representative of Diesel contamination and Diesel contamination could be detected at 0.5%v/v considering the analysis uncertainty. However, the measurement of FAME does not seem suitable to detect Diesel contamination in all cases because it depends on the FAME content of diesel.

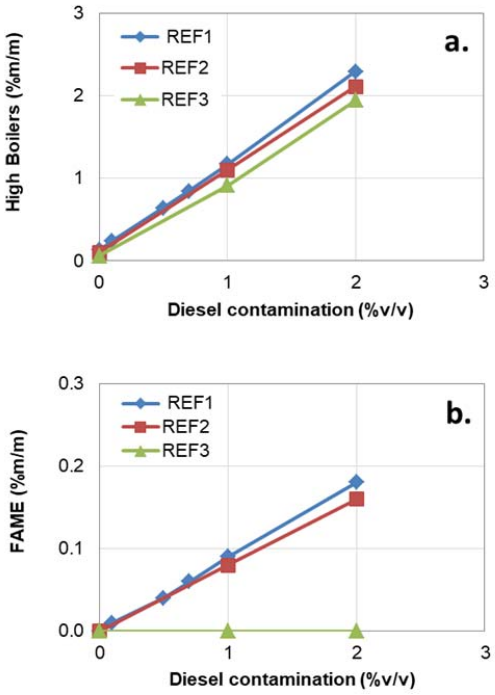

Figure 10: Variation of A. High boiling components (HB) and B. FAME with the addition of Diesel contamination to reference gasoline estimated by EN16270.

VDA 265

Figure 11.a presents the results of High boiling components HB variation with the addition of Diesel measured by VDA265. Results are very similar to those obtained by EN16270. Diesel could be detected at a lower content by VDA265 (0.1 %v/v) considering the lower uncertainty error. FAME variation with the addition of Diesel is represented in Figure 11.a. The result show very similar trends to EN16270 technique with a linear increase of FAME with the addition of Diesel fuel. This criterion is dependent on the content of FAME in the Diesel fuel. Finally, Diesel content derived from the GC analysis, is plotted in Figure 11.c. Results show qualitatively a linear increase of diesel content with the diesel contamination. Quantitatively, a good agreement is obtained as presented in Appendix 5.

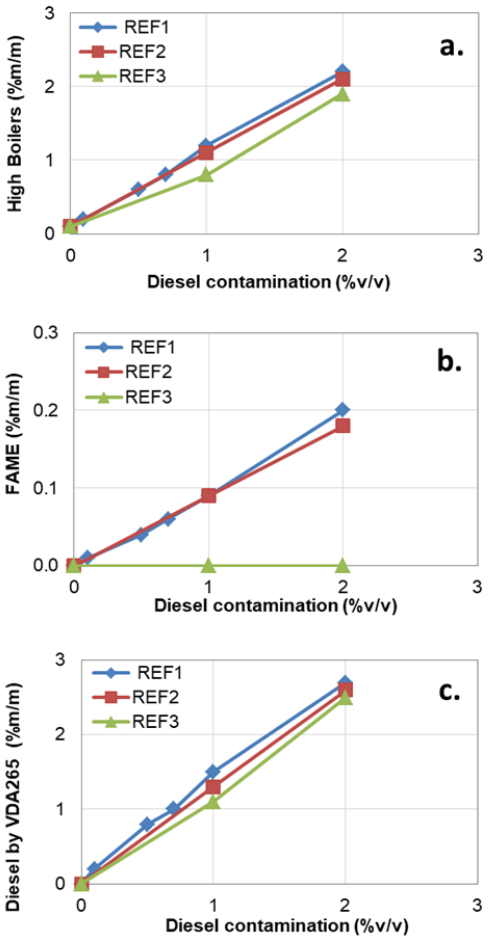

Figure 11: Variation of High boiling components with the addition of Diesel contamination to reference gasoline by VDA265. A: High Boilers, B. FAME, C. Diesel

3.2.4. Filterable contamination

Filterable contaminants FC of REF1 and Diesel fuel DF1 are measured in a first step. Results, presented in Figure 12.a, show a small amount of FC in the reference gasoline fuel that equals 0.21

mg. This suggests that the reference gasoline contains a small amount of particulates such as solid contaminants or gums that could be trapped by 0.45 µm filtration. Interestingly, FC in pure Diesel fuel are more than two orders of magnitudes higher than gasoline fuel (29 mg). This trend suggests that the Diesel fuel contains higher amount of particulates that can be retained by filtration. These contaminants are mainly organic. Solvency tests were carried out showing they were almost entirely soluble in common solvents such as pentane, heptane, dodecane, ethanol, methanol and toluene. In summary, the results of FC obtained in this study suggest a large difference between the reference gasoline in one hand and Diesel fuel (DF1) in the other hand. This large difference supports the working assumption put forward initially and might help the detection of Diesel in gasoline fuel.

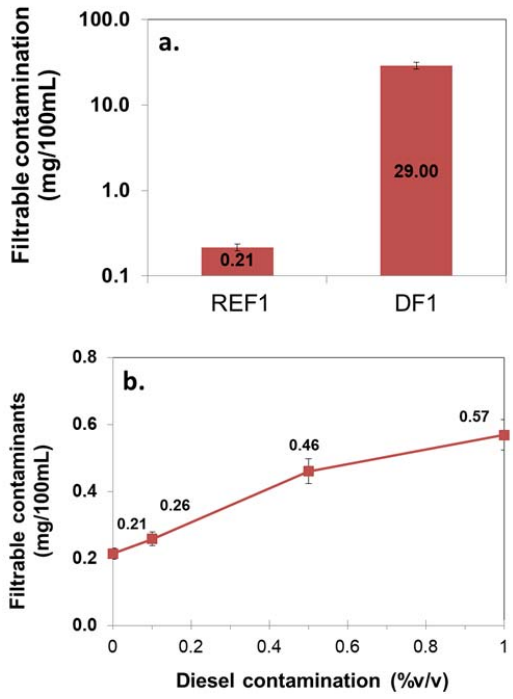

Figure 12: Filterable contamination by IFPEN method. a. Filterable contaminants of gasoline fuel REF1 and Diesel Fuel DF1, b. Variation of Filterable contaminants of REF1 gasoline fuel blended with Diesel fuel DF1

The measurement of the FC of Diesel/Gasoline blends is presented in Figure 12.b. The addition of Diesel increases the level of FC almost proportionally to the mass fraction of the Diesel fuel added. Diesel fuel can be detected since 0.5%v/v considering the measurement uncertainty.

This suggests a lower detection limit than the gums measurement using ISO 6246 protocol (1-2%v/v). Nevertheless, these results seem sensitive to the initial FC content of gasoline and Diesel fuels. Hence, an evaluation of the variability of Filterable contaminants for a representative database of market gasoline and diesel fuels is needed in order to define more accurately the normal levels and discriminate contaminated fuels.

3.2.5. NIR spectroscopy

NIR spectra were obtained for reference fuels (REF1, REF2 and REF3) and Diesel contaminants (DF1) and their blends. Principal Component Analysis was first applied to analyse qualitatively the effect of Diesel contamination in Gasoline.

Figure 13 presents the fuel matrix projection in the first score plot of the PCA (PC1, PC2). The points are arranged in the correct order with respect to the concentration of the contaminant from dark blue if there is no contaminant to yellow for the highest concentration of diesel. This result is interesting and shows a good sensitivity of this approach to detect contamination with diesel fuel. In summary, results confirm the potential to detect qualitatively the presence of Diesel in gasoline fuel by NIR associated to PCA.

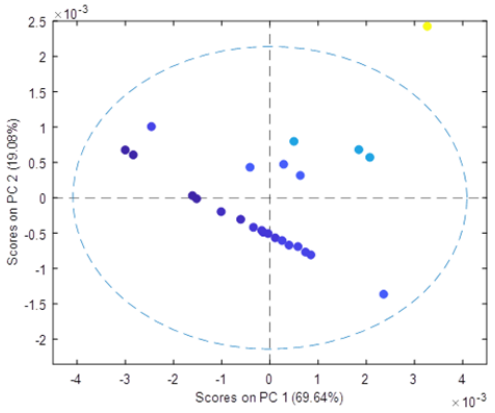

Figure 13: Characterization of the contaminated gasoline fuels with NIR Spectroscopy associated to Principal Component Analysis. Representation of the fuel projection in the plan (PC1, PC2) highlights the effect of Diesel contamination.

Partial Least Squares Analysis

To quantify the concentration of contaminants, Partial Least Squares PLS analysis was carried out in this study as described in section 2.3.2. A PLS model was developed for Diesel contaminant using the dataset presented in Appendix 3. The main properties of the model developed are provided in Table 4 below. Note that data from REF3 were not included in the calibration set.

Table 4: PLS models : Main characteristic and performance on the calibration dataset

Spectral range	4900-9000 cm^{-1}
X-Pre-processing	Baseline (WLB, order=2), 1st Derivative (order: 2, window: 15 pt), Mean Center
Y-Preprocessing	Mean center
Nb of spectra	27
Nb of latent values	5
RMSEC	0.028
RMSECV	0.045
BIAS Cal	0.0

Results of the model performance are presented in Figure 14 and Figure 15. Parity plot presented in Figure 14, shows a good correlation between the predicted and the reference values on the calibration dataset. Diesel concentration in gasoline is predicted with good agreement in the range 0.3-5%v/v with a confidence interval of 0.06% v/v.

Using the validation dataset presented in Figure 15, all the blends of Diesel DF1 with REF1 and REF2 (in the range of 0.1%v/v -1%v/v) are reasonably well predicted.

In summary, diesel contamination could be detected at concentration as low as 0.3 %v/v with a confidence interval of 0.06%. Further work is needed to validate these initial findings on a larger database of fuels including different grades and compositions of gasoline and diesel fuels.

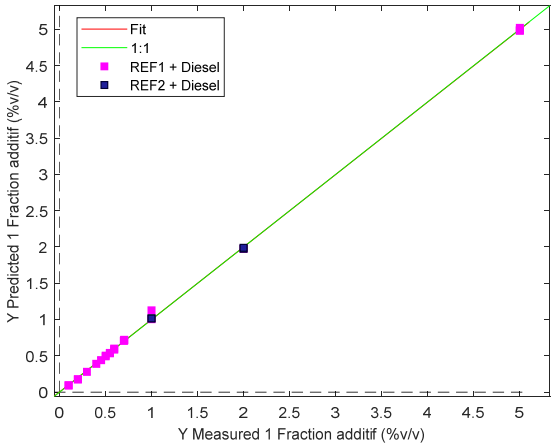

Figure 14: Prediction of Diesel contamination in gasoline by PLS analysis. Diesel Model performance on the calibration dataset

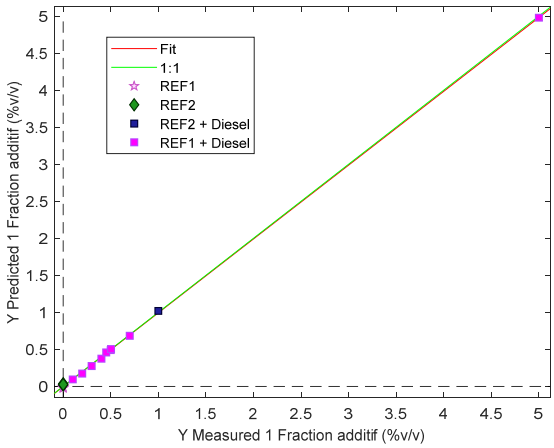

Figure 15: Prediction of Diesel contamination in gasoline by PLS analysis. Diesel Model performance on the Validation dataset

4. Synthesis

This study had two objectives. First, it aimed at evaluating through vehicle tests the impact of Diesel contamination on tailpipe particle emissions. Second, in order to quantify such contamination in gasoline fuel with simple techniques, several experimental approaches were investigated. The main results of this study are:

- Vehicle tests were carried out on WLTP using two Euro6-b vehicles equipped with a turbocharged direct-injection

gasoline engines. PN emissions were approximately 10% higher PN were obtained for 1%v/v of Diesel in gasoline.. 2% of diesel let to an additional emission increase.

- The FBP presented a good correlation with diesel contamination. However, the variation remains within EN228 limits for all tested fuels. Hence, distillation does not seem suitable to detect small amount of diesel in gasoline (<0.5%v/v).
- High boiling components by EN16270 and VDA265 were found interesting to detect small amount of Diesel contamination in gasoline: High boilers criterion was found sensitive to Diesel addition at 0.5%v/v using EN16270 and 0.1 %v/v using VDA265. Nevertheless, the use of these techniques in routine analysis might raise some practical concerns such as the need for a specific GC column and a technical expertise for the treatment of GC chromatograms.
- Unwashed gums UWG by ISO6246 were found sensitive to diesel contamination. However, the detection of Diesel was not always achievable at 1%v/v. The detection limit varies from 1-2%v/v depending on the gasoline and diesel fuel used. Washed gums was also unable to capture diesel contamination at concentration as low as 1%v/v in all cases. Thus standard gums seems also irrelevant to detect small amount of diesel in gasoline.
- Alternative techniques were developed in this study to address these concerns, namely 1) Filterable contaminant obtained by filtration, a widely used technique for fuel cleanliness control with a relatively low cost and technical expertise requirement and 2) Near Infrared Spectroscopy which is a relatively new technique but presents a practical benefit including low test duration and the possibility to use it in portable devices.
- Filterable contaminants allowed to detect diesel contamination at concentration as low as 0.5%v/v.
- NIR spectroscopy was successfully used to evaluate first, qualitatively the presence of Diesel in Gasoline through Principal Component Analysis (PCA), then, quantitatively, through Partial Least Square Modelling (PLS). PLS Analysis allowed to achieve the quantification of Diesel contamination at concentration as low as 0.3 %v/v. Further work is still needed to enlarge the calibration and validation database. More specifically, to upgrade the model with new parameters that account for differences between gasoline fuels and diesel fuels in the market.

5. Conclusions

This study highlighted the critical impact of diesel contamination in gasoline on pollutant emissions from future spark ignition engines. In this context, this work aimed at providing original data regarding the role of diesel on PN emission increase and developing laboratory tests which could contribute to better control the fuel quality.

Two original methods were developed for measuring Diesel contamination in market gasoline fuels based on Near Infrared spectroscopy and Filtration. These methods presented a good compromise between detection precision and ease of implementation. The study demonstrated that their sensitivity is low enough to detect a significant amount of diesel contamination regarding PN emission increase.

Further work is needed to validate these techniques on a larger fuel database. More specifically, to take into account the sources of variability of gasoline fuels and diesel fuels in the market. This work is on-going and will be the object of future publications by our group.

Lab Tests	Method	Diesel Detection	Standar-dization	Ease of use	Sug-gestion
Distillation	ISO 3405	Not detected	In EN228	Easy	
Washed Gums	ISO 6246	Not detected	In EN228	Easy	
Unwashed Gums	ISO 6246	≥1-2%v/v	Not in EN228	Easy	*
Filterable contaminants	IFPEN	≥0.5%v/v	New	Easy	+ +
High boiling components	VDA265	≥0.1%v/v	Not in EN228	Expensive	+
	EN16270	≥0.5%v/v			+
NIR	IFPEN	≥0.3%v/v	New	Not expensive	+ +

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Definitions/Abbreviations

GDI	Gasoline Direct Injection
PN	Particulate Number
RDE	Real Driving Emissions
PM	Particulate Matter
GHG	Greenhouse Gases
NIR	Near InfraRed
PCA	Principal Component Analysis
PLS	Partial Least Square
GC	Gas Chromatography
DTGS	Deuterated triglycine sulfate
WLB	White light bronchoscopy

Appendix

Appendix 1: Selected properties of the base Gasoline fuels and Diesel contaminants used to build the fuel matrix

Fuel name	Standard	REF1	REF2	REF3	DF1
Density (g/L)	NF EN ISO 12185	750.3	748.2		836.2
RON	NF EN ISO 5164	97.2	97.9		
MON	NF EN ISO 5163	85.8	86.2		
DVPE (kPa)	NF EN 13016-1	53.9	57		
Unwashed gums (mg/100mL)	NF EN ISO 6246	1.5	<0.5	58	
Washed gums (mg/100mL)	NF EN ISO 6246	0.5	<0.5	<0.5	
Smoke point (mm)	ASTM D1322	16.3	18	<14.7	19.7
Distillation	NF EN ISO 3405				
IBP		35.2	35.1	31.2	182.8
5		50.2	50.5	45	208.4
10		54.8	54.5	52.7	223
20		59.6	59	63.9	246.9
30		64.1	63.8	75.9	263.8
40		68.6	67.5	89.6	275.5
50		93	90.9	105.6	285.2
60		103.5	102.7	118.4	294.6
70		109.8	108.3	131.5	304.9
80		118.4	116.6	147.5	316.7
90		141.3	140.3	162.4	332.7
95		164.6	167.4	172.8	345.4
FBP		181.9	181.4	185.4	356.4
Residue (%v/v)		0.8	1.2	1	NA
LOSS (%v/v)		0.8	0.5	1.1	NA
E70 (%v/v)		40.6	41.1	25.1	0.0
E100 (%v/v)		56.7	57.7	46.5	0.0
E130 (%v/v)		85.1	85.7	68.9	0.0
E150 (%v/v)		91.9	91.8	81.7	0.0
E170 (%v/v)		96.6	95.9	93.7	0.0
Composition (%m/m)	ASTM D6733*				
n-Paraffins		6.1	6.2	5.8	7.8
i-Paraffins		35.2	35.2	37.5	32.0
Naphthenes		9.6	8.8	3.5	29.7
Aromatics		32.2	32.4	41.9	25.2
Olefins		7.0	7.2	11.3	
Oxygenated		9.9	10.1	0.0	5.4
Hydrocarbons C15+		0.0	0.0	0.0	
Unknowns		0.0	0.0	0.0	
Total		100.0	100.0	100.0	100.0
Composition (%v/v)	ASTM D6733*				
n-Paraffins		6.8	6.9	6.7	NA
i-Paraffins		39.0	39.2	41.5	NA
Naphthenes		9.4	8.6	3.4	NA
Aromatics		27.6	27.8	35.8	NA
Olefins		7.8	8.0	12.6	NA
Oxygenated		9.4	9.5	0.0	NA
Hydrocarbons C15+		0.0	0.0	0.0	NA
Unknowns		0.0	0.0	0.0	NA
Total		100.0	100.0	100.0	NA

Appendix 2 : Inventory and comparison of the GC methods used in this study

	EN16270	VDA 265
Quantification	Absolute areas	Relative areas
Calibration	One external for all gasoline types Heptane+1-MN, nC32, FAME	Every gasoline type has to be calibrated Calibration function 3xDiesel/3xFAME in gasoline, RT of 1-MN and nC26
Definition of HB	Above 1-MN (included) to nC32	Above 1-MN (excluded) to nC26
Injector	PTV/COC	Sample size : 1.0 µl
	Sample size : 1.0 µL	Splitter vent: 50mL/min
Column	10m x 0.53mm ID x 0.88µm T program: 40-350°C, 35°C/min He : 26 mL/min	30m x 0.25mm IDx0.1µm T program: 40 °C (1 min. hold), 40-260°C, 8°C/min; 260-375°C, 10°C/min He: cst pressure 40kPa
Validity range	HB : 0.7-2.5 %m/m FAME : 0.2 – 2%m/m Diesel : Not defined	HB : 0.1-1.0 %m/m FAME : 0.1-1.0%m/m Diesel : 0.1-1.0%m/m
Identification /	HB* : 0.01%m/m FAME : 0.01% (m/m)	HB: * : 0.1% (m/m) FAME : 0.01% (m/m)

Appendix 3: Inventory of the samples used in the calibration and validation databases for the PLS models

PLS model - Diesel		
Sample references	**Calibration**	**Validation**
REF1		5
REF1 + DF1 (0.1%v/v)	2	1
REF1 + DF1 (0.2%v/v)	2	1
REF1 + DF1 (0.3%v/v)	1	1
REF1 + DF1 (0.4%v/v)	1	1
REF1 + DF1 (0.45%)	1	1
REF1 + DF1 (0.5%v/v)	2	2
REF1 + DF1 (0.55%v/v)	2	
REF1 + DF1 (0.6%v/v)	2	
REF1 + DF1 (0.7%v/v)	4	1
REF1 + DF1 (1%v/v)	2	1
REF1 + DF1 (2%v/v)	1	
REF1 + DF1 (5%v/v)	3	1
REF2		3
REF2 + DF1 (1%v/v)	2	1
REF2 + DF1 (2%v/v)	2	

Appendix 4: Summary of the laboratory test results by Standard Techniques: Distillation by ISO3405, Unwashed Gums UWG and Washed Gums WG by ISO6246; High boiling components by EN16270 and VDA265

	ISO 3405 Distillation														
Fuel name	0	5	10	20	30	40	50	60	70	80	90	95	100	Residue	Loss
	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	%v/v	%v/v
REF1	35.2	50.2	54.8	59.6	64.1	68.6	93.0	103.5	109.8	118.4	141.3	164.6	181.9	0.8	0.8
REF1+DF1 (0.1%v/v)	35.1	51.0	55.0	59.9	64.2	68.3	93.3	103.9	109.4	118.4	143.0	165.3	184.4	0.9	0.2
REF1+DF1 (0.5%v/v)	36.5	51.8	55.6	60.5	64.9	69.1	94.7	104.9	110.9	120.2	144.5	168.5	197.6	1.0	0.5
REF1+DF1 (0.7%v/v)	34.8	50.8	55.1	59.9	64.2	68.3	93.6	103.9	110.2	118.9	144.3	167.7	193.1	1.0	0.6
REF1+DF1 (1%v/v)	36.0	50.7	55.0	59.7	64.3	68.3	93.7	104.1	110.4	119.9	144.4		199.7	0.8	1.0
REF1+DF1 (2%v/v)	36.5	49.8	54.5	59.6	64.1	69.4	93.5	104.3	110.9	120.8	147.8	171.2	208.8	1.1	1.6
REF1+DF1 (5%v/v)	36.4	52.1	55.5	60.4	65.0	72.1	97.8	105.5	114.0	126.9	163.6	199.8	220.0	3.0	0.6
DF1	182.8	208.4	223.0	246.9	263.8	275.5	285.2	294.6	304.9	316.7	332.7	345.4	356.4	NA	NA
REF2	35.1	50.5	54.5	59.0	63.8	67.5	90.9	102.7	108.3	116.6	140.3	167.4	181.4	1.2	0.5
REF2 + DF1 (1%v/v)	37.6	49.8	54.4	59.5	64.0	68.4	91.4	103.2	109.5	117.8	144.0	169.9	195.7	1.0	1.8
REF2 + DF1 (2%v/v)	36.3	50.2	54.5	59.5	64.0	68.4	92.7	103.6	110.0	119.1	146.9	173.3	202.4	1.1	1.3
REF3	31.2	45.0	52.7	63.9	75.9	89.6	105.6	118.4	131.5	147.5	162.4	172.8	185.4	1.0	1.1
REF3 + DF2 (1%v/v)	29.9	45.7	52.7	63.9	76.0	90.1	105.2	119.5	132.7	148.6	163.8	174.0	199.4	1.2	0.6
REF3 + DF2 (2%v/v)	30.0	45.5	53.0	64.6	76.7	91.0	106.8	120.9	133.9	149.8	165.4	176.4	201.2	1.5	0.8

	ISO 6246		EN16270		VDA265		
Fuel name	UWG	WG	High boilers	FAME	High boilers	DF1	FAME
	mg/100mL	mg/100mL	%m/m	%m/m	%m/m	%m/m	%m/m
REF1	1.5	0.5	0.13	<0,01	0.10	<0.1	<0.01
REF1+DF1 (0.1%v/v)			0.24	0.01	0.2	0.20	0.01
REF1+DF1 (0.5%v/v)			0.64	0.04	0.6	0.8	0.04
REF1+DF1 (0.7%v/v)			0.84	0.06	0.8	1.0	0.06
REF1+DF1 (1%v/v)	0.5	<0.5	1.17	0.09	1.2	1.5	0.09
REF1+DF1 (2%v/v)	5.0	4.0	2.29	0.18	2.2	2.7	0.20
REF1+DF1 (5%v/v)	31.0	4.0	5.37	0.45	5.4	6.9	0.47
DF1			>>	>>	>10 (82)	>>	>>
REF2	<0.5	<0.5	0.10	<0,01	0.1	<0.1	<0,01
REF2 + DF1 (1%v/v)	6.5	6.5	1.10	0.08	1.1	1.3	0.09
REF2 + DF1 (2%v/v)	76.5	3.0	2.11	0.16	2.1	2.6	0.18
REF3	<0.5	<0.5	0.06	<0,01	0.1	<0.1	<0,01
REF3 + DF2 (1%v/v)	<0.5	<0.5	0.91	<0,01	0.8	1.1	<0,01
REF3 + DF2 (2%v/v)	3.0	<0.5	1.94	<0,01	1.9	2.5	<0,01

Appendix 5: Measurement of High Boilers by VDA265 and EN16270 in REF1 and REF2 contaminated with diesel. Measurement of Diesel content by VDA265 in REF1 and REF2 contaminated with diesel. Diesel contamination is given in mass fraction.