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Preliminary investigation of experimental conditions and precision of an alternative method to determine high boiling point components in motor gasoline

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ABSTRACT

This work describes a new method that can be used for the determination of high boiling point components in motor gasoline. Heavier components in the range of diesel fuel, if present in the gasoline, do not completely burn during the combustion cycle of spark ignition engines and increase exhaust emissions and deposits formation in the combustion chamber. The method used for the determination of heavy residue in gasoline is the atmospheric distillation test, according to EN ISO 3405 (similar to the classic ASTM D86) test method. The volume of distillation residue is recorded. This residue must be below 2% V/V according to EN 228 standard. The presence of heavy components is caused mainly by remnants in tanks and pipelines or bad housekeeping in the fuel distribution and supply chain. In this paper, a new alternative method is used. The residue is determined as mass percentage of the test sample after evaporation of a small quantity of the sample in a proper container put in an oven. Results show that at oven temperature of 220 °C and residence time of 20 min repeatable results can be obtained. The test method was also tested in gasoline sample that was intentionally mixed with automotive diesel, in concentrations up to 5% m/m, in an attempt to simulate a possible incident in the gasoline supply chain distribution system. Regarding the quantification of the amount of heavier fraction that was present in the fuel, the obtained results suggest that the new method gave better results in comparison to the classic EN ISO 3405 distillation test method.

1. Introduction

Fuel quality is critical to the operation of spark ignition engines with respect to both performance and emissions [1,2]. Fuel composition will continue to grow in importance in an attempt to reach the target of near-zero-emission vehicles [3,4]. In European Union (EU), several directives [5,6] set technical specifications for fuels used on market. Gasoline is the lighter of the liquid transport fuels used worldwide. The mixture of hydrocarbons (and oxygenates) in a gasoline determines its physical properties and engine performance characteristics, which affect driving performance. A critical gasoline characteristic for good driveability is volatility. It is important to note that there is no single best volatility for gasoline, but it must be adjusted for the altitude and seasonal temperature of the location where the fuel will be used [7]. Gasoline volatility is measured by the use of vapor pressure (Reid vapor pressure or equivalent methods), distillation profile and vapor lock index. Distillation profile is measured by ASTM D86 test method (American Society for Testing and Materials - ASTM) or the equivalent EN ISO 3405 test method (International Standardization Organization - ISO) [8,9]. The distillation profile and particular back end volatility is adjusted to provide good fuel economy after engine warm-up, to eliminate the formation of deposits, and to minimize the fuel dilution of crankcase oil [10]. Gasoline must not contain high boiling point components, because these components negatively affect the quality characteristics of the fuel and increase exhaust emissions from gasoline engines. The increase of back end volatility (expressed in terms of E150 or T90 distillation points) contributes toward the reduction of hydrocarbons (HC) emissions, but leads to some rise in carbon monoxide (CO) and nitrogen oxides (NOx) emissions [11]. These remarks correlate with the presence of higher molecular mass compounds in the fuel which do not burn completely; due to the large size of their molecule, they don't have enough time in order to be fully burnt in the combustion chamber [12,13]. The contamination of motor gasoline with heavier components is mainly an issue dealing with good working practice and good housekeeping procedures in the refining, storage and

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distribution supply chain of motor fuels. The presence of heavier hydrocarbon in gasoline is an indication of mix in small quantities with heavier fuels, in pipelines, tank trucks, and fuel stations tanks. Due to the importance of the issue, a new European standard has been recently issued by the European Committee for Standardization (CEN), for the determination of high boiling point components in gasoline [14]. This standard describes a method for the determination of high boiling components in gasoline by capillary gas chromatography using flame ionization detection.

An alternative method for the determination of high boiling point components in gasoline is presented by the authors. The method is based on the evaporation of a small amount of gasoline under specific conditions, and gravimetric determination of the residue after the evaporation stage has been finished. The results obtained are in good relation with the amount of heavier component (diesel fuel in this case) that was added to the gasoline sample used in concentrations 1.0, 2.0, 3.0, 4.0, and 5.0% m/m. The measurements with EN ISO 3405 also showed that the presence of high boiling point components in gasoline affects mainly the back end volatility of the fuel and more specifically final boiling point (FBP), T95, and T90. Samples with 4.0 and 5.0% m/m diesel fail the FBP specification that sets maximum value of 210 °C according to EN 228 standard [15]. A slight decrease was noticed in E100 and E150 while E70 was not affected. Distillation residue increased as diesel concentration increased but only samples containing 4.0% and 5.0% m/m diesel had residues exceeding the acceptance limit of 2% V/V [16,17]. The comparison of the results from the proposed method with results from EN ISO 3405 test method showed that the proposed method was unable to quantify the presence of high boiling point components at low concentrations (below 3.0% m/m), where EN ISO 3405 method failed in these low concentrations.

2. Experimental section

2.1. Base fuels

In order to evaluate the efficiency of the EN ISO 3405 method to determine the presence of high boiling point components in gasoline, a typical gasoline sample that meets the EN 228 standard requirements was used as base fuel. A typical automotive diesel fuel that meets the requirements of the EN 590 [18] standard was added in the gasoline. Blends containing 1.0, 2.0, 3.0, 4.0, and 5.0% m/m diesel in gasoline were prepared. The main characteristics of the two base fuels used in this series of experiments are shown in Tables 1 and 2.

2.2. Distillation measurements

All samples were analyzed for their distillation characteristics by EN ISO 3405 method. In order to check the precision of the measurements each sample was measured in 3 different automatic distillation units. 2 distillation tests were performed in each sample, giving a total number of 6 runs per sample. According to EN 228, the volume of the distillation residue is recorded, which must be below 2% V/V for conformity reasons. The mass of distillation residue was also measured by weighing the final mass of the flask.

2.3. Residue determination measurements

All the samples were also tested for their residue according to the new method that is under consideration. A brief description of the method is as follows: A small amount (4 ml) of the test fuel is added in a glass container that has a narrow neck. Coking bulbs used for the determination of Ramsbottom carbon residue were used as sample containers [19]. The fuel sample is transferred to the container by use of hypodermic syringe. The amount of the fuel added is determined with precision on laboratory balance. The glass container with sample is placed in an upright position in a thermostated oven for a determined time period. The oven used for the test is the Ramsbottom test block [19]. The apparatus is located in a hood equipped with fire proof electric equipment. A fire extinguishing system is available in the hood for safety reasons. The oven temperature is relevant to the maximum allowable according to EN 228. During this residence time in high temperature, the fuel is evaporated and a very small amount of residue remains in the container. The residue is determined as a percentage by mass of the test sample.

Table 1
Main properties of the gasoline sample.

Property	Units	Value	Expanded uncertainty	Limits		Test method
				Min.	Max.	
Research Octane Number, RON		95.5	0.3	95		EN ISO 5164
Motor Octane Number, MON		85.6	0.3	85		EN ISO 5163
Density (at 15 °C)	kg/m^3	744.3	0.1	720	775	EN ISO 12185
Sulfur content	mg/kg	6.1	1.1		10	EN ISO 20846
Hydrocarbon type	% (V/V)					EN 14517
Content		10.9	2.1		18.0	
Olefins		31.8	1.8		35.0	
Aromatics						
Benzene content	% (V/V)	0.88	0.02		1	EN 14517
Oxygen content	% (m/m)	2.15	0.12		2.7	EN 14517
Oxygenates content	% (V/V)					EN 14517
MTBE		7.7	0.4		15.0	
TAME		4.1	0.4		15.0	
Vapor Pressure (VP)	kPa	78.4	0.7	50.0	80.0	EN 13016-1
Distillation						EN ISO 3405
% evaporated at 70 °C, E70	% (V/V)	36.2	0.9	22.0	50.0	
% evaporated at 100 °C, E100	% (V/V)	62.1	0.7	46.0	71.0	
% evaporated at 150 °C, E150	% (V/V)	89.7	0.7	75.0		
Initial Boiling Point (IBP)	°C	34.6	1.9			
T10	°C	49.6	1.7			
T50	°C	83.5	0.8			
T90	°C	151.0	1.1			
T95	°C	164.5	2.0			
Final Boiling Point (FBP)	°C	186.2	2.6		210	