Chapter 4

Distillation: Basic Test in Quality Control of Automotive Fuels

Ma Mercedes del Coro Fernández-Feal,
Luis R. Sánchez-Fernández and
Blanca Sánchez-Fernández

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/67140

Abstract

The petroleum-derived automotive fuels available on the market today have different characteristics from those that were available a decade ago, mainly due to the promotion of the use of biofuels. However, the study of their distillation curves remains a basic test for their quality control. The ISO 3405 Standard has been the basis of the test procedure for the determination of the distillation characteristics of petroleum-derived automotive fuels at atmospheric pressure. This test is essential for the quality control of this type of products because of the extensive information that can be extracted from the interpretation of its results. The introduction of biofuels (bioethanol, biodiesel) in the new automotive fuel formulations, petrol and diesel fuels, made imperative to review ISO 3405:2000 in 2011. This paper studies the most significant changes between the two versions of the ISO 3405. The latest edition of the Standard is broader in scope; it has been modified in order to include the new fuel formulations which result from biofuel mixtures and the new criteria for repeatability and reproducibility calculation. This paper studies the most significant changes between the two versions of the ISO 3405 Standard together with a field study of commercial automotive fuel samples selection (with and without biofuel blend) and certified reference materials.

Keywords: distillation, volatility, quality control, fuel, biofuel

1. Introduction

'Distillation is the most widely used separation technique in the petroleum industry' [1].

At present, petroleum remains the major source of energy resources, and for more than 100 years, it has been the main source of fuels used in alternative internal combustion engines in auto-motion as well, both for spark ignition engines (SIE[1]), traditionally known as petrol engines, and for compression ignition engines (CIE[2]), or diesel engines. Nevertheless, we must bear in mind that differences in the operation of spark ignition and compression ignition engines require very different types of fuels.

When we speak about petroleum-derived fossil fuels, used as automotive fuel, we must remember that in a given series of hydrocarbons the ignition temperature decreases as the molecular weight increases because the cracking of large molecules needs less activation energies [1], whereby:

1. The SIE require low boiling hydrocarbons, with a soft combustion temperature and a relatively high spontaneous ignition temperature.
2. In the CIE, hydrocarbons with low spontaneous ignition temperatures are preferable, whereby the compounds of low boiling points are unsuitable.

From the chemical composition viewpoint, petrol is a blend of hydrocarbons between C4 and C11, with boiling points between 25 and 210°C and in which we can find all types of hydrocarbons: paraffins, isoparaffins, olefins, aromatics, naphthenes, etc. They may also contain oxygenated compounds such as ethers (MTBE, ETBE, TAME[3]) and pure alcohols in variable proportions: minimum amounts of sulphur and nitrogen as well as additives (detergents, anti-knock, etc.).

From the chemical composition viewpoint, the diesel fuels are a blend of different components obtained from different refining processes, with a majority of hydrocarbons between C10 and C16, with boiling ranges between about 160 and 360°C, and low amounts of sulphur and nitrogen. Additives are also present in their formulations [2–4].

Petroleum is, even today, the source of energy most used worldwide, but it is not an inexhaustible source of energy; this fact, together with the need to protect the environment, has led to the search for new automotive fuels and for the modification of the characteristics of the existing ones. One of the paths chosen in recent years has been to include biofuels in the formulation of conventional automotive fuels given their great capacity for blend with petroleum-derived fuels [5].

Incorporating biofuels and/or bioethanol to petrol and biodiesel (FAME[4]) to diesel is a path to a more sustainable energy future and involves a great R&D effort since it is necessary to study how blending modifies fuel characteristics in the search for optimal behaviour in any automobile engine [6].

As a general rule, according to international specifications, petrol can be combined with bioethanol in a percentage not exceeding 10% by volume and diesel with biodiesel up to a maximum of 7% in volume without informing consumers about it. There are also specially designed vehicles that can support a mixture of petrol with 85% by volume of bioethanol (E85) and taxis or buses that use a mixture of diesel and biodiesel in a proportion of 70:30% by volume (B30) [7].

Now, any fuel which is in the market should guarantee that their use in an engine will provide the projected energy performance that it will satisfy any other capacity inherent to their

[1]SIE—spark ignition engine
[2]CIE—compression ignition engine
[3]Methyl tert-butyl ether, ethyl tert-butyl ether, tert-amyl methyl ether
[4]FAME—fatty acid methyl esters

use and it will perform to the environmental quality level required. In order to comply with these conditions, those fuels must comply with certain specifications, i.e. a set of physical and chemical characteristics with maximum or minimum specified values, obtained through test procedures or standards [8, 9], including their volatility.

With the aim of controlling engine performance and the formation of vapours which may form explosive mixtures with air or escape to the atmosphere as emissions (VOCs—volatile organic compounds), most of the specifications for petroleum distillate products, specially the main automotive engine fuels, limit the values of certain distillation characteristics (volatility).

A fuel distillation range provides decisive information about its composition, its use and its behaviour during storage.

2. State of the art

2.1. Volatility versus fuel type

Among the wide variety of features to consider when establishing the quality of a fuel used in auto-motion, volatility stands out as one of the most critical ones since it is a characteristic directly related to engine performance and pollutant emissions [2–4].

2.1.1. Petrol

Petrol is a fuel which is a liquid state in the fuel tank and in the fuel injectors (or carburettor on older engines) and which is nebulized with air before being injected into the combustion chamber:

- If the volatility of fuel is low, the petrol does not exist in the gas phase, and there will be difficulties with the starting up of the engine and the behaviour of the engines in cold regimes.
- If the volatility is high, the petrol can be vaporized in the tank itself or in the pipelines ('vapour lock'). As a consequence the injection rate is inadequate, and the engine drowns.

2.1.2. Diesel

The volatility characteristics of a diesel have a great influence on the performance of diesel engines:

- If the volatility is low, then high distillation end points are obtained, which are indicative of high combustion times and poor combustion of heavy hydrocarbons. This will lead to the formation of smoke, loss of power and increased fuel consumption.
- If the volatility is high, then the fuel can cause incidents of 'vapour lock' in the lines.

2.2. Measure of volatility: distillation curve

Volatility is not a physical magnitude that can be measured directly; it is necessary to define methods of evaluating it. One universally used method to determine the volatility of a fuel is the distillation test [10, 11] that offers different information according to the type of fuel tested.

2.2.1. Petrol

The distillation test measures the percentage of vaporized fuel as the temperature increases. The test result is a curve obtained under standardized conditions of temperature versus percentage of evaporated fuel (**Figure 1**) wherein the different sections of the curve allow us to interpret the different behaviours of the product:

- At least 20% V/V fuel must be vaporized below 70°C to ensure good cold start capability. If this percentage is lower, then difficulties may occur at start-up; if it is too high, evaporation losses will occur in the fuel tank, and vapour bubbles may form in the intake manifold of the vehicle.
- The temperature at which 50% V/V of fuel is vaporized is a critical parameter, since if it is too low it can cause the solidification of water vapour contained in the intake air resulting in formation of ice on elements forming the blend.
- If the temperature at which 90% V/V of the fuel is vaporized is too high, then the fuel can remain in liquid form within the cylinder, displacing the lubricant and coming to cause oil dilution. Additionally, combustion may be hampered, causing irregular operation of the engine. Also, the presence of hydrocarbons of high boiling point in the petrol is decisive for the generation of polluting emissions.

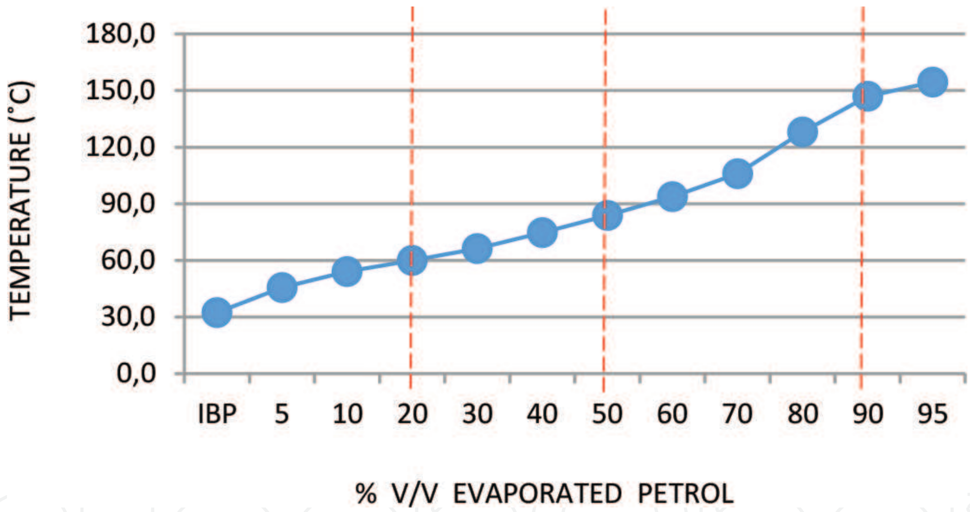


Figure 1. Distillation curve of petrol.

The percentages of fuel evaporated at 70, 100 and 150°C are limited. Additionally, a limitation in the final boiling point of to 210°C is also implemented in the regulations, ensuring the complete combustion of hydrocarbons and the non-formation of deposits in the combustion chamber and spark plugs.

2.2.2. Diesel

In a CIE, the volatility problems that may be present are notably different from those in SIE. In the regulations, there are no limitations in the light section of the curve but only for the end zone, where the fractionation of the components occurs.

The distillation test, in this case, measures the percentage of fuel which is recovered as the temperature increases. The test result is a curve obtained under standardized conditions of temperature versus percentage recovered (**Figure 2**). In these, fuel is important to note:

- The temperature at which vaporization ends, since if this is very high, combustion of the less volatile components will be incomplete, fuel droplets may reach the cylinder walls and dilution of the lubricating oil may take place, thereby increasing wear and producing coke deposits in the combustion chamber and waste segments [3].
- The end point of the fractionation of the components. This parameter is established so as 65% V/V must not have distilled before 250°C; 85% V/V should be distilled before 350°C,and 95% V/V before 360°C.

Figure 3 shows the distillation curves associated to both types of automotive fuels, petrol and diesel.

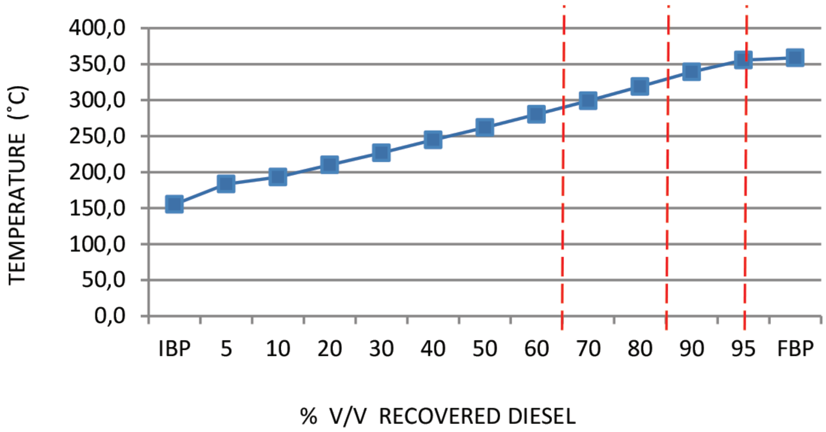


Figure 2. Distillation curve of diesel.

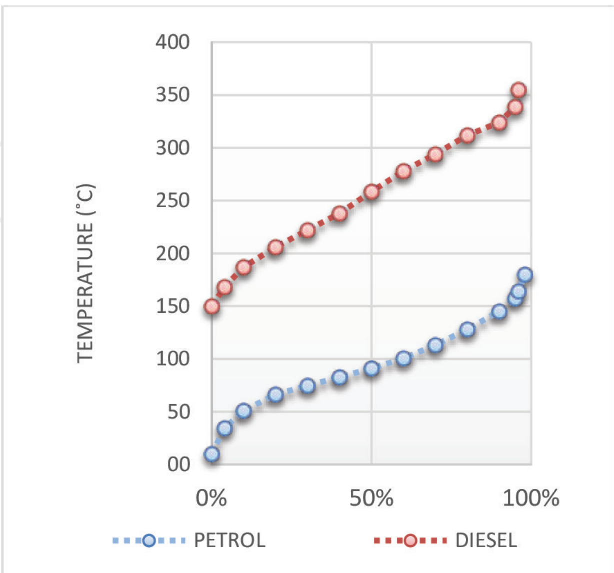


Figure 3. Comparison between distillation curves of petrol and diesel.

2.3. ISO 3405: petroleum products—determination of distillation characteristics at atmospheric pressure

ISO 3405 International Standard has been adopted by the European Standard EN ISO 3405, and it received the rank of the National Standard, by publication in the national language of an identical text under the responsibility of a member of CEN (European Committee for Standardization): UNE-EN ISO 3405 (Spain), DIN-EN ISO 3405 (Germany), etc.

This procedure aims to establish the steps '*for determining the distillation characteristics of light and middle distillates derived from petroleum having initial boiling points above 0°C and end points below approximately 400°C*'.

There are standards similar to ISO 3405 developed by other agencies with the same objective, such as ASTM D86: Standard Test Method for Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure, whose first version dates from 1978, or IP 123: Petroleum Products—Determination of Distillation Characteristics at Atmospheric Pressure.

The test samples are classified into 'groups' based on their composition and the characteristics of expected volatility. In the case of fuels for automotive engines, petrol with up to 10% V/V ethanol is included in Group 1 and diesels with up to 20% V/V biodiesel in Group 4 (**Table 1**). Belonging to a particular group defines the setup of the equipment to be used and the condenser temperature. Finally, it determines the operation conditions to be used in the process of distillation by ISO 3405 (**Table 2**).

	Group 1	**Group 4**
Type of sample	Petrol	Diesel
Reid vapour pressure (kPa)	≥65.5	<65.5
Characteristics of expected volatility		
Initial distillation point, IDP (°C)	–	>100
Final boiling point, FBP (°C)	≤250	>250

Table 1. Sample type by group and expected volatility characteristics.

	Group 1	**Group 4**
Temperature of condensador bath (°C)	0–1	0–60
Temperature of medium around recovered receiving cylinder (°C)	13–18	±3 of charge
Time from the first heat to IBP (min)	5–10	5–15
Time from IBP to 5% (V/V) recovered (s)	60–100	–
Uniform average rate from 5% (V V) of recovered to 5 mL in the flask (mL/min)	4–5	4–5
Time from 5 mL residue in the flask to FBP (min)	≤5	≤5

Table 2. Test conditions.

During the testing process, a 100 mL test portion is distilled under the specified conditions appropriate to the fuel group, and systematic observations of thermometer readings and volumes of condensate recovered are made.

2.4. Precision ISO 3405: automated apparatus

The introduction of new formulations in automotive fuels made necessary the adaptation of the standard in effect at the time of their appearance (ISO 3405:2000), and, given the volatility characteristics of the new formulations, it was also necessary to validate the test method again based on new precision criteria.

The new version of the ISO 3405 standard (2011) establishes new criteria, based on the group to which it belongs the sample tested, to determine the validity of two results obtained under the same conditions by one operator using the same apparatus, in the same operating conditions, on the same day, on identical samples (repeatability, r) or obtained by different operators working in different laboratories on identical material test (reproducibility, R).

In the case of petrol and bioethanol blends (Group 1), these criteria are listed in **Tables 3** and **4** and in the case of diesel and biodiesel blends (Group 4) in **Tables 5** and **6**.

2000	Evaporated % (V/V)	2011	
Repeatability Group 1		**Repeatability Group 1**	**Valid range (°C)**
3.9	IBP	0.0295 (E + 51.19)	20–70
r_2 + 0.56	10	1.33	35–95
r_2	50	0.74	65–220
r_2	90	0.00755 (E + 59.77)	110–245
4.4	FBP	3.33	135–260

r_2 is a constant function of the slope, ΔC/ΔV, at each distillation point, with values calculated from $r_2 = 0.673\ (\Delta C/\Delta V) + 1.131$.
E is the temperature at the percentage evaporated within the prescribed valid range.

Table 3. Repeatability (Group 1).

2000	Evaporated % (V/V)	2011	
Repeatability Group 4		**Repeatability Group 4**	**Valid range (°C)**
3.5	IBP	0.018 T	145–220
1.42 (ΔC/ΔV) + 1.2	10	0.0094 T	160–265
1.42 (ΔC/ΔV) + 1.2	50	0.94	170–295
1.08 (ΔC/ΔV) + 1.1	90	0.0041 T	180–340
1.08 (ΔC/ΔV) + 1.1	95	0.01515 (T–140)	260–340
3.5	FBP	2.2	195–365

Slope: ΔC/ΔV
T is the temperature at the percentage recovered within the prescribed valid range.

Table 4. Repeatability (Group 4).

2000	Evaporated % (V/V)	2011	
Reproducibility Group 1		Reproducibility Group 1	Valid range (°C)
7.2	IBP	0.0595 (E + 51.19)	20–70
$R_2 + 0.72$	10	3.20	35–95
R_2	50	1.88	65–220
$R_2 - 1.90$	90	0.019 (E + 59.77)	110–245
8.9	FBP	6.78	135–260

R_2 is a constant function of the slope, ΔC/ΔV, at each distillation point, with values calculated from $R_2 = 1.998\ (\Delta C/\Delta V) + 2.617$.

E is the temperature at the percentage evaporated within the prescribed valid range.

Table 5. Reproducibility (Group 1).

2000	Evaporated % (V/V)	2011	
Reproducibility Group 4		Reproducibility Group 4	Valid range (°C)
8.5	IBP	0.055 T	145–220
2.64 (ΔC/ΔV) + 3.0	10	0.022 T	160–265
3.97 (ΔC/ΔV) + 2.9	50	2.97	170–295
2.53 (ΔC/ΔV) + 2.0	90	0.015 T	180–340
2.53 (ΔC/ΔV) + 2.0	95	0.04227 (T–140)	260–340
10.5	FBP	7.1	195–365

Slope: ΔC/ΔV

T is the temperature at the percentage recovered within the prescribed valid range.

Table 6. Reproducibility (Group 4).

3. Materials and methods

Step 1.

A sample selection of automotive fuel (petrol, diesel) with and without blend of biofuel (bioethanol, biodiesel) for a field study is used. The variations in product volatility as a result of the presence of biofuel in its composition are checked.

Each sample is tested in duplicate by two operators.

Step 2.

The changes in criteria established for repeatability and reproducibility in Standard ISO 3405 are studied; certified reference materials are used.

http://dx.doi.org/10.5772/67140

3.1. Test description

3.1.1. Reagents and materials

- Acetone: cleaning solvent.
- Certified reference material (CRM).
- Distillation flasks: flasks should have a capacity of 125 mL and be constructed of heat-resistant glass, according to the dimensions and tolerances given in Standard ISO 3405:2011.
- Receiving cylinder: graduate cylinder of 100 mL capacity, with a mark at 100 mL and metal base.
- Residue cylinder of 5 mL capacity.
- Certified temperature-sensor pt100 to an accuracy of 0.01C.
- Centring device, for centring the temperature sensor, adjusts the neck distillation flask, allows to centre the temperature sensor and prevents steam leaks.

3.1.2. Apparatus

- Automated equipment for petroleum product distillation satisfies the requirements established in the Standard ISO 3405:2011; the maximum error tracking device level is 0.3 mL.

3.1.3. Preparation of apparatus

- Clean the condenser tube, employing acetone. Dry thoroughly to remove any portion of acetone used for cleaning the device.
- Check that the temperature probe is properly seated in the centring device. Check your state and proper cleaning.
- Choose the support plate of the flask as the orifice diameter thereof according to the type of sample to be tested (**Table 7**).
- Check that the value of atmospheric pressure recorded by the apparatus is coincident with that indicated by the recording barometer atmospheric pressure in the laboratory.

	Group 1	**Group 4**
Diameter of hole in flask-support board (mm)	38	50
Temperature at start of test (°C)		
Flask and thermometer	13–18	≤ambient
Flask-support board and shield	≤ambient	–
Receiving cylinder and sample	13–18	13 at ambient

Table 7. Preparation of apparatus.

3.1.4. Procedure

- Measure the test portion precisely to the 100 mL mark of the receiving cylinder, and then transfer it as completely as practical to the distillation flask, taking care that none of the liquid flows into the vapour tube. If irregular boiling (bumping) is expected, add a small volume of clean and dry boiling chips to the test portion.
- Fit the flask vapour tube, provided with a silicone rubber stopper, tightly into the condenser tube. Adjust the distillation flask in a vertical position so that the vapour tube extends into the condenser tube for a distance of 25–50 mm. Raise and adjust the flask-support board to fit snugly against the bottom of the flask.
- Fit the receiving cylinder with a drip deflector, through which the distillate is going to drip.
- Place the receiving cylinder that was used to measure the test portion, without drying, into the bad under the lower end of the condenser tube so that the end of the condenser tube is centred in the receiving cylinder and extends therein for a distance of at least 25 mm.

After the choice of the method, which has been specifically developed to the distillation test according to **Table 2** and the corresponding group, follow the steps indicated by the system software. Any distillation that does not meet above conditions must be repeated, as well as those in which the actual loss differs by more than 2 mL from the estimated value.

3.1.5. Calculations

The data required for calculations is recorded in the range between the initial and the final boiling point, with an accuracy of 0.1 mL for all the readings on the receiving cylinder and with an accuracy of 0.1°C for all the readings on the temperature sensor.

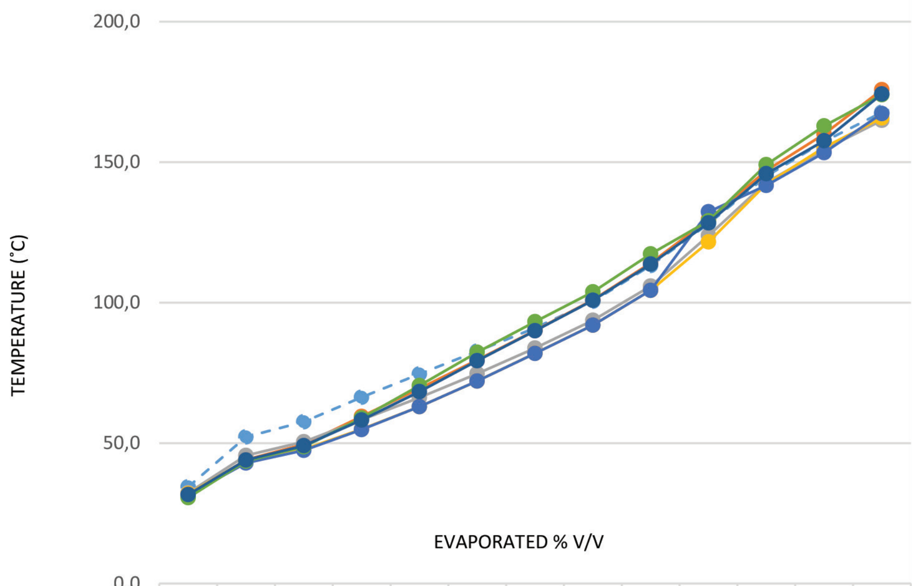
Distillations carried out with automated instrument do not require manual calculation; the system software makes the appropriate calculations according to the corrective measures established by the Standard. However, it is certainly right to check the atmospheric pressure value does not differ by more than ±10 hPa from the value provided by the barometer in the laboratory.

3.2. Results obtained

3.2.1. Step 1: Samples of petrol—distillation curves obtained

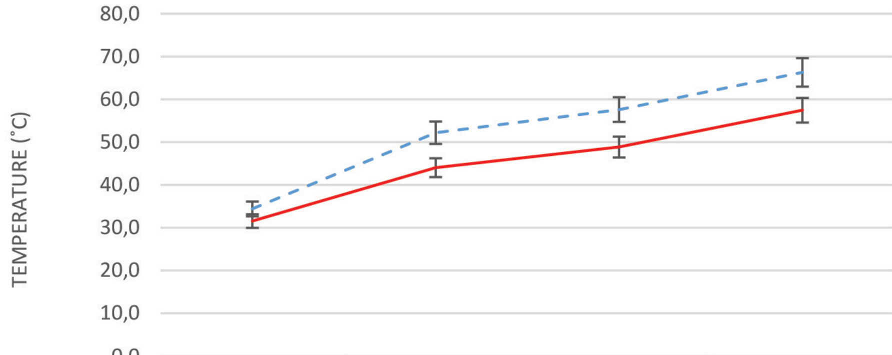
Distillation test is carried out on 24 petrol samples with a bioethanol percentage that varies between 0.0 and 4.0% V/V, obtaining their corresponding distillation curves. Among these curves, we have selected seven for being analyzed and included in the present paper. Obtained results are shown in **Figure 4**.

After studying the trend and as the different sections of the curve give the opportunity to interpret the different product performances, a particular observation of each section is developed, making a graphic comparison on the basis of an average value (**Figures 5–7**).



	IBP	5	10	20	30	40	50	60	70	80	90	95	FBP
0,0%V/V	34,4	52,2	57,6	66,3	74,6	82,7	91,0	100,5	113,2	128,1	145,0	157,4	167,7
1,0%V/V	31,2	44,1	49,6	59,5	69,4	79,6	90,1	101,0	114,1	129,6	147,0	160,0	175,8
1,5%V/V	32,3	45,6	50,5	58,3	66,2	74,7	83,8	93,7	105,9	123,9	142,8	154,5	164,9
2,1%V/V	32,0	43,9	47,8	55,0	63,0	72,1	82,0	92,0	104,4	121,6	142,2	155,3	165,7
2,5%V/V	31,5	42,9	47,4	54,8	63,0	72,1	81,9	92,0	104,4	132,3	141,7	153,4	167,3
3,5%V/V	30,6	43,6	48,7	58,9	70,5	82,3	93,2	103,8	117,3	129,1	149,1	162,9	174,0
4,0 %V/V	31,7	44,0	49,1	58,2	68,3	79,3	90,0	100,8	113,7	128,4	145,9	157,6	174,3

Figure 4. Distillation curves: petrol and blends with bioethanol (0.0–4.0% V/V).

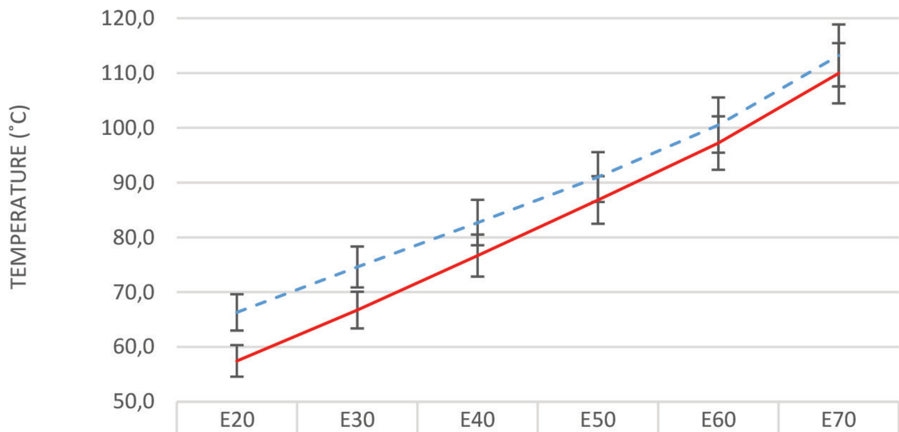


	IBP	E5	E10	E20
PETROL	34,4	52,2	57,6	66,3
PETROL WITH BIOETHANOL	31,6	44,0	48,9	57,5

Figure 5. Initial section (IBP-E20). Distillation curves of petrol samples.

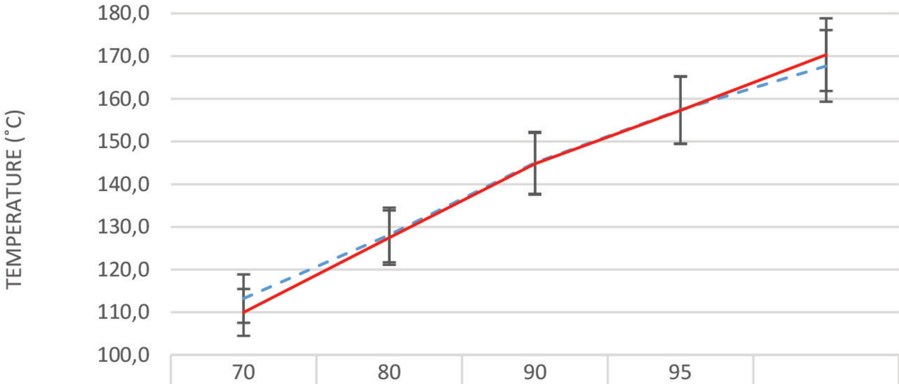
3.2.2. Step 1: Diesel samples—distillation curves obtained

Distillation test is carried out on 24 diesel samples which contain a different biodiesel percentage (FAME), obtaining their corresponding distillation curves. Among these curves, we have selected seven for being analyzed and included in the present paper; six of them correspond to diesel samples with a usual biodiesel percentage, between 0.0 and 7.0% V/V. However, the other one corresponds to a diesel sample with a 30% V/V biodiesel percentage; this is outside the Standard scope. Obtained results are shown in **Figure 8**.



	E20	E30	E40	E50	E60	E70
PETROL	66,3	74,6	82,7	91,0	100,5	113,2
PETROL WITH BIOETHANOL	57,5	66,7	76,7	86,8	97,2	110,0

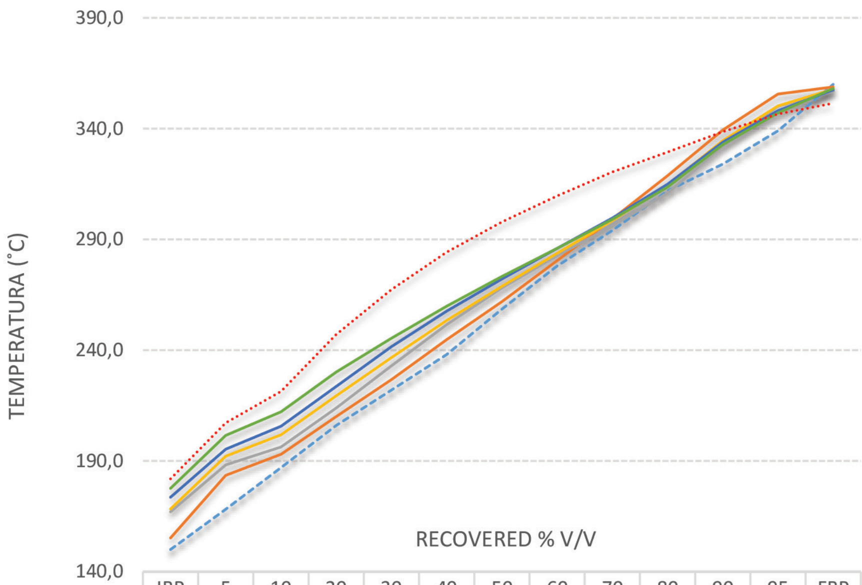
Figure 6. Middle section (E20-E70). Distillation curves of petrol samples.



	70	80	90	95	
PETROL	113,2	128,1	145,0	157,4	167,7
PETROL WITH BIOETHANOL	110,0	127,5	144,8	157,3	170,3

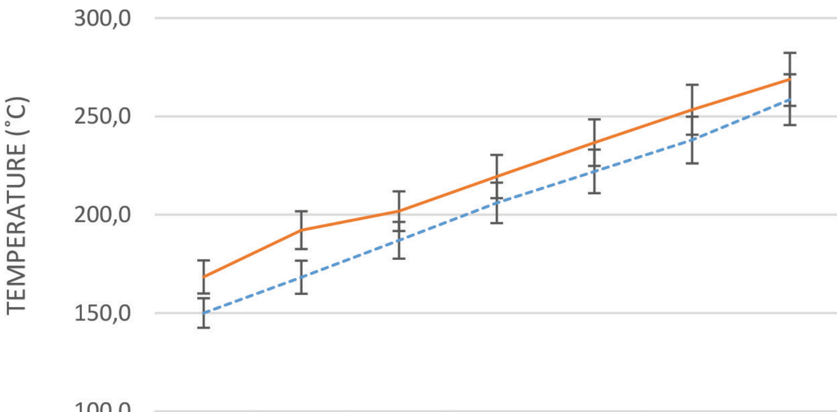
Figure 7. Final section (E70-FBP). Distillation curves of petrol samples.

As in the case of petrol samples, here we study the trend and the different sections of the distillation curve. However, in this case, the distillation curve will be divided for its study in two different sections: the first one comprises from the initial distillation point until 60% of the total volume is collected, whereas the second one comprises from this point to the final distillation point. A graphic comparison on the basis of an average value is also used here to illustrate the results, making a graphic comparison on the basis of an average value (**Figures 9** and **10**).



	IBP	5	10	20	30	40	50	60	70	80	90	95	FBP
0,0%	150,0	168,2	187,0	206,0	222,0	238,0	258,5	278,0	294,0	312,0	324,0	339,0	360,0
1,0 %	155,2	183,5	193,0	210,0	226,7	244,7	261,9	280,4	299,2	318,8	339,4	355,6	358,8
3,0%	167,0	188,2	196,3	213,9	232,9	251,5	268,1	282,7	296,1	311,0	332,1	350,1	356,9
4,0 %	168,4	192,1	201,8	219,4	236,7	253,4	268,9	283,7	298,5	314,6	334,6	350,2	357,8
5,0 %	173,6	195,3	205,7	223,6	241,6	257,6	272,1	285,9	299,6	314,9	333,9	348,1	357,5
7,0 %	177,6	201,5	212,2	230,1	245,4	259,8	273,3	285,9	299,0	313,6	332,8	347,1	358,1
30,0%	181,9	207,2	221,4	247,1	267,3	284,2	297,9	309,6	320,4	329,4	338,6	346,6	351,5

Figure 8. Distillation curves: diesel and blends with FAME (0.0–30.0% V/V).



	IBP	R5	R10	R20	R30	R40	R50
DIESEL	150,0	168,2	187,0	206,0	222,0	238,0	258,5
DIESEL WITH FAME	168,4	192,1	201,8	219,4	236,7	253,4	268,9

Figure 9. Initial section (IBP-R50). Distillation curves of diesel samples.

3.2.3. Step 2: Repeatability and reproducibility

In order to know and be able to check the quantitative change derived from the precision requirement set in the new edition of the Standard, which involves repeatability and reproducibility, two different certified reference materials are used; one of them matches with the petrol boiling range, whereas the other one matches with the diesel boiling range.

Two analysts are involved in the test process; each using a different distillation automated equipment, in the same laboratory, and maintaining the required operation conditions for the standardized calculation. Distillation test is carried out in duplicate, and their results are shown in **Figures 11–14**.

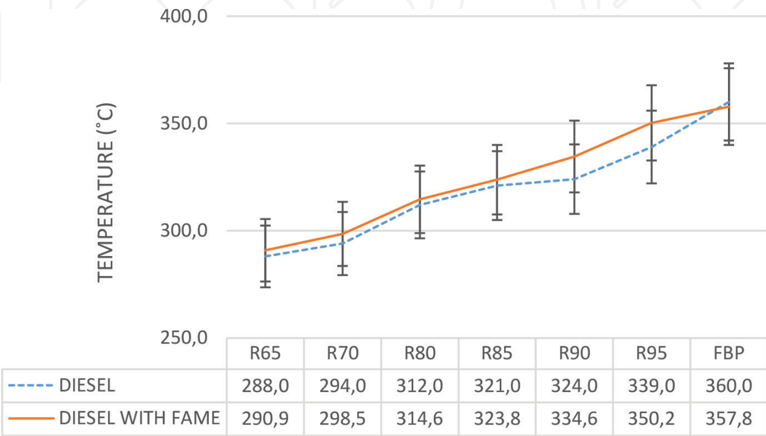


Figure 10. Final section (R65-FBP). Distillation curves of diesel samples.

QUALITY CONTROL - PETROL - CRM - ISO 3405:2000												
EVAPORATED %V/V	CERTIFICATE VALUE	ANALYST	TEMPERATURE (°C) MEASURED VALUES	AVERAGE OF ANALYST	DIFFERENCE BETWEEN AVERAGE OF ANALYST AND CERTIFICATE VALUE	AVERAGE OF ANALYSTS	DIFFERENCE BETWEEN AVERAGE OF ANALYSTS AND CERTIFICATE VALUE	TOLERANCE RANGE SIMPLE	DIFFERENCE BETWEEN VALUES BY ANALYST	REPEATABILITY	DIFFERENCE BETWEEN VALUES BY ANALYSTS	REPRODUCIBILITY
PI	32,2	1	33,2	33,80	1,20	32,68	1,60	5,09	1,20	3,90	3,10	7,2
		1	34,4									
		2	31,8	31,55	0,50		0,65		0,50			
		2	31,3									
10%	49,3	1	49,0	49,20	0,40	49,00	0,10	4,67	0,40	2,79	0,60	6,60
		1	49,4									
		2	48,8	48,80	0,00		0,50		0,00			
		2	48,8									
50%	83,7	1	83,6	83,70	0,20	83,73	0,00	3,08	0,20	1,72	0,20	4,35
		1	83,8									
		2	83,7	83,75	0,10		0,05		0,10			
		2	83,8									
90%	143,9	1	144,2	144,00	0,40	144,00	0,10	2,64	0,40	2,15	0,40	3,73
		1	143,8									
		2	143,8	144,00	0,40		0,10		0,40			
		2	144,2									
PF	166,3	1	165,8	165,95	0,30	165,93	0,35	6,29	0,30	4,40	0,30	8,90
		1	166,1									
		2	166,0	165,90	0,20		0,40		0,20			
		2	165,8									

Figure 11. Quality control according to ISO 3405:2000; petrol-CRM.

http://dx.doi.org/10.5772/67140

EVAPORATED %V/V	CERTIFICATE VALUE	ANALYST	TEMPERATURE (°C) MEASURED VALUES	AVERAGE OF ANALYST	DIFFERENCE BETWEEN AVERAGE OF ANALYST AND CERTIFICATE VALUE	AVERAGE OF ANALYSTS	DIFFERENCE BETWEEN AVERAGE OF ANALYSTS AND CERTIFICATE VALUE	TOLERANCE RANGE SIMPLE	DIFFERENCE BETWEEN VALUES BY ANALYST	REPEATABILITY	DIFFERENCE BETWEEN VALUES BY ANALYSTS	REPRODUCIBILITY
PI	32,2	1	33,2	33,80	1,20	32,68	1,60	3,51	1,20	2,46	3,10	5,0
		1	34,4									
		2	31,8	31,55	0,50		0,65		0,50			
		2	31,3									
10%	49,3	1	49,0	49,20	0,40	49,00	0,10	2,26	0,40	1,33	0,60	3,20
		1	49,4									
		2	48,8	48,80	0,00		0,50		0,00			
		2	48,8									
50%	83,7	1	83,6	83,70	0,20	83,73	0,00	1,33	0,20	0,74	0,20	1,88
		1	83,8									
		2	83,7	83,75	0,10		0,05		0,10			
		2	83,8									
90%	143,9	1	144,2	144,00	0,40	144,00	0,10	2,74	0,40	1,54	0,40	3,87
		1	143,8									
		2	143,8	144,00	0,40		0,10		0,40			
		2	144,2									
PF	166,3	1	165,8	165,95	0,30	165,93	0,35	4,79	0,30	3,33	0,30	6,78
		1	166,1									
		2	166,0	165,90	0,20		0,40		0,20			
		2	165,8									

Figure 12. Quality control ISO 3405:2011; petrol-CRM.

QUALITY CONTROL - DIESEL - CRM - ISO 3405:2000												
RECOVERED %V/V	CERTIFICATE VALUE	ANALYST	TEMPERATURE (°C) MEASURED VALUES	AVERAGE BY ANALYST	DIFFERENCE BETWEEN AVERAGE OF ANALYST AND CERTEFICATE VALUE	AVERAGE BY ANALISTS	DIFFERENCE BETWEEN AVERAGE OF ANALYSTS AND CERTEFICATE VALUE	TOLERANCE RANGE SIMPLE	DFFERENCE BETWEEN VALUES BY ANALYST	REPEATABILITY	DFFERENCE BETWEEN VALUES BY ANALYSTS	REPRODUCIBILITY
PI	172,9	1	178,1	179,35	6,45	178,63	4,40	6,01	2,50	3,50	4,40	8,50
		1	180,6									
		2	176,2	177,90	5,00				3,40			
		2	179,6									
10%	209,2	1	210,4	210,25	1,05	209,98	1,20	5,49	0,30	3,76	1,20	7,76
		1	210,1									
		2	209,2	209,70	0,50				1,00			
		2	210,2									
50%	274,4	1	274,9	275,00	0,60	274,48	1,40	6,19	0,20	3,30	1,40	8,76
		1	275,1									
		2	273,7	273,95	0,45				0,50			
		2	274,2									
90%	339,2	1	341,3	341,05	1,85	339,78	3,40	4,93	0,50	3,22	3,40	6,97
		1	340,8									
		2	337,9	338,50	0,70				1,20			
		2	339,1									
95%	354,9	1	356,2	355,30	0,40	353,55	4,80	6,34	1,80	4,08	4,80	8,97
		1	354,4									
		2	351,4	351,80	3,10				0,80			
		2	352,2									
PF	364,2	1	359,4	359,60	4,60	359,60	3,20	7,42	0,40	3,50	3,20	10,50
		1	359,8									
		2	358,0	359,60	4,60				3,20			
		2	361,2									

Figure 13. Quality control according to ISO 3405:2000; diesel-CRM.

QUALITY CONTROL - DIESEL - CRM - ISO 3405:2011											
RECOVERED %V/V	CERTIFICATE VALUE	ANALYST	TEMPERATURE (°C) MEASURED VALUES	AVERAGE OF ANALYST	DIFFERENCE BETWEEN AVERAGE OF ANALYST AND CERTIFICATE VALUE	AVERAGE OF ANALYSTS	DIFFERENCE BETWEEN AVERAGE OF ANALYSTS AND CERTIFICATE VALUE	TOLERANCE RANGE SIMPLE	DIFFERENCE BETWEEN VALUES BY ANALYST	REPEATABILITY	DIFFERENCE BETWEEN VALUES BY ANALYSTS	REPRODUCIBILITY
PI	**172,9**	1	178,1	179,4	6,45	178,63	5,72	6,72	2,50	3,11	4,40	9,51
		1	180,6									
		2	176,2	177,9	5,00				3,40			
		2	179,6									
10%	**209,2**	1	210,4	210,3	1,05	209,98	0,78	3,25	0,30	1,97	1,20	4,60
		1	210,1									
		2	209,2	209,7	0,50				1,00			
		2	210,2									
50%	**274,2**	1	274,9	275,0	0,80	274,48	0,28	2,10	0,20	0,94	1,40	2,97
		1	275,1									
		2	273,7	274,0	0,25				0,50			
		2	274,2									
90%	**339,2**	1	341,3	341,1	1,85	339,78	0,57	3,60	0,50	1,39	3,40	5,09
		1	340,8									
		2	337,9	338,5	0,70				1,20			
		2	339,1									
95%	**354,9**	1	356,2	355,3	0,40	353,55	1,35	6,42	1,80	3,26	4,80	9,08
		1	354,4									
		2	351,4	351,8	3,10				0,80			
		2	352,2									
PF	**364,2**	1	359,4	359,6	4,60	359,60	4,60	5,02	0,40	2,20	3,20	7,10
		1	359,8									
		2	358,0	359,6	4,60				3,20			
		2	361,2									

Figure 14. Quality control according to ISO 3405:2011; diesel-CRM.

4. Discussion

4.1. ISO 3405:2011 versus ISO 3405:2000

The fourth edition of ISO 3405 Standard came into force on 15 January 2011. This fourth edition cancelled and replaced the third edition, which had come into force on 1 March 2000. It is noteworthy that the text of this new edition is in line with the American Standard ASTM D86, widely used throughout the petroleum industry.

The fourth edition of ISO 3405 Standard introduces significant changes which are the result of the new formulations of automotive fuels and which are listed below:

The latest edition of the Standard is wider in scope. It has been modified in order to include the new fuel formulations, obtained from mixtures of biofuels and petrol (containing up to 10% V/V of ethanol) and diesel (containing up to 20% V/V of biodiesel). Additionally, it establishes a clear definition of 'light distillates' and 'middle distillates'.

Petrol from direct distillation (the petroleum fraction obtained by distillation at atmospheric pressure) no longer has their own group (the former Group 0, since the latest edition of the

http://dx.doi.org/10.5772/67140

Standard refers only to four distillation Groups 1, 2, 3 and 4), instead of the former five Groups 0, 1, 2, 3 and 4. Petrol and their mixtures with bioethanol belong to Group 1, while diesel and their mixtures with biodiesel belong to Group 4.

This Standard specifies an assay method, utilizing either manual or automated equipment. However, its latest edition sets the automated alternative as the reference method in the event of a dispute, unless otherwise agreed.

The latest edition of the Standard includes a specific point related to the test procedure utilizing automated equipment. Although the former edition allowed the use of this type of equipment, the procedure had not been defined so far. Nowadays, most distillation tests are carried out utilizing automated equipment. Once programmed, the procedure is performed in an autonomous way by the instrument, but programming them is not easy. It requires an absolute control and knowledge of the process as well as of the conditions required for each specific sample. The validity on the findings remains dependant on performing a validation study.

The latest edition of the Standard requires the establishment of new criteria for calculating repeatability and reproducibility.

The latest Standard specifies the percentages of distillate required at specific temperatures for petrol. Accordingly, the Standard includes a normative annex (Annex C) which provides values of reproducibility of petrol percent volume evaporated at 70, 100, 150 and 180°C. These reproducibility statements were estimated for the specification temperatures and percentages from the data collected in an inter-laboratory study:

- E70 → R = 2.7% V/V.
- E100 → R = 2.2% V/V.
- E150 → R = 1.3% V/V.
- E180 → R = 1.1% V/V.

4.2. Biofuel impact on fuel volatility

4.2.1. Petrol

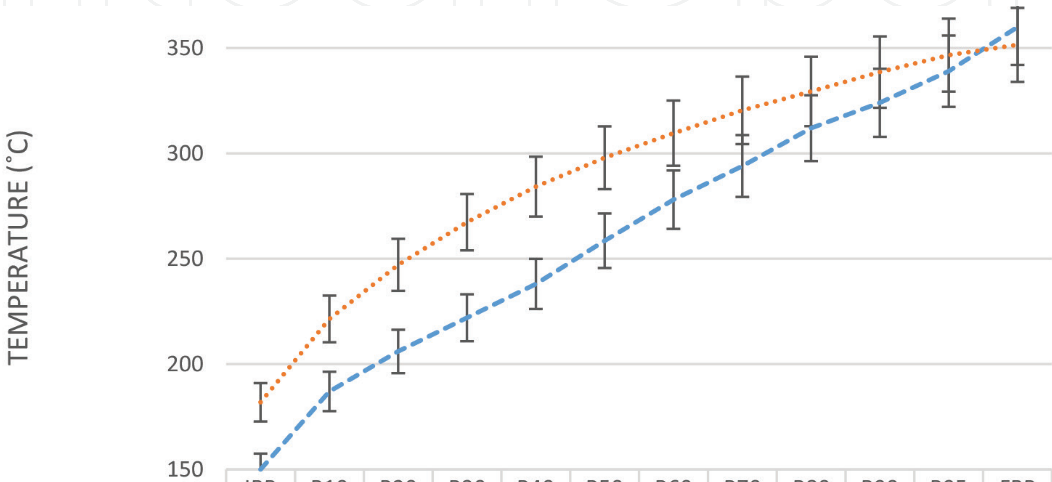
As we set before, the petrol distillation curve study was developed through its analysis in three different sections. From the study of the two first sections (IBP-E20; E20-E70), we conclude that the evaporated percentage is higher in blends. So, in the range between 30 and 90°C, which comprises from IBP to the middle boiling point, the petrol volatility increases from bioethanol addition. In the final section, the sample distillation curves coincide to a great extent, and there are no any significant changes, as might be expected from the bioethanol boiling point.

4.2.2. Diesel

For diesel blends, containing up to 7% V/V biodiesel, the study of the distillation curve indicates the recovered percentage has risen slightly in the first section, while we can observe a bigger variation in the last one, where the fractioning of the heavy components of the samples takes place; this is between R90 and R95.

Diesel blends, containing 30% V/V biodiesel, are outside the ISO 3405:2011 Standard scope. Distillation test has been carried out, considering them as part of Group 4 and, then, accordingly to the conditions established for that group.

Distillation curve for diesel blends, containing 30% V/V biodiesel, indicates clearly the volatility diminution from the own characteristics of the biodiesel: high boiling point and low volatility (**Figure 15**). As in this type of products, the volatility diminution is directly related to the viscosity; the use of this type of blends in the engines is intimately related to their operation and performance.



	IBP	R10	R20	R30	R40	R50	R60	R70	R80	R90	R95	FBP
0,0% FAME	150	187	206	222	238	259	278	294	312	324	339	360
30,0% FAME	181,9	221,4	247,1	267,3	284,2	297,9	309,6	320,4	329,4	338,6	346,6	351,5

Figure 15. Diesel distillation curves, 0.0% V/V and 30.0% V/V FAME.

4.3. Estimation of variation suffered by the accuracy of the automated method based on criteria of repeatability and reproducibility.

The latest edition of the Standard, ISO 3405:2011, establishes new repeatability and reproducibility criteria. This new criteria has reduced measure variations allowed in the whole range, affecting petrol (Group 1) and diesel (Group 4). Relatively small variations are allowed in the middle section of the distillation curve, whereas a more significant variation is allowed in the IBP and FBP determination, as shown in **Figures 16** and **17**.

4.4. Future prospects

The EU has promoted turning plants into fuel as a way to reduce carbon emissions from transport for the last 10 years. Today however, some say that biofuels have become part of the problem and actually have generated more CO_2 than they saved, as the demand for crops needed to produce them has led to the destruction of forests. The EU now wants to limit the amount of fuel produced from food crops and shift to biofuels that are produced from non-food sources, such as waste.

QUALITY CONTROL - CRM GASOLINE								
CRM			ISO 3405:2011			ISO 3405:2000		
CERTIFICATE VALUE (˚C)	TOLERANCE RANGE CERTIFICATE (˚C)	EVAPORATED %V/V	TOLERANCE RANGE SIMPLE	REPEATABILITY	REPRODUCIBILITY	TOLERANCE RANGE SIMPLE	REPEATABILITY	REPRODUCIBILITY
32,2	3,5	PI	3,54	2,46	5,00	5,09	3,90	7,20
49,3	2,3	10%	2,26	1,33	3,20	4,67	2,79	6,60
83,7	1,3	50%	1,33	0,74	1,88	3,08	1,72	4,35
143,9	2,7	90%	2,74	1,54	3,87	2,64	2,15	3,73
166,3	4,8	PF	4,79	3,33	6,78	6,29	4,40	8,90

Figure 16. The values of repeatability and reproducibility for the same petrol-CRM, according to ISO 3405:2011 and ISO 3405:2000.

QUALITY CONTROL - CRM DIESEL								
PAC-1037			ISO 3405:2011			ISO 3405:2000		
CERTIFICATE VALUE (˚C)	TOLERANCE RANGE CERTIFICATE (˚C)	EVAPORATED %V/V	TOLERANCE RANGE SIMPLE	REPEATABILITY	REPRODUCIBILITY	TOLERANCE RANGE SIMPLE	REPEATABILITY	REPRODUCIBILITY
172,90	6,00	PI	6,72	3,11	9,51	6,01	3,50	8,50
209,20	5,80	10%	3,25	1,97	4,60	5,49	3,76	7,76
274,20	6,10	50%	2,10	0,94	2,97	6,19	3,30	8,76
339,20	4,80	90%	3,60	1,39	5,09	4,93	3,22	6,97
354,90	7,00	95%	6,42	3,26	9,08	6,34	4,08	8,97
364,20	7,40	PF	5,02	2,20	7,10	7,42	3,50	10,50

Figure 17. The values of repeatability and reproducibility for the same diesel-CRM, according to ISO 3405:2011 and ISO 3405:2000.

The EU is committed to meeting 10% of its transport fuel needs from renewable sources, mostly biofuels, by 2020. But pressure is growing to change this policy by limiting the amount of food-based biofuels.

In response to these concerns, the European Parliament voted in favour of a compromise deal with the Council to limit the amount of fuel produced from food crops such as rapeseed and palm oil. The new legislation will enter into force in 2017 [12].

The future liquid automotive fuel formulations will remain dependant on distillation test as a powerful quality control tool. It provides useful information, which can be employed to establish optimal conditions of use in the appropriate engines, as well as to establish safe conditions for storage, transportation and delivery.

5. Conclusion

In 2011, the addition of up to 10% V/V bioethanol in petrol and up to 20% V/V of biodiesel in diesel, as a result of biofuel promotion, has prompted a careful review of the

ISO 3405 Standard: Petroleum Products. Determination of Distillation Characteristics at Atmospheric Pressure.

Changes include:

1. The broadening of the scope to cover these new products
2. The adjustment of the calculations related to the method accuracy

Standard relating to test standardization, which establishes the procedure to determine the distillation characteristics of petroleum products at atmospheric pressure, remains open to future review and updating.

Author details

Mª Mercedes del Coro Fernández-Feal*, Luis R. Sánchez-Fernández and Blanca Sánchez-Fernández

*Address all correspondence to: coro.ffeal@udc.es

Fuels Laboratory, University of A Coruña, Spain

References

[1] Satou, M., Itoh, D., Hattori, H., Yoshida, T. Evaluation of ring size distribution in a heavy oil based on boiling point and molecular weight distributions. Fuel. 2000; **79**(3-4):339-348. DOI: 10.1016/S0016-2361(99)00168-4.

[2] Lluch Urpí, J. Tecnología y margen del refino de petróleo (Technology and petroleum refining profit). España: Ediciones Díaz de Santos; 2008. 464 pp. ISBN: 9788479788759.

[3] Álvarez Flórez, J.A., Callejón Agramunt, I., Forns Farrús, S. Motores Alternativos de Combustión Interna (Alternative Internal Combustion Engines). España: Ediciones UPC; 2005. 513 pp. ISBN. 9788483018187.

[4] Wilfrid, F. Los combustibles y su Tecnología (Fuels and their Technology). Bilbao, España: Ediciones Urmo S.A.; 1969. 688 pp. ISBN: 9788431400095.

[5] Sánchez-Fernández, B., Bouza-Fernández, S., Sánchez-Fernández, L.R., Seoane-López, L.R., Seoane-López, S., Fernández-Feal, M.L., Fernández-Feal, M.C. Biodiésel en el Mercado Gallego (Objetivo 2010) como consecuencia del Plan de Fomento de Energías Renovables (Biodiesel in the Galician Market (Objective 2010) as a result of the Plan for the Promotion of Renewable Energies). In: Proceedings World Economy Meeting XII; Santiago de Compostela, España; 2010. ISBN 9788415026068.

[6] Aburudyna, A., Karonis, D., Zannikos, F., Lois, E.. Impact of biodiesel addition on distillation characteristics and cetane number of diesel fuels. Journal of Energy Engineering. 2015; 141(2). DOI: 10.1061(ASCE) EY.1943-7897.0000244.

[7] Daganzo, J.M. Blog de Innovación Tecnológica (REPSOL). [Internet]. 05.01.2012 [Updated: 22.07.2016].Available from: http://blogs.repsol.com/innovacion/combustibles-convencionales-y-biocombustibles-un-ejemplo-de-convivencia [Accessed: 20.05.2016].

[8] EN 228:2012. Automotive fuels. Unleaded petrol. Requirements and test methods.

[9] EN 590:2013. Automotive fuels. Diesel. Requirements and test methods.

[10] ISO 3405:2000. Petroleum products. Determination of distillation characteristics at atmospheric pressure.

[11] ISO 3405:2011. Petroleum products. Determination of distillation characteristics at atmospheric pressure.

[12] Parlamento Europeo. En portada. Punto de mira. [Internet]. 14.04.2015 [Updated: 05.05.2016]. Available from: http://www.europarl.europa.eu/news/es/news-room/20130719STO17435/Nueva-pol%C3%ADtica-de-biocombustibles-menos-CO2-y-m%C3%A1s-seguridad-alimentaria [Accessed: 15.07.2016].

IntechOpen