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TNO report

TNO 2020 R10138

Petrol fuel and blending ethanol analyses

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Copy no	2020-STL-REP-100330310
Number of pages	19 (incl. appendices)
Sponsor	Ministry of Infrastructure and Water Management
Project name	Aanvullend onderzoek benzine kwaliteit
Project number	060.35698

Samenvatting

Dit rapport bevat twee opeenvolgende studies (fase 1 en fase 2) waarin benzine en ethanol monsters geanalyseerd zijn. Deze onderzoeken volgen op een eerder onderzoek uit 2016, waarin er mogelijke zorgen omtrent de aanwezigheid van water in benzine en de verbrandingswaarde van benzine naar voren zijn gekomen.

Het doel van deze onderzoeken is het vaststellen van de CO_2 uitstoot bij het praktijkgebruik van benzineauto's. Daarvoor zijn de koolstofinhoud, de bio-bijmenging, en de verbrandingswaarde van belang.

In totaal zijn er 68 benzinemonsters en 14 ethanolmonsters genomen in de twee fases samen.

De conclusies zijn de volgende:
- Deze studie bevestigt eerdere bevindingen dat de hoeveelheid water in benzine hoger is dan op basis van de ethanol en de fossiele brandstof verwacht mag worden.
- De bron van het water in benzine is niet achterhaald. De oorzaak uit fase 1: een ethanolmonster met veel water, is in fase 2 niet bevestigd.
- Alle E5 brandstoffen hebben een nauwe bandbreedte van de ethanol tussen 4,38% en 4,61% volume fractie.
- De verbrandingswaarde van de 12 gemengde monsters E5, 42.07 MJ/kg en 42.50 MJ/kg. De fossiele fractie ("EuroBOB") had een verbrandingswaarde van 43,22 MJ/kg en 43,40 MJ/kg.
- De koolstofmassa van de fossiele fractie varieert tussen 84,5% en 86,0%.

Ten aanzien van de mogelijkheid om referentiebrandstof voor de typekeuringstest te optimaliseren voor lage CO_2 uitstoot kan gesteld worden dat ongeveer 0,7% lagere CO_2 uitstoot bereikt kan worden, ten opzichte van gangbare referentiebrandstoffen.

Hieronder volgen de samenvattingen van de twee fases.

Fase 1: (2017)
Een jaar lang zijn er benzinemonsters verzameld van diverse merkpompen in geheel Nederland, en gecombineerd tot maandgemiddelden voor chemische analyse. Elke maand werden vier tot zeven monsters gecombineerd, om met een beperkt aantal van 12 chemische analyses een goed beeld te krijgen van de gemiddelde marktbrandstof. De gemiddelde onder-stookwaarde van benzine, op basis van ongeveer 60 monsters, is 42,5 MJ/kg, met een spreiding van 0,3 MJ/kg (bandbreedte). De verwachting is dat per individuele tankbeurt de stookwaarde ongeveer 2% varieert. Er zijn geen wettelijke eisen aan de verbrandingswaarden van brandstoffen voor wegvervoer.

De ethanolfractie is erg constant in de benzinemonsters, en daardoor niet de oorzaak van de spreiding in verbrandingswaarden. Als de ethanolfractie wordt weggenomen, is de verbrandingswaarde van de fossiele component ongeveer 43,3 MJ/kg. Dit is hoger dan op basis van de vorige studie is ingeschat op 42,5 MJ/kg.

Naast benzinemonsters zijn er ook ethanolmonsters genomen, omdat dat mogelijk de oorzaak is van het geobserveerde water in de benzine. Inderdaad, had één van de drie monsters van ethanol, bedoeld voor bijmenging in benzine, veel meer water dan de bedoeling is. In plaats van de vereiste fractie onder de 0,3% volgens de norm EN-15376 had dit monster meer dan 2% water. Mogelijk is dus water in ethanol de oorzaak van de aanwezigheid van meer water dan verwacht in marktbenzine. Deze ligt rond de 0,03% ligt, in plaats van de te verwachten 0,015% maximaal in E5 benzine.

Fase 2: (2018 – voorjaar 2019)
In een vervolgonderzoek, na de bevindingen uit Fase 1 hierboven, zijn er meer ethanolmonsters genomen, en monsters van de fossiele brandstof, “EuroBOB”, die met ethanol gemengd worden. Ook is er voor een nieuwe set marktbrandstoffen het aandeel water bepaald. Het aandeel water in de marktbrandstoffen wordt niet verklaard door de hoeveelheid water die in ethanol in gevonden en de waterhoeveelheid in de fossiele brandstof. De gevonden hoeveelheid water, in een kleiner aantal monsters, is met 0.025% wel wat lager in 2019 dan dat in 2018. De verbrandingswaarde van de fossiele component komt goed overeen met de eerdere inschatting van 43,3 MJ/kg.

Er is onderzocht wat de mogelijke marge is in CO_2 uitstoot op de typekeuringstest door de variatie in de samenstelling van de referentiebrandstof. De nauwere specificaties van referentiebrandstof voor benzine in de typekeuringstesten, laat nog steeds ongeveer 1% marge op de CO_2 uitstoot. Een 0,7% afname ten opzichte van typische referentiebrandstof is gehaald. Een grootste deel van deze marge wordt veroorzaakt door de variatie in koolstofinhoud van de brandstof, maar de bandbreedte in verbrandingswaarden speelt ook een rol. De referentiebrandstoffen kunnen door de hoge ondergrens van 29% aan de aromaten niet een hele lage CO_2 uitstoot hebben ten opzichte van marktbrandstoffen.

Summary

This study reports on two programs (phase 1 and phase2) in which petrol and ethanol fuel samples were investigated. These programs are the follow up of a program in 2016 in which some concerns were raised on the combustion value and water content of E5 petrol fuel.

The objectives of the two programs (2017-2019) were to determine the average properties including the combustion value and carbon content and whether they fulfil the formal specifications.
An additional objective of the phase 2 program was to investigate the possibility to tune fuels to a lower CO_2 emission (measured in the exhaust flow) during the type-approval test.

In total 68 petrol and 14 ethanol samples were taken during the two phases.

The conclusions are as follows:
- This study confirms the finding of the earlier 2016 study, that the water content of E5 petrol is systematically higher than can be expected based on the maximum allowable water content of ethanol. It is on average about 0.1 weight % higher, which would reduce the energy content also by about 0.1%.
- The precise reason for the high water content could not be identified with certainty. According to the phase 1 samples the most likely reason is too high water content in ethanol, but this was not confirmed by the phase 2 samples.
- The E5 fuels showed a small band width in ethanol volume fraction: 4.38% to 4.61%.
- The combustion values of 12 mixed monthly E5 samples showed a range from 42.07 to 42.5 MJ/kg (phase 1). The four EuroBOB[1] samples varied from 43.22 to 43.40 MJ/kg.
- The carbon content of the EuroBOB samples ranged from 84.5% to 86.0%.

With respect to the possibility to lower the CO_2 emissions during the type approval test, it is concluded that the CO_2 emission can be lowered by about 0.7% compared to an average standard reference fuel, by optimising the fuel for lower specific CO_2 emissions.

Below follows a summary of the two programs.

Phase 1, 2017:
For a full year petrol samples were collected randomly from different brands and at different locations. The samples collected in one calendar month were combined to a monthly average sample. Each average contained four to seven samples with equal fractions. The results show an average heating value of 42.5 MJ/kg, with a variation of 0.3 MJ/kg. This would mean that the fuelling-by-fuelling variation in heating value is in the order of 2%. There are no requirements for the heating value of fuels.

[1] Base petrol at distribution station before ethanol is blended

Given the volume fraction of 4.6% of ethanol in the collected samples, the heating value of the fossil component would have been around 43.3 MJ/kg. This is slightly higher than the estimate of 43.0 MJ/kg based on the previous study.

Separately, the three ethanol samples collected from companies which supply ethanol for bio-blending, show variable results for the amount of water. Two of the samples are below the 0.3% water content limit, according to standard EN-15376, for ethanol intended for blending. The third sample contains more than 2% water. Too high water content in ethanol is possibly the cause of the higher than expected water content of market petrol. This is about 0.03% while 0.015% is the maximum that can be expected in E5 petrol.

Phase 2, 2018 – spring 2019:
After the findings in phase 1, more samples of ethanol were collected in the autumn 2018. Moreover, four samples of the fossil part of the petrol blends were collected. No new sample with high water content was found. The energy content of the fossil petrol was 43.3 MJ/kg (LHV), well in line with the market fuel energy content, corrected for ethanol.

Also further samples of market petrol were collected, in spring 2019, and analyzed on water content. The average water content was 0.025%, slightly lower than the samples collected in 2018. The sample was much smaller, but the spread was low.

A specialized laboratory made a special blend of reference fuel, intended for low CO_2 emissions. Within the narrow bandwidth of reference fuel specifications, it is possible to achieve a reduction of 0.7%, with respect to average reference fuels. Reference fuels themselves are at the low end of the range of CO_2 per energy, due to the lower bound on aromatics fraction of 29% weight fraction.

Contents

1 Introduction

On the basis of the study: "Dutch market fuel composition for GHG emissions" (TNO report 2016 R10700), there were concerns about the quality of petrol for mobility. First, the lower heating value, or amount of energy in a litre or kilogram of petrol fuel varied greatly. Furthermore, the values were typically much lower than used in the national energy statistics.[2] Second, the amount of water in petrol was higher than could be expected from the maximum water content in the ethanol blended into the fossil product to make petrol.

Due to the outcomes of the 2016 study, the Ministry of Infrastructure and Waterways ordered a more extensive fuel investigation program with the following objectives:

- To investigate the average fuel properties including the combustion value and carbon content,
- Whether they fulfil the formal specifications to determine the average and variation in heating value
- To evaluate possible side effects of ethanol blending, such as increased water content
- To investigate the possibility to tune fuels to a lower CO_2 emission (measured in the exhaust flow) during the type-approval test.

The reason for the last objective is the fact that this possibility may be used to obtain a lower CO_2 value during the type approval.

This report summarizes the results of this study, in two phases. The phase 1 results are presented in the section 4 and 5. The phase 2 results are reported in the sections 5, 6 and 7.

It should be noted that water content and heating values of petrol are not regulated explicitly. Hence, this report has no bearing on the Fuel Quality Directive or even the EN-228 standard. Moreover, in the literature, different values are cited, regarding normal heating value of petrol. The Dutch petrol heating values are on the lower end of the typical range.

For the water content of petrol, there was historically no reason to have strict regulation, as even a small fraction of water in hydrocarbons would produce a clouded appearance. With the admixture of ethanol the situation has changed, and petrol with ethanol can contain significant amounts of water, before turning cloudy. The water in ethanol should be below a limit of 0.3% [weight] on the basis of standard EN-15376.

[2] Adjustment of heating values and CO_2 emission factors of petrol and diesel, CBS memo 14 December 2017.

2 Measurement program

2.1 Phase 1

Over 2017 petrol samples were taken, and four to seven samples per month were mixed in equal fractions, to a single average petrol sample. With the mixing of multiple samples a better average on the basis of a limited number of analyses can be achieved. On the basis of about 60 separate samples 12 chemical analyses were carried out, to have an overview of the petrol composition and heating value over the course of 2017.

Moreover, three ethanol samples were taken. In those samples the water content was determined. The sampling itself, of both petrol and ethanol, was carried out by the Dutch Human Environment and Transport Inspectorate (ILT). The samples were mixed at TNO, on the basis of equal volume fractions. The petrol samples were taken from consumer petrol stations all over the country and from different petrol companies. The ethanol samples were taken from suppliers of ethanol for blending with petrol, as registered by the Dutch Emissions Authority.

2.2 Phase 2

On the basis of the first phase of this project, the Ministry requested a follow-up with more ethanol samples collected. The companies were involved in this sampling. And at the same time fossil components of petrol were collected, to be examined as a possible source of water. Moreover, given the large variation in heating value, the possibility to generate low CO_2 emissions in the type-approval, by special fuel blends, was examined as well in this project.

Table 2-1: Overview of petrol and ethanol samples used for phase 1 and phase 2.

	Phase 1: 2017		**Phase 2: 2018- spring 2019**	
	Market petrol	Ethanol	EuroBob petrol	Ethanol
Taken samples	60	3	4	8
Analysed samples	12	3	4	8
Samples taken and analysed by third parties				3

3 Results of the petrol samples

About sixty samples of petrol were taken over the course of end 2016 until end 2017. The Inspection was asked to supply samples from different parts of the country and from different brands of petrol stations. The Inspection ensured the broad coverage. In some months this resulted in the minimum number of four samples, in other months more samples were taken, up to seven.

The samples were supplied in metal 1 litre containers, filled to the rim. These samples were stored at room temperature of about 15-18^{o}C for a batch to be taken to the laboratory. Four to seven samples were monthly taken. These were mixed prior to the analysis. From each sample an equal amount was taken for the combined sample.

Table 3-1: The results of the chemical analyses of the monthly average samples.

	minimum	maximum	average	standard deviation	unit
heating value	42.07	43.36	42.50	0.31	MJ/kg
ethanol fraction	4.38	4.96	4.61	0.17	% [vol]
water content	210	370	291	55	mg/kg
oxygen content	1.85	3.42	2.43	0.48	% [weight]

In most samples around 2%-3% MTBE was found (higher MTBE content in the winter fuels than the summer fuels). This affected the oxygen content of the fuel, on top of the oxygen in the ethanol. For the greater part MTBE is a fossil component. Ethanol is the dominant bio-admixture. The fraction of ethanol is very constant.

Table 3-2: The result of the chemical analyses for each of the samples.

sample	heating value [MJ/kg]	ethanol %[volume]	water mg/kg	oxygen % [weight]
dec-16	42.468	4.38	260	2.40
jan-17	42.340	4.61	210	2.35
feb-17	42.074	4.59	230	2.22
mrt-17	42.560	4.58	290	2.18
apr-17	42.450	4.53	310	2.09
jun-17	42.340	4.55	320	2.11
jul-17	42.460	4.49	370	2.04
aug-17	42.325	4.46	340	2.03
sep-17	42.438	4.96	330	2.30
okt-17	43.360	4.59	310	2.25
nov-17	42.495	4.89	340	2.41
dec-17	42.645	4.63	280	2.38

Analyses were carried out according to: ISO 12937 for water content, ISO 22854 for composition (ethanol and oxygen), and ASTM D 240 for heating value.

The 12 months of data collection, started at the end of 2016 and ran till the end of 2017. The twelve samples have the net heating value, water content, ethanol, and oxygen fraction, presented in Table 3-2. Net heating value is the amount of heat produced by combustion where the combustion products are in the gaseous phase.

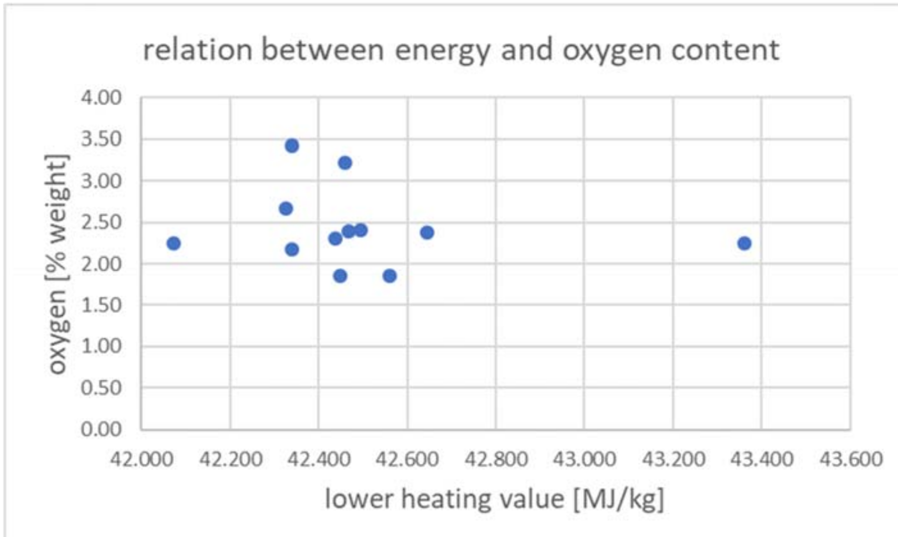

Figure 3-1: There is no clear relation between the oxygen content and the heating value of the mixed petrol samples.

The cause of the variation in heating value is not simply the lower heating value of the blended MTBE and ethanol. If the oxygen content, as the primary indicator of blending of oxygenated components is plotted, in Figure 3-1, against the heating value, no relation is observed. The heating value varies, most likely, due to the mix of fossil hydrocarbons.

4 Results of the ethanol samples

Ethanol was collected from three suppliers in February 2018. The ethanol samples were taken from batches intended for blending with the fossil petrol to produce market petrol fuel (E5). This sample collection is not a standard task of the Inspection. The companies were found through the registration of biofuels, as required by the Renewable Energy Directive. The Dutch Emission Authority is responsible for this reporting task.

The requirements of a maximum of 0.3% [weight] water in ethanol, according to EN-15376, were met by two of the three samples:

Table 4-1: The water content of the three ethanol samples.

water content in ethanol:

sample 1	0.183 % [weight]
sample 2	2.65 % [weight]
sample 3	0.288 % [weight]

The water content was determined according to procedure EN 15489, prescribed in EN 15376.

The amount of water in the second sample was substantially higher than acceptable. Adding this ethanol to fossil petrol, could lead to more than 1000 mg/kg water (0.1% [weight]) in the market blend. These values are not observed in market fuels sampled, probably also due to the mixing of four to seven samples prior to the analysis. However, a significant fraction of such ethanol batches in the blending, would explain the average 291 mg/kg (0.029% [weight]) water content in market petrol (Table 2-1).

5 Second set of ethanol and base petrol samples

On the basis of the first results, reported in Chapter 2 and Chapter 3, with only three ethanol samples were collected and further evidence was needed.
The Ministry has extended the project to collect more results (phase 2). In the autumn of 2018 and the spring of 2019, four further analyses were carried out. First, more ethanol samples were collected. Second, the fossil part of petrol was examined separately. Third, more market fuel samples were collected to determine the water content. Fourth, a reference fuel for the determination of factory value of CO_2 emission of vehicles, was examined for the flexibility to achieve low CO_2 emissions during type-approval. The last two topics are reported in separate chapters.

5.1 Ethanol samples

With the help of the fuel producers a larger set of ethanol samples was collected at the location where ethanol is mixed with the fossil fuel. In part the samples were collected by the Inspection (7 samples: average water content 1735 mg/kg, range 1370 mg/kg -1960 mg/kg), one sample was collected by the quality control engineers (1500 mg/kg), and in parts test reports from the normal quality control procedures were provided (3 samples, average 987 mg/kg, samples: 880, 940, 1140 mg/kg). The average of all samples is 1510 mg/kg (i.e., 0.151% weight), well below the limit of 0.3% (3000 mg/kg). No second sample with high water content, like in phase 1 of the study, was discovered among these 11 samples in phase 2.

Table 5-1: Water content of 11 additonal ethanol samples (phase 2). Limit value is 3000 mg/kg.

Water content	Min.	Max.	Average	Unit
7 by Inspection	1370	1960	1735	mg/kg
4 by quality control	880	1500	1115	mg/kg
Total			1510	

It can be concluded that the water content of all ethanol samples fulfilled the requirements.

5.2 The fossil fuel samples (“EuroBOB”)

At the same time and location also the fossil component was sampled. The four samples of fossil petrol, to be mixed with ethanol were analysed. Three of the four samples had a RON lower than 95. The corrected RON numbers were 93.3, 93.3, 94.1, and 95.1. The samples did contain oxygen in the molecular form of MTBE: 3.74 to 4.95% volume. The carbon content is not substantially reduced by the presence of MTBE: 84.5%, 85.1%, 85.7%, and 86.0% are the carbon weight fractions.

The net heating values of the fossil fuels are 43.22, 43.23, 43.34, and 43.40 MJ/kg, average 42.29 MJ/kg. These values are lower than the values used for fossil fuel in the past. The fossil component examined here does explain the lower net heating values in market petrol fuels found in this and earlier studies.

It can be concluded that the variations in carbon content and combustion value of the four base petrol samples (without ethanol) are relatively small: max. respectively 1.5% and 0.4% variation.

6 Margins in fuel for type-approval tests CO_2 values

Since the heating value and Carbon content of market fuels show a large variation, the question arises if the variation can be utilized in the type-approval testing to achieve low CO_2 emission values. The reference fuel in type-approval testing is within stricter margins than the market fuels according to EN228, but a certain range remains. In particular, the carbon content and the heating value are not specified, although they are central to the actual CO_2 emissions.

TNO has asked a laboratory specialized in producing reference fuels and special blends to provide a sample of fuel which is expected to have the lowest CO_2 emission in a WLTP test. Specifically, they provided a sample within the E5 reference fuel specification with a low carbon content per energy content, leading to low CO_2 emissions. The laboratory recognized substantial margin in the reference fuel in multiple aspects. First, the aromatic content is high in carbon and low in energy per kg. This is the majority of the margin in the reference fuel and not delimited much by other specifications. Second, the long hydrocarbon chains add to the energy. So the laboratory prepared a sample with low aromatics content, from which the specifications are presented in Table 5-1. This table also shows four random batches of reference fuels used for type-approval testing. The aromatics content of these batches varies from 30.7% to 34.5%, compared to 29.6% for the special low carbon batch (C per MJ energy).

A simple exercise can give an indication how the margins can be utilized:

- Using toluene (C_7H_8, molar mass 92 $g\cdot mol^{-1}$) as a proxy for aromatics:
  - Lower Heating Value: 40.6 MJ/kg
  - Carbon content: 91%wt
- Compare these values with the typical properties of petrol, from Chapter 2:
  - Heating value: 42.6 MJ/kg → 5% lower for toluene
  - Carbon content: 84.5%wt → 11% higher for toluene
- The reference fuel has a margin of 29%-35%vol aromatics (UNECE Regulation 83 revision 4 and 5). Hence, a bandwidth of 6% in aromatics translates to:
  - 6% * 5% = 0.30% bandwidth in heating value in the reference fuel
  - 6% * 11% = 0.66% bandwidth in carbon content in the reference fuel
- Hence, in total 0.96% flexibility in the CO_2 emissions on the basis of the margins in the reference fuel.
- Ethanol (C_2H_6O) may vary in E5 from 4.7% v/v tot 5.3% v/v, i.e., 0.6% bandwidth. The heating value is substantially lower but so is the carbon content, such that the net effect is very limited.

It should be noted that in EN228 the margins are much wider, as there is no lower limit for aromatics, but the upper limit of 35% is the same as for reference fuel. Hence, higher heating values should be possible.

Against typical samples of reference fuel, the special batch has a heating value which is 0.32% higher, and a carbon content which is 0.41% lower. So, the CO_2 emission in a type-approval test can be lowered by 0.73% compared to an average standard reference fuel, by optimising the fuel for lower CO2 emissions. The net heating value of the standard reference fuels (determined through method ASTM D240) is with 42.26 MJ/kg close to the market average of 42.3 MJ/kg, after subtracting ethanol.

Table 6-1: The results compared with the reference fuel specification. In the last 4 columns other batches of reference fuels are added for comparison.

						comparable results			
Test	**Method**	**Unit**	**Euro-5 reference**		**Result**	***Result A***	***Result B***	***Result C***	***Result D***
			Min	**Max**					
						Result PrefixResult (Fixed)	*Result PrefixResult (Fixed)*	*Result PrefixResult (Fixed)*	*Result PrefixResult (Fixed)*
Appearance	Visual		Report		C&B	*C&B*	*C&B*	*C&B*	*C&B*
RON ·	EN ISO 5164		95.0	-	96.6	*96.0*	*96.8*	*96.8*	*98.2*
MON ·	EN ISO 5163		85.0	-	87.7	*86.1*	*86.3*	*87.5*	*87.7*
Density @ 15°C #	EN ISO 12185	kg/L	0.7430	0.7560	0.7447	*0.7492*	*0.7508*	*0.7476*	*0.7505*
DVPE @ 37.8°C	EN 13016-1	kPa	56.0	60.0	57.1	*59.6*	*57.8*	*59.8*	*59.5*
Sulfur #	EN ISO 20846	mg/kg	-	10.0	1.5	*2.6*	*2.4*	*1.8*	*3.0*
Water Content	EN ISO 12937	% v/v	-	0.015	0.010	*0.013*	*0.015*	*0.015*	*0.015*
Aromatics	ASTM D1319	% v/v	29.0	35.0	**29.6**	*30.7*	*34.5*	*32.3*	*32.1*
Olefins	ASTM D1319	% v/v	3.0	13.0	3.8	*8.2*	*6.3*	*7.4*	*5.4*
Saturates	ASTM D1319	% v/v	Report		61.6	*55.8*	*54.5*	*55.5*	*57.4*
Benzene	ASTM D6730 mod	% v/v	-	1.00	0.06	*0.21*	*0.22*	*<0.1*	*0.22*
Oxygenates									
Methanol	ASTM D6730 mod	% v/v	Report		<0.1	*<0.1*	*<0.1*	*<0.1*	*<0.1*
Ethanol	ASTM D6730 mod	% v/v	4.7	5.3	5.0	*5.3*	*4.7*	*4.8*	*5.2*
MTBE	ASTM D6730 mod	% v/v	Report		<0.1	*<0.1*	*<0.1*	*<0.1*	*<0.1*
ETBE	ASTM D6730 mod	% v/v	Report		<0.1	*<0.1*	*<0.1*	*<0.1*	*<0.1*
Other	ASTM D6730 mod	% v/v	Report		<0.1	*<0.1*	*<0.1*	*<0.1*	*<0.1*
Oxygenates - Total	ASTM D6730 mod	% v/v	Report		5.0	*5.3*	*4.7*	*4.8*	*5.2*
Oxidation Stability	EN ISO 7536	min	480	-	>480	*>480*	*>480*	*>480*	*>480*
Copper Corrosion (3h at 50ºC)	EN ISO 2160	Rating	Class 1	-	1A	*1A*	*1A*	*1A*	*1A*
Existent Gum - Washed	EN ISO 6246	mg/100mL	-	4	<1	*<1*	*<1*	*<1*	*<1*
Lead ·	EN 237	mg/L	-	5.0	<2.5	*<2.5*	*<2.5*	*<2.5*	*<2.5*
Phosphorus ·	ASTM D3231	mg/L	-	1.30	<0.20	*<0.20*	*<0.20*	*<0.20*	*<0.20*
Carbon	ASTM D6730 mod	% m/m	Report		84.52	*84.79*	*85.07*	*84.82*	*84.78*
Hydrogen	ASTM D6730 mod	% m/m	Report		13.64	*13.27*	*13.20*	*13.40*	*13.33*
Oxygen	ASTM D6730 mod	% m/m	Report		1.84	*1.94*	*1.73*	*1.78*	*1.89*
H/C Mole Ratio	Calculation		Report		1.92	*1.86*	*1.85*	*1.88*	*1.87*
O/C Mole Ratio	Calculation		Report		0.02	*0.02*	*0.02*	*0.02*	*0.02*
Gross Calorific Value	ASTM D3338 mod	MJ/kg	Report		45.00	*44.78*	*44.72*	*44.90*	*44.80*
Gross Calorific Value ·	ASTM D240	MJ/kg	Report		45.68	*45.11*	*45.02*	*N/A*	*N/A*
Net Calorific Value	**ASTM D3338 mod**	**MJ/kg**	**Report**		**42.11**	***41.96***	***41.92***	***42.06***	***41.97***
Net Calorific Value	**ASTM D240**	**MJ/kg**	**Report**		**42.79**	***42.29***	***42.22***	***N/A***	***N/A***
Distillation (Evaporated) #									
E70	EN ISO 3405	% v/v	24.0	44.0	32.5	*31.4*	*29.1*	*32.5*	*28.8*
E100	EN ISO 3405	% v/v	48.0	60.0	**49.3**	*56.0*	*54.8*	*53.6*	*51.7*
E150	EN ISO 3405	% v/v	82.0	90.0	**83.0**	*87.5*	*87.6*	*83.0*	*85.4*
E180	EN ISO 3405	% v/v	Report		94.9	*93.9*	*93.9*	*91.4*	*91.9*
IBP	EN ISO 3405	ºC	Report		33.7	*32.4*	*37.5*	*33.0*	*36.2*
10% Volume Evaporated	EN ISO 3405	ºC	Report		52.6	*53.4*	*55.2*	*52.1*	*56.5*
20% Volume Evaporated	EN ISO 3405	ºC	Report		57.4	*59.6*	*60.9*	*57.9*	*61.6*
30% Volume Evaporated	EN ISO 3405	ºC	Report		65.2	*67.8*	*71.3*	*65.3*	*72.0*
40% Volume Evaporated	EN ISO 3405	ºC	Report		84.8	*83.7*	*85.7*	*83.7*	*88.0*
50% Volume Evaporated	EN ISO 3405	ºC	Report		101.1	*94.6*	*95.8*	*96.3*	*98.5*
60% Volume Evaporated	EN ISO 3405	ºC	Report		115.5	*103.7*	*104.7*	*106.1*	*106.7*
70% Volume Evaporated	EN ISO 3405	ºC	Report		128.8	*113.5*	*113.6*	*117.0*	*115.7*
80% Volume Evaporated	EN ISO 3405	ºC	Report		144.2	*126.0*	*126.1*	*137.2*	*129.8*
90% Volume Evaporated	EN ISO 3405	ºC	Report		165.9	*164.0*	*163.5*	*176.9*	*173.2*
95% Volume Evaporated	EN ISO 3405	ºC	Report		180.4	*183.5*	*184.2*	*188.2*	*187.9*
FBP	EN ISO 3405	ºC	190.0	210.0	193.6	*197.2*	*202.5*	*204.5*	*202.0*
Residue	EN ISO 3405	% v/v	-	2.0	0.8	*1.0*	*0.5*	*1.0*	*0.9*

7 Water content in market fuels in spring 2019

In February, March, and April 2019 the Inspection has collected more samples petrol fuel. These samples were collected together with the regular sample collection by the Inspection for the Fuel Quality Directive. In total 20 samples were collected. Each sample was analysed separately, so the results do not have the (good) statistical significance such as the 60 samples in the first phase of the study.

The average water content of all samples is 0.0246% of the mass with a variation of 16% with respect to the average. The range is 0.018% - 0.032%. The first and second period of sampling in the Spring show no systematic difference. The water content is lower than the results of the market fuels obtained in 2018, as reported in Chapter 2.

Given the 5% volume content of ethanol in petrol, the 0.3% mass fraction of water in ethanol for bio-admixture would result in 0.015% water in petrol. Current values would mean, that on average 0.010% weight of water is from the fossil component. The highest water content in the fossil part, i.e., 100 mg/kg is equal to 0.01% weight. However, in the recent samples of ethanol, an average water content of 1510 mg/kg was observed. This would result in 0.0075% water in petrol from the ethanol.

Consequently, it can be concluded (or it is very likely) that based on the current samples, the about half of the water in market petrol has a different source, not explained by the results of the fossil sample, nor by the typical water content in ethanol.

8 Discussion

From the 2017 analyses of petrol, it is clear that a range in heating values is to be expected, when fuelling a vehicle. The average heating value of the samples taken is 42.5 MJ/kg which corresponds to a heating value of the fossil component of 43.3 MJ/kg. In the past a heating value of 44 MJ/kg for the fossil fuel was used for the Dutch statistics, also for the fossil component in blending. However, this has recently been adapted to a more plausible 43 MJ/kg[3]. The variations in heating value was +/- 0.3 MJ/kg. The cause of the variation is largely unknown.
The oxygenated components, e.g., from biofuels like ethanol and MTBE, bring the petrol to market quality and it may allow for variations in the fossil part. The most plausible explanation is a variation in heating values of the base fossil petrol (EuroBOB) used for blending with ethanol or other oxygenates.

The ethanol used for blending may be the cause of the high average water content of 290 mg/kg in petrol. One out of the three ethanol samples contained almost nine times more water than is specified in the standard EN-15376 for ethanol. Taking the average of the three samples leads to water contents similarly as observed based on the ethanol blending fraction of 4.61%[volume]. However, the sample size of 3, and the variation therein of a factor 10, can only be taken indicatively of ethanol as the source of water in petrol. Further study, with 11 additional samples collected, with the help of the fuel producers, did not yield more samples with high water content. Based on the water content found in the fossil component and the water content in the ethanol samples, some additional water is systematically present in market fuels. This amount of water is, however, limited to about 50% higher than can be expected from the ethanol and fossil fuel.

The collection of 4 fossil samples, confirmed the hypothesis that the lower heating value of 43.3 MJ/kg of fossil fuel is the main cause of the lower than previously used heating values for petrol in the national energy statistics. This situation is remedied based on the preliminary findings from this study, after phase 1.

The apparent range in heating value of petrol for the same weight and atomic composition may be exploited to yield higher or lower CO_2 emissions in a standard type-approval emission test. A special blend was made by a specialized laboratory which could be used to determine the official CO_2 of a vehicle model, according to Annex 10 of Regulation 83, lower than the same test with an average market fuel. The regulation does not specify heating value, nor request reporting of heating value. This is a flexibility in type-approval tests since Euro-5/6, which allows for testing with “E5/E10” reference fuels, under varying specifications. The impact of this flexibility is about 0.7% on the CO_2 emissions, compared to typical reference fuels blends. Separately, current market fuels generally do not satisfy the latest density range of the E5 reference fuel between 743 kg/m^3 and 756 kg/m^3. In particular winter fuels have a lower density, with less energy per litre.

[3] Dit is gelijk aan de waarde in bijlage III van de RED.

9 Conclusions

Petrol fuel and ethanol samples were investigated to determine a) the average properties including the combustion value and carbon content, and b) whether they fulfil the formal specifications. This leads to the following conclusions:

- This study confirms the finding of the earlier 2016 study, that the water content of E5 petrol is systematically higher than can be expected based on the maximum allowable water content of ethanol. It is on average about 0.03 weight % higher, which would reduce the energy content also by about 0.03%.
- The precise reason for the high water content could not be identified with certainty. According to the phase 1 samples the most likely reason is too high water content in ethanol, but this was not confirmed by the phase 2 samples.
- The E5 fuels showed a small band width in ethanol volume fraction: 4.38% to 4.61%.
- The combustion values of 12 mixed monthly E5 samples showed a range from 42.07 to 42.5 MJ/kg (phase 1). The four EuroBOB[4] samples varied from 43.22 to 43.40 MJ/kg.
- The carbon content of the EuroBOB samples ranged from 84.5% to 86.0%.

With respect to the possibility to lower the CO_2 emissions during the type approval test, it is concluded that the CO_2 emission can be lowered by about 0.7% compared to an average standard reference fuel, by optimising the fuel for lower specific CO_2 emissions

[4] Base petrol at distribution station before ethanol is blended

10 Signature

The Hague, 31 January 2020

TNO

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