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# Problems of assessment of the petrol propensity to combustion chamber deposits forming according to methods specified in Worldwide Fuel Charter: M 111 test and BZ-154-01

The Worldwide Fuel Charter established to harmonize fuel quality world-wide, classified fuel markets according to the severity of the requirements for emission control or other market demands. Petrol standards for markets of categories 2, 3 and 4 contain additional requirements concerning intake valve cleanliness and combustion chamber deposits (CCDs). Two tests CEC-F-20-A-98 (engine test Mercedes Benz M 111) or TGA – FLTM BZ-154-01 (laboratory test) can be used to appreciate the effect of petrol quality on the formation of deposits in the combustion chamber. In the TGA method a coefficient of unwashed gums decomposition at 450°C is determined. Petrol propensity to form combustion chamber deposits (CCDs) is a crucial parameter in the case of the introduction of a new additive package. The basic M 111 test engine enabling quantitative evaluation of this property is very expensive, besides, reproducibility of the test results is low in some cases. For these reasons some attempts have been made to replace the test or to find a complement to it. In the presented work a model describing the rate of CCDs formation as a function of unwashed gums content and their decomposition coefficient, has been proposed. For 11 samples of petrol the following tests have been performed: engine test M 111, a test determining unwashed gums content and TGA measurements. Correlation of the obtained experimental results with the model have been assessed. It was found that the M 111 engine test can't be substituted by the measurement of unwashed gums content and TGA of these gums. These methods can be only considered as complementary, nevertheless they can be helpful in preliminary estimation of the potential ability of petrol to form deposits.

Key words: petrol, chamber deposits, engine, Worldwide Fuel Charter.

## Problemy badania skłonności benzyn do tworzenia osadów w komorze spalania silnika metodami przywołanymi w światowej karcie paliw: M 111 oraz BZ-154-01

Światowa Karta Paliw jest wyrazem dążności do ujednolicenia standardów paliw silnikowych w zakresie emisji w zależności od wymagań rynków. Dzieli ona benzyny silnikowe na cztery kategorie w zależności od dodatkowych wymagań w zakresie czystości zaworów silnika oraz tworzenia osadów w komorze spalania. Do oceny skłonności benzyn do tworzenia osadów w komorze spalania silnika stosowane są dwie metody badawcze: test silnikowy CEC-F-20-A-98 (Mercedes M 111) oraz metoda termograwimetryczna opracowana przez koncern Ford FLTM BZ-154-01. W metodzie termograwimetrycznej oznaczany jest współczynnik rozkładu żywic nieprzemywanych w temperaturze 450°C. Skłonność benzyn do tworzenia osadów w komorze spalania jest kluczowym parametrem w przypadku stosowania nowoczesnych pakietów dodatków do paliw. Podstawowy test M 111 jest kosztowny i słabo odtwarzalny, co sprawia, że poszukuje się innej, prostszej i tańszej metody do oceny tego parametru. W niniejszej publikacji zaproponowano matematyczny model tworzenia osadów w komorze spalania silnika bazujący na funkcji termicznego rozkładu żywic nieprzemywanych oraz ich zawartości w paliwie. Dla 11 próbek benzyn zbadano skłonność do tworzenia osadów metodami M 111 oraz BZ-154-01. Dokonano oceny korelacji uzyskanych wyników z obu metod. Stwierdzono, że test M 111 nie może być wprost zastąpiony metodą BZ-154-01. Obie metody mogą być rozważane jako komplementarne, niemniej jednak metoda BZ-154-01 może być przydatna do wstępnej oceny skłonności do tworzenia osadów.

Słowa kluczowe: benzyna, osady w komorze spalania, silnik, Światowa Karta Paliw.

## Introduction

There is a significant tendency in the modern world to harmonize fuel quality worldwide and to unify the standards. Requirements given in the Worldwide Fuel Charter (WWFC) [19] are the result of this trend. The draft of the fifth edition has been available since December 2012 [20]. This document is authorized by four world organizations: ACEA (European Automobile Manufactures Association), Alliance (Alliance of Automobile Manufactures), EMA (Engine Manufactures Association) and JAMA (Japan Automobile Manufactures Association). Creation of the document indicates that both engine and vehicle manufacturers recognize the importance of a common policy concerning fuels quality.

Implementation of the recommendations contained in the Worldwide Fuel Charter should help to protect the environment by reducing vehicles emissions and benefit customers with optimal fuel consumption and higher vehicle performance. The fifth edition of Charter proposes five different quality categories for unleaded petrol and diesel fuel. The main criterion of such division was the legal situation on the market concerning emissions controls. The categories are described below:

1) markets with no or first level of emission control (e.g., US Tier 0, EURO 1),
2) markets with requirements for emission control (e.g., US Tier 1, EURO 2, EURO 3),
3) markets with more stringent requirements for emission control (e.g., US LEV, California LEV or ULEV, EURO 4, JP 2005),
4) markets with advanced requirements for emission control (e.g., US Tier 2, US Tier 3 (pending), US 2007/2010 Heavy Duty On-Highway, US Non-Road Tier 4, California LEV II, EURO 4, EURO 5, EURO 6, JP 2009,
5) markets with highly advanced requirements for emission control and fuel efficiency (e.g., emission standards for markets with Category 4, with additional requirements as US 2017 light duty fuel economy, US heavy duty fuel economy, California LEV III).

Requirements concerning intake valve cleanliness and combustion chamber deposits have been introduced into categories 2–5. For the evaluation of these parameters the Charter recommends the following methods:

- CEC-F-20-A-98 – Deposits forming tendency on intake valves and in combustion chambers of petrol engines (Mercedes Benz M 111 engine test),
- or FLTM BZ-154-01, an alternative method – Thermogravimetric analysis (TGA) of petrol gums (Ford Laboratory Test Method).

For markets classified as categories 2, 3, 4 and 5 requirements concerning intake valve cleanliness and combustion chamber deposits have been introduced. There are some differences within the limits of the parameters determined by these methods in each category from 2–5. The requirements for the individual categories are given:

- for the method CEC-F-20-A-98 combustion chambers deposits maximal value – category 2: 3500 mg/engine, category 3, 4 and 5: 2500 mg/engine,
- for the method TGA-FLTM BZ-154-01 „*A*” coefficient (% mass at 450ºC) maximal value for all categories is defined as 20%.

The fuels are classified according to the results of the M 111 test and the BZ-154-01 analytical test. Analysis of the test methods indicates that a correlation between their results may exist; nevertheless a firm connection has not yet been found.

In our former paper results of investigations concerning the introduction of BZ-154-01 thermal analysis with Labsys TM apparatus into the lab practice have been presented [13].

## Effect of the deposits on engine work

Deposits in the combustion chambers formed as an effect of fuel combustion cause problems with auto ignition – as a result the engine's octane demand increases. Besides problems with engine start appear, engine power decreases and fuel consumption and emission of toxic components of exhaust fumes increase [5–12, 14, 15]. Petrol treated with additive packages reduced the intake valve deposits and decreased the CO and HC emissions, whereas the same additive packages increased combustion chambers deposits. The dosage of multifunctional additive packages in petrol should be optimized for reducing IVD and CCD in order to maintain the engine performance and emission characteristics over a period of time [17].

The introduction of oxygenates and petrol detergent packages into the petrol and application of direct gasoline injection contribute to problems connected with pollution. Packages containing polymeric additives substantially contribute to combustion chambers sediments formation but there are few data addressing this problem. Problems resulting from deposits formation in engine combustion chambers are serious enough to deal with the subject. The additional reason is that costs of the engine tests are very high whereas the application of thermal analysis is incomparably less expensive.

## Petrol composition and deposits forming in the engine combustion chambers

Theories and opinions concerning formation of deposits in the engine combustion chambers have been modified as the changes in petrol composition appeared (including modification of the group composition, lead and sulfur content, application of oxygenates and new additive packages) [5–12].

According to [5] it is believed that the main process of deposits formation takes place on the cooler parts of the combustion chamber where the partially oxidized fuel, lubricating oil and additives condense. Relative share of each of these sources depends on the engine construction, operation conditions, duration of the engine test or the distance in the case of road tests. After the initial fast growing, of the amount of deposits on the surface of the engine chamber the second slow period of their gathering occurs, until the equilibrium state is achieved, in which the rate of deposits formation is equal to the rate of their decomposition [5].

There are two ways to estimate the quantity of deposits – either the mass of the deposits or the thickness of the deposits layer in the engine chambers are measured. In the article [9] many examples documenting correlation between mass and deposits layer thickness have been presented.

The Mercedes Benz M 111 engine test (acc. to CEC-F-20-A-98) takes 60 hours and is the basic test for assessment of the deposits mass in the combustion chambers.

To find the reasons for deposits formation in the engine chambers the following parameters have been taken into consideration: fuel group composition, unwashed gums (UWG) content and information obtained from TGA of the unwashed gums – characteristics of the UWG obtained with TGA.

Diolefins and aromatics promote CCDs formation. Ethanol contained in petrol enhances deposits amount whereas for MTBE such correlation was not found [11].

Researchers reports [11] that mechanisms which cause petrol additives to affect CCDs formation are complicated. The correlation between CCDs amount and gums content is difficult to find, as the additives contain components of different chemical composition. In articles [5] the plot depicting unwashed gums contents versus CCDs thickness has been shown. It was assessed that the relation of these two quantities was difficult to define. Also given [12] were the results of CCDs mass measurements and the coefficient TGA 10. TGA 10 is defined as the product of unwashed gums content and the amount of residue after 10 minutes of heating at 300ºC, expressed in %. The correlation between these two values was not found. Nevertheless the TGA measurement temperature equal to 300ºC is for certain too low in comparison with the engine temperature, so in our opinion in this case, conditions in the engine were not properly simulated.

The authors in [1] present the research results of the relationship between thermal stability of petrol additive packages and their effect on CCDs. In the authors opinion [1] there are no clear correlations between CCDs and the degree of decomposition of UWG from additized petrol obtained in the DTA analysis.

Data analysis conducted by the authors [4] in terms of CCDs, the results of UWG content and results of thermogravimetric analysis (TGA) of these UWG for various fuels indicated that the UWG does not allow for predictions of CCDs. It isn't also possible to use the UWG content or results obtained from the TGA analysis to assess the tendency to form CCDs from randomly selected fuels.

In the article [18] the authors presented the fuel research results in the standard engine which simulate various road conditions. It studied the effect of different individual fuel parameters on their possiblity to predict CCDs. These parameters were TGA residue, UWG, T95, sulfur content, aromatics content. Research has shown that none of the tested fuel parameters behaved as a good predictor of CCDs thickness. This assessment should involve the use of complex physical and chemical models.

IVD and CCDs in spark-ignition engines affect nitrogen oxides ($NO_x$) emission and octane requirement increases (ORI). The first reason of these phenomena is difficulty to transfer the heat from the combustion chamber and the second is the increase in the compression ratio. Currently additives to control the tendency to form IVD and CCDs and methods used for assessing the weight and thickness of sludge are being studied widely. The authors insist [17] that the weight and thickness measurement of these deposits without considering the shape and position of the deposits is not able to reflect the

CCDs effect on the ORI. In the paper [17], the testing results of several fuels according to the ORI engine test procedure is presented. In these studies [17] the impact of the same characteristics of deposits such as weight, thickness, shape and location of CCDs on the ORI was assessed.

The authors of another article [3] point out that petrol components play a prime role in the formation of deposits on engine components, so petrol producers dope the multifunctional additives to reduce the deposit forming tendency of the fuel. For the propensity of the fuel to form deposits the engine test method CEC F-20-A-98 on Mercedes Benz M 111 was used. In article [3] the authors attempt to differentiate the types of additives and their effects on emission characteristics. The IVD and CCDs formation and exhaust emissions depended upon the treat rate and components of multifunctional additives blended with petrol.

The work [16] gives the results of the characteristics of deposits formed on the intake valves and combustion chambers of a new petrol engine DISI as compared to the results obtained in the PFI engine. The characteristics of these deposits have been investigated using elemental and thermal analytical techniques. The authors have found that both fuel and engine lubricant contribute to the composition of deposits. DISI composition consisted of inorganic elements such as Ca, Mo, Zn, P and S and the amount of these inorganic elements in DISI IVD deposit were higher than in the PFI IVD. Significant differences in deposit volatility and the amount of inorganic components were observed between CCDs, when additives containing mineral base oil or synthetic base oil were applied. Elemental composition of CCDs was not significantly changed by the presence or absence of the fuel additives. The inorganic composition of DISI engine CCDs showed no significant differences when compared with PFI engine CCDs.

The introduction of oxygenates and petrol detergent packages into the petrol and application of direct gasoline injection contribute to problems connected with pollution. Packages containing polymeric additives substantially contribute to combustion chambers sediments formation but there are few data addressing this problem. Problems resulting from deposits formation in engine combustion chambers are serious enough to deal with the subject. The additional reason is that the cost of the engine tests are very high whereas the application of thermal analysis is incomparably less expensive.

However, in work [2] the authors presents new methodology to evaluate IVD and CCDs formation on port injection flexible fuel spark-ignition engines. This methodology was adapted from the ASTM 6201 standard, using a commercial Brazilian flexifuel engine. The ASTM D 6201 standard is the method recommended by the WWFC as a third method to evaluate IVD and CCDs in engines. This methodology will also be used to evaluate the efficiency of detergent additives to clean intake valves and combustion chambers after petrol additivation.

## Experimental procedures

### *Thermal analysis BZ-154-01*

In our past work [20] some detailed problems concerning the method BZ-154-01 have been discussed. The method enables determination of the degree of unwashed gums decomposition at 450ºC.

The degree of gums decomposition is determined with *A* coefficient defined as follows (1):

$$A = \frac{(M_{450} - m_{450})100\%}{M_{150} - m_{150}} \tag{1}$$

where:

$M_{450}$ – mass of gums left in the crucible at 450ºC, obtained from TGA,

$M_{150}$ – mass of gums in the crucible at 150ºC, obtained from TGA,

$m_{450}$ – base line correction at 450ºC (empty crucible),

$m_{150}$ – base line correction at 150ºC (empty crucible).

Temperature of gums decomposition equal to 450ºC and *A* coefficient which should not exceed 20% were given in Worldwide Fuel Charter [19, 20].

### *Proposed model of CCDs formation*

Deposits formation in combustion chambers resembles the physical adsorption of particles on the surface of solids. The physical adsorption phenomenon occurs due to intermolecular van der Waals forces forming on the surface of the potential energy field in which particles of the matter take positions at energy minima. However, in the case of an engine the temperature gradient occurs. The engine wall is cooler than its interior so unburnt, heavier substances may condense on the wall.

Such a general approach to the problem can be found in publications [5–12, 15]. Based on this analogy an attempt at quantitative description of CCDs formation has been taken.

High boiling substances present in petrol and being the main component of unwashed gums are burnt and subjected to decomposition in the engine chambers. The amount of substances from which the deposits can be formed in the chambers is a function of gums content in the petrol and *A* coefficient (defined above, describing the effect of combustion and decomposition of these gums).

For the model describing the CCDs formation the following assumptions have been made:

- in the engine fuelled with given hydrocarbon petrol the achieved distributions of temperature and pressure are statistically reproducible,
- the rate of CCDs formation depends on: the coefficient of the engine chambers covered with the deposits and coefficient of unwashed gums decomposition.

With these assumptions the rate of deposits formation on the combustion chambers surface can be described with the equation (2):

$$r = k_1(1 - \theta)AZ \tag{2}$$

where:
$k_1$ – constant, characteristic for the given system (petrol + gum substance + wall of the engine); the constant describes the ability of the burnt and decomposed unwashed gums to aggregate on the inside surface of the engine,
$A$ – coefficient of the unwashed gums decomposition,
$Z$ – content of the unwashed gums in gasoline (mg/100 ml),
$\theta$ – coefficient of the engine chambers covered with the deposits given by the equation (3):

$$\theta = \frac{m}{m_{\max}} \tag{3}$$

where:
$m$ – deposits mass in the chambers,
$m_{\max}$ – maximum deposits mass in the chambers.

Beside deposits gathering the reverse process, deposits decomposition (‘desorption’), also occurs on the engine chambers surface. The rate of this process can be described by the equation:

$$r_{des} = k_2 \cdot \theta \tag{4}$$

where:
$r_{des}$ – rate of the deposits ‘desorption’ from the chambers surface,
$k_2$ – constant, characteristic for the system (gum + chamber surface); the constant describes the ‘ability’ of the deposits for desorption from the engine chambers surface.

At equilibrium the rates of deposits forming and deposits ‘desorption’ are equal (5).

$$r = r_{des} \tag{5}$$

Therefore (6):

$$k_1(1 - \theta)AZ = k_2\theta \tag{6}$$

so the equation is obtained (7):

$$\theta = \frac{bAZ}{1 + bAZ} \tag{7}$$

or (8):

$$\frac{m}{m_{\max}} = \frac{bAZ}{1 + bAZ} \tag{8}$$

where:
$b$ – constant, equal (9) to:

$$b = \frac{k_1}{k_2} \tag{9}$$

The equation (7) formally resembles the Langmuir equation describing gas absorption on the solid surface.

For the given petrol containing a proper additive, maximum amount of deposits is achieved.

A state of saturation of the engine chambers surface with deposits is, or at least should be achieved in the M 111 engine test. Therefore (10):

$$m = m_{\max} \tag{10}$$

Then (11):

$$\frac{m}{m_{\max}} \approx \frac{bAZ}{1 + bAZ} \approx \frac{bAZ}{bAZ} = 1 \tag{11}$$

(with the assumption that $b \cdot A \cdot Z >> 1$)

From (11) it can be found that for the saturation state the following relation can be obtained (12):

$$m_{\max} = b \cdot A \cdot Z \tag{12}$$

The $m_{\max}$ quantity is equal to the amount of deposits determined with the M 111 engine test, provided that the equilibrium state (saturation with the deposits) has been achieved in the test. Parameter $b$ is a measure of the ability of decomposed unwashed gums to aggregate into deposits (carbon build-up) in the engine chambers. The equation (12) may explain the relation between the M 111 engine test results and the decomposition degree of unwashed gums (parameter $A$), which is mentioned in the Worldwide Fuel Charter [19, 20].

The process of deposits formation is probably more complicated than it was described above, nevertheless the presented considerations can help to clear up the phenomenon mechanism and explain the correlation between the M 111 engine test results and parameter $A$.

It is significant that in the equation (12) variables $A$ and $Z$ describes generally the petrol propensity to deposits formation. They can be considered as independent variables. Coefficient $b$ is not an independent variable. How much the coefficient $b$ is specific for the given (petrol + engine) system is considered below.

#### *Determination of unwashed gums (UWG)*

Determination of unwashed gums was performed with the classic apparatus according to PN-EN ISO 6246 standard.

#### *Thermal analysis*

The DTA/DTG study was performed with SETARAM LABSYS™ apparatus. The heating module consists of a resistance furnace with operating temperature of up to 1600°C. During the measurement the oven can be purged with air or inert gas.

#### *Petrol samples*

Samples of petrol represented were made by leading concerns present in the Polish fuel market and from the experimental petrol blended in the Oil and Gas Institute. All of the petrol samples containing the proper additive packages were investigated with the M 111 engine test.

#### *Procedure*

The Oil and Gas Institute testing method, according to the BZ-154-01 procedure, was used. As the tested samples were of organic origin the test was performed in platinum crucibles of 100 µl. In the chosen samples unwashed gums (UWG) content was determined (*Z*) and next the coefficient of their decomposition (*A*) was found [13, 14].

### Results and discussion

Table 1 contains the results obtained from TGA (*A*), contents of unwashed gums (*Z*), values from the M 111 engine test and the results of calculations of the total amount of substances which theoretically may deposit in the engine chambers. This value expressed in grams is a product of the amount of petrol used in the test (*l*), unwashed gums content and thermal decomposition coefficient $A \cdot 10^{-4}$. The obtained value was compared with the results from the M 111 test. Unfortunately in such comparisons usually single results are given because of the high cost of the test (about 400 $dm^3$ of petrol).

It should be also stated that uncertainties of the thermal decomposition coefficient *A* obtained in TGA measurements are significant. The repeatability of the unwashed gums test (*Z*) usually didn't exceed 2 mg/100 ml. Estimated uncertainties are shown in figures 1÷3 as vertical lines limiting the average result of the measurement. Analogically the uncertainty range for the M 111 engine test is depicted as horizontal lines and for the whole observed measurement range it was taken as equal to about ±11% of the measured value.

Because of these facts results of the whole statistical analysis should be treated only as a kind of approximation. Their reliability is closely related to the size of the tested sample population and because only 11 M 111 engine test results were available the relations described below should be treated as indication of some tendencies of the possible relations. Their verification needs further gathering of the tests results.

For example in Table 1 the results of the assessment of linear correlation between the M 111 engine test results and thermal decomposition coefficient (M111(*A*)), unwashed gums content (M111(*Z*)) and a product of these values (M111($A \cdot Z$)) correspondingly have been presented for all the used petrol blends. The tested relations have been also depicted in Figures 1–4.

In Figures 3 and 4 the obtained lines are the result of regression analysis ($A \cdot Z$) versus the M 111 engine test. In

Table 1. Results of the M 111 engine test, TGA analysis and unwashed gums content

| M 111 engine test result [mg/engine] | Coefficient *b* | *A* gums decomposition coefficient, [%] | *Z* unwashed gums content, [mg/100 ml] | Product $A \cdot Z$ | Amount of petrol used in the M 111 test [$dm^3$] | Calculated total amount of a substance which can be deposited in the engine chambers [g/engine] |
|---|---|---|---|---|---|---|
| 4269 | 14.3 | 9.60 | 31 | 298 | 382 | 11 |
| 4631 | 11.8 | 9.06 | 43 | 393 | 384 | 15 |
| 11058 | 18.7 | 14.69 | 40 | 590 | 378 | 22 |
| 8736 | 1.2 | 19.42 | 363 | 7048 | 385 | 271 |
| 12685 | 1.6 | 20.86 | 372 | 7761 | 388 | 301 |
| 3721 | 7.0 | 13.72 | 39 | 528 | 391 | 21 |
| 3588 | 6.6 | 14.32 | 38 | 546 | 393 | 21 |
| 4100 | 10.8 | 11.00 | 35 | 390 | 390 | 15 |
| 4366 | 9.4 | 12.56 | 37 | 467 | 389 | 18 |
| 4045 | 13.1 | 8.85 | 35 | 308 | 378 | 12 |
| 4125 | 18.0 | 2.34 | 98 | 229 | 375 | 9 |

Figure 4 sample No. 3 has been omitted to show how much a single M 111 engine test result may affect the interpretation of the tested relation. The value of $R^2$ (determination coefficient) changes from about 0.56 (Fig. 3) to nearly 0.92 (Fig. 4). Besides omitting the results of tests 4 and 5, it may suggest that no correlation exists between the product of coefficient $A$ and $Z$ ($A \cdot Z$) and the M 111 engine test results.

Table 2. Results of the linear correlation testing

| Type of the relation | $R^2$ determination coefficient |
|---|---|
| M111($A$) | 0.48 |
| M111(Z) | 0.51 |
| M111($A \cdot Z$) | 0.56 |
| M111($A \cdot Z$) – without sample No. 3 | 0.91 |

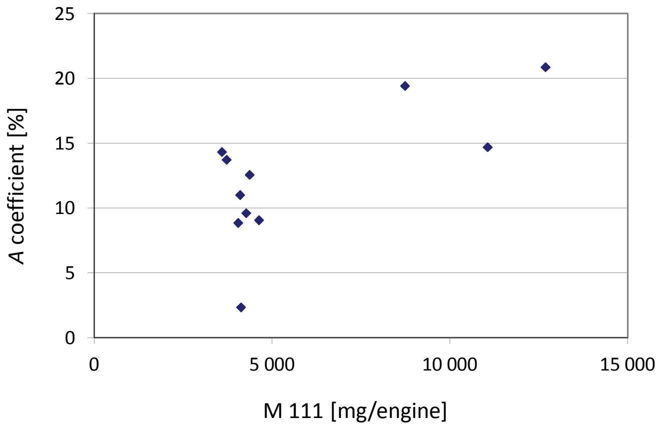


Fig. 1. (A) coefficient versus M 111 engine test results

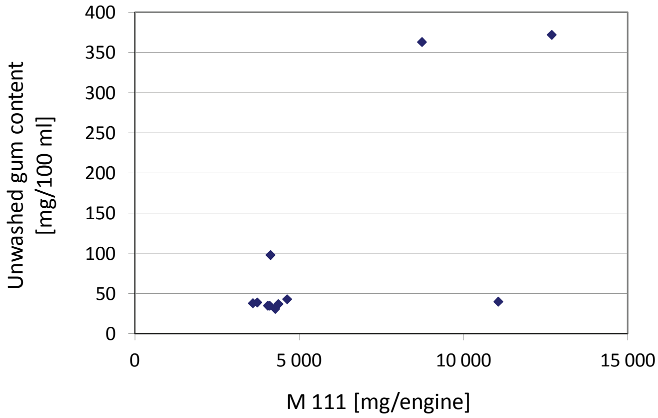


Fig. 2. Gums content ($Z$) versus M 111 engine test results

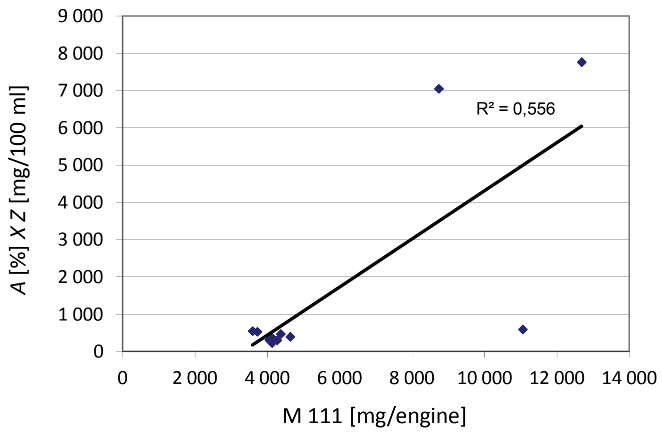


Fig. 3. Regression analysis ($A \cdot Z$) versus the M 111 engine test results

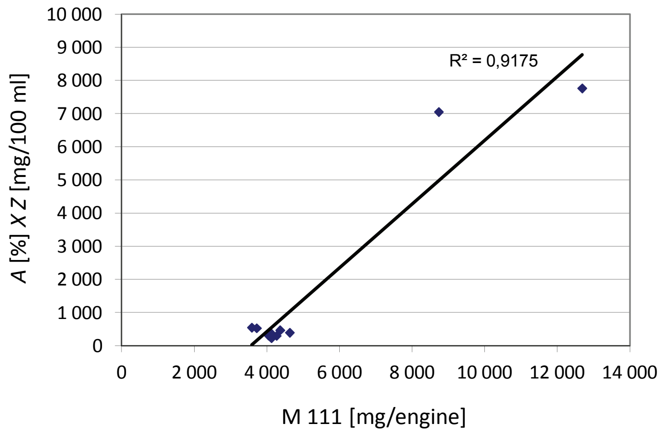


Fig. 4. Regression analysis ($A \cdot Z$) versus the M 111 engine test results (without sample No. 3)

## Correlations

Regression analysis of the relations M111($A$), M111($Z$) and M111($A \cdot Z$) has shown that for the obtained experimental data set, the linear correlations practically doesn't exist (Tables 1 and 2). It should be noted that the highest value of the determination coefficient was obtained for the relation M111($A \cdot Z$).

Considering the relation between the amount of CCDs obtained in the M 111 test and factors cited in the proposed equation (12).

It should be expected that $R^2$ coefficients for linear correlations will be lower for M111($A$) and M111($Z$) than for M111($A \cdot Z$). Actually such a result was obtained.

Besides the regression analysis results (given in Table 1) for the tested petrol the values of $b$ factor have been calculated taking the M 111 test result as equal to $m_{max}$. The calculation results are presented in Table 1. The obtained $b$ factor values differ significantly and are contained within the range [1.2 to 18.7].

Interpretation of the obtained results on the base of the proposed math model leads to the conclusion that factor $b$ has significant meaning to describe CCDs formation. At equilibrium it determines the ratio of the rate constant of CCDs formation on the engine chambers surface to the constant describing the deposits decomposition ability. So factor $b$

is specific for the given sample of petrol containing proper additives but the observed relatively wide range of $b$ values (see Table 1) suggests that the M 111 engine test result is far from the equivalence point with different extent. Alternatively the physical character of the formed deposits, because of the kind of detergent additive used and especially its interaction with the deposits may affect the test result. For example accidental mechanical losses may occur (deposits breaking) besides thermal decomposition processes of the non volatile substances gathered in the engine chambers. Also a phenomenon of deposits washing off the cylinder surface may take place during their contact with the engine oil.

The range of $b$ values suggests that the value is affected not only by the non-volatile components deposition and thermal degradation of the deposits, but also other phenomena which occur during fuel combustion in the engine.

## $A \cdot Z$ product

The analysis results show that it's much better to consider the relation between the M 111 engine test results and the product of $A$ and $Z$ than to the $A$ value alone. It can be observed in Table 1 for petrol No. 11 which has a very low factor $A$ and a big value of factor $Z$. For this petrol the mass of CCDs formed in the M 111 engine test was high. If only factor $A$ value was considered lower test results could be expected.

As mentioned above, the population of results used in the presented work was small because of the high costs of the M 111 engine test. It seems that the product of $A$ and $Z$ may be useful as a preliminary measure of petrol washing properties. The fact that elimination of one petrol from the tested population significantly enhanced the coefficient of determination $R^2$ (from 0.6 to 0.92) supports the thesis. Based on the presented results it can be accepted as a first approximation that for the petrol with $A \cdot Z > 1000$ the M 111 engine test will also show a significant amount of CCDs. The volume of petrol which was used in each of the performed engine test was known (380÷390 $dm^3$) and used to calculate the amount of substances from which the deposits were formed in the combustion chamber. These values are shown in Table 1. They are usually 2÷5 times higher than the deposits amounts determined in the M 111 engine test with the exception of petrol No. 4 and 5 for where these ratios were equal to 24 and 31.

The M 111 engine test results and their interpretation with the application of the proposed math model indicate that when the deposits are formed from the burnt and decomposed substances originating from unwashed gums the additional segregation processes (specific for the given petrol) occur before the basic deposits formation in the engine chambers takes place. Factor $b$ range confirms this thesis.

## Conclusions

Eleven samples of petrol with different chemical compositions were tested using the M 111 engine test and TGA according to BZ-154-01.

It was observed that correlation between the amounts of CCDs obtained from the M 111 engine test and UWG content in the gasoline does not exist. The same was found for M111($A$). Nevertheless it was found that the correlation between the M 111 test result and a value of the product of $A$ and $Z$ ($A \cdot Z$) exists.

Math model showing the relatively weak correlation of the amount of deposits determined in the M 111 engine test to the product of unwashed gums content ($Z$) and a coefficient of their decomposition ($A$) obtained by TGA has been proposed. The value of $b$ was taken as a proportionality constant which according to a physical interpretation is the limit of the ratio of a formation rate constant to a decomposition rate constant.

The weak correlation found for the whole population of the tested samples of petrol and its sharp change after exclusion of one of them indicates that either a random error occurred or that there were some other factors not considered in the model. Therefore systematic gathering of the data is necessary to enlarge the results population.

For preliminary assessment of the CCDs formation propensity it seems possible to use the abovementioned product ($A \cdot Z$). It can be expected that the petrol with $A \cdot Z > 1000$ will have a high tendency to form CCDs.

The results obtained at this stage indicate that the qualifying M 111 engine test can't be completely replaced by simple classical analyses like UWG determination and TGA of these gums. Nevertheless the premises exist that such methods can be used as screening tests and can be applied at the preliminary fuel testing stage enabling avoiding of the expensive M 111 engine test. Further investigations are necessary with more and more types of engine petrol. Especially any observed deviations from the proposed model should be analyzed for its proper modification.

Please cite as: Nafta-Gaz 2014, no. 3, pp. 176–184

### Acronyms

ACEA – European Automobile Manufactures Association
Alliance – Alliance of Automobile Manufactures
CCDs – Combustion Chamber Deposits
CEC – Coordinating European Council for the Development of Performance Tests for Transportation Fuels, Lubricants and Other Fluids
CO – Carbon Monoxide
DISI – Direct Injection Spark Ignition
EMA – Truck and Engine Manufactures Association
FLTM – Ford Laboratory Test Method
HC – Hydrocarbons
IVD – Intake Valve Deposits
JAMA – Japan Automobile Manufactures Association
$NO_x$ – Oxides of Nitrogen
ORI – Octane Requirement Increasing
PFI – Port Fuel Injection
TGA – Thermal Gravimetric Analysis
UWG – Unwashed Gums
WWFC – Worldwide Fuel Charter

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