# INFLUENCE OF RME CONTENTS IN DIESEL FUELS ON CETANE NUMBER DETERMINATION QUALITY

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***Abstract***

*Increasing RME contents in Diesel fuels has an adverse impact for engine combustion chamber deposits formation as well on fuel injection system components.*

*In the article discussed issues concerning with Cetane number determination of Diesel fuels about increased RME contents. Described troubles caused by difficulties in keeping stable engine running during making Cetane number determination by using of engine test bed. The influence of these issues for repeatability of obtained results has been also examined. Presented great own experience in the assessing the usefulness of engine test bed type Waukesha CFR for biofuels Cetane number determination. Comparison of repeatability obtained results Cetane numbers depending on the quantity of RME contained in Diesel fuel has been also performed.*

*View of CFR test bed for Cetane number determination according to ASTM D 613 and picture engine's combustion chamber for the determination of Waukesha CFR Cetane number and piston assembly, view of injector hole pintle nozzle coking field of CFR engine for Cetane number determination, carbon deposit on piston crown and piston skirt, comparison of spraying stream fuel distribution through injector of CFR Waukesha test engine after biofuels determinations with standard distribution according to ASTM D 613, results of CN are presented in the paper.*

***Keywords:*** *biofuels, RME, combustion chamber deposits, Cetane number*

## 1. Introduction

Since January 1st 2007 year Act of August 25th 2006 year, regarding liquid biocomponents and biofuels, is in force in Poland. The goal of Regulations of this Act is to implement provisions of European Parliament 2003/30/WE Directive of May 8th 2003 year regarding supporting the use in transport biofuels and other renewable fuels (U.E Official Gazette – Polish Special Edition, chapter 13, volume 31). Although the provisions of the Directive are not obligatory, they determine the pace of the increase of the share of energy from renewable sources, in fuels used in countries – members of European Union. Plans of this increase during consecutive years are included in The National Index Target – NIT (Polish; Narodowy Cel Wskaźnikowy – NCW), determining minimal share of biocomponents and other liquid fuels as well as renewable fuels in the total amount of liquid fuels and liquid biofuels consumed by transport means during calendar year, calculated on the base of calorific value. In the system of establishing index targets for consecutive years, continuous increase of their share is being assumed. According to NIT guidelines the share of biocomponents and other liquid fuels and renewable biofuels should reach the level of 10%. It is consistent with European Commission Communication „Europe Energy Policy”, marking out the achievement of this share of biocomponents in the market of fuels consumed by transport means of each of country member till 2020 year, as obligatory.

The possibility of execution the set target amounts in practice to the necessity of further verification of EN 590:2009 specification: Automotive fuels – Diesel – Requirements and methods of test, determining Diesel fuels quality through gradual increase of permitted amount of biocomponent (Fatty Acids Methyl Esters – FAME) in the fuel, and to the introduction on the market new type of fuels, as yet non used in Europe. Present EN 590:2009 Diesel oil B7 standard, sets FAME amount to non higher than 7,0% (*V/V*). This standard is should be considered as a temporary step which had to be made before the implementation of M/393 and M/394 mandates, ordering standardization of B10 Diesel oil containing up to 10% (*V/V*) FAMER and/or FAEE.

Raw materials for FAME manufacturing are vegetable oils, animal fats, as well as waste vegetable fats. Vegetable oils are a mixture of fatty acids glycerine esters in the form of multimolecular structures responsible, among other things, for severe deposits in engine combustion chambers and contained there elements of fuel injection system, as a result of thermal cracking of some fuel part. When a vegetable oil is subject of the transesterification process, by the action of ethanol or methanol one gets methyl of ethyl esters of vegetable oil fatty acids, having smaller molecules and lower viscosity. RME – Rapeseed Methyl Esters, are a mixture of higher fatty acids methyl esters and could be used either alone as a biodiesel, or added in different amounts to Diesel oil forming biofuels (Diesel oil with RME content above 7.0% (*V/V*). It should be underlined that the condition of keeping required quality, thus biofuels utilitarian and exploitation properties, is complete removal out of biofuel all contaminants formed during manufacturing process, and assuring maintenance of required biofuel quality during transport and distribution operations.

Already some years Oil and Gas Institute takes part in the national program of fuel quality monitoring. This monitoring covers, among other things, determination of Cetane number (CN). Increased content of biocomponents in fuels for Diesel engines and often also poor quality of such fuels caused many problems and inconveniences connected with keeping in required technical shape the test engine used to determine Cetane number. This problems together with difficulties resulting from different origin and biocomponents content in fuels make difficult obtaining results repeatability required by ASTM D613 standard. Now, it is to remind that the biofuels Cetane number is greatly influenced by their chemical properties, and especially by fatty acids distribution in initial vegetable oil or fat used to produce biocomponent [1]. In general, the longer fatty acids carbon chains and more unsaturated molecules, the higher Cetane number (Geller and Goodrum, 2004). The number of FAME double bonds indicates their unsaturation grade. With decrease of unsaturation grade (decrease of double bonds number), increases CN. CN changes also with the type and origin of raw material used to produce biocomponent, thus with fuel chemical composition and could influence engine starting abilities, its noise and level of harmful components emission [1, 2]. Moreover, unstable FAME easily oxidize, what within time leads to the formation of different oxidation products and could contribute to the CN increase [3]. It should be kept in mind that CN is a dimensionless, nonlinear measure of fuel capability to the self-ignition but only for fuels characterized by the same dependence of ignition delay period on the combustion chamber temperature, as used in tests on Waukesha CFR engine reference fuels. Taking into consideration that vegetable oils do not meet this condition, it is not possible to foretell exactly their capability to self-ignition [5]. Of course, difficulties with precise determination of biofuels self-ignition capability increase with increasing of biocomponent content in the fuel.

In Oil and Gas Institute for the determination of Cetane number the standard CFR test engine, manufactured by Dresser Waukesha Company (USA), equipped with single-assembly fuel injection pump (Fig. 2), simple – cylindrical combustion chamber and injector with a pintle nozzle (Fig. 3) is utilized.

Those structural solutions have not been changed till today, and CFR Waukesha USA engines are, at present time the only test engines accepted and approved by fuels manufacturers for the determination of octane and Cetane numbers of internal combustion piston engines.

In 1997 year Institute of Petroleum Processing (now part of Oil and Gas Institute) was admitted to the CEC PF-022 Task Force (Cetane Quality), having as a target modification of the hardware of ASTM D 613 standard, in order to improve repeatability and reproducibility of determination results, carried out in accordance with this standard. This CEC Task Force cooperated closely with

Waukesha company, with regard to proposed changes of the test stand for the determination of the

*Fig. 1. View of CFR Waukesha engine test bed for Cetane number determination according to ASTM D 613 (O&GI Cracow)*

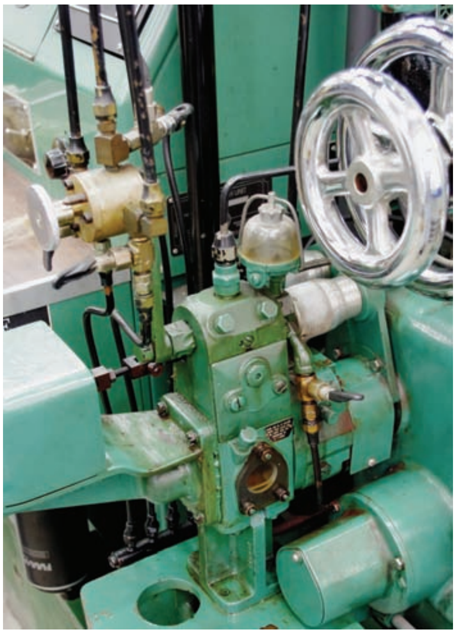

*Fig. 2. Single-assembly fuel injection pump of CFR Waukesha engine for Cetane number determination according to ASTM D 613 (O&GI Cracow)*

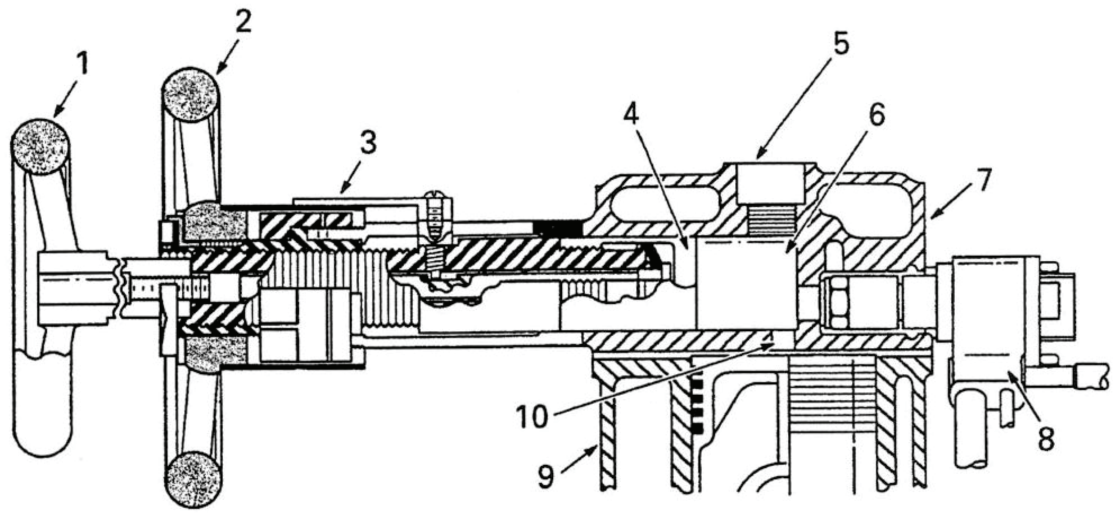


*Fig. 3. Review picture engine's combustion chamber for the determination of Waukesha CFR Cetane number and piston assembly of the handwheel is used to change the volume of the combustion chamber:1- variable compression plug –locking wheel; 2- variable compression plug –handwheel; 3- variable compression plug – micrometer; 4-variable compression plug, 5-combustion pickup hole; 6-precombustion chamber, 7-cylinder head; 8-injector nozzle assembly; 9-cylinder; 10-turbulence passage (ASTM D 613)*

Cetane number, taking into consideration present tendencies in the structure of self-ignited engines, strategy of combustion processes course and fuel manufacturing methods. Unfortunately, described above ambitious intentions of this Task Force were subject to the marked slow-down when English company LUCAS (carrying out for the CEC PF-022 Task Force many prototype elements of injection systems, at its own expense) after joining the international concern DELPHI. One of the after-effects of this fusion was significant limitation of LUCAS company commitment into current works of the Task Force, which in turn were brought to a stop by the lack of sufficient financial means from other companies participating in these works, what in 2003 year caused giving up modification of the test engine stand, and then closing the CEC PF-022 Task Force [6]. As a consequence, widely accepted engine method of CN determination, described in ASTM D 613 standard and based on it EN ISO 5165 and PN-EN ISO 5165 standards, shows many „congenital" defects; large quantity of fuel needed to carry out the determination, long determination time, relatively high cost and poor results repeatability as well reproducibility.

## 2. Research part

Growing trends towards the diversification of manufactured fuels and lowering the emission level of harmful components in Diesel engines exhaust gases and also the necessity to fulfil goals of the National Index Target (NIT), caused appearing on the Polish market different components of vegetable origin mixed with hydrocarbon fuels – biofuels.

As a consequence there was a marked rise of biofuel samples passed to evaluate octane number (ON) and Cetane number (CN), both by external customers and within the confines of the national fuels monitoring, including biodiesel B100.

During the determination of Cetane number of biodiesel blends and biocomponents alone (biodiesel B100) there was stated the necessity of changing certain settings of injection system of test engine for the determination of Cetane number, in comparison with settings used in CN determination of Diesel oil without biocomponents. Discrepancies of those settings grow with the growing share of biocomponent in biofuel.

Specifically, in the above cases it was necessary to increase the amount of delivered fuel dose (Table 1), angle of injection advance, and also to change settings of the handwheel, necessary to reach the self-ignition delay angle recommended by ASTM D 613 standard [7].

*Tab. 1. Fuel charge difference of fuel injection pump of test engine for Cetane number determination in case of biofuels determination versus diesel fuel (without biocomponents)*

| Fuel used | Difference in the amount of injection pump fuel dose in the case CN determination of different biofuels, relative to the dose of Diesel oil without biocomponents (B0) |
|---|---|
| Diesel oil B7 | increase of 0.04 [ml/min] |
| Diesel oil B30 | increase of 0.2 [ml/min] |
| Diesel oil B100 | increase of 0.4 [ml/min] |

As the time of carrying out Cetane number determinations of biodiesel blends went by, gradual deterioration of possibilities to reach standardized self-ignition delay of the fuel injected to the test engine combustion chamber was stated. Also characteristic sound signals of nozzle operation with cold engine (during start-up) appeared. Check-up investigation using reference fuel carried out according to ASTM D 613, revealed deviations of determined values, exceeding permissible value given in the standard, and at the same time deterioration of the angles of injection advance and fuel self-ignition delay. There were also difficulties with changing of test engine combustion chamber volume, caused by growing resistance of rotating the setting handwheel.

Engine and accessories servicing operations carried out (especially fuel injection system) revealed heavy coke formation, both on pintle tip and on the area close to the opening of the fuel nozzle (Fig. 4), and carbon deposit on piston head and crown, and on the piston of handweel (Fig. 5).

*Fig. 4. View of injector hole pintle nozzle coking field of CFR engine for Cetane number determination (O&GI Cracow)*

*Fig. 5. Carbon deposit on piston crown and piston skirt of manual setting wheel for change of test engine combustion chamber volume (O&GI Cracow)*

Moreover, examination of the fuel system revealed small deposits in the injection pump feeding tank, dissolved protective varnish of metal fuel lines (Fig. 6), and dripping (unsealing) of fuel valve.

*Fig. 6. Biofuels influence on fuel pipes protective coating of CFR Waukesha test engine for Cetane number determination (O&GI Cracow)*

Inspection of the test engine fuel injector operation (spraying), revealed serious deviations from the model distribution spraying stream required by ASTM D 613 standard and engine manufacturer. Lack of the central part of stream was found, and irregular peripheral fuel spraying (Fig. 7). The deterioration of fuel spraying quality could influence both difficulties in stabilizing engine operation and also incomplete course of combustion process, what influenced Cetane number determinations – value as well as repeatability.

a) b)

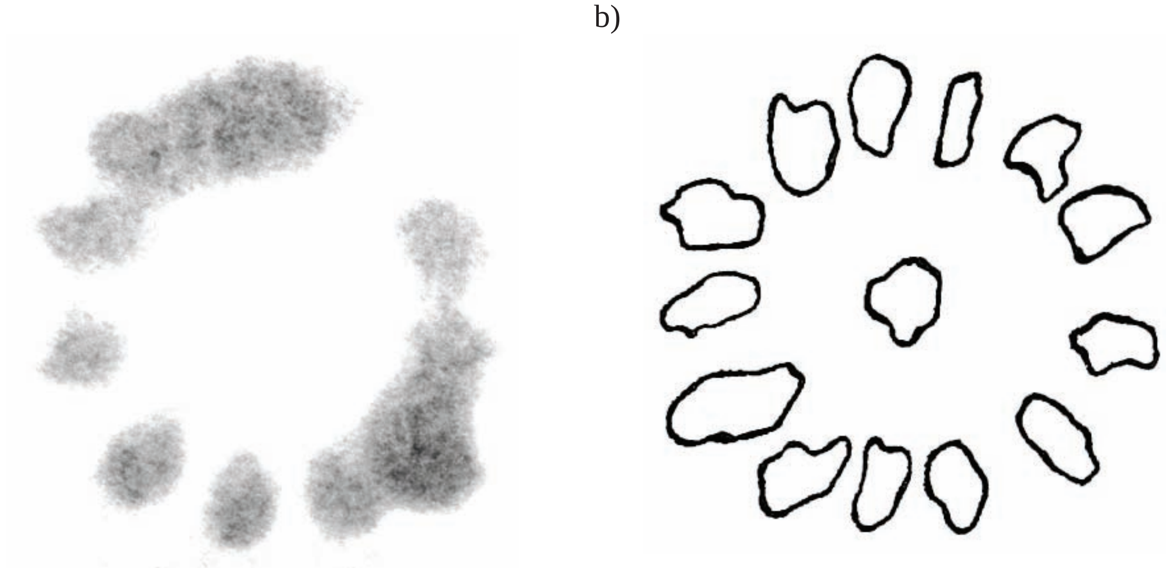

*Fig. 7. Comparison of spraying stream fuel distribution through injector of CFR Waukesha test engine after biofuels determinations (a) with standard distribution according to ASTM D 613 (b) – (O&GI Cracow)*

Practical observations described above, based on the very large number carried out determination indicate high probability of greater contamination of test engine fuel system and its combustion chamber by carbon deposits, lacks and large coke deposits in the case of determining CN of Diesel oils containing higher amount of biocomponents or only biodiesel, in comparison with typical Diesel oils. To establish influence of those negative phenomena on the determinations carried out it was decided to define the time range (measured by the number of determinations carried out) of test engine stable operation, when determining CN of fuels with growing share of biocomponents, together with pure biodiesel (B 100), and of Diesel oil without biocomponents. Chosen results of CN determination of these fuels are given in Tab. 2 and presented on Fig. 8-11.

*Tab. 2. Determination stability of CN carried out on Waukesha CFR test engine according to ASTM D 613 depending on biocomponents content in biofuel*

| Cetane numbers determinations | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Diesel oil | CN 1 | CN 2 | CN 3 | CN 4 | CN 5 | CN 6 | CN 7 | CN 8 | CN 9 | CN 10 |
| B0 | CN = 51.2 | CN = 51.3 | CN = 51.1 | CN = 51.1 | CN = 51.3 | CN = 51.0 | CN = 51.1 | CN = 51.2 | CN = 51.2 | CN = 51.3 |
| B7 | CN = 51.8 | CN = 51.8 | CN = 51.7 | CN = 51.9 | CN = 52.0 | CN = 52.7 | CN = 52.2 | CN = 52.9 | CN = 52.8 | CN = 52.9 |
| B30 | CN = 52.1 | CN = 52.0 | CN = 52.2 | CN = 51.8 | CN =52.4 | CN = 53.1 | CN = 52.0 | CN = 54.1 | CN = 51.4 | CN = 52.5 |
| B100 | CN = 54.1 | CN = 54.5 | CN = 54.2 | CN = 54.6 | CN = 53.4 | CN = 55.2 | CN = 55.7 | CN = 53.0 | CN = 55.0 | CN = 52.3 |

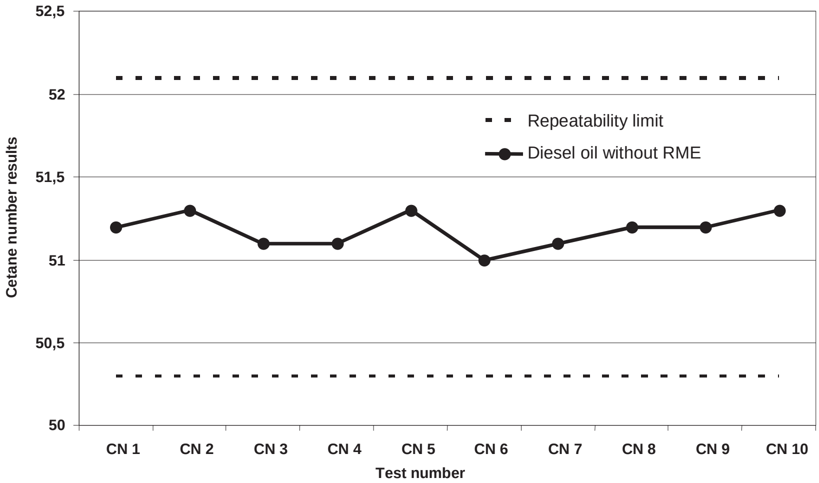


*Fig. 8. Results of CN determination for B0*

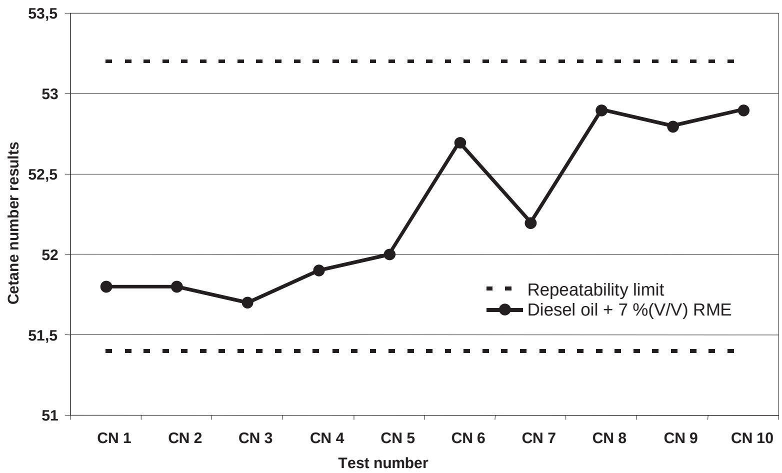


*Fig. 9. Results of CN determination for B7*

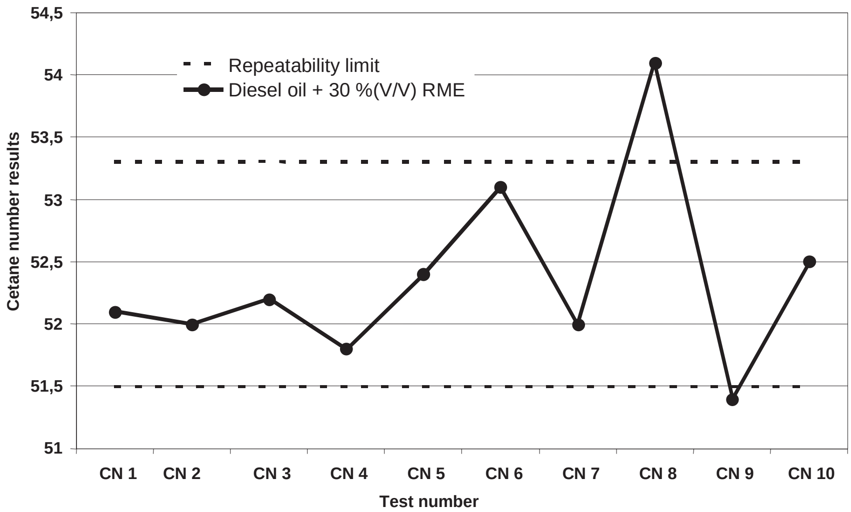


*Fig. 10. Results of CN determination for B30*

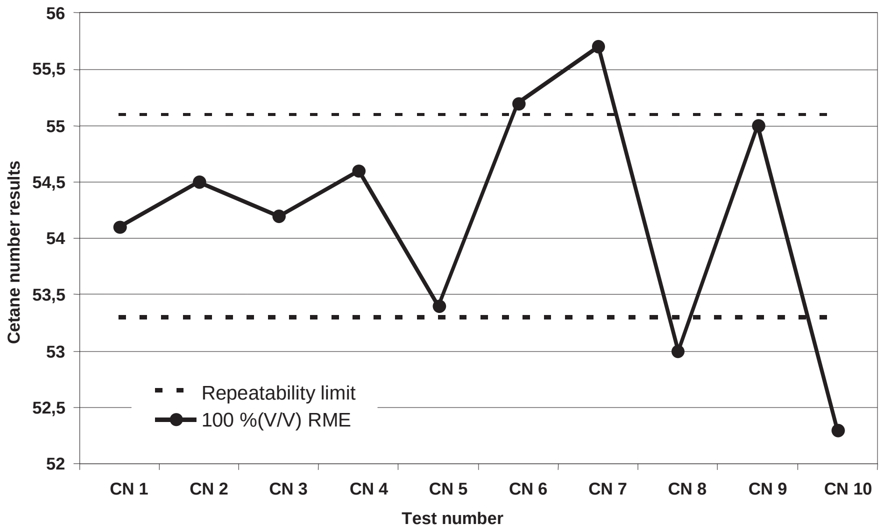


*Fig. 11. Results of CN determination for B100*

## 3. Research results

When evaluating results of comparative Cetane number determinations carried out (Tab. 2) it should be stated that in the case of biofuel B30 repeatedly determined Cetane number twice exceeded permissible limits of results repeatability (ASTM D 613; Fig. 10), and in the case of biodiesel B100 such a situation took place four times (Fig. 11).

On the base of Cetane number determinations carrier out for fuels with different amount of RME (Tab. 2), limiting determinations number was evaluated; after exceeding this number the deterioration of angles of injection advance readings and fuel self-ignition delay takes place, what seriously impedes unambiguous and reliable CN determination.

In the case of Cetane number determinations of B0 and B7 fuels the limiting determinations number was not evaluated because permissible limits of CN determination results repeatability according to ASTM D 16, within the range of repetitions carried out were not exceeded (Fig. 8-9). In the case biofuel B39 Cetane number determination the situation was different, and limiting determinations number was fixed as 7 (Fig. 10), and for biodiesel B100 as 5 (Fig. 11). In practice it means the necessity of carrying out engine technical service after performing mentioned above number of determinations, especially cleaning nozzle tip, and if required, removing deposits out of the engine combustion chamber. On Fig. 12 a and 12 b are showed nozzles of CFR Waukesha test engine, after determination CN of oils containing 30% and 100% RME (V/V).

When performing evaluation of CN of fuels with different biocomponent amounts and in accidental order (without repetition possibility), the evaluation of determinations limiting number – when exceeded we observe deterioration of engine operation stability, what can influence the quality of determinations carried out, is much more difficult and requires skilled operator.

To guard against such a situation, the time range of performing engine servicing operations given by ASTM D 613 standard was shortened and in order to keep current quality control of determinations carried out, it was decided to take part in the international research program, enabling systematic monitoring of determinations correctness, run by the Energy Institute UK.

Energy Institute (EI) constitutes British research centre formed as a result of fusion of two scientific institutes, i.e. Institute of Petroleum and Institute of Energy, with separation from this new structure – Energy Institute Laboratory Correlation Scheme (EILCS).

For about 20 years EILCS organizes international round robin tests of motor fuels for the determination of octane and Cetane numbers, sending appropriate samples in a monthly cycle, to the laboratories participating in tests. After collecting results EILCS analyzes them and prepare, in a tabular form monthly report, sent to participating in tests. These investigations, due to the large number of participants and high frequency of determinations, enable constant and reliable evaluation of the quality of determinations carried out, and at the same time confirmation of mastering research technique. Partial reports sent by EILCS enable conducting up to date monitoring correctness of determinations carried out and form valuable documentation of laboratory competence, especially for centres having accreditation.

a) b)

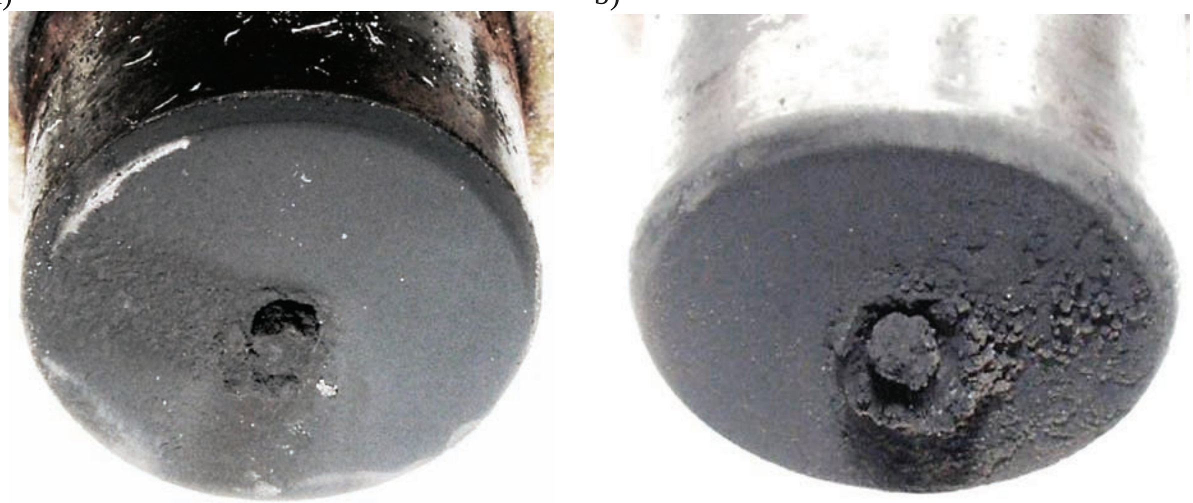

*Fig. 12. The injectors of CFR Waukesha test engine after determinations CN for biofuel B30 (a) and biodiesel B100 (b) – (O&GI Cracow)*

## 4. Summary

Greater and greater biocomponents share in fuels, spreading of biofuels and also diverse quality of biocomponents used creates problems, among others in the field of Cetane number determination for Diesel engines fuels. As a consequence there is a necessity to verify range and frequency of Waukesha CFR test engine technical servicing, in relation to ASTM D 613 standard recommendations. These actions are absolutely necessary taking into consideration the necessity to preserve the required quality of performed CN determination. Moreover, there is also advisable additional monitoring of performed determinations, e.g. by participation in EILCS inter-laboratory round robin tests, forming authoritative confirmation of obtained results reliability.

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