# COMPARISON OF UNBURNT HYDROCARBON EMISSIONS FOR DIESEL ENGINES FUELED BY DIESEL OIL AND RAPESEED FUEL

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### Abstract

*The article presents the results of the of the HC emissions composition for the compression ignition - diesel engine fuelled with rapeseed fuel (a mixture of methyl esters of fatty acids - RSME). The investigations were conducted on a turbocharged, four-cylinder compression-ignition engine type T370 (of 80 kW power at 2400 rpm engine speed and maximum torque of 400 Nm at 1440 rpm engine speed, with bore / stroke 110 mm /120 mm, displacement volume 4560 cm$^3$, compression ratio 17). For the exhaust toxicity investigations the equipment of Signal and AVL companies was used, and for composition of nonregulated hydrocarbons emissions investigations the Hewlett Packard Company chromatograph type HP-5890II was used. The investigations were conducted under engine full load at maximum torque speed and for engine rotational speed of the rated power. Chromatographic test for emissions were collected using special equipment and special procedures. The article presents the results of chromatographic investigations focused on: benzene, toluene and acetaldehyde. It was found that the percentage of emission of individual components in the total emissions of HC was independent of the fuel used. However, due to the fact that in the case of rape fuel, emission of unburned HC was smaller and smaller were the absolute amounts of emissions components. Thus, emissions from combustion of rape fuel are less harmful than emissions from the engine fuelled with diesel oil.*

*Keywords: transport, CI internal combustion engines, motor fuels, alternative fuels, toxic exhaust emissions*

## 1. Introduction

Unburned hydrocarbons (HC) are officially limited exhaust components, whose content is determined in almost all motor tests and during testing of automotive vehicles. In these studies, however, the total quantity of hydrocarbons is determined, properly organic components of exhaust, without specifying the individual components, which are several hundred in the HC emissions range, and the harm of which for the environment and humans is very different. Some of these compounds, such as paraffin compounds are physiologically inert, while others, such as polycyclic aromatic hydrocarbons are carcinogenic.

One of the hydrocarbons whose carcinogenic effects are well documented is the benzopirene. In relation to other are serious suspicions, but the evidence of their harmful effects requires extensive research. The most harmful components of HC emissions are considered now: benzene, toluene, isobutene, 1,3 butadiene, and aldehydes, but this follows from the fact that they are present in the exhaust gas in significant quantities.

In recent years, one sees a growing interest in using biofuels to power internal combustion engines [10]. This interest is due to possible restriction of the greenhouse effect in this way, because $CO_2$ emissions during engine work would be reduced per annum to nearly zero, because of its absorption in the vegetation of plants, from which fuel would be produced [6].

The Aviation Institute in Warsaw, conducted several studies on the use of rapeseed fuel (rapeseed oil methyl ester - RSME) [5, 8-10] including both the dynamometer test, as well as the controlled exploitation. In addition, the investment actions were taken in Poland, by running experimental production plants, producing rape fuel on the small-scale, according to developed industry standards. Therefore, it seemed advisable to determine the composition of unburned

hydrocarbons, in order to assess whether the use of rape fuel, despite the lower CO and HC emissions, poses no greater threat to health and the environment, to further emphasize the advisability of investing in this area.

The mechanism of hydrocarbons formation is fairly well understood, in terms of the impact of various factors on the formation of unburned HC, but the problem is more complicated in terms of chemical kinetics. For example, Heywood [4] examines in some detail the impact of some 50 factors on the emissions of unburned hydrocarbons, taking into account: the design of engines and components, working conditions, flows, the impact of lubricant oil and fuel. In turn, Lefebvre [7] by analyzing the formation mechanism of the officially regulated toxic components of exhaust emissions (CO, HC, NOx) gives even a semi-empirical model which allows to calculate the emissions of CO and NOx in the exhaust gas, while for HC emissions performs only phenomenological analysis.

This is due to a very complex chemical kinetics of the hydrocarbons oxidation, including in relation to each of the hydrocarbons the hundreds and thousands of transition reactions [3, 12]. At the same time, in the fuel composed of many hydrocarbons the reactions are running simultaneously, influencing one another.

For example, one can specify that during burning of the simplest hydrocarbon which methane is, occurs almost two thousand transition reactions, which has been disclosed so far.

Even so, at current capabilities of computer technology the inclusion of such number of reactions becomes difficult, which makes that models are limited to several tenths and maximum of several hundred reactions, which, although leads to large discrepancies in determining even the aggregate HC emissions, not to mention the breakdown for individual components.

Therefore, it seems that the motor tests are in fact more effective method of determining the composition of unburned HC.


## 2. Object and research methodology

The object of the study was turbocharged, four-cylinder compression ignition automotive engine, type T370, with the following parameters:
- ore/stroke [mm]                   110/120
- Displacement volume [cm3]         4560
- Compression ratio                 17
- Nominal power [kW]                 80
- Rated power speed [rpm]            2400
- Maximum torque [Nm]                400
- Maximum torque speed [rpm]         1440
- Fuel pump                         PEW4-07, inline
- Injectors                         Nk-3140
- Turbocharger                      B65/5.65

T370 engine was mounted on the test stand at the Institute of Aviation and coupled with the Schenck eddy-current brake type W450 and all the necessary systems were connected for testing.

This was followed by preliminary investigations using the factory regulations, during which the characteristics of the engine power output with diesel fuel and rapeseed fuel were set out.

The contents of the main components of these fuels are presented in Tab. 1 and 2

Therefore, the characteristics of an engine supplied with fuel other than fuel specified in the engine instruction manual may be more favourable with other regulations than the factory regulation, the optimization investigations were performed, which resulted in the ignition timing best chosen from the perspective of engine output power.

The study was conducted in conditions of maximum engine torque speed (full engine load, speed 1440 rpm) and rated power engine speed (full load, speed 2400 rpm).

*Tab. 1. Summary of the main components (n-alkanes) of diesel fuel*

| Item | Name of substance | Designation (number of carbon atoms) | CAS | Part [%] |
|---|---|---|---|---|
| 1 | n-octane | C8 | 111-65-9 | 0.21 |
| 2 | n-nonane | C9 | 111-84--2 | 0.66 |
| 3 | n-decane | C10 | 124-18-5 | 1.98 |
| 4 | n-undecane | C11 | 1120-21-4 | 5.02 |
| 5 | n-dodecane | C12 | 112-40-3 | 5.08 |
| 6 | n-tridecane | C13 | 629-50-5 | 6.82 |
| 7 | n-tetradecane | C14 | 629-59-4 | 5.20 |
| 8 | n-pentadecane | C15 | 629-62-9 | 4.85 |
| 9 | n-hexadecane | C16 | 544-76-3 | 4.10 |
| 10 | n-heptadecane | C17 | 629-78-7 | 3.63 |
| 11 | n-oxadecane | C18 | 593-45-3 | 3.06 |
| 12 | n-nonadecane | C19 | 629-92-5 | 2.74 |
| 13 | n-eicosene | C20 | 112-95-8 | 2.32 |
| 14 | n-heneicosene | C21 | 629-94-7 | 1.35 |

*Tab. 2. Composition of rapeseed fuel*

| Item | Name of substance | Acid designation | CAS | Part [%] |
|---|---|---|---|---|
| 1 | Palmitic acid methyl ester | C16:0 | 112-39-0 | 4.78 |
| 2 | Linoleic acid methyl ester | C18:2, cis 9,12 | 112-63-0 | 16.56 |
| 3 | Linolenic acid methyl ester | C18:3, cis 9,12,15 | 301-00-8 | 7.78 |
| 4 | Oleic acid methyl ester | C18:1, cis 9 | 112-62-9 | 60.37 |
| 5 | Elaidic acid methyl ester | C18:1, trans 9 | 1937-62-8 | 4.04 |
| 6 | Stearic acid methyl ester | C18:0 | 112-61-8 | 2.16 |
| 7 | Gondoic acid methyl ester | C20:1, cis 11 | 3946-08-5 | 1.78 |
| 8 | Arachidonic acid methyl ester | C20:0 | 1120-28-1 | 0.65 |
| 9 | Erucic acid methyl ester | C22:1, cis 13 | 1120-34-9 | 1.59 |
| 10 | Behenic acid methyl ester | C22:0 | 929-77-1 | 0.30 |

## 3. Investigations of hydrocarbon emissions composition

The hydrocarbon investigations were carried out using a Hewlett-Packard gas chromatograph type HP-5890II equipped with mass detector type HP-MSD-5972, the chamber injector (Split/splitless type) and a capillary column HP-PONA with a length of 50 m, diameter 0.2 mm with stationary phase filter with thickness 0.5 μm.

Samples for analysis of hydrocarbons were collected during the engine performance (under the conditions stated in the previous chapter), on Institute of Aviation engine test bed stand, using the suction pump type 224-PCEX4 U.S. manufactured by SKC LTD.

Exhaust gas to identify the hydrocarbons was collected by a calibrated divider in the amount of 5 dm3 directed to tubes filled with activated carbon manufactured by SKC LTD U.S. Cat. No. 226-01, and for the identification of aldehydes, the amount of 0.5 $dm^3$ of the exhaust gases was collected in tubes filled with 2-hydroksymetylopiperidine, manufactured by SKC LTD U.S. Cat. No. 226-117.

Then the samples were subjected to chromatographic analysis to identify the individual components of an emission.

In the first place gas chromatograph was subjected to calibration by injecting a standard mixture to chromatography column (pure sorbent tube without exhaust gas) and then taken for analysis exhaust gas sample was injected.
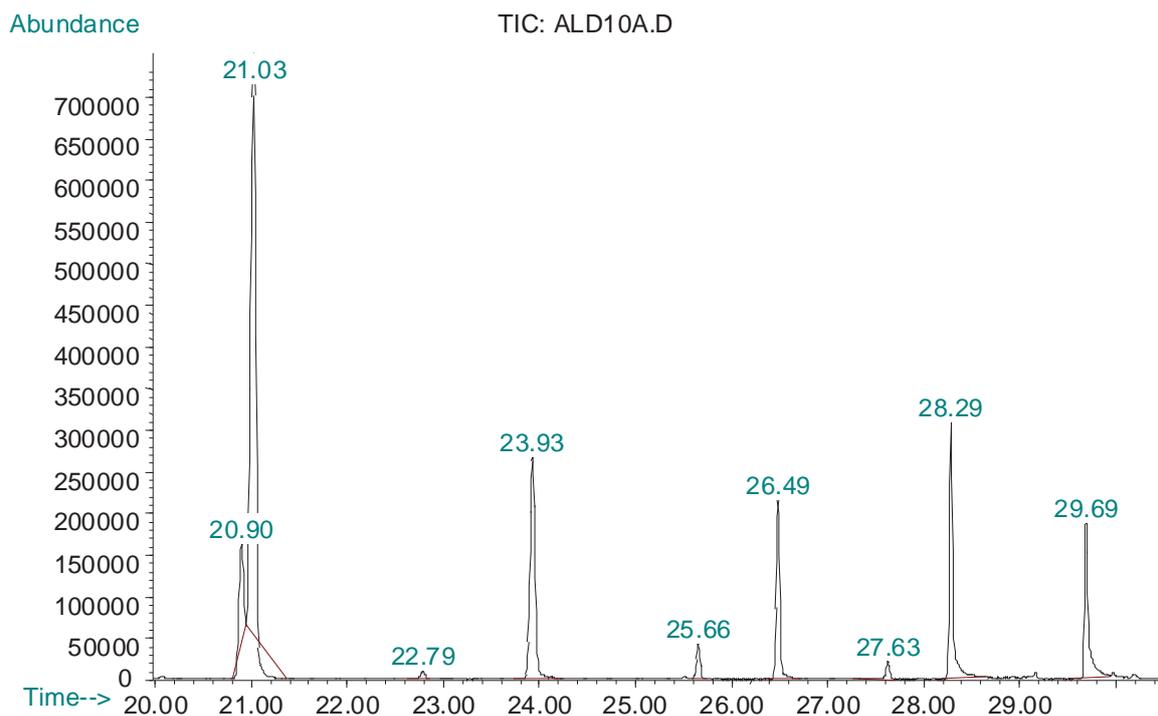
*Fig. 1.  Chromatogram of standard mixture of derivatives of aldehydes: Retention times: 20.90 min - acetaldehyde HMP; 21.03 minutes - formaldehyde HMP; 23.93 minutes - propionic aldehyde acrolein and HMP; 26.49 min - n-butyric aldehyde HMP; 28.29 min - n-valeric aldehyde HMP; 29.69 min - aldehyde Hexanoic HMP*

Figure 1 shows an sample standard chromatogram for mixture of aldehydes derivatives, and Fig. 2 shows chromatograms of four exhaust samples taken on the engine test stand from engine supplied with diesel fuel (sample no. IL991A and IL992A) and rapeseed fuel (sample no. IL993A and IL994A) and blank sample in order to compare the contents of acetaldehyde and formaldehyde in the engine exhaust.
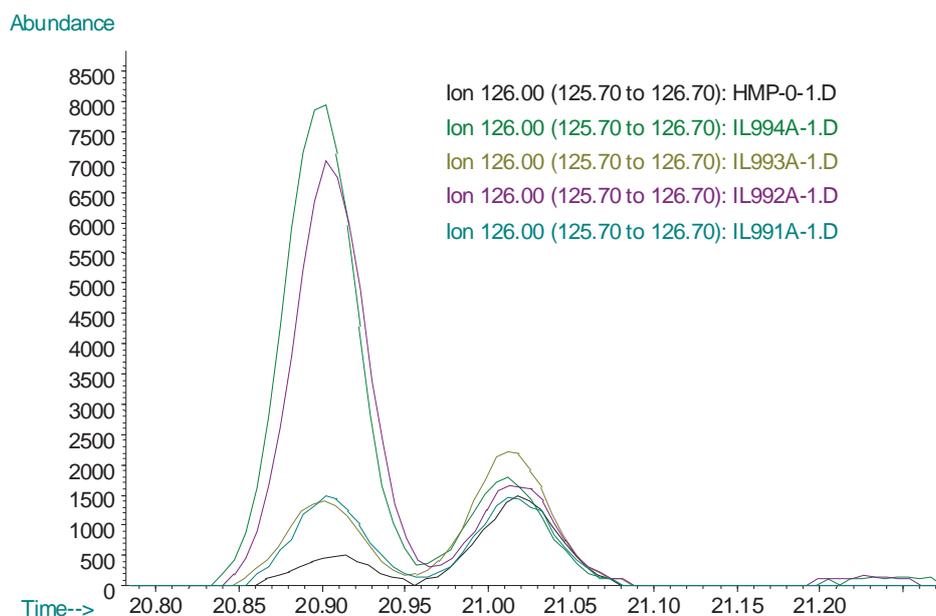


*Fig. 2.  Gas chromatograms of four samples taken at test stand and the blank (zero) sample, the retention time of 20.78 minutes to 21.5 minutes (acetaldehyde - retention time 20.90 min, and formaldehyde - retention time 21.03 min)*

For example, on Fig. 3-5 are shown the gas chromatograms of samples taken at the same test parameters when the engine speed was at 2400 rpm and engine was supplied with diesel and rapeseed fuel, in order to detect polycyclic hydrocarbons and compare their contents, depending on type of fuel supplied to the engine.

A comparison shows that the identified hydrocarbon content is similar, in terms of benzene (retention time 8.71 min, Fig. 4) and toluene shows a clear difference in favour of the rapeseed fuel in toluene content (Fig. 5 - retention time 11.54 minutes ).
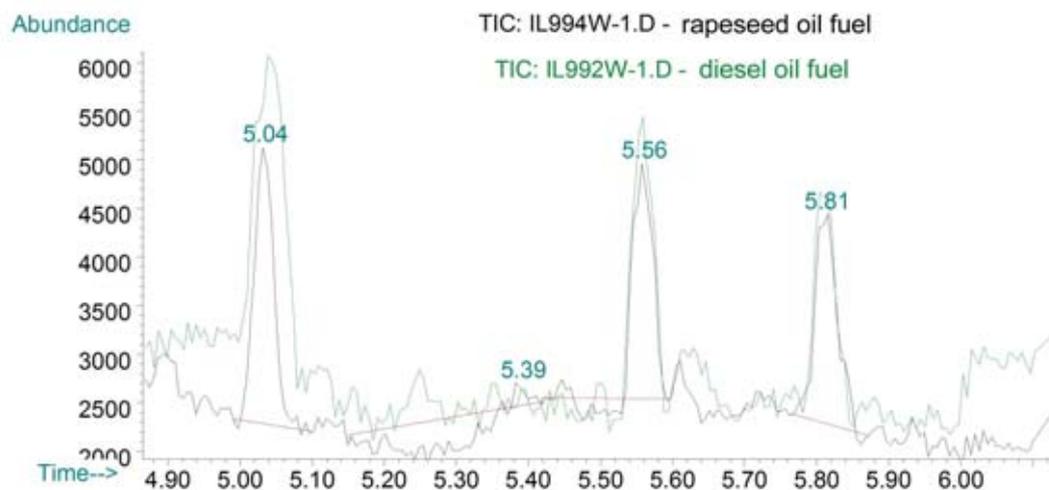


*Fig. 3. Comparison of gas chromatograms of exhaust samples taken during the engine performance at 2400 rpm speed, supplied with rapeseed and diesel oil fuel (retention time of 4.90 min to 6.00 min: 5.04 min – 2-methylpropene-1, 5.56 min - acrolein or pentene-2, 5.81 min - penten-1)*
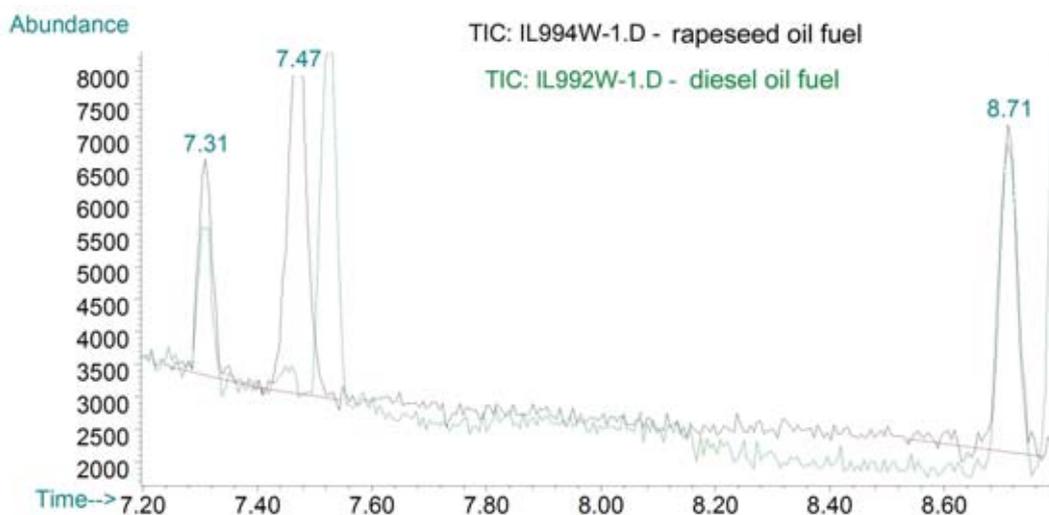


*Fig. 4. Comparison of gas chromatograms of exhaust samples taken during the engine performance at 2400 rpm speed supplied with rapeseed and diesel oil fuel (retention time from 7.2 min to 8.8 min - 7.31 min - hexene-1, 7.47 min - methyl acrylate, 8.71 min - benzene).*

Table 3 summarizes the results of the computation for components of HC emissions for diesel oil fuel and Tab. 4 for the rapeseed fuel.

Due to the fact that there are many components of HC exhaust emissions, but they are present in a small amounts, in the tables are published only their total content in exhaust gas samples, although it is possible to identify each component in relation to: benzene, toluene, acrolein, methyl acrylate, acetaldehyde, formaldehyde, propionic aldehyde, N-butyric aldehyde, N-valeric aldehyde, Hexanoic aldehyde and many other hydrocarbons identified in the chromatographic tests.
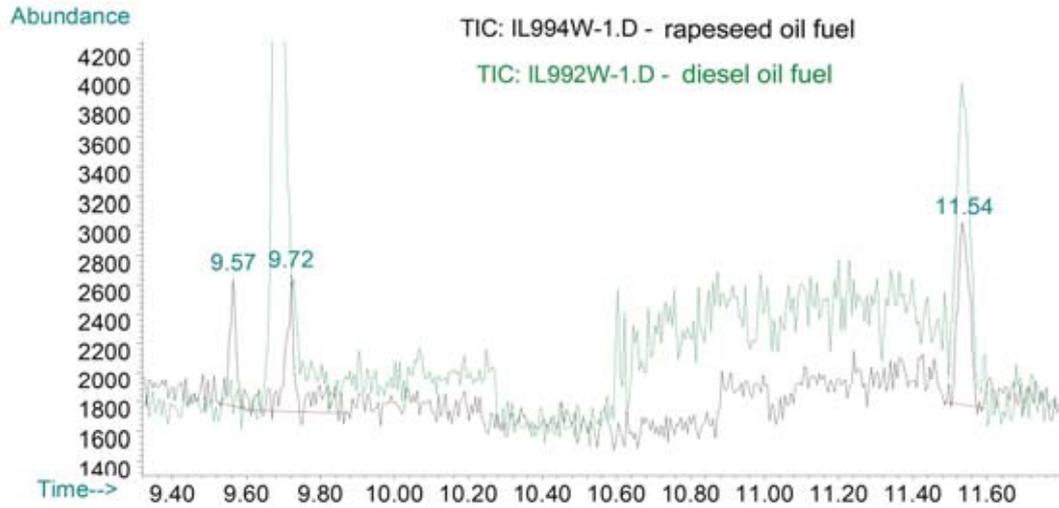
*Fig. 5. Comparison of gas chromatograms of exhaust samples taken during the engine performance at 2400 rpm speed supplied with rapeseed and diesel oil fuel (retention time from 9.3 minutes to 11.8 minutes - 11.54 minutes - toluene)*

*Tab. 3. Results of calculations of the relative emissions of some toxic components of compression ignition test engine exhaust supplied with diesel oil fuel*

| Rotational Speed | Investigated toxic component of the exhaust | Relative Emissions $\left[\dfrac{g_t}{kWh}\right]$ | Ratio $\dfrac{e_t}{e_{HC}}[\%]$ |
|---|---|---|---|
| n = 1440 rpm | benzene | 0.002 | 0.22 |
| | toluene | 0.030 | 3.90 |
| | total HC | 0.763 | 100 |
| | acetaldehyde | 0.027 | 3.60 |
| n = 2400 rpm | benzene | 0.010 | 0.87 |
| | toluene | 0.050 | 4.60 |
| | total HC | 1.097 | 100 |
| | acetaldehyde | 0.153 | 13.98 |

*Tab. 4. Results of calculations of the relative emissions of some toxic components of compression ignition test engine exhaust supplied with rapeseed fuel*

| Rotational Speed | Investigated toxic component of the exhaust | Relative Emissions $\left[\dfrac{g_t}{kWh}\right]$ | Ratio $\dfrac{e_t}{e_{HC}}[\%]$ |
|---|---|---|---|
| n = 1440 rpm | benzene | 0.001 | 0.19 |
| | toluene | 0.015 | 3.02 |
| | Total HC | 0.509 | 100 |
| | acetaldehyde | 0.032 | 6.31 |
| n = 2400 rpm | benzene | 0.004 | 0.35 |
| | toluene | 0.039 | 3.51 |
| | Total HC | 1.109 | 100 |
| | acetaldehyde | 0.105 | 9.44 |

## 6. Conclusion

1.  The task of this publication is not to present the content of all, identified in the investigations, substances included in the HC emission, since it would exceed the volume of this article, but rather to show the way for the designation of HC emissions components that was applied to the

engine investigations, in case when diesel oil and rapeseed fuel is used to supply engines and publication of basic research results.

2. The most important components of HC emissions was benzene, toluene and acetaldehyde, which stems both from its harmfulness to the environment, as well as their relatively high content in the engine exhaust gases and the researchers main attention was focused on them.

3. It was found that the content of cyclic aromatic hydrocarbons of benzene and toluene in the exhaust was similar for both diesel oil fuel and rapeseed fuel.

4. The share of emissions of acetaldehyde in HC emissions is considerable and ranges from a few to several percent depending on engine operating parameters.

5. With an increase in engine speed followed a significant increase in emissions of acetaldehyde, both in relation to engine supplied with diesel oil fuel, and engine supplied with rapeseed fuel.

6. Emissions of benzene and toluene, when it comes to their content in HC emissions changed little with changes in engine speed.

7. Contribution of individual components in the emission of HC was slightly dependent on the fuel type used, what is important, because the absolute emission of HC in the case of rapeseed fuel usage is much smaller than emission from the usage of diesel oil fuel. So this means that the absolute amount of the most dangerous components of HC emissions with engine supplied with rapeseed fuel is less than the amount from engine supplied with diesel oil fuel.

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