# THE EFFECTS OF CETANE NUMBER AND FUEL SULPHUR CONTENT ON EXHAUST EMISSIONS FROM THE EURO III DIESEL VEHICLE

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## INTRODUCTION

Internal combustion engines, operating primarily on petroleum-based fuels, dominate land transportation propulsion. They also play a major role in marine and light aircraft propulsion. Due to the lower fuel costs associated with diesel engines, these engines are used extensively in transportation systems. It is well known that the direct-injection (DI) diesel engine is the most effective among internal combustion engines because of its excellent thermal efficiency and durability. Direct injection diesel engines minimise the green house effect because its low fuel consumption leads to low  $CO_2$  emission. The use of diesel engines is continually increasing even in high speed passenger cars (Fig. 1). On the other hand, a further significant reduction of particulate matter (PM) and nitrogen oxides (NO<sub>x</sub>) to meet stringent environment regulations remains to be addressed.



To meet new, unusually severe norms of emissions (for instance: Euro III, IV and V, Tier 2, ULEV, LEV II) a single solution will no longer be sufficient. Complex activities including: optimisation of the process of fuel combustion in the engine by an improvement of its construction, introducing systems (e.g. EGR) restraining the formation of pollutants, use of effective catalytic systems for emission control and finally appropriate blending of fuels are necessary [13].

Fuel composition as well as physical and chemical parameters have, apart from the type of engine and its condition, a decisive influence on the quantity and constitution of emissions. Each parameter of fuel affects emissions chiefly in three key areas [2]:

- by influence on injection parameters,
- by connection with creation of pollutants in an engine,
- by influence on efficiency of emission control systems.

It has been demonstrated repeatedly that engine exhaust emissions are largely dependent on the characteristics of an engine and its ability to utilize the fuel over the operating cycle. However, when engine emissions are reduced to lower levels the effect of fuel properties on engine emissions becomes significant. Many studies have shown (e.g. [7] and [15]), that fuel properties have serious impact on engine exhaust emissions. Among various fuel properties the ones which are frequently shown in various studies to have significant effect on engine emissions are: sulphur content (especially for modern engines) and cetane number.

In most studies [10, 11, 12, 15, 16, 17, 18] cetane number has been found to affect all engine emissions. The effect of cetane number on engine emissions is also found to be both fuel and engine dependent. The research programmes described in literature [1, 3, 5, 6, 9, 19, 20] concerning an influence of fuels on emission levels, confirm the negative sulphur effect on exhaust emissions, however, it is also characteristic, that the sulphur effect on particulate emissions depends on other parameters of diesel fuel properties and on the engine type. So far there has been no research in the field of an influence of diesel fuel properties on exhaust emissions, taking into account the Polish conditions e.g. the specification of Polish vehicles fleet as well as Polish fuels. Moreover, the available foreign data in this field with regard to light-duty diesel vehicles (especially the latest ones) are sparse. Therefore it was difficult to predict potiential ecological benefits due to the quality improvement of Polish diesel fuels. The goal of the research project described in this paper was to fill this gap.

The permissive regulations of the PN-EN 590:1999 standard (Table 1) which is currently valid in Poland in relation to diesel fuel were the second reason which made the authors undertake the study concerning an influence of the diesel fuel properties on exhaust emissions. In fact, the requirements of the PN-EN 590:1999 standard only slightly consider the aspect of the influence of fuel composition on the formation of exhaust emissions. In such situation, in Poland there is a high potential for reducing the exhaust emissions through an improvement of fuels. It has to be remembered, that there is still a significant number of old vehicles in operation in Poland, for which using the eco-fuels can be the only reasonable way to limit noxious emissions. Facing the decision of joining the European Community, Poland will have to adjust the quality of its fuels to that of Europe.

	PN-EN	EURO III	EURO IV	WFC <sup>3)</sup>
	590: 1999 <sup>1)</sup>	$(2000)^{2)}$	$(2005)^{2)}$	Category 4
Cetane number	min 49	min 51	min 51	min 55
Sulphur, ppm	max 500	max 350	max 50/10 <sup>4)</sup>	max $5-10^{5}$
Polyaromatics,% m/m	-	max 11	max 11	max 1.0
Density @15°C, kg/m <sup>3</sup>	820-860	max 845	max 845	820-840
Distillation	F370 = min 95% (y/y)	$T95 = max 360^{\circ}C$	$T95 = max 360^{\circ}C$	$T95 = max 340^{\circ}C$

Table 1. Comparison of requirements for diesel fuels [4, 14, 19]

<sup>1)</sup> Polish Standard, <sup>2)</sup> European Directive 98/70, <sup>3)</sup> Worldwide Fuel Charter,<sup>4)</sup> diesel fuel with a maximum sulphur content of 10 ppm must be marketed and be available, <sup>5)</sup> accurate maximum will be defined

A number of previous studies have investigated the effect of diesel fuel properties on steady-state and transient emissions, but the sulphur content was not usually taken into account as experimental variable and the sulphur effect was distorted by other fuel properties. In the present work sulphur content is the only fuel design variable and is varied from 2000 ppm down to sulphur free (less then 5 ppm S). In the research the test fuels without ignition improver additives were used. The natural cetane number of a diesel fuel is correlated with other fuel properties such as distillation temperatures, density etc, hence it is a difficult task, if not impossible, to completely isolate the cetane number effects from the effects of other fuel properties on emissions. In the whole research the test fuels from Polish refineries only were used.

#### **RESEARCH PROGRAM**

The tests were conducted on a passenger car equipped with 1.9 litre direct injection (Common Rail) turbocharged engine, representing the latest technology in production at the start of the research program. Major data on the vehicle are shown in Table 2.

Table 2. Specifications of the est venice				
Vehicle Type	Passenger Car			
Dry Weight	1300 kg			
Engine Type	Diesel, 4-cylinder in-line			
Displacement	1.9 litre			
Injection / Combustion Type	Direct injection Common Rail, turbocharged (intercooled)			
Exhaust Gas Recirculation	Electronically controlled (closed-loop)			
Emission control	Oxidation catalyst			
Calibrated to	EURO III			

Table 2. Specifications of the test vehicle

The new vehicle homologation procedure introduced in the Directive 98/69/EC, so-called New European Driving Cycle (NEDC) was selected as a representative test for this research. The test was Urban Driving Cycle (UDC) (cold start), followed by the high-speed Extra Urban Drive Cycle (EUDC) (hot

start). Tests were undertaken in order to determine the influence of both parts of NEDC on exhaust emissions.

A test fuel matrix consisting of eight diesel fuels was designed to investigate the effect of sulphur and cetane number on exhaust emissions from the test vehicle. To evaluate the influence of sulphur contained in diesel fuel on the exhaust emissions, four different test fuels with the sulphur content varying from less than 5 ppm through 50 ppm (EURO IV) and 350 ppm (EURO III) up to 2000 ppm were prepared. These four test fuels were identical except for the sulphur content, which was varied. The test fuels were blended on the basis of sulphur free (< 5 ppm S) diesel fuel. The expected level of sulphur content was being obtained after an addition of the right amount of thiophene (C<sub>4</sub>H<sub>4</sub>S). The properties of test fuels with different sulphur content are shown in Table 3. To evaluate the influence of cetane number on the exhaust emissions, another four different test fuels with the cetane number varying from 45 through 50 and 55 up to 63 ppm were prepared. These test fuels were blended from refinery streams to match the desired cetane numbers. The properties of the test fuels with different cetane numbers are given in Table 4. Fuel TF-2C represents typical Polish commercial diesel fuel.

Table 3. Properties of test fuels with different sulphur content

Fuel code		TF-1S	TF-2S	TF-3S	TF-4S
Sulphur, ppm		2000	350	50	<5
Cetane number		52	52	52	52
Density	/@15°C, g/ml	0.815	0.815	0.815	0.815
Aroma	tics, % (v/v)	5.1	5.1	5.1	5.1
ation	IBP, °C	172.0	172.0	172.0	172.0
	T50, °C	255.9	255.9	255.9	255.9
still	T90, °C	303.6	303.6	303.6	303.6
Di	FBP, °C	340.5	340.5	340.5	340.5

 Table 4. Properties of test fuels with different cetane numer

Fuel code		TF-1C	TF-2C	TF-3C	TF-4C
Cetane number		45	50	55	63
Density @15°C, g/ml		0.8084	0.8282	0.8244	0.8270
Sulph	ur, ppm	300	300	200	<100
ч	IBP, °C	164	174	172	201
tioi	T10, °C	182	196	196	230
illa	T50, °C	206	236	260	308
list	T90, °C	242	313	344,5	363
Д	FBP, °C	320	348	368	377

### TEST RESULTS AND DISCUSSION

The influence of the sulphur content in diesel fuel on the CO, HC,  $NO_x$  and PM emission in the NEDC test and its individual phases is presented in Figures 1, 2, 3 and 4.

The CO emission in the NEDC test (Fig. 2), irrespective of the sulphur content in diesel fuel was kept at the similar level of 0.570-0.590 g/km. In the first phase of the NEDC test, i.e. UDC phase, any significant difference in the CO emission for the individual test fuels has not been noted, either. However, a distinct differentiation of the CO emission depending on the sulphur content in fuel occurred in the second phase of the NEDC test, i.e. EUDC phase. The smallest CO emission of 0.043 g/km was obtained for the diesel fuel of a sulphur free type. In case of fuels of intermediate sulphur content (50 and 350 ppm) the CO emission was by about 0.01 g/km higher. However, for fuel with the sulphur content of 2000 ppm the CO emission was of the 0.063 g/km level, i.e. nearly 50% higher than for the fuel with the smallest sulphur content.

The influence of sulphur content in fuel on the CO emission is experienced mainly by its effect on the efficiency of the catalyst. On one hand the high CO emission results from the worse combustion characteristics for a cold engine, and on the other hand from the lack of the operation of the catalyst. In practice in the UDC phase, when the catalyst light-off temperature has not been reached yet, the oxidation of CO in the catalyst does not occur and therefore any significant effect of sulphur on the CO emission level is not recorded there.



Fig. 2. CO emission during UDC, EUDC and whole NEDC as a function of diesel fuel sulphur content

In the EUDC phase the engine reaches its thermal stability that significantly limits the formation of CO in a combustion process. Similarly, the catalyst is already warmed-up and the highly efficient oxidation of CO occurs there. Both these effects result in the low and relatively steady level of the CO emission. At this moment the CO emission is mainly determined by the catalyst efficiency which depends, among other things, on the sulphur content in fuel. The serial catalyst of a test vehicle, despite the short time of the test, appeared to be very sensitive to the sulphur content – the difference in the CO emission in the EUDC phase for the sulphur free fuel and the fuels with the intermediate sulphur content (2000 ppm) reached up to about 50%.

When analysing the CO emission in the whole NEDC test one can see that the influence of sulphur on the CO emission is "masked" by the high CO emission in the first phase of the test, and the serious relative differences in the second phase of the NEDC test, due to low absolute CO emission during EUDC, are of small importance.

With regard to the HC emission (Fig. 3) it is difficult to indicate a clear-cut effect of the sulphur content in fuel on the obtained emission levels. In the UDC phase the differences in the HC emission from test fuels have not exceeded the values of a few percent, and moreover, the lowest emission was obtained for the fuel with the highest sulphur content. It gives evidence of a lack or a small influence of sulphur on the emission in the first phase of the NEDC test, the same as in case of CO. Slightly higher differences for the HC emission were recorded in the EUDC phase. The lowest emission was recorded for the lowest sulphur content, however, for other fuels the HC emission was higher by about 15% and in practice it was kept at the same level of 0.041-0.042 g/km. In the whole NEDC test the obtained results were close to the ones obtained in its first phase.



Fig. 3. HC emission during UDC, EUDC and the whole NEDC as a function of diesel fuel sulphur content

In case of the HC emission similarly as for the CO emission the most evident effect of sulphur occurred in the EUDC phase, which should be explained in the same way as above by the influence of sulphur on the catalyst efficiency. However, one should notice the nature of the sulphur influence on the HC emission is definitely different from that of CO. For HC the differences of emission for fuels with the extreme sulphur content are much lower and also no influence on the emission in case of sulphur content changes in the range of 50-2000 ppm was found.

The influence of the sulphur content in diesel fuel on the  $NO_x$  emission is presented in Figure 4. Both in the first phase and in the second phase of the NEDC test the lowest emission was recorded for the fuel with the lowest sulphur content. In general, the  $NO_x$  emission intensified as the sulphur content increased. The differences of emission for the fuels with the extreme values of sulphur content were most significant in the EUDC phase and of about 10% value. In the UDC phase and in the whole NEDC they were smaller by factor 2.



Fig. 4. NOx emission during UDC, EUDC and whole NEDC as a function of diesel fuel sulphur content

Although the results of the tests proved the negative effect of sulphur on the  $NO_x$  emission as well as the evident increase of this effect in the second phase of the NEDC, it is difficult to state definitely what they resulted from. The test vehicle was not equipped with the  $NO_x$  reduction catalyst. It was possible that the sulphur content influenced the  $NO_x$  emission by affecting the operation of the exhaust gas recirculation system.

The highest PM emission during the whole NEDC (Fig. 5) was obtained at the highest sulphur content in diesel fuel. For other fuels the PM emissions were of a similar value and about 20% lower than for the case with 2000 ppm sulphur content. For fuels with the 350 and 50 ppm sulphur content the same PM emission levels were recorded which were higher by only less than 4% than for diesel oil of a sulphur-free type.



Fig. 5. PM emission during UDC, EUDC and whole NEDC as a function of diesel fuel sulphur content

When analysing the PM emissions during the UDC test, which makes up the first part of the NEDC test, it should be stated that the PM emission differences obtained here for the fuels with the extreme values of sulphur content are lower

than for the complete NEDC test. It is probably due to a low temperature of the catalyst and exhaust gas in this test, resulting from the cold start and small engine loads. It follows that the formation of the sulphates occurs with reduced intensity and affects the total PM emission level to a smaller extent.

In the second part of the NEDC test, namely during the EUDC, the linear relation between the PM emission and the sulphur content in fuel was obtained. It should be concluded that the exhaust gas and catalyst temperatures were higher (hot start, higher load) than during the UDC test and as a result the increased formation of the sulphates were decisive.

The influence of the cetane number (CN) of diesel fuel on the CO, HC,  $NO_x$  and PM emission is presented in Figures 6, 7, 8 and 9.



Fig. 6. CO emission during UDC, EUDC and whole NEDC as a function of cetane number of diesel fuel

The effect of an increase of the cetane number of diesel fuel on the CO emission is definitely advantageous (Fig. 6). In the first phase of the NEDC the significant reduction of the CO emission started above the cetane number of 50; the difference of the emission for fuels with the extreme values of cetane number was 0.522 g/km, i.e. about 26%. The reduction of the CO emission in the UDC phase is of a special advantage, since due to the cold engine in this phase it is difficult to decrease the CO emission by use of the catalyst; the reduction of the CO emission, especially at the very beginning of the UDC phase, is possible to be achieved only by reducing the intensity of CO formation in the engine working cycle. In the EUDC phase the influence of the cetane number on the CO emission was nearly linear, the relative emission difference for fuels with cetane numbers of 45 and 63 was even higher than in UDC and was of about 41%. It gives evidence of the smaller amount of CO being formed during the combustion of fuel with the higher cetane number, and probably to some extent, it proves the higher efficiency of the obtained catalyst due to the higher temperature of exhaust gas.

The characteristics of the HC emission in the UDC phase as a function of the cetane number of fuel (Fig. 7) shows a great similarity to the characteristics of the CO emission discussed above. The significant reduction of the emission is also

seen here above the CN = 50, whereas the characteristics of the HC emission in the EUDC phase is quite different. Despite the lowest HC emission value which was recorded for the highest cetane number, the highest emission was obtained for fuels with the intermediate value of this parameter (CN = 50 and 55). The highest HC emission in the whole NEDC test was obtained for CN = 50, when increasing CN up to 63 the HC reduction by 25% was obtained.



Fig. 7. HC emission during UDC, EUDC and whole NEDC as a function of cetane number of diesel fuel

The influence of the cetane number of diesel fuel on the NO<sub>x</sub> emission is presented in figure 8. In the UDC phase for the CN range from 45 to 55, the NO<sub>x</sub> emission slightly decreases as CN increases. The increase of CN from 55 to 63 results in the quite substantial (by 6%) reduction of the NO<sub>x</sub> emission. In the EUDC phase the increase of CN from 45 to 50 and 55 results in a slight (by 2%) increase of the NO<sub>x</sub> emission; the further increase of CN up to 63 no longer influences the NO<sub>x</sub> emission. In the whole NEDC test the lowest NO<sub>x</sub> emission was obtained for the fuel with CN = 63, for other fuels the NO<sub>x</sub> emission was by 3-4% higher and the recorded values were similar.



Fig. 8. NOx emission during UDC, EUDC and whole NEDC as a function of cetane number of diesel fuel



Fig. 9. PM emission during UDC, EUDC and whole NEDC as a function of cetane number of diesel fuel

The influence of the cetane number on the PM emission is presented in Figure 9. In the UDC and EUDC identical PM emission values were recorded for fuels with CN = 45 and 50. In case of those fuels the PM emission was lower than for fuels with higher cetane numbers (CN = 55 and 63), especially in the UDC phase where the difference was of about 25%. In the EUDC phase (and also in the whole NEDC test) definitely the highest PM emission was obtained for the fuel with the CN = 55, whereas for other fuels of both higher and lower cetane numbers the PM emission was by about 15% lower.

#### CONCLUSIONS

– Considering the NEDC test as a whole it should be noted that the lowering of the sulphur content in diesel fuel was of the greatest influence on the reduction of the PM emission, and to smaller extent resulted in the reduction of the  $NO_x$  emission as well. No serious correlation between the sulphur content in diesel fuel and the CO and HC emission in the whole NEDC test was found; the CO and HC emission was kept at a similar level irrespectively of the sulphur content.

– From two phases of the NEDC test the second phase – the EUDC – is more sensitive to the diesel fuel sulphur content. Within the EUDC test the catalyst reaches its nominal work temperature and the engine loads are higher. In the EUDC phase for all toxic substances (CO, HC,  $NO_x$  and PM) the highest emission was obtained in case of the fuel with the highest sulphur content.

In the EUDC phase a significant influence of the sulphur content on the CO emission was recorded; for fuels with the extreme values of sulphur content (< 5 and 2000 ppm) the CO emission difference of nearly 50% was recorded. In this phase CO is efficiently combusted in the catalyst; the significant differences of its emission prove the high disadvantageous influence of the sulphur content on the CO oxidizing ability of the catalyst (especially when considering the fact that</p>

fuel affected the catalyst for short time only). The above mentioned differences of the CO emission do not apply to the whole NEDC test, because during the UDC phase the average CO emission is more than 30 times higher than the one of the EUDC phase, that determines the total emission in whole NEDC test.

- The fact that the reduction of the emissions by the reduction of the diesel fuel sulphur content is not accompanied by an increase of other regulated emission components and fuel consumption is of great importance.

- The increase of the self-ignition ability of fuel (cetane number) was of the greatest influence on the reduction of the CO emission. It applies both to the UDC phase and to the EUDC one, and proves that the intensity a of the CO formation in the combustion chamber is smaller at the higher cetane number of fuel. The reduction of the CO emission was especially significant at the cetane number values above 50.

– The characteristics of the HC emission as a function of the cetane number was similar to the one of the CO emission. In the whole NEDC test the differences of the emission for the fuels with the cetane number extreme values (CN = 45 and 63) were of 27% and 25% for CO and HC respectively. The reduction of the CO and HC emission in the UDC phase is of special importance, as in fact CO and HC are no longer combusted after leaving the engine due to a low temperature of the catalyst.

– The advantageous effect of higher CN values on the NO<sub>x</sub> emission occurred only in the UDC phase. In the EUDC the NO<sub>x</sub> emission was almost identical for all fuels. For the whole NEDC test the lowest NO<sub>x</sub> emission was recorded for the fuel with CN = 63; for other fuels the NO<sub>x</sub> emission was higher by 3-4%.

- No direct correlation between the cetane number values and the PM emission was found. The lowest PM emissions in EUDC, and especially in UDC, were recorded for fuels with the lowest cetane number values, i.e. CN = 45 and 50, and the highest for the fuel with CN = 55.

- Although the emissions reduction is lesser than could be achieved by the most modern engine technology or alternative fuels, the immediate net effect of fuel parameters improvement on the emissions is significant, since it takes place over the whole vehicle population.

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#### SUMMARY

A great reduction of diesel engine emission limits in the future, especially of PM and  $NO_x$ , forces to develop means to comply with stringent legislation. Environmentally friendly fuels are regarded as effective means to decrease emissions. Although the emissions reduction is lower than could be achieved by the most modern engine technology or alternative fuels, the immediate net effect of reformulated diesel fuel on the emissions is significant, since it takes place over the whole vehicle population.

The effect of diesel fuel properties and composition on regulated emissions was investigated in a DI Common Rail, turbocharged passenger car, equipped with an oxidation catalyst and electronically controlled exhaust gas recirculation, representing the latest technology in production at the start of the research programme. Attention was focused primarily on the fuel properties such as: sulphur content and cetane number. To evaluate the influence of fuel properties on emissions, eight different test fuels were prepared: four fuels with the sulphur content varying from less than 5 ppm up to 2000 ppm and four fuels with the cetane number varying from 45 up to 63. The new vehicle homologation procedure introduced in the Directive 98/69/EC, the so-called new European driving cycle (NEDC) was selected as a representative test for this research.

Experimental results indicated that fuel sulphur level had a significant impact on all the regulated emissions, especially on PM. Out of the two parts of the NEDC test the second part – the EUDC test – was more sensitive for the diesel fuel sulphur content.

Testing fuels of different ignition qualities showed that HC and CO emissions of high cetane number fuels were significantly lower than the emissions of low cetane number fuel. We also observed a small decrease in  $NO_x$  emissions with an increase in cetane number. The effect of cetane number on particulate emissions was more complex, the highest emission was obtained for medium-cetane number fuel.