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LUBRICATING PERFORMANCE OF CARBON NANOTUBES IN INTERNAL COMBUSTION ENGINES – ENGINE TEST RESULTS FOR CNT ENRICHED OIL

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ABSTRACT−The main purpose of this research is to reduce friction losses by adding carbon nanotubes to engine oil. Extremely favorable tribological properties of carbon nanotubes have been extensively studied on the microscopic scale and using tribometers, have not yet been verified in the engine. Enriching oil with nanotubes can lead to significant, exceeding 7 %, reduction in the motoring torque of the engine at low crankshaft rotational speed. The phenomena associated with the dispersion of carbon nanotubes in the engine are stated and discussed. It has been shown that the oil shear during normal operation of the engine can effectively improve the dispersion of nanotubes. At the same time the oil filtration system removes agglomerates of nanotubes very quickly.

KEY WORDS : Combustion engines, Carbon nanotubes, Engine oil, Friction

1. INTRODUCTION

Article relates to the use of carbon nanotubes (CNTs) as an additive for motor oil, the main aim is to reduce friction losses and thus fuel consumption (NanoLab Inc., 2016; Golloch, 2005; Holmberg, 2012; Tung and McMillan, 2004; Deuss *et al*., 2010, 2011a, 2011b). The relationship between the efficiency of internal combustion engines operating conditions and their fuel consumption have already been discussed in an earlier article (Kałużny, 2013) and will not be repeated here in detail. Contrary to popular belief reciprocating internal combustion engines are, and in the coming decades are likely to remain the dominant part of powertrain in cars. This is due to the well-to-wheel energy balance and the total emissions estimate performed by including all the stages in the production and distribution chain (Bossdorf-Zimmer *et al*., 2012; Spicher, 2012; Ernst *et al*., 2014; Jeong *et al*., 2016; Loiselle-Lapointe *et al*., 2017; Lee and Choi, 2016).

CNTs are a relatively recently discovered and intensively studied material (Baughman *et al*., 2002; De Volder *et al*., 2013; Yan *et al*., 2015); their often reported unique features are extremely beneficial tribological properties (Bhushan, 2010; Chauveau, 2010; Servantir and Gaspard, 2006; Vander Wall *et al*., 2005; Lucas *et al*., 2009; Cook *et al*., 2013). One can find many papers where the results of CNT research in idealized conditions are presented, carried out outside the engine with the use of a tribometer. The paper proposes considering CNTs as an additive for engine oil, such a use is subject to patent (Habeeb and Bogovic, 2013), and a CNT containing liquid oil additive is commercially available.

The authors found no outside publications, which would discuss in detail test results of experiments performed on an engine using CNTs as an oil additive. Such studies are justified, because the conditions in the engine can only to a limited extent be reproduced in a tribometer. In experiments performed outside an operating engine it is impossible to study and take into account aspects such as:

- The diverse conditions for different friction components of the engine, from boundary lubrication to elastohydrodynamic lubrication regime
- Diversity of friction surfaces materials; in almost every engine there are friction components made of aluminum, various grades of steel, including chrome-plated steel and hardened steel, cast iron, bearing alloys, non-ferrous metals, and polymers
- Cyclic thermal loads, the occurrence of extremely high temperatures, e.g. in the upper piston ring area
- Oil contamination with fuel and combustion products.

The conviction that there is a need to verify the results of tribological investigations of engine oil with the addition of CNTs was the motivation for undertaking this research. This incentive was further reinforced by the findings of the authors and the previously described tests of abrasive layers of CNTs deposited on the piston skirt (Kałużny,

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2013). The obtained results may indicate the dominant role of the CNTs scratched off the piston skirt and carried by oil to other friction components, in limiting the total friction losses there.

Due to the need to lower the tribologically induced CO_2 emissions the engine oil viscosity was reduced significantly in the last years. The next step could be the replacing of standard lubricating oil with diesel fuel, or diethylenglycol used already as engine coolant or other fluids. The detailed computer simulation and tribological research of such engine lubricant substitutes was presented in Hadler *et al*. (2016) showing impressive potential in engine friction reduction. Thus, the additional issue explored in this article is the dispersion of CNT's in hydrocarbons and diethylene glycol.

2. RESEARCH OF CARBON NANOTUBES AS AN ADDITIVE TO LUBRICATING OIL

Adding micro- and nano-particles of substances such as copper, tungsten, molybdenum, and molybdenum disulfide to the lubricating oil is a well-established method of reducing the engine friction. Under certain conditions the friction deposition process of these substances on the surfaces of the working elements, leads to reduced friction forces (Kotnarowski, 2009; Liu *et al*., 2004). Similarly, a layer of CNTs on the surface of the piston skirt might be formed spontaneously by the settling of CNTs contained in the lubricating oil (Pottuz *et al*., 2004). In another research project, no adsorption of CNTs on the skirt surfaces was observed, the CNTs were chemically inert (Chauveau, 2010; Chaveau *et al*., 2012).

In the study (Pottuz *et al*., 2004) single-walled carbon nanotubes (SWCNTs) were added to the lubricating oil, and a reduction in the friction forces between contacting metal surfaces was observed. With the mass fraction of CNTs at 1 % in a range of different unit pressures the lowest coefficient of friction equal to 0.08 was achieved. Based on the results in Pottuz *et al*. (2004) of frictional force in successive tribometer tests it can be concluded that the optimal mass fraction of CNTs is 1 %, and any higher concentrations are ineffective. At the same time the change of the coefficient of friction recorded for the mass concentration of CNTs limited to 0.5 % shows a significant reduction of friction forces only after many tribometer cycles. As a result of similar tests performed (Cursaru *et al*., 2012) the friction coefficient value of 0.087 was obtained when the mass fraction of CNTs in the oil was kept at 0.5 %.

The results of the tests described in Pottuz *et al*. (2004) clearly show that CNTs added to the oil reduce friction more effectively than graphite and C60 fullerene. On the other hand, test conditions applied in Hwang *et al*. (2011) lead to the opposite findings, nano-oils with the fibrous particle additives (e.g. CNT) showed higher friction coefficients than the nano-oils with spherical nanoparticle additives. Article (Hwang *et al*., 2011) discusses the hypothesis given in Tao *et al*. (1996) that the nanoparticles perform rolling or ball bearing role.

The results of research provided in Hwang *et al*. (2011) lead to the conclusion that the lubrication performance clearly improved with the decrease in size of the particles suspended in the mineral oil. However, the lubrication was worse than that of raw mineral oil when the average size of the suspended particles was greater than several micrometers. The quoted study suggests the existence of an effect that is widely described in Chauveau (2010) and Chaveau *et al*. (2012) consisting of the oil flow being blocked in the convergent zone by the trapped agglomerates having a diameter greater than the film thickness. This effect is strongly related to the entrainment and starvation velocity.

From the point of view of the conditions prevailing in the engine the effect described in Chauveau (2010) and Chaveau *et al*. (2012) consisting of dramatically increasing the thickness of the oil film in the conditions of low entrainment velocity can have a particularly preferred significance. This effect was observed for the oil with concentration of CNTs as small as 0.01 – 0.1 %.

Study of the effect of CNTs on the rheological parameters of the oil was described in Ettefaghi *et al*. (2013). In the context of an engine the improvement of the thermal conductivity resulting from the addition of CNTs to an oil may have a large positive significance (Ettefaghi *et al*., 2013; Phan *et al*., 2014).

The concept of adding CNTs or other nanoparticles like molybdenum disulfide to the lubricating oil is a related issue (Kogovšek *et al*., 2013; Kalin *et al*., 2012).

3. CARBON NANOTUBE DISPERSION IN HYDROCARBON LIQUIDS

CNTs, like other nanomaterials are characterized by a strong tendency to agglomerate. The large surface area of CNTs makes them attract each other to form visible agglomerates of the size of many tens or hundreds of microns. In the studies of friction components presented in the literature it is clearly shown that engine oil in which such large agglomerates of CNTs are suspended has inferior tribological properties in comparison to oil in which the CNTs are well dispersed (Chauveau, 2010; Chaveau *et al*., 2012; Hwang *et al*., 2011). While in the case of tribometer research the agglomeration of CNTs only lead to the reduction of the positive effect of the addition of CNTs on friction losses and wear, its effect on the internal combustion engine as a whole can be much more severe. The major portion of the agglomerates of CNTs will be stopped within a short time by the oil filter, whose pores have a diameter of tens of micrometers; the blocked filter ceases to fulfill its function, Figure 1. In addition, the remaining agglomerates are likely to block the flow of oil in small diameter oil supply pipes, for example

Figure 1. Picture of a new oil filter (left) and an oil filter after two minutes of operation in an engine, with CNT remnants left after previous tests (right).

to the turbocharger or the valve timing control. This can cause damage to important parts of the engine or, in extreme cases the complete destruction by seizing. Achieving a good dispersion of CNTs in the oil is therefore essential for the success in using CNTs to reduce friction losses in internal combustion engines.

The authors have only used CNTs produced in the CVD process in their study, given that due to the possibility of mass production, the method is most suitable for future automotive applications.

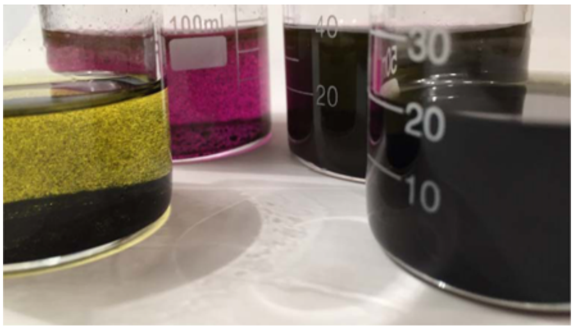

Figure 2. Comparison of pristine MWCNT, long (5 – 20 μm, two on the left) and short (1 – 3 μm, two on the right) dispersion in ethylene glycol (Volkswagen brake fluid DOT 4 two at the front and G13 cooling liquid concentrate two at the back).

Pristine SWCNTs form “bundles” out of parallel-arranged, adjacent side walls of the CNTs. Multi-walled carbon nanotubes (MWCNT) are entangled in a chaotic tethered pattern of crossed fibers forming a mesh configuration (Chauveau, 2010; Xie *et al*., 2003; Huang and Terentjev, 2012). The number of contacts which can form between neighboring MWCNTs increases dramatically with the length of the CNTs. Therefore, the binding of a clustered network of long MWCNTs is extremely strong, where each contact effectively acts as a cross-link fixing the network together (Huang and Terentjev, 2012). The use

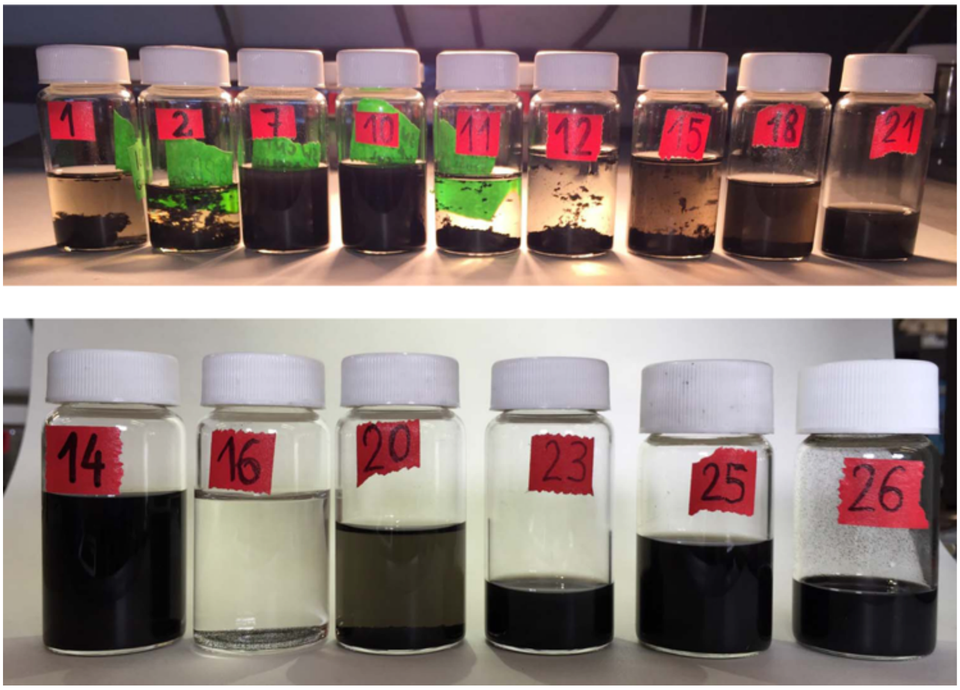

Figure 3. Commercial gasoline and reagent grade ethanol: a comparison of the dispersion of different types of SWCNTs and MWCNTs subjected to chemical treatment, or with the addition of surfactant according to NanoLab procedures. Pictures were taken 24 hours after sample preparation.

of short CNTs therefore seems to be a simple and effective way that allows for obtaining a good dispersion. Figure 2 shows a comparison of the samples with ethylene glycol to which pristine MWCNTs were added. The CNTs were obtained using the same CVD process, but some of them have undergone a longer mechanical milling process, so that their length is much shorter. After adding the pristine CNTs the samples were only shaken by hand, they were not sonicated at all.

Ethylene glycol, same as ethyl alcohol, are hydrocarbons which helps to relatively easily achieve a good dispersion of CNTs with. Figure 3 shows a comparison of dispersion of different types of CNTs in ethanol and gasoline. In the case of gasoline, visual inspection shows that CNT agglomerates are visible in each of the samples. The same initial set of experiments allowed to obtain three different methods for dispersing CNTs in ethanol (samples 14, 23 and 25), in a way that no agglomerates can be seen in the vials.

In order to prepare the sample for SEM to investigate the dispersion of CNTs in hydrocarbons a drop of the colloid was applied on an aluminum foil and evaporated at room temperature. The process of evaporation was associated with a temporary critical increase in the concentration of CNTs and as a result could have led to the agglomeration of CNTs on the surface of the aluminum foil, thus positively falsifying the results. It could certainly not, however, give a falsely negative test result for the presence of agglomerates.

Figure 4 compares the results obtained for a sample of ethanol, shown as sample No. 14 in Figure 3, and the sample of gasoline from the second test phase, not shown in Figure 3 (the presence of agglomerates couldn't be visually determined for this sample either).

In the presented cases, a good dispersion in ethanol was obtained through chemical modification of the surface of bamboo-CNTs using COOH groups, for petrol satisfactory results were achieved after applying a Nanosperse surfactant produced by NanoLab Inc. (2016). The point of both of these methods is to obtain similar electrical charge on the surface of the nanotubes which, thanks to the existence of this charge, repel each other thus inhibiting the phenomenon of agglomeration. COOH groups attached to the surface of carbon nanotubes lose hydrogen and become negative ions when placed in any liquid having a pH of less than 8 or 9. The other method comprises of adding a colloidal solution of carbon nanotubes in the target liquid – in this case gasoline nanosperse surfactant. Wrapping pristine nanotubes with molecules that can ionize will accomplish the same result. Sodium polyacrylate is one poly-anionic molecule that can be wrapped around a nanotube. In suspension, the sodium ionizes and disperses in the gasoline, while the remaining backbone chain (which is wrapped around the nanotube) acquires a negative charge (NanoLab Inc., 2016).

The conducted study indicates the need to define the criterion for assessing the dispersion of CNTs in a hydrocarbon liquid that is adequate to the requirements of engine application. In the case of most of the samples shown in Figure 3 visual inspection carried out immediately after the process of sonicating showed no presence of agglomerates. These have formed and precipitated to the bottom of the vials within 24 hours, while all the compounds showed a differentiated morphology. The most undesired nature of the agglomerates seems to be clearly visible at the bottom of the sample No. 16, because their re-dispersion by shaking the vial is completely ineffective. Much more beneficial is the "fluffy" structure as can be seen for example in sample No. 12, where the CNTs precipitated to the bottom of the glass to occupy a large volume, but their re-dispersion can be easily achieved through a light shaking of the sample, or even thermal movement shortly after turning the lights on to take the sample picture.

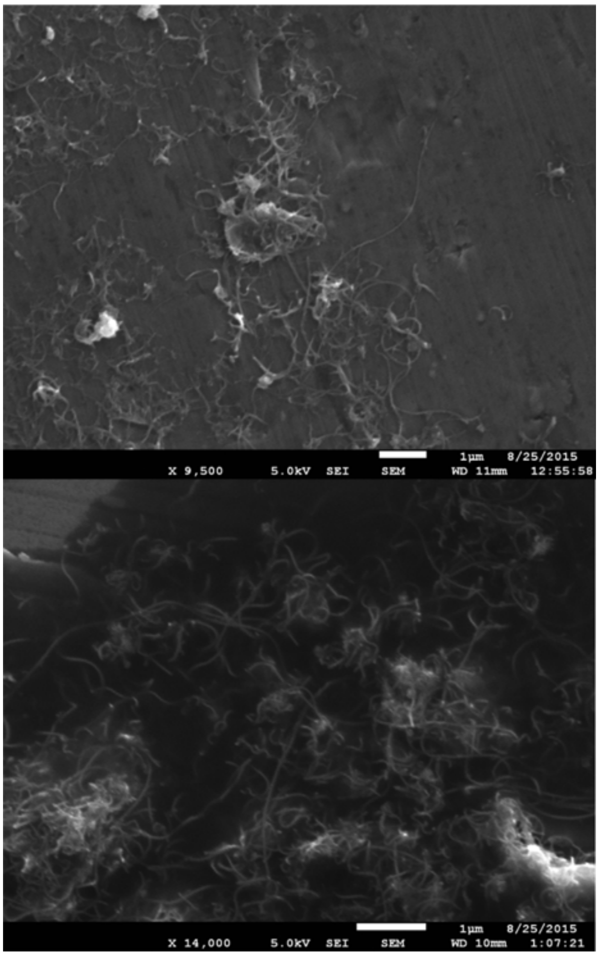

Figure 4. CNT dispersion in ethanol (higher) and in gasoline, selected SEM images of samples of the evaporated hydrocarbons on the aluminum foil. The nanotubes were dispersed in ethanol thanks to functionalization with COOH group, surfactant nanosperse was used in gasoline, which appears as a dark spot in the SEM picture.

Using a standard scanning electron microscope (SEM) is

Figure 5. MWCNT in the engine oil, a drop of oil on a piece of paper; oil taken from the sump immediately after stopping the engine; large CNT agglomerates visible (Volkswagen TDI engine, AXD type).

limited to samples with very low vapor pressure – that is why the samples containing hydrocarbons such as petrol or ethanol were subject to evaporation prior to SEM testing. Application of this method cannot therefore be easily extended to the colloidal CNT solution in the engine oil. Radically simplified version of the method involves applying a drop of the colloid onto a piece of paper and observing it with an optical microscope or even taking a picture with a standard camera Figure 5.

The dispersion of CNTs in liquids of low viscosity, such as gasoline and ethanol can be effectively supported by the sonicating process. Ultrasonicating can effectively break SWCNT aggregates without damaging their structure; in the case of MWCNT effective breakdown of agglomerates is associated with the shortening of length of the CNTs predicted by theoretical considerations (Huang and Terentjev, 2012) as well as confirmed in several independent experiments. Both theoretical considerations (Huang and Terentjev, 2012) and experiments (Chauveau, 2010) indicate that after a long sonicating time a defined target length of the CNTs is obtained and the process of further shortening does not occur.

The authors' own experiments show that the sonicating process is not effective in the case of viscous liquids such as lubricating oil or diesel fuel. Even a many hour long sonication of lubricating oil, aided by its heating, does not yield a satisfactory dispersion of CNTs. In contrary to sonication, using dispersion by shear-mixing occurring in the engine lubrication system was effective, but only in some experiments. The high viscosity characteristic of lubricating oil is indeed a factor impeding the obtaining of a satisfactory dispersion of CNTs, but at the same time it also slows down the process of re-aggregation, creating a relatively stable colloidal system.

Motor oils, especially oils for compression-ignition engines contain many additives, including dispersants. Their role is to keep the soot, which is a product of combustion and enters into the oil, in a dispersed form (Chauveau, 2010; Dikio, 2011; Manoj *et al*., 2012). More detailed studies indicate that among the many forms of carbon contained in the products of combustion engines CNTs also appear (Lagally *et al*., 2012).

4. STUDIES OF THE FRICTION LOSSES IN THE WORKING ENGINE

4.1. Research Concept

The analysis of the literature in the field of tribological investigations of oil with the addition of CNTs, and especially the results of experimental studies of pistons, performed by our research group (Kałużny, 2013), were the inspiration to carry out the research described below. The concept of the study is to examine the effect of the addition of CNTs dispersed in the engine oil on the friction losses of entire engines installed on a test bench. The study used standard MWCNTs produced in industrial grade CVD process at NanoLab in Waltham. The tests were performed on two modern engines, examining oil containing 1 % of CNTs by weight and another oil with a smaller addition of CNTs, of about 0.5 %. Oil with a higher concentration of CNTs was poured into a four-cylinder FIAT JTD engine with a displacement of 1.3 dm^3; the oil with a lower concentration of CNTs was tested in five-cylinder Volkswagen TDI AXD type engine, with a displacement of about 2.5 dm^3. Both tested turbocharged compression ignition engines were combined with dynamic brakes, enabling braking or motoring the engine. The FIAT engine is mainly used in small passenger vehicles, the Volkswagen engine is used to power commercial vehicles. The FIAT engine was not new at the start of the research – it previously operated with the engine dyno for over 1,000 h; the Volkswagen engine previously worked only a few dozen hours.

The use of the electrical machine allows for both adding load and motoring of the internal combustion engine. In order to unambiguously determine the actual transmission power it was consistently assumed in the following part of the paper that when the engine is motored to the measured torque is negative.

The aim of the study was to examine whether the addition of CNTs to the oil may constitute a simple and effective method to reduce friction losses in the internal combustion engine.

4.2. Experimental Setup

Detailed specifications of the engines tested, and a description of their construction can be found in the literature (Hadler *et al*., 2004; Volkswagen Selbststudienprogramm 305, 2003; FIAT 1.3 Multijet Engine, 2016).

The torque measurement which was key to these studies

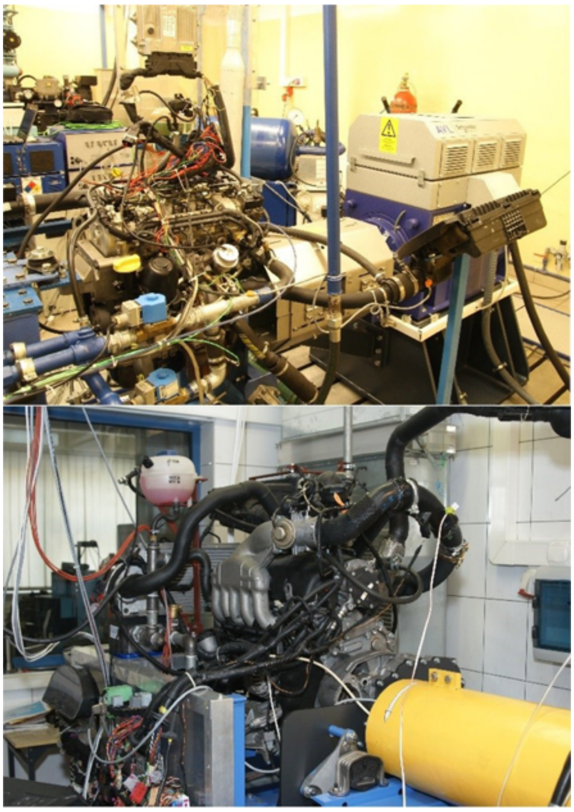

Figure 6. Engine dynamometers with FIAT JTD (higher) and Volkswagen TDI (lower) engines.

was made using torque meters mounted on the shaft connecting the engine with the dyno; it was a KTR 42/1000 measuring shaft for the Volkswagen engine and HBM flange for the FIAT engine (KTR 42/1000 Torque Measuring Shaft, 2016; HBM T40B 1 kNm Torque Measuring Flange, 2016). Figure 6 shows a view of the engine dynamometers where the tests were conducted. The engines were liquid-cooled with a water/water heat exchanger, with an external regulation system. The TDI engine uses an external coolant pump and additional 20 kW electric heaters. Prior to conducting the research described in the paper no CNTs have been used in any of the engines tested.

4.3. Results of the Research of the Volkswagen Engine

The comparison tests between standard oil and oil with CNTs have been performed on the Volkswagen engine first. The initial part of the study is the registration of the motoring torque in 16 minutes of the engine warm-up. During this time, the engine was powered by the dynamometer maintaining a constant engine speed of 1,030 rpm, at the same time engaging electric heaters of the engine coolant setting the coolant temperature to be kept at 90 °C. Before the tests the engine was prepared to ensure the high repeatability of the results: glow plugs circuit was disconnected, the throttle and exhaust gas recirculation valve were opened completely, an external battery charging system was connected. Before the tests the engine was shut down and thermally conditioned for 24 hours, 2 hours

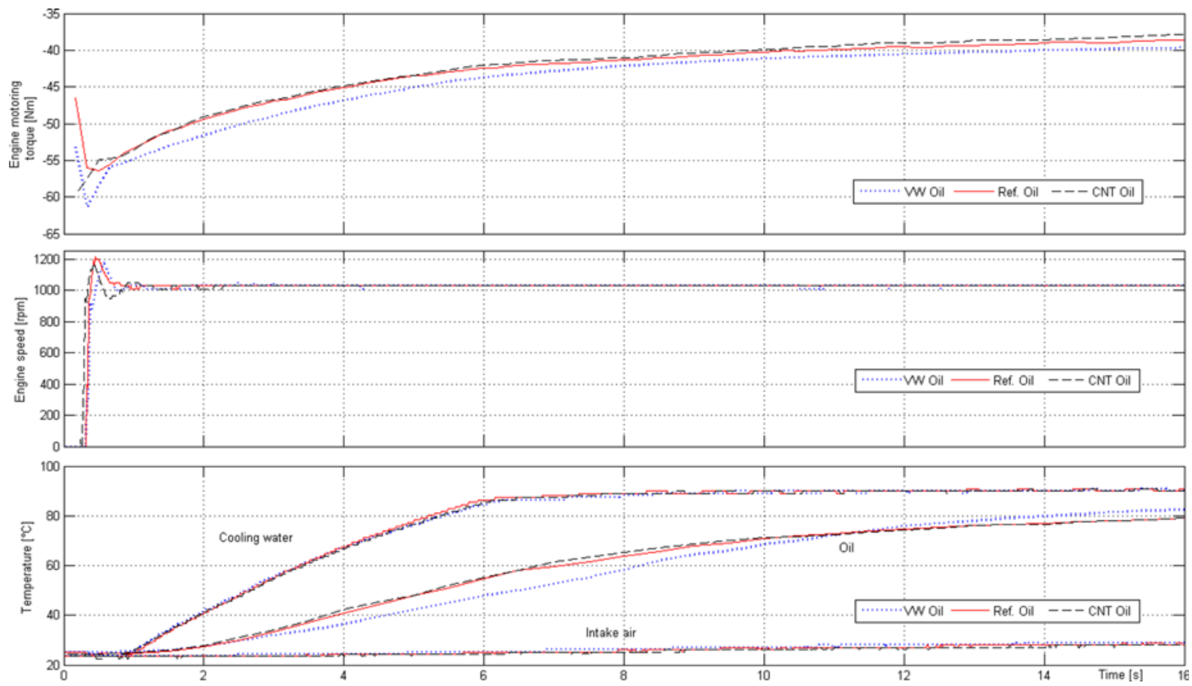

Figure 7. Impact of the lubricating oil on the engine motoring torque; comparison between the original VW oil, Shell reference oil and cnt-enriched Shell oil; immediately after each oil was filled in the sump the engine was started and motored at a constant 1,030 rpm, while the electrical coolant heater allowed to simulate engine warm-up conditions.

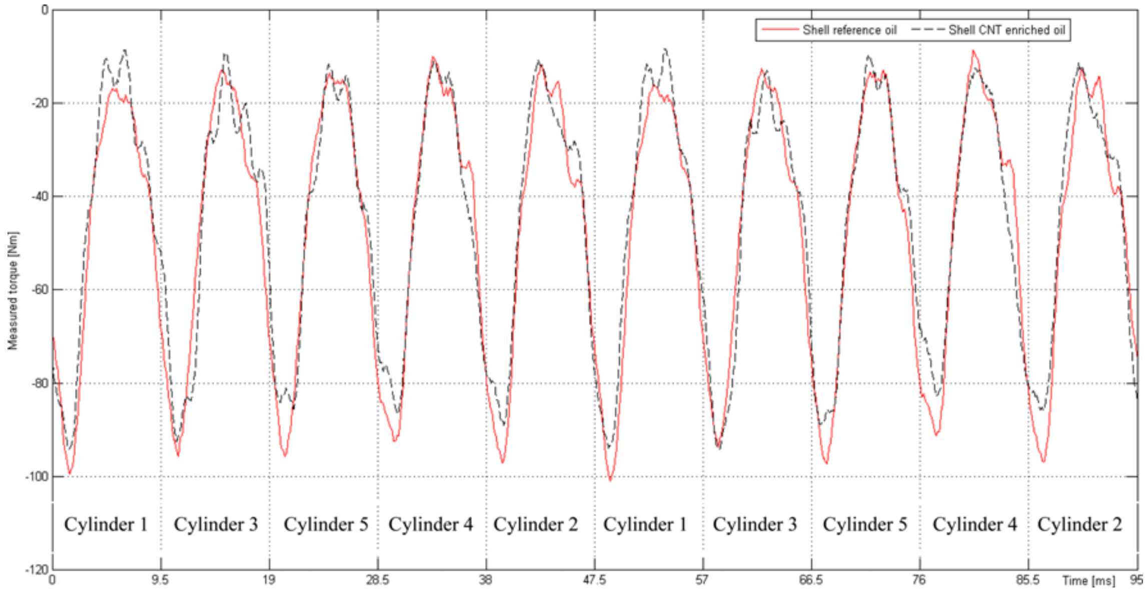

Figure 8. Instantaneous torque values recorded at a speed of about 2,500 rpm for the engine lubricated with reference oil and oil with the addition of cnt; portion of work cycle for 4 crankshaft revolutions, shows a clearly visible repeatability of the cycles after 47.5 ms (this time corresponds to 2 revolutions of the crankshaft, which is the equivalent of one full work cycle of a 5-cylinder 4-stroke engine).

before the start of the test the torque measuring shaft was activated and conditioned. The oil level was always exactly the same. To avoid CNT agglomerates from being filtered out the oil filter has been removed for the duration of the tests, including when the oils without the addition of CNT were tested to ensure comparability. There were three series of measurements, first using the standard engine oil Volkswagen LongLife III with viscosity grade 5W/30 and designation VW 504 00/507 00, replacing it later with reference Formula Shell oil with viscosity grade 10W/30 and quality rating API SN. In the last series of measurements the same Shell oil with the addition of CNTs was examined. The oil and coolant operating temperature, the torque, and other selected engine parameters that were recorded during the test are shown in Figure 7.

Moreover, in the second part of the experiment after several tens of minutes of continuous engine drive further tests of friction losses for the constant speed of 1,000 rpm and 2,500 rpm were conducted for every oil. In this part of the experiment torque output was recorded with a maximum torque measuring transducer sampling rate equal to 10 kHz, each measurement consisted of 25,000 torque sampling points. Each of such recordings was repeated three times. The results are shown in Table 1 and in the Figure 8.

It should be noted that in the case of this research various quasi-fixed temperature values of the reference oil and oil with the CNTs were obtained, while the CNT oil temperature was always slightly higher. The temperature of the cooling water was controlled and always equal to 90 °C.

Regardless of the type of test after filling the engine

Table 1. Comparison of the values of the motoring torque of the engine lubricated with reference oil and oil with the addition of the CNTs, the results for a fully warmed up engine.

Engine speed	1,000 rpm		2,500 rpm	
Oil type	Without CNT	With CNT	Without CNT	With CNT
Oil temperature	80 °C	81 °C	83 °C	86 °C
Torque in test No.1 (Nm)	− 36.37	− 33.85	− 47.16	− 45.13
Torque in test No.2 (Nm)	− 36.61	− 33.92	− 47.22	− 45.21
Torque in test No.3 (Nm)	− 36.74	− 34.10	− 47.13	− 45.25
Average torque (Nm)	− 36.57	− 33.96	− 47.17	− 45.19
Torque: Reduction %		7.15		4.19

sump with oil containing CNTs a significant noise reduction of the engine operation was observed. Previously it was never observed that the change in the type of oil would affect the level of engine noise as significantly. This result was a complete surprise, which is why the preparations for measurement of vibration and noise turned out to be inadequate. This observation is indirectly confirmed by the graph in Figure 8, indicating a noticeable decrease in the amplitude of the torsional vibrations of the engine crankshaft after introducing cnt into the oil.

After completing the measurements the engine sump was flushed several times using the standard Volkswagen oil, allowing for a relatively easy purification of the oil-lubricated engine space of all the CNT agglomerates, which was observed using an endoscope.

The flushed agglomerates quickly clogged the oil filter (see Figure 1). The final measurement of the friction losses with the standard Volkswagen oil gave the same results as the measurements prior to CNT oil tests. Given this result the spectroscopic studies of friction surfaces was abandoned, assuming a permanent friction-relevant layer of CNTs could not have formed. After completing the study of CNTs the engine was used for other experiments and no faults or any consequences of earlier CNT presence in the lubricating oil have been detected. Dismantling the oil sump performed several months after the completion of the study of CNTs revealed that despite many hours of engine operation and oil changes a few deposits of CNTs remained in places sheltered from the oil flow.

4.4. Results Analysis for the Volkswagen Engine

Comparative studies of the friction losses for reference oil and oil with the addition of CNTs were performed by means of engine motoring test. In the warm-up phase no significant differences were obtained, neither in the runs of the motoring torque nor other engine parameters. The exception is the oil temperature of the standard Volkswagen oil, whose temperature profile differs significantly from the temperature profile of Shell oils. It is significant that temperature profiles of Shell oils seem to be very similar in the tests regardless of whether the CNTs were included in the oil or not. A different temperature profile of the Volkswagen oil can be explained in that the oil is a different viscosity grade than the Shell oil. The change in viscosity at low temperature can effectively change the circulation of oil in the engine.

At no time of using the CNT oil the motoring torque was seen to increase, but CNT also did not provide any strongly favorable results in comparison with the reference oil. Some slight benefit from the use of CNTs become noticeable in the final testing phase. Comparing the average torque values of the last five minutes of the test a value of – 39.13 Nm for the reference oil and – 38.52 Nm for the CNT oil was obtained. This is only a difference of about 1.5 %, although excluding the impact of random errors on the results would require multiple repetitions of the test.

Much better, because reaching up to 7 %, were the results obtained for the oil with the addition of CNTs after a few tens of minutes of operation, for the engine in the conditions of thermal equilibrium and for low engine speed. After a longer operating time of the engine the previously not noticeable difference in the temperature of the reference oil and the oil with CNTs was observed, especially for higher engine speeds. These results may indirectly indicate the achievement of better dispersion of CNTs in the engine oil as a result of a longer operating time, higher speed of oil pump driven by the crankshaft and higher shear stress. The results of tribological tests show that the dispersion of CNTs in the oil is a key factor in determining the friction conditions (Chauveau, 2010; Chaveau *et al*., 2012), and in the studies available the problems of achieving a good dispersion of CNTs in the engine oil can be found (see Figure 5).

At a speed of 1,000 rpm a significantly greater benefit was obtained from the use of CNTs in the oil than at a speed of 2,500 rpm (7.1 % vs 4.2 %). From the viewpoint of improving engine performance under the most common operating conditions, it is a preferred result. At low engine speeds conditions are not favorable to the formation of an oil film or reduce its thickness and strength in multiple friction components. The obtained result may indicate the benefits of using CNTs are higher in boundary friction regime than in elastohydrodynamic regime. A similar conclusion can be derived from the engine motoring torque graph example shown in Figure 8. For both the speed of 1,000 rpm and for 2,500 rpm adding carbon nanotubes to oil caused not only a decrease in the mean engine motoring torque but also a significant reduction in the maximum values observed in the regular engine work cycle.

4.5. Results of the Research of the FIAT Engine

The FIAT engine was used to carry out a comparative study of the engine oil with a relatively large, equal to 1 % addition of Industrial Grade MWCNTs, produced with the CVD process by NanoLab Waltham, USA. Mobil 1 New

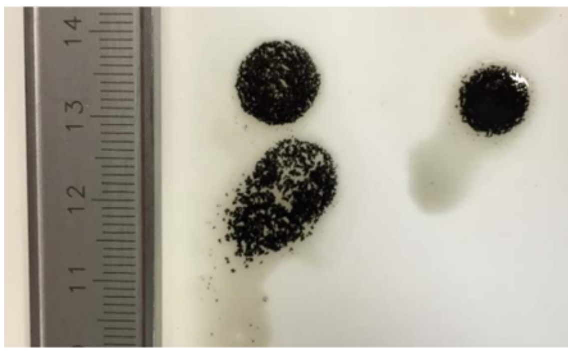

Figure 9. Mobil 1 oil containing 1 % MWCNT, before applying it in the engine; the majority of the CNTs formed agglomerates, but the flowing oil probably also contains well dispersed CNTs, as indicated by its darker shade.

Table 2. FIAT JTD engine test cycle used in comparative studies of reference oil and CNT oil.

No.	n (rpm)	M (Nm)	Time (min)	Cumulative time (min)
1	1000	Engine motoring	2	2
2	idle	0	2	4
3	1000	25	2	6
4	1000	50	2	8
5	idle	0	2	10
6	2000	25	2	12
7	2000	100	2	14
8	3000	25	2	16
9	3000	125	5	21
10	1000	Engine motoring	2	23
11	3000	Engine motoring	2	25

Life with viscosity grade 0W/40 and quality rating API SN/CF was used as the reference oil. CNTs were sonicated for approximately 12 hours, while oil was heated to 80 °C. The procedure used proved to be inefficient (Figure 9). Despite not obtaining a good dispersion of CNTs the oil was poured into the engine expecting an effective dispersion to occur in the process of shear-mixing occurring naturally during engine operation. The oil filter was removed for the duration of the experiment to ensure comparable conditions between the studied oil with CNTs and the reference oil.

The adopted high concentration of CNTs was chosen based on the unambiguously positive results of tribological tests performed for the high concentration of CNTs in the oil, which have been described in Kotnarowski (2009), Liu *et al*. (2004), Hwang *et al*. (2011) and Phan *et al*. (2014). It should be noted, however, that there is a second group of publications which indicate clearly the potentially adverse effects of increasing the concentration of CNTs in the oil (Chauveau, 2010; Chaveau *et al*., 2012; Ettefaghi *et al*., 2013) and proposes the concentration of CNTs to be substantially less than 0.5 %.

In research conducted in a fully automated test bench the test cycle described in Table 2 was used. The study was performed for the reference oil and then for the same oil with the addition of CNTs.

The test was carried out smoothly when the engine was working on the reference oil. The experiment was repeated after cooling the engine and filling it with the oil with the addition of CNTs, immediately after sonicating and oil cooling. The results are shown in Figure 10; the attempt was aborted because after the engine has warmed up, during operation at high speed there was a dangerous drop of oil pressure in the lubrication system.

After the engine cooled off, the oil filter cover and oil sump were disassembled, and it was observed that the oil

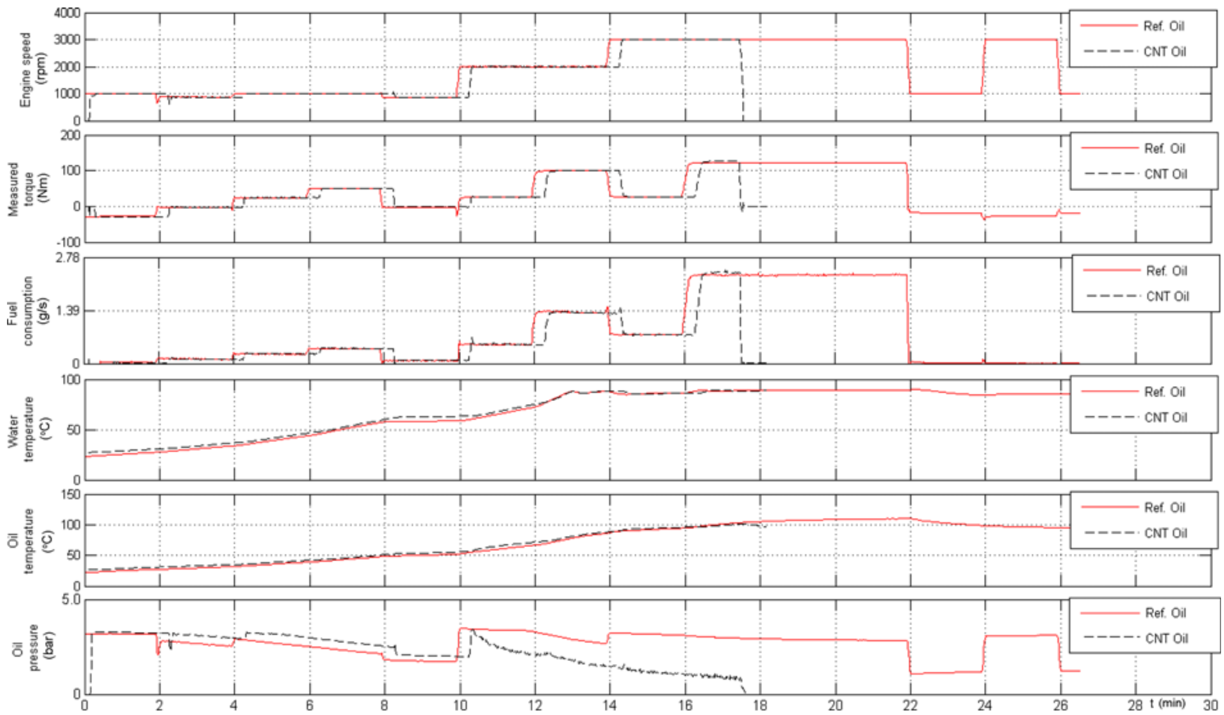

Figure 10. Selected engine parameters recorded during the engine test using the reference oil and the oil with the additin of CNTs.

Figure 11. Interior of the oil filter housing after the test with oil containing 1 % MWCNT; oil changed its consistency to resemble stiff grease and was not flowing back from the filter housing to the oil sump.

changed its physical state and reminded the consistency of grease (Figure 11), wrapping the horizontal and vertical surfaces inside the crankcase. The thickened oil was removed, and after mounting the oil sump the engine was filled several times with fresh oil relatively easily cleaning the engine. Finally the test was repeated in accordance to the protocol in Table 2 and no differences were observed compared with the results before the application of CNTs. The following months of operation of the engine revealed no faults. A sample of oil with modified consistency exhibited stability. Within one year after the engine tests took place the sample only formed a very thin layer of clear, uncolored oil on the surface.

4.6. Results Analysis for the FIAT Engine

The aim of the research conducted on the FIAT engine, was to check the properties of oil with a high content of MWCNTs. Bearing in mind the practical aspects of the widespread use of such an oil in the automotive industry, a standard engine oil and the cheapest variant of MWCNTs were used in the experiments, their dispersion in the heated oil was obtained only by using an ultrasonic disintegrator.

The conducted engine tests show that the oil prepared in this way, characterized by the presence of large CNT agglomerates, does not reduce the engine friction. This can be concluded from the comparison of the torque recorded in the first two minutes of the engine test with the reference oil and the CNT oil.

Over the next eight minutes the warming up the engine worked in the speed range of up to 1,000 rpm, the load varied from idle to moderate values. At that time, there were no irregularities in the operation of the engine and no significant influence of the type of oil used on fuel consumption.

After ten minutes from the start of the test the engine speed was increased to 2,000 rpm for low load. At that point a gradual decrease in oil pressure in the lubrication system was immediately observed for the engine oil with CNTs. The next two phases of the test consisted of increasing the load and speed, and each of these phases led to a deepening of the pressure drop. The test was stopped to prevent damage to the engine.

Both the increase in speed and load leads to increased shear load which the oil lubricating the cylinder wall and the crankshaft bearings are subjected to. It can be assumed therefore, that these factors have led to the effective dispersion of CNTs, which resulted in a drastic reduction in the liquidity of the oil and the loss of pumpability.

Later attempts also suggest that a similar effect can be achieved outside of the engine, by adding sufficiently many CNTs to oil and conducting an intensive and lengthy sonicating process. A similar phenomenon was also mentioned in Chauveau (2010).

The experiment points to the desirability of significantly reducing the CNT content in engine oil in future studies. At the same time a relatively good stability of the obtained grease-similar colloidal system of oil – CNT can be treated as a motivation to explore such a lubricating substance's applications outside the engine.

5. CONCLUSION

The evolution of expectations with respect to the CNTs and their practical applications can be followed in publications (Baughman *et al*., 2002; De Volder *et al*., 2013). It should be emphasized that while the literature provides a number of publications about the unique properties of CNTs in certain chosen aspects, like for example: tensile strength or electric current density, these features do not ensure a successful application in engineering. However, no matter how outstanding any one property of CNTs would be, each of the functionally significant features must meet certain minimum conditions for successful engineering application. Numerous studies have shown favorable tribological properties of CNTs, while the research work presented in this article was aimed to search for optimal exact solutions enabling the use of CNTs in the engine oil.

The research results presented in the article lead to the following concluding remarks:

(1) The use of an oil supplemented with about 0.5 % of its mass with MWCNTs obtained from low-cost mass production CNT process leads to a noticeable reduction in friction losses. Research carried out on the hot TDI engine led to registering a decrease in the total motoring torque by about 4 % at engine speed equal to 2,500 rpm and up to 7 % at 1,000 rpm.

(2) Non-engine tribological tests show that the addition of CNTs to the oil leads to a reduction in friction, both in terms of boundary lubrication regime and elastohydrodynamic regime (Chauveau, 2010). More favorable results obtained at low engine speed may indicate a particularly high positive significance of

CNTs in boundary lubricating regime. Due to the expected benefits in terms of engine performance and the fuel consumption this effect is preferred.

(3) During the first few minutes of the VW engine warm-up, conducted immediately after pouring oil with CNTs that were previously dispersed using only the sonicating process, initially showed no differences in friction losses between the reference oil and the oil enriched with CNTs. The difference in favor of the oil with CNTs became first noticeable only after about 10 minutes of operation. Although this effect may be associated only with the engine temperature, it is more likely that the conditions in the engine led to shear mixing and an effective increase in the dispersion of CNTs in the oil. Such a hypothesis is confirmed by the results of the test carried out on the FIAT engine.

(4) The large, amounting to 1 % of the oil mass, concentration of CNTs observed in some of the tribological studies mentioned in the article cannot be used in the engine oil, as the oil loses its pumpability and ceases to perform its function.

(5) Adding CNTs to the engine oil can significantly reduce the friction losses of the engine. Moreover, greater thermal conductivity of oil (Phan *et al*., 2014) is likely to play a key role in the cooling of critical engine parts such as pistons (Dörnenburg *et al*., 2010; Backhaus, 2009; Ottliczky *et al*., 2011). Achieving these benefits, however, must be preceded by the development of an effective method of dispersion of CNTs in oil, even at the expense of a compromise involving a substantial reduction of the concentration of CNTs in oil.

(6) In none of the engines tested the addition of CNTs to the oil, even in amounts leading to the loss of oil pumpability, resulted in engine damage. Remaining CNTs can be removed easily by several oil changes. The friction losses measured after the CNT experiment were the same as before the study, which seems to indicate that the formation of stable layers of CNTs on friction surfaces does not occur.

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