Influence of engine oils dilution by fuels on their viscosity, flash point and fire point

D. Ljubas, H. Krpan, I. Matanović

In this project the influence of dilution of synthetic and mineral engine oils with two commercial fuels – gasoline (type Eurosuper 95) and diesel fuel (type eurodiesel) was studied. The situation that could really occur in the automotive engine was simulated – a breakthrough of unburned fuel to engine oil and its mixing and dissolution. Viscosity, fire point and flash point were chosen as the most important parameters to follow the changes in oil-fuel mixtures. The dilution range was between 0 and 10 wt% of fuel in the oil-fuel mixture. The samples used in this investigation were bought directly from the two producers present on the Croatian market, without further modification. The samples were multigrade mineral and synthetic oils – mineral oil with SAE gradation 15W-40 and synthetic oil with SAE gradation 5W-30. The changes of oil properties were too high for assumed safe use in engines in the case of oil dilution with 10 wt% of gasoline. The dilution of oil with 5 wt% of gasoline was maximal level of dilution that could be expected to be still adequate for use in engines, because the flash points of these mixtures were mostly near 150 °C, which is assumed as maximal allowed working temperature of engine oil. The properties of mixtures of the same oils with diesel fuel showed smaller changes than mixtures with gasoline.

Key words: engine oil, fuel, viscosity, flash point, fire point

1. Introduction
Very important component for safe and undisturbed functioning of any internal combustion engine is a sound lubrication of vital parts with engine (motor) oil. Simultaneously with engines development, new requirements were also set for engine oils in order to get more power from the engines - to withstand higher working temperatures, wear and load and to last longer. At first mineral engine oils were used, but synthetic engine oils that could fulfill the highest requirements are more and more implemented. Nowadays, technically and commercially, engine oils have gained more than 60% of market share on the global market of lubricants.

For proper functioning of the engine, engine oil must fulfill five basic requirements: minimizing wear; assisting in cooling, keeping the compression ratio, reducing corrosion and friction and controlling the deposits. The highest rate of wear arises by starting the engine, because oil could not reach immediately all the critical parts of the engine. When the engine is warmed up, oil should not become too low viscous, i.e. the oil film should keep proper thickness to ensure adequate wear protection of the engine.

Owing to different reasons, fuels in Otto and Diesel engines do not always burn completely. Higher part of this unburned and/or partially burned fuel leaves the engine with exhaust gasses, but a smaller part could reach the housing of the engine and mix with, or dissolve in engine oil. That could cause total or partial dissolution of the fuel in oil (solubility of fuels in engine oils depends on a variety of parameters, including the fuel chemical composition, the oil chemical composition, the temperature, the engine cold-start frequency, the compression ratio, presence of foreign particles in oil, water, soot, etc.) that could cause a change in engine oil properties and even a drastic case could occur - engine oil contaminated with fuel could become inadequate for use. A solution of unburned fuels (gasoline “Eurosuper 95” and diesel fuel “Eurodiesel” are used in this study) in engine oils (mineral and synthetic) causes changes of oil properties that should be followed with adequate analyses. In this study the authors assumed that for practical use it could be important to analyze the following properties of oil-fuel mixtures: viscosity (in order to follow oil film stability) and flash and fire point (in order to follow the lubrication system safety).

According to the published results, oil films should be stable up to 10 wt% of fuel dilution. Some authors followed certain specific parameters of oils in the case of dilution with fuel – e.g. friction moment in dependence with the load: mineral oils even at 1% of fuel dilution loose their properties considerably and at 7% dilution they lose their properties of wear protection totally. In the same experiment synthetic oils showed better stability resistance, but also with 7% of dilution with fuel they lose most of their lubrication properties. Other authors observed that for gasoline-fueled engines the maximal level of oil dilution is 4%, but some of them give general warnings, e.g. amount of fuel in engine oil of 5% is high enough to lower considerably the flash point or to weaken considerably the oil film stability.

The goal of this research was to investigate the change of properties of pure engine oils (two mineral and two synthetic engine oil samples that are present on the Croatian market) when they are diluted by (mixed with) different amounts of different commercial fuels – gasoline (type Eurosuper 95) and diesel fuel (type Eurodiesel) and to observe the critical amounts of fuel in oil-fuel mixtures that could cause problems in exploitation.
1.1 Engine oils viscosity

Viscosity is one of the most significant properties of any lubricating oil.\(^{15,20}\) It is the measure of internal friction in a fluid which acts as a resistance to molecule position’s changes in moving fluid exposed to shear stress. Since they are used in a wide spectra of application, lubricating oils must keep their properties in different working conditions, but viscosity of the best oils should change minimally in the working temperatures range. The viscosities classification of engine oils was grounded by SAE (Society of Automotive Engineers) in the document SAE J300 engine Oil Viscosity Classification.\(^{14,15}\)

In this study the viscosity of oils was determined at 20.0 and 40.0 °C. To calculate the viscosity at 100.0 °C, an extrapolation of the empirical Ubbelohde-Walther equation was used, which represents the linear relationship of viscosity with temperature\(^{1,15}\) and is described in more detail in DIN 51563\(^6\) and DIN 53017.\(^5\) At first the viscosity-temperature slope \(m\) was determined according to equation (1) and after that the viscosity at other temperatures could be calculated:

\[
m = \frac{W_{t_2} - W_{t_1}}{\log T_{t_2} - \log T_{t_1}}
\]  

where \(m\) is the viscosity-temperature slope, \(W_{t_i} = \log \left(\nu_{t_i} + 0.8\right)\), \(\nu_{t_i}\) and \(\nu_{t_2}\) [mm\(^2\)/s] are kinematic viscosities at temperatures \(T_{t_1}\) and \(T_{t_2}\) [K].

The density of the oils was measured at 20°C. Densities at other temperatures were calculated according to equation (2) and (3), proposed in DIN 51 757 – Appendix B:\(^6\)

\[
\rho(15°C) = \frac{\rho(15°C)}{K_2} + \frac{\rho(15°C)}{K_1}
\]

where \(\alpha(15°C)\) is the coefficient of thermal expansion [°C\(^{-1}\)], \(\rho(15°C)\) is density at 15 °C [kg/m\(^3\)] and \(K_0\) and \(K_1\) are specific constants according to DIN 51 757 [kg/m\(^3\)°C].

Volumetric thermal expansion coefficient at temperature \(\theta = \beta_0\) was calculated using the equation (3):

\[
\beta_0 = \frac{\rho(\theta)}{\rho(15°C)} = \exp\left[-\alpha(15°C) \cdot \Delta \theta \cdot (1 + a(15°C) \cdot 0.8 \cdot \Delta \theta)\right]
\]

where \(\rho(\theta)\) is density at measured temperature [kg/m\(^3\)], \(\rho(15°C)\) is density at 15 °C [kg/m\(^3\)] and \(\Delta \theta\) is the temperature difference (\(\theta - 15\)) [°C].

1.2 Flash point and fire point

The flash point of oil is the lowest temperature of oil at which the application of defined test flames causes the vapors above the surface to ignite and the release of vapors at this temperature is not sufficiently rapid to sustain combustion.\(^1,12,18\) However, if heating is continued, a temperature will be reached at which vapors are released rapidly enough to support combustion longer than 5 s. This temperature is called the fire point and for engine oils is usually 20-30 higher than flash point.

Flash and fire tests are significant to consumers under certain circumstances for safety considerations, as can be seen in Table 1. In the inspection of used oil, a significant reduction in the flash point usually indicates contamination with fuel or other lower flash point fluid. Depending on the flash point, liquids are divided in four groups, i.e. classes of hazard, Table 1. Normally, engine oils have flash points above 200 °C and therewith they are out of classification as hazardous liquids and out of expected working temperatures, usually between 100 and 150 °C. However, small amounts of fuel could make the oil/fuel mixture hazardous according to Table 1 or its fire point could fall in the working temperatures interval, which should be avoided.

2. Experimental

2.1 Apparatus

The fuel/oil mixtures were prepared using digital balance AG240 from METTLER and magnetic mixer Rotamix MM5 from TEHTNICA. Thermostatic bath M3 from LAUDA was used to ensure constant temperatures for viscosity measurements. For dynamic viscosity measurements rheomat RM 180 from METTLER was used, according to the standard DIN 53018, Part 3.\(^5\)

Flash and fire points above 100 °C were measured using Cleveland-Semi Automatic system with open cup from WALTER HERZOG, and for flash and fire points under 100 °C Pensky-Martens Semi Automatic System from WALTER HERZOG with closed cup was used. The procedure of measurement followed the standards DIN ISO 25925 and DIN 51758.\(^7\) Atmospheric pressure during the flash and fire point measurements was controlled with barometer No. 99060 from G. LUFFT MESS-UND REGELTECHNIK.

Table 1. Flash point and classes of hazard\(^{1,19}\)

<table>
<thead>
<tr>
<th>Hazard class</th>
<th>Flash point [°C]</th>
<th>Method</th>
<th>Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.</td>
<td>below + 21</td>
<td>Closed cup Abel - Pensky</td>
<td>DIN 51755</td>
</tr>
<tr>
<td>II.</td>
<td>below + 55</td>
<td>Closed cup Abel - Pensky</td>
<td>DIN 51755</td>
</tr>
<tr>
<td>III.</td>
<td>Below +100</td>
<td>Closed cup Pensky – Martens</td>
<td>DIN 51758</td>
</tr>
<tr>
<td>No hazard</td>
<td>over +100</td>
<td>Open cup- Cleveland</td>
<td>DIN ISO 2592</td>
</tr>
</tbody>
</table>

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2.2 Fuel and engine oil mixtures

Two mineral and two synthetic engine oils from two producers that are present on the Croatian market were chosen.

For further analyses they are marked as follows:

a) Producer A: mineral oil (SAE 15W-40, API SJ/CF) is marked with “MO-A”;

b) Producer A: synthetic oil (SAE 5W-30, API SL/CF) is marked with “SO-A”;

c) Producer B: mineral oil (SAE 15W-40, API SG/CD) is marked with “MO-B”;

d) Producer B: synthetic oil (SAE 5W-30, API SL/CF) is marked with “SO-B”

The fuel samples used in this study were commercial samples of motor gasoline - type Eurosuper 95 (ES 95) and of diesel fuel – type Eurodiesel (ED), taken in summer period, without further modification.

ES 95 is unleaded motor gasoline that completely meets the requirements of the European standard EN 228:2004 and ED meets the requirements of the European standard EN 590:2004. Both fuels are in compliance with EURO IV requirements on quality and emissions, too.

The following mixtures of oils and fuels were prepared and examined:

1. MO-A + ES 95 (0, 0.5, 1.0, 3.0, 5.0 and 10.0 wt %)
2. MO-A + ED (0, 0.5, 1.0, 3.0, 5.0 and 10.0 wt %)

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### Table 2. Overview of dynamic viscosity $\mu$, density $\rho$ and kinematic viscosity $\nu$ of pure oils at different temperatures

<table>
<thead>
<tr>
<th>$\delta$, °C</th>
<th>MO-A</th>
<th>SO-A</th>
<th>MO-B</th>
<th>SO-B</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu$ [Pa·s]</td>
<td>20</td>
<td>0.2797</td>
<td>0.862</td>
<td>0.851</td>
</tr>
<tr>
<td>$\rho$ [kg/dm³]</td>
<td>40</td>
<td>0.0837</td>
<td>0.0959</td>
<td>0.838</td>
</tr>
<tr>
<td>$\nu$ [mm²/s]</td>
<td>100</td>
<td>0.0115</td>
<td>0.0009</td>
<td>0.801</td>
</tr>
</tbody>
</table>

### Table 3. Overview of flash point, fire point and viscosity index of pure oils

<table>
<thead>
<tr>
<th></th>
<th>MO-A</th>
<th>SO-A</th>
<th>MO-B</th>
<th>SO-B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flash point, °C</td>
<td>224.5</td>
<td>226.5</td>
<td>222</td>
<td>219</td>
</tr>
<tr>
<td>Fire point, °C</td>
<td>245.0</td>
<td>241.0</td>
<td>241</td>
<td>243</td>
</tr>
<tr>
<td>Viscosity index (VI)</td>
<td>134.0</td>
<td>157.0</td>
<td>141</td>
<td>153</td>
</tr>
</tbody>
</table>

### Table 4. Overview of dynamic viscosity $\mu$, density $\rho$, kinematic viscosity $\nu$ and flash point of pure fuels at different temperatures

<table>
<thead>
<tr>
<th>GASOLINE EUROSUPER 95 (ES 95)</th>
<th>DIESEL FUEL EURODIESEL (ED)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu$, Pa·s (20 °C)</td>
<td>0.003</td>
</tr>
<tr>
<td>$\rho$, kg/dm³ (20 °C)</td>
<td>0.745</td>
</tr>
<tr>
<td>$\nu$, mm²/s (20 °C)</td>
<td>4.030</td>
</tr>
<tr>
<td>Flash point, °C</td>
<td>&lt; 0</td>
</tr>
</tbody>
</table>

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Fig. 1. Properties change of oil-gasoline mixture: (a) quantity of gasoline amounts up to 10 wt% in mineral oil, (b) quantity of gasoline amounts up to 10 wt% in synthetic oil

Sl. 1. Promjene svojstava smjese ulje-benzin: (a) do količine 10 wt% benzina u mineralnom ulju MO-A i (b) do količine 10 wt% benzina u sintetičkom ulju SO-A
3. MO-B + ES 95 (0, 3.0 and 5.0 wt %)
4. MO-B + ED (0, 3.0 and 5.0 wt %)
5. SO-A + ES 95 (0, 1.0, 3.0 and 5.0 wt %)
6. SO-A + ED (0, 1.0, 3.0 and 5.0 wt %)
7. SO-B + ES 95 (0, 3.0 and 5.0 wt %)
8. SO-B + ED (0, 3.0 and 5.0 wt %)

After weighing of oil and adding of fuel, every sample was mixed in a magnetic mixer for min. 60 minutes in well-stoppered bottles.

3. Results and discussion

Dynamic viscosity was determined by rotational viscometer (rheomat) at 20.0 and 40.0 °C. Kinematic viscosity was calculated using the data from dynamic viscosity measurements and from the data for density. Density was measured at 20 °C and for other temperatures it was calculated using the procedure described in DIN 51757 – Appendix B and equations (2) and (3). Equation (1) was used to calculate kinematic viscosity at 100.0 °C.

Atmospheric pressure in a laboratory during the flash and fire point determination was controlled with barometer. The pressure varied between 994 and 1001 hPa and it was not necessary to correct the measured results.

3.1 Properties of pure oils and fuels

The parameters of pure oils, i.e. unmixed with fuels, are shown in tables 2 and 3 and parameters of fuels can be seen in Table 4.

Viscosities of oils are significantly different for mineral and synthetic oils (as a result of author’s choice of different oil gradations), but flash and fire points are very close to each other. All the parameters for Eurodiesel fuel are higher than for gasoline Eurosuper 95.

3.2 Determination of dilution limits of fuels

The samples MO-A+ES95 and SO-A+ES95 are prepared with 0.5, 1.0, 3.0, 5.0 and 10.0 wt% of gasoline. The results are shown in Figure 1.

Figure 1 shows that fire point and flash point of both oil-fuel mixtures are too low for adequate use in the engine for both types of engine oils in the case of 10 wt% gasoline content. The 10 wt% mixture is in hazard class III (according to Table 1). Such a content of gasoline in MO-A and SO-A is too high for normal exploitation in the engine (up to 150 °C). Figure 1 also shows that fire and flash points of oil-fuel mixtures with 3 wt% of gasoline are above the limit for exploitation (above 150 °C) and mixtures with 5 wt% of gasoline are close to, or already in the area of working oil temperatures. Therefore the authors decided to investigate oil-fuel mixtures up to 5 wt%, assuming that higher fuel contents are not adequate for practical use and should be avoided.

3.3 Results of measurement of oil-fuel mixtures with 5 wt% of fuels

Parameters of all oils mixed with all fuels with 5 wt% are shown in the tables 5, 6, 7 and 8.

From Tables 2, 3, 5 - 8 it can be seen that both dynamic and kinematic viscosities of mineral oils are considerably higher than viscosities of synthetic oils and with increase of temperature this difference decreases. Since the fuels are of different viscosities and flash and fire points, properties of oil-fuel mixtures show the same

<table>
<thead>
<tr>
<th>Table 5. Overview of dynamic viscosity, density and kinematic viscosity of the 5 wt% mixture of gasoline ES 95 with oils at different temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ, °C</td>
</tr>
<tr>
<td>20</td>
</tr>
<tr>
<td>40</td>
</tr>
<tr>
<td>100</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 6. Overview of flash point and fire point of the 5 wt% mixture of gasoline ES 95 with oils</th>
</tr>
</thead>
<tbody>
<tr>
<td>η, °C</td>
</tr>
<tr>
<td>Flash point, °C</td>
</tr>
<tr>
<td>Fire point, °C</td>
</tr>
</tbody>
</table>

* - exceeds class „no hazard” and enters the hazard class III

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trend – lower viscous gasoline mixed with the same oil gives a mixture that has lower overall viscosity than a mixture of diesel fuel and the same oil. The same situation is observed in flash and fire points. Significant decrease of flash point (to 91.5 °C) is observed in combination of SO-A with 5 wt% of ES 95 assuming that this mixture is no more adequate for use in the engine. Other flash point results, when dilution fuel is gasoline, are rather close to each other and range from 144-156 °C.

In case of dilution of engine oils with 5 wt% of diesel fuel ED flash points remain rather high and still adequate for use in the engine. This lower decrease of flash points is expected since the flash point of pure ED is higher than the flash point of gasoline (Table 4).

### 3.4 Influence of gasoline content on engine oil viscosity

In Figure 2 can be seen that quantities of ES 95 in the mixture with mineral engine oils even below 3 wt% are capable to make the oil inadequate to keep the proposed SAE gradation SAE 40 (15W-40), because their kinematic viscosities drop below 12.5 mm²/s.

In synthetic oils, a critical dose of gasoline ES 95 that could cause the oil inadequacy for proposed SAE classification is 5 wt%. In case of SO-A the mixture does not satisfy the proposed gradation and the second mixture with SO-B becomes very close to the proposed limit of minimum 9.3 mm²/s.

### 3.5 Influence of diesel fuel content on viscosity of engine oil

In Figure 3 can be observed that quantities of ED in the mixture with synthetic engine oils up to 5 wt % satisfy the proposed SAE classification (5W-30) and stay in the interval from 9.3 to 12.5 mm²/s. In case of mineral oils, critical dilution amount of fuel is 3 wt% for MO-B and 5 wt % of ED for MO-A.

### 3.6 Influence of gasoline fuel content on flash and fire points of engine oils

In Figure 4 can be seen that the values of flash points in the case of 3 wt% of ES 95 in oil are regularly less than 200 °C and in the case of 5 wt% of ES 95 close to 150 °C. The SO-A with 5 wt% of gasoline shows the highest drop of flash point– from 226.5 °C to 91.5 °C and therefore in hazard classes of liquids enters from “no hazard” class to class gradation III (Table 1). The second synthetic oil SO-B has similar characteristics of flash and fire points decrease as mineral oils.

| Table 8. Overview of flash point and fire point of the 5 wt % mixture of fuel oil ED with oils |
|--------------------------------------|-------------------------------------|--------------------------------------|
|                                      | MO-A + 5% ED                       | SO-A + 5% ED                        | MO-B + 5% ED                        |
| Flash point, °C                      | 201.5                              | 194.5                               | 204.0                               |
| Fire point, °C                       | 216.5                              | 215.5                               | 221.5                               |
A possible reason for high decrease of flash point for SO-A mixed with 5 wt% of ES 95 could be the fact that very small amounts of lighter gasoline fractions could remain undissolved in oil and cause an effect identical to flash point. However, heavier fractions of gasoline ES 95, obviously well miscible with oil, remain in the oil-fuel mixture and give a decrease of fire point similar to other mixtures.

Fire point values for all the samples are close, with slightly lower values for synthetic oils.

3.7 Influence of diesel fuel content on flash and fire points of engine oils

The changes of flash and fire points for mixtures of oils with ED are shown in Figure 5.

The dilution of engine oils with diesel fuel ED affects the flash and fire points of the mixture less than does the dilution of oils with gasoline ES 95 – Figures 4 and 5.

3.8 Following the stability of oil-fuel mixtures

The stability of fuel-oil mixtures was followed by measuring and comparing the dynamic viscosities of the 4 freshly prepared samples of oil MO-A and SO-A with 5 wt% fuel and viscosities of the same samples after they were kept 180 days in closed glass bottles in the dark, without mixing. The comparison of results is shown in Figure 6.

(Figure 6)

Figure 6 shows that viscosity changes of oil-fuel mixtures even after a long time remain relatively small, on average less than 4%. Since the samples were kept without mixing, and pouring of the samples in measuring device was done carefully and without intensive mixing, it could be assumed that oil-fuel mixtures up to 5 wt% of fuels are stable mixtures, i.e. significant separation of components was not observed.

4. Conclusions

In this study three parameters important for characterization of engine oils during exploitation were followed: viscosity, flash point and fire point.

Experiments carried out on mineral (SAE classification 15W-40) and synthetic engine oils (SAE classification 5W-30) from two producers present on the Croatian oil market and two types of fuel – gasoline and diesel fuel, led us to the following conclusions:

A) The chosen mineral engine oils have higher viscosity and lower viscosity index than synthetic oils. Both types of oils show close values for flash and fire points, around 225 and 245 °C, respectively.

B) The oil-fuel mixtures with 5 wt% of fuel even after 180 days of keeping in the dark without mixing seem to be stable, i.e. the observed viscosity changes are less than 4%.

C) Viscosities and flash and fire points of oils decrease with amounts of added gasoline and diesel fuel. Higher viscosity decrease is observed when oil is diluted with gasoline than with equal amount of diesel fuel.

The viscosities of both mineral oils with 5 wt% of fuel do not satisfy the proposed viscosity range of SAE 40 gradation according to the SAE J300 classification system and they change the gradation from SAE 40 to SAE 30.

Both synthetic oils by dilution with up to 3 wt% of gasoline and up to 5 wt% of diesel fuel keep their proposed gradation SAE 30, but with 5 wt% of gasoline a change to gradation SAE 20 is possible.

D) A breakthrough of unburned gasoline to engine oils MO-A and SO-A in the amount of 10 wt% causes the oil flash and fire points decrease to values that are no more acceptable for use (less than 50 °C).
The fire points of oils diluted with 5 wt% of fuels are mostly above the maximal expected working temperature of 150 °C, which suggests that these amounts of fuel in oils could be adequate for use for short periods of time.

The obtained results are in agreement with the relevant published data for fuel-engine oil mixtures, where amounts of fuels in oils of up to 4 or 5% are foreseen as acceptable levels, while amounts of 7 to 10% of fuels in oils are considered as unacceptable levels.

5. Literature

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