APPRAOCHIMATE TEST OF THE THERMAL DEGRADATION OF ENGINE OIL

J. Pošta, B. Peterka

Department for Quality and Dependability of Machines, Faculty of Engineering, Czech University of Life Sciences Prague, Czech Republic

Abstract
Engine oils are one of the most stressed operating fluids of combustion engines. European manufacturers of combustion engines are creating degradation models of engine oils taking into account the operational conditions of each of vehicle. The engine oil is checked and changed on the base of these models. For stationary working gas engines of cogeneration units, these models are not fully suitable. This kind of combustion engines has very high requirements on the quality of engine oils, especially on the thermo-oxidative stability. Modern oils with high portion of additives are commonly used. In this case, tribodiagnostic does not serve as predictive utility, but serves as confirmation of properly chosen service period of engine oil.

Experiment was set to prove the possibility of evaluation of thermo-oxidative degradation of synthetic, hydrocracked and mineral oils. The change of colour, caused due to high temperature and presence of air, was chosen as evaluation criteria. The aim of article was to set time course of colour changes. This paper presents results for synthetic, hydrocracked and mineral oils.

Key words: engine oil, thermo-oxidation, colour changes, image analysis.

INTRODUCTION
Engine oils are one of the most stressed operating fluids of combustion engines. Operating conditions are more difficult and requirements for engine oils are ever growing. European manufactures of engine oils are involved in searching of optimal service period of engine oils replacement. Manufacturers are creating degradation models of engine oils taking into account the operational conditions of each of car type. The engine oil is checked and replaced on the base of these models.

Combustion engines are also used in very different applications. Then, the operation condition of combustion engine is very different than in a vehicle. In those cases, the engine oils degradation models used for cars are not fully suitable, so it is necessary to seek for more suitable models. Such as gas combustion engines of cogeneration units of biogas plants are continuously working 24 hours per day while high load and constant speed. This operating conditions result in thermal stress of engine oil, which is also exposed to acid products mainly created from sulphurous parts of biogas combustion process. This operational mode has extremely high requirements on engine oils, especially on their thermo-oxidative stability. Therefore, high quality and high additive containing oils belonging to Group II and Group III are most used. The need to replace oil filling is relatively soon in case of those oils. According to engine type, the service period is in range of 500 to 2000 operating hours. The engine has to be stopped due to oil change. Engine oil and oil filters are changed and the centrifugal cleaner must be cleaned.

In most of bio-gas stations, the change of engine oil is controlled such that small sample of used oil is taken and subjected to tribological analysis. This analysis is commonly done in independent and accredited laboratory. Based on analysis results and taking into account the content of sulphur in biogas obtained during simplified operation monitoring, the service period is appropriately changed. Thus applied tribotechnical diagnostic is not predictive in nature and only serves as feedback of the accuracy of estimated time of oil change.

MACHALIKOVA ET. AL. (2013) states, that detonation level of engine oil can be determined using comparative differential spectroscopy of original oil and degraded oil. Therefore, it is possible to relatively compare the content of oxidative, nitrating and sulphating products, water content, fuel content, coolant content and decrease of content of anti-oxidation additives. Due to both temperature stress and water in oil leakage, the exhaustion of base anti-wear and anti-oxidative additives occurs. The oil change is recommended in case of decrease of the content below 20% compared to content of additives in new oil.

Spectroscopy analysis uses complex equipment. Result of analysis is available in relatively long time and operation itself is relatively expensive. Therefore, it
would be useful to have at least approximate method for easy, fast and inexpensive evaluation of change of operating conditions of given oil. This would enable correction of real operational time in particular operating conditions.

It is known that the degradation process of engine oil, which will require its change, pass in different ways in case of various types of engine oils. As an example CERNY (2005) states that exploited oil keeps lubricating and load-carrying capacity can be even higher as effect of polar oxidation products formed while machine operation. Waste oil has to be changed for other reasons than lubricity loss. Waste oils contain, in most cases, mechanical wear particles and lot of soot particles in case of diesel engines. Petrol engines oils can be excessively oxidative deteriorated and they may effect significantly corrosion, etc. SVOBODA (2015) states that lubrication of oil is crucial in term of boundary friction. But CERNY (2015) also states that while oil oxidation there are created numerous oxidation products, i.e. while nitrification organic nitrates are formed. These substances have polar character and affect positively on carrying-load capacity of lubricating film and lubricity of oil in general. On the other side during operation there is loss of synthetic antiwear and friction modifiers additives which act also as antioxidants. The final effect is that intensity of oil lubricity degradation after decrease of additives concentration is faster. NOVACEK (2013) states that transition of actual oils from Group I to Group II and III was accompanied with general changes in oil composition. New generation of oils mentioned above deteriorate another way as traditional oils. Nonlinear degradation of most of modern lubricants is determined by antioxidants additive selection and oxidation stability of base oils belonging to Group II and III. This base oils show lower oxidation stability than Group II and III. This kinds of oils deteriorate rapidly when they lose antioxidant additives. As consequence, most of standard oil analyses gives none of alert when the oil begins deteriorate or exhibit oil deposits.

It is obvious, that thermo-oxidation of engine oil in initial stages does not mean a significant risk of lubricity loss. As the thermo-oxidation process continues, the oxidation products are polymerising and creating strongly adhesive deposits that could affect function of combustion engine. Increasing content of polymerised oxidation products in engine oil is accompanied by a change of colour of engine oil – oil darkening.

VUTAN HIEN (2016) states that change in colour can be evaluated by image analysis of spot that engine oil will leave on the filtration membrane. The coloured spot can be obtained either by filtering of specified amount of oil or by dropping the oil onto filtration paper. Partial influence of permanent thermal stress on the process of darkening of engine oil was experimentally proved. Results of this experiment are described in this article.

MATERIALS AND METHODS

Materials

Experiment was performed using mineral oil Group I, hydrocracked oil Group II and synthetic oil Group III. Base technical parameters of tested engine oils are shown in Tab. 1.

Mineral oil under test is declared as oil with low content of sulphated ash intended for use in stationary gas engines and for use in engines without turbocharger. Hydrocracked oil under test is declared as oil with mid-range content of sulphated ash, without content of Zn, intended for use in all types of stationary gas engines. Synthetic oil under test is declared as oil without content of Zn, containing very low sulphur and phosphor content, intended for use in diesel engine equipped with a turbocharger, engines of commercial vehicles and engines equipped with exhaust gas treatment.

Methods

Engine oil samples of volume 80 ml were kept at temperature 132°C (±3°C) for 382 hours. At 24 hour interval the drop of oil from each of particular sample was dropped in the centre of Macherey-Nagel MN 1640w filtration paper. After next 12 hours was the resultant colour spot digitzed by scanner to TIF file with 24 bit of colour depth and 1200 dpi resolution. Evaluation of images was performed in Zoner Photo Studio software. The evaluated area was taken as centred circle of 500 pixels in diameter. Using the Advanced histogram function, the evaluation in RGB colour space was performed for each of additive primary colours. Intensity and colour distribution for each of luminosity (intensity), red (R), green (G) and blue (B) components was obtained.
In RGB colour space model each pixel can be represented as combination of three colours (RGB), while intensity of each component ranges from 0 to 255. With this system, 16,777,216 (256^3) discrete combinations of R, G and B values are specified.

For the RGB model, this is represented by a cube using non-negative values within a 0–255 range, assigning black to the origin at the vertex (0, 0, 0), and with increasing intensity values running along the three axes up to white at the vertex (255, 255, 255), diagonally opposite black.

A colour histogram of an image represents the distribution of the composition of colours in the image. It shows different types of colours appeared and the number of pixels in each type of the colours appeared.

Fig. 2 show examples of luminance histogram and colour histograms of all RGB colour components for one particular colour spot of oil under test.

Tab. 1. – Base technical parameters of tested engine oils

<table>
<thead>
<tr>
<th>Properties</th>
<th>Units</th>
<th>Mineral oil</th>
<th>Hydrocracked oil</th>
<th>Synthetic oil</th>
<th>Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAE classification</td>
<td>-</td>
<td>40</td>
<td>---</td>
<td>5W-30</td>
<td>SAE J300</td>
</tr>
<tr>
<td>Density at 15°C</td>
<td>kg.m⁻³</td>
<td>893</td>
<td>866</td>
<td>861</td>
<td>DIN 51 757</td>
</tr>
<tr>
<td>Flash point</td>
<td>°C</td>
<td>240</td>
<td>260</td>
<td>238</td>
<td>DIN ISO 2592</td>
</tr>
<tr>
<td>Pour point</td>
<td>°C</td>
<td>-15</td>
<td>-35</td>
<td>-45</td>
<td>DIN ISO 3016</td>
</tr>
<tr>
<td>TBN</td>
<td>mgKOH.g⁻¹</td>
<td>5.5</td>
<td>8.9</td>
<td>---</td>
<td>DIN ISO 3771</td>
</tr>
<tr>
<td>Sulphate ash</td>
<td>% hm.</td>
<td>0.45</td>
<td>0.7</td>
<td>0.99</td>
<td>DIN 51 575</td>
</tr>
<tr>
<td>Kinematic viscosity at 40°C</td>
<td>mm².s⁻¹</td>
<td>149</td>
<td>105.00</td>
<td>71.8</td>
<td>DIN 51 562-1</td>
</tr>
<tr>
<td>Kinematic viscosity at 100°C</td>
<td>mm².s⁻¹</td>
<td>14.5</td>
<td>13.40</td>
<td>12.16</td>
<td>DIN 51 562-1</td>
</tr>
</tbody>
</table>

Fig. 1. – RGB colour model

Fig. 2. – Example of histograms
RESULTS
Results of image analysis of synthetic oil Group III, hydrocracked oil Group II and mineral oil Group I are shown in Fig. 4, Fig. 5 and Fig. 6 respectively.

**Fig. 3.** — Intensity of RGB components of spot picture of synthetic oil Group III, error bars shown for each graph

**Fig. 4.** — Intensity of RGB components of spot picture of hydrocracked oil Group II, error bars shown for each graph
DISCUSSION
As NOVACEK (2013) states, degradation of almost all of modern lubricants depends on additives selection and on oxidation stability of base oil as well. Oxidation stability of base oils of Group II and Group III is naturally worse than Group I so, when this oils lose antioxidant additives, they deteriorate rapidly. As consequence, most of standard oil analyses gives none of alert when the oil begins degraded or exhibit oil deposits.
In case of synthetic oil Group III with high anti-oxidation additive content, it can be expected that degradation will rise very slowly at the beginning and will rise very progressively when all of additives are exhausted. In case of hydrocracked oil Group II which is also highly doped with anti-oxidation additives, similar behavior can be expected. In case of mineral oil Group I with naturally better anti-oxidation properties and lower content of additives, linear progression of degradation can be expected from the beginning of operating time.
Experimental results correspond with these assumptions. Progress of thermo-oxidation process characterized by colour changes of oil when other influences are omitted, corresponds with statements of NOVACEK (2013), CERNY (2015) and MACHALIKOVA ET AL. (2013)
Progression of degradation of synthetic oil, Fig. 3, corresponds to expected slow degradation rate at the beginning of operating time. Therefore, we can assume that in this particular case, the content of anti-oxidation additives was not exhausted. Progression of degradation of hydrocracked oil, Fig. 4, is from the beginning of operating time relatively faster as is in case of hydrocracked oil Group III with high content of additives, but degradation rate is slight. Progression of degradation of mineral oil, Fig. 5, is faster from the beginning of operating time than in case of hydrocracked and synthetic oil.

CONCLUSIONS
It is obvious, that initial stages of thermo-oxidation process of engine oils do not pose significant risk of loss of lubricity. In case of modern engine oils which are massively highly doped with anti-oxidation additives, the degradation is determined by content of this additives. Degradation rate of this kind of oils is slow at the beginning of operating time, but it can be indirectly monitored as colour change of oil compared to his initial colour.
Experimentally obtained rate of thermo-oxidation which is expressed as change of colour (darkening) during experiment was 4.1% in case of Group I, 8% in case of hydrocracked oil Group II and 10.3% in case of mineral oil. These findings can serve for development of degradation models of engine oils of biogas combustion engines.
ACKNOWLEDGEMENT
This proceeding originated within the project of long time development of IGA CULS Prague 2016: 31190/1312/3117 Effect of mixtures of biofuels on production of nitrogen oxide and smoke of combustion engine during NRSC.

REFERENCES

Corresponding author:
prof. Ing. Josef Pošta, CSc., Department for Quality and Dependability of Machines, Faculty of Engineering, Czech University of Life Sciences Prague, Kamýcká 129, Praha 6, Prague, 16521, Czech Republic, phone: +420 22438 3266, e-mail: posta@tf.czu.cz