Evaluating petrol engine oil deterioration through oxidation and nitration parameters by low-cost IR sensor

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Abstract

For the proper working of the internal combustion engine, engine oil plays a significant role. The performance of the engine is greatly affected by oil that has degenerated. In order to determine the optimal gap between oil changes, it is crucial to measure the deterioration in the engine oil. Multiple parameters like oxidation, nitration, viscosity and so on are brought into use. One of the methods used to quantify the deterioration in the engine oil is the Fourier Transform Infrared (FTIR) spectroscopy. The main parameters of the engine oil are distinguished by this method by utilizing Infrared (IR) absorption at different bandwidths. The two significant parameters in engine oil deterioration are oxidation and nitration. However, the limitation of the FTIR method is that it is more expensive and since it uses huge machinery, it requires a lot of area. Hence, the use of this method is not possible in the field area due to the need for space. It is this major limitation that is the motivation for proposing an inexpensive, yet handy system, using an IR sensor set up, in this paper. This system is used for measuring the transmittance of engine oil that has degenerated. For this paper, we collected random samples at various times from service stations that were specifically authorized. These samples were used in experiments based on the FTIR spectroscopy and UV spectrophotometer and the results were compared using the IR sensor setup. Investigation of the experimental results showed that monitoring oil transmittance using an IR sensor setup is possible, and a robust relationship between oxidation and nitration and the transmittance of the oil was observed. Moreover, a pattern of deterioration for a specific engine oil (SAE 5W30) which is utilized for passenger cars and light duty vehicles was also established.

Keywords Engine oil · Oxidation and nitration · IR sensor · Oil deterioration

Introduction

In order for an internal combustion engine to maintain high levels of performance and yet stay durable, the engine oil that is used is of great significance. Nevertheless, the degradation of oil greatly accelerates if the engine is operated under severe conditions such as very high temperatures, starting up the engine when it is cold or high pressure [1]. To attain the different functions of the engine oil, the parameters of the deterioration in the engine oil undergo multiple

changes. As these parameters of deterioration alter, they have a bearing on the quality of the engine oil. As a result, once these parameters reach a specific value, the oil cannot be used in the engine without affecting the performance and working of the engine. For the purposes of prolonging the period for which the oil can be used, different additives are combined with the oil which in turn make the oil a complex hydrocarbon compound. Even as the oil ages, there are many contaminants such as wear debris, soot, water, glycol which are added to the oil when it is serviced. Given the situation, determining and measuring the level of deterioration in the engine oil becomes very complicated. The two other factors that play a role in this process of deterioration are the driving conditions as well as the engine condition. The manufacturers of the vehicles provide instructions and guidelines as to when to change the engine oil. However, these recommendations assume standard driving conditions. If, however, the distance travelled by the vehicle is less than the kilometre range provided by the manufacturer, and proper

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driving conditions are maintained, chances are that the oil may not deteriorate to the point where it has to be changed. Since India needs to import a large portion of the crude oil that is needed in the manufacture of engine oil, there is a great need to quantify the level of deterioration of the oil before it is replaced during servicing. Besides, keeping track of the deterioration levels also supplies pertinent information about coolant or fuel leakages or extreme wear and tear in the engine which may lead to engine failure thereby reducing the gap between service periods of the vehicle. Multiple methods of measuring the levels of deterioration in the laboratory exist. These methods depend on various parameters like sulfonation, nitration, viscosity, oxidation and hence the total acid as well as total base numbers, the content of glycol and water can be determined. The content of the antioxidants in the oil can also be determined. The use of these methods provides the true levels of deterioration. However, since these methods are destructive in nature, it is far cheaper to change the engine oil, especially in the case of light duty vehicles. Hence, there is a great need to quantify the deterioration of engine oil cheaply, utilizing a testing method that is not ruinous.

Engine oil that is being used can be monitored either offline or it can be monitored online. Engines that are large in size and are stationary, definitely need monitoring in the online condition. For obvious reasons, it is more expensive to do online condition monitoring rather than offline condition monitoring. For engines that are up to 1200 cc and are used in light-duty vehicles or passenger cars or vans, determination of the condition of the oil in the engine can be done by an approximation based on parameters of the vehicle. These parameters can be the length of the travel, the speed of the vehicle, the temperature of the engine and so on. One of the limitations of offline analysis that is done in the laboratory is that a lot more time is required for sampling as well as analysing the results.

Sensors can be used for monitoring some chemical as well as physical parameters of the engine oil which can quantify the level of deterioration. One of the tools that has proven to be very powerful as well as practical for analysis of used oil is IR analysis. IR absorption spectrum can detect the deterioration of multiple oil components. Some of these are nitration, oxidation, etc. IR can also detect various contaminants contained in the oil such as anti-wear components, fuel, soot, sulphate by products, glycol, etc. [2, 3]. One of the most critical parameters that is monitored using FTIR spectroscopy [4–6] in the analysis of used oil is the oxidation index, or the oxidation number. When the temperatures are high and there is oxygen present in the air is when the process of oxidation occurs. It is because of the oxidation that a number of compounds that contain carbonyl like carboxylic acids are formed. The chemical effect of oxidation results in the oil becoming acidic because of the presence

of carboxylic acids, which leads to corrosion. A physical change that oxidation causes is that the viscosity of the oil rises depending on the amount of oxygen that is used up as a result of the process [7, 8]. Based on the type of anti-wear components, sulfonate detergents, material antioxidants, carbonyl compounds, hydroxyl and so on, there is infrared radiation absorption at a characteristic wavelength in all of the covalent chemical bonds in organic molecules [9]. Maleville et al. [8] showed how the process of oxidation is influenced by the aromatic and sulphur content as well as the composition of the oils because of the consumption of oxygen and thin film oxidation tests. Measurements taken of variations in the concentration profiles through the carbonyl (C=O) absorption region ($1820\text{--}1650\text{ cm}^{-1}$), it is found that the by-products mentioned above all have vibrations that are highly characteristic in this region, namely, ketones ($1725\text{--}1705\text{ cm}^{-1}$), carboxylic acid ($1725\text{--}1700\text{ cm}^{-1}$), and ester ($1750\text{--}1725\text{ cm}^{-1}$) [10–12]. The following ASTM standards have been developed based on the huge amount of information that can be got from the IR spectrum as well as the reliable results: ASTM E2412, D7412, D7414, D7415, D7418, and D7624. This includes determining of the scope of the oil tests using the FTIR method [13]. Literature survey shows that near wave numbers 860 cm^{-1} and 970 cm^{-1} is where absorption is the highest and this was related to the oxidation times and for each of these oxidation times, the absorbance rate was quite different from all of the other times [9]. The wavenumbers mentioned above are closer to the IR spectra and measurements of this can be easily taken with the UV spectroscopy method. This method is referred to as a method of absorption spectroscopy/reflectance spectroscopy. For the region that is closer to the IR range measurement and for light in the visible region, this measurement region is used. In order to portion calculable determination of various analytes, this technique is used. Moreover, FTIR method [14] or IR spectral data [15] can be used to determine the total acid number of used mineral oils. In order to monitor oxidative desulphurization of light cycle oil [16] FTIR spectroscopy can also be used. Antioxidants which are possible to be determined by ultra-microelectrodes [17] affect the oxidation of engine oil.

Besides, current literature has also announced partially quantitative supervision of additive depletion (zinc dialkylidithiophosphates) as well as other additive degradation products in an oil matrix that is complex and that emerges from the formulation of oil, deterioration and contamination that includes wear particles, polymerized degradation products as well as soot [18]. Many other types of sensors like inductive, conductive [19] optical and acoustic sensing, integrated sensors for measuring multiple oil properties [20, 21] are used for quantification of engine oil deterioration. For detection of base oil oxidation and for increase in acidity [22], thick film (TF) potentiometric

sensors which depend on ion-selective electrodes are used. Great potential is shown by optical measurement techniques to monitor the quality of oil, particularly in the IR spectral region. An example of this is the multi-channel non-diffractive-infrared (NDIR) absorption or IR spectroscopy [23]. This technique is also utilized in laboratories thereby permitting an improved correlation of online data and the results obtained from the lab. Bley et al. [23] displayed a diminished multi-channel IR sensor system to show the difference between rising oxidation and rising contamination of water for synthetic motor oil [23].

As mentioned in the literature published earlier, the development of an infrared sensor that makes use of attenuated total reflectance (ATR) makes possible the supervision of lubricants online [24]. Rauscher, et al. [25] came up with a sensor that is based on the principle of non-dispersive infrared absorption measurement along with a setup of transmission that is made up of two thin-film infrared emitters as well as two, four-channel pyroelectric detectors. There are seven types of optical bandpass filters that are brought into use for monitoring alterations in the absorption of the infrared spectrum of marine gearbox oil as well as wind turbine oil.

It would be interesting to know if a study of an analysis of engine oil deteriorated in the laboratory would still hold true for samples taken from the field. There are reports done earlier by researchers on experimentally tested oil that was degraded in the laboratory in an environment that was controlled [2, 7, 9, 23, 26]. Studies that have been published in the existing literature show how the existence of a diesel particulate filter (DPF) influences the contents of the contaminants such as Fe, Cr, Ni, Pb as well as the extent of alterations in the physical and chemical parameters like Total Base Number, Total Acid Number, kinematic viscosity during the service life of the engine oil [27]. The primary purpose of this study was to come up with an inexpensive solution to measure the degradation of engine oil using a comparison of the results of the analysis attained from a couple of devices that enabled a rather quick assessment of the quality of the lubricating oils while they were being used with the help of the FTIR technique as well as the transmittance measurement utilizing the UV spectrophotometer. This was in relation to the inexpensive IR sensor setup where transmittance (T) was the amount of light that was transmitted through a solution. The changes that occurred in the specific physiochemical properties of the engine oils while they were being used actually made up the basis of the assessment. The results and discussion section of the paper puts forth information graphically on the intensification and direction of changes in the said physiochemical attributes like the degree of oxidation, the extent of nitration, the alteration in transmittance.

Experimental details

The goal of this paper is to discuss the use of the three techniques, namely, FTIR spectroscopy, UV spectrophotometer and IR sensor method in the identification of engine oil degradation in terms of the changes in Oxidation (D7414/ASTM E2412), Nitration (D7624/ASTM E2412), Transmittance (ASTM 1421 99). The research work reported in this paper is on the basis of the FTIR method. This method is utilized to measure the degradation in the engine oil in relation to alterations in oxidation and nitration. The UV spectrophotometer technique is used to discover the transmittance of the used engine oil which changes because of the degradation in the engine oil. Samples of oil were gathered from cars at random intervals post an oil change to try out the viability of the IR sensor setup to measure the transmittance of the used oil. The oil that was used was 5W30 engine oil. Authorized service stations in the city of Pune were used to collect the samples. For the purposes of the experimentation, the samples of oil were sorted into various classes based on a servicing number which was assigned according to the use of the vehicle in kilometres or months. Samples of oil were taken from the first three servicing cycles.

According to the schedule set up for servicing, the first samples were taken between 0 and 10,000 km or 12 months whichever comes first. The second sample is usually taken from 10,000 to 20,000 km that is to say after a span of 10,000 km after the very first servicing or 12 months before the servicing, whichever comes first. Samples of the oil for the third time were taken from 20,000 to 30,000 km that is to say, 10,000 km after the second servicing or 12 months, whichever comes first. For the purposes of this study, Shell 5W30 (API SM) oil samples are utilized as they are ideal for light commercial vehicles, passenger cars and vans. During the sample collection period as per the availability of vehicles for servicing basis, we got 43 samples for the first servicing. Sample range for the first servicing was from 2323 to 12,432 km i.e. in spite of a specific schedule being provided, some vehicles covered more distance than the recommended distance before servicing or some vehicles were available for servicing because of the duration before next the servicing as per the schedule which was 12 months. Similar to earlier discussion for second servicing 28 samples were available from 2248 to 21,896 km because either the distance was covered or duration between second and first servicing was more than 12 months. Since some of the vehicles that were tested were not driven as much during the first and the second servicing periods, the kilometre range is lower than the kilometre range of the specific servicing period. Oxidation and Nitration measurements of

the FTIR spectrometer method, which is a very common method, are compared to measurements taken using the IR sensor setup for change in oil transmittance.

Experimental method

The most obvious properties that can possibly be used to separate used oils from the new oils are the optical properties of the engine lubricants. Some of these optical attributes include reflection, refractive index, transparency and absorbance. Engine oil that has never been used is able to transfer light through without much resistance. As and when degradation sets in, this transmittance reduces due to the presence of impurities like water, fuel and particulate contamination in the lubricant. There are other factors such as nitration, oxidation and so on which also have an impact on the engine oil deterioration. Any alteration in the transmittance of the engine oil is a sign of changes in the oxidation and nitration of the engine oil.

To begin with, measurements for oxidation and nitration are undertaken using the FTIR spectrometer (make: “Nicolet iS10” FT IR spectrometer). The testing is done at the testing laboratory of Valvoline Cummins Pvt. Ltd., Ambernath, Thane. Figure 1 illustrates the FTIR spectrometer. This is an instrument that is highly sensitive to the working environment and therefore it needs to be operated indoors in a laboratory facility where the temperature can be controlled and the moisture is at a minimum. As the first step in the experiment, nitrogen gas purging is carried out. Next, IR window cleaning is done. This is followed by cell calibration (zinc selenide) with 99.99% purity heptane for a correct path length of 0.01. Desiccators are used to extract moisture and the instrument is recalibrated in case the results are incorrect. At this point, the instrument is all set for readings.

Nicolet iS10 FT IR spectrometer is manufactured by Thermo Scientific Company with OMNIC and Integra software is used for analysis and interpretation of the obtained results.

For analysis of solid samples, the OMNIC software is recommended whereas for analysis of oil, the Integra software is recommended. The OMNIC software can provide FTIR measurement spectra only for two samples. The Integra software, on the other hand, monitors change in the nitration and oxidation values directly using the data stored in the library as reference. There is provision made in this equipment for a reference library that is made up of samples of standard engine oil. However, for exact results, a sample from the first barrel of fresh engine oil is tested and saved in the library with details such as the grade of the oil, the specification, details of additives and the manufacturer and so on. Moreover, this setup also comes with TQ software for the quantification in terms of percentage of the contamination of the parameters such as diesel fuel, glycol water and so on in the engine oil sample. Once each sample is tested the background is verified using *n*-pentane. Hence the background spectrum has to match the reference. Next, the sample of the deteriorated oil is injected with a syringe in a cell for the purposes of measurement as depicted in Fig. 1. There is a restriction of up to 5% soot contaminated deteriorated oil sample for the measurements of this instrument. Due to the sensitivity of the instrument, care must be taken to ensure that preparation of samples using any chemical should not be done close to the instrument. There should not be any air bubbles present while the oil is filled into the sample cell. The instrument uses the Integra software to compare the oil sample spectra that are deteriorated with the fresh engine lubricant sample spectra data from the library. Having done this, the instrument provides results about the different degradation parameters. A very clear peak can be seen in the IR spectrum of a mineral oil that is oxidised at a specified wavenumber range. Once the fresh oil spectrum is subtracted from the old oil spectrum in

(a) FTIR spectrometer

(b) Zinc solenoid cell for engine oil sample

Fig. 1 Nicolet iS10 FT-IR spectrometer

this region, the oxidation is stated as the IR absorption which is referenced to a thickness absorbance per centimeter (abs/cm) of 1 cm of the oil layer. This refers to how much of the infrared beam is absorbed in a particular wavelength.

The second alternative technique that is proposed for measuring the deterioration in the oil is the alteration in transmittance. Transmittance (T) refers to the amount of light that is transmitted through a solution. The definition of transmittance is that it is the ratio of the light energy that is transmitted through a sample (I) to the energy that is transmitted through the reference blank. As the compound that is being tested is not there in the reference blank, the transmittance of the reference blank (oil sample) is defined as 100% T .

$$T = \frac{I}{I_0}. \quad (1)$$

This number is multiplied by 100 to determine the percentage transmittance (% T), the percentage of light transmitted by the substance relative to the reference blank.

$$\%T = \frac{I}{I_0} \times 100. \quad (2)$$

Transmittance measurement is measured through UV Spectrophotometer (make: 'LABINDIA UV 3000') as shown in Fig. 2.

Work mode defines that there are two modes of measurements, i.e. Absorbance mode or transmittance mode. The wavelength range of the instrument is from 190 to 1100 nm. The cuvette is composed of a quartz which is of optical grade. It has two sides that are opaque and two sides that are clear. For the sample, about 11 ml of the oil is taken. Based on literature that has been published earlier [9] the range that is selected is from 850 to 1100 nm for 10 samples. The range for the performance of the trials was from 850 to 1100 nm and for each repetition, it was increased by 100 nm. After four repetitions of the experiments for 4 wavelengths that is, 850 nm, 950 nm, 1050 nm and 1100 nm, we shifted to a wavelength range of 1000–1100 nm. The transmittance value that corresponded to the wavelength was also noted and the trend was plotted against oxidation and nitration. Moreover, transmittance that was measured by a UV spectrophotometer was also noted and its trend was plotted against any change in transmittance that was measured by the IR sensor setup.

Figure 3 illustrates an IR Transmitter which is fixed on an acrylic, transparent, horizontal sheet. This is the third

Fig. 2 LABINDIA UV 3000+ UV/VIS Spectrophotometer

Fig. 3 a Schematic representation of change in transmittance measured by IR sensor. b Actual setup photo

proposed IR sensor setup. It is because of this arrangement that most of the other wavelengths that may impact the measurements are not used. The oil sample which is 3 ml under measurement is put in a glass beaker and positioned between the abovementioned transmitter and receiver pair. Its transmittance is affected due to the degradation of the engine oil. Hence, any alteration in the transmittance (mv as output between the IR transmitter and IR receiver pair) will have to be compared with the UV spectrophotometer and the FTIR spectrometer.

Making use of the different devices, the engine oil deterioration reflected in terms of nitration, oxidation, any change in transmittance was measured and the results are discussed in the following section.

Results and discussions

To begin with, a set of used oil samples which cover a wide range of nitration and oxidation are gathered. Table 1 lists the measurements taken for the samples from the first servicing. It is due to the first servicing, that there are more than 30 samples. Based on the data provided by the manufacturers of engine oils, the permissible limit for both, nitration (abs/cm) and oxidation (abs/cm) is 25 (abs/cm). For any value beyond that, the engine oil (5W30) has to be replaced. Based on the literature that has been published so far [1], the oxidation [abs/(0.1 mm)] has to be within the range i.e. less than 0.4. Table 2 lists the measurements taken for the samples from the second servicing. Tables 1 and 2 show the bold values for measured parameters which are beyond permissible limit.

Figure 4 shows FT-IR absorbance spectra of the engine oils. All these graphs are taken from OMNIC software module which was provided with FTIR setup. Figure 4a shows spectra of fresh engine oil with an overlap of 10E sample used engine oil with a nitration value of 9 (abs/cm) and an oxidation value of 11 (abs/cm). Figure 4b shows spectra of fresh engine oil with an overlap of 14G sample used engine oil as it was observed that the pick for nitration and oxidation was lower than the 10E sample ID engine oil. Therefore the nitration value for the sample was 8 (abs/cm) and the oxidation value was 5 (abs/cm). Figure 4c shows higher picks with respect to fresh engine oil with an overlap of 18D sample used engine oil which showed a nitration value of 29 (abs/cm) and an oxidation value of 15 (abs/cm). Figure 4d shows a maximum pick, hence with respect to fresh engine oil with an overlap of 18O sample used engine oil the nitration value was also higher 49 (abs/cm) and the oxidation value was 28 (abs/cm). As per a discussion in the FTIR spectrometer measurement procedure the results were automatically compared with respect to fresh engine oil reference and by using Integra software results were directly provided for nitration as well as oxidation. No manual calculations or pick point

was required for this model of FTIR spectrometer. This spectra analysis graph is used as a reference to observe the difference in picks at the particular region for nitration and oxidation parameter measurement on FTIR spectrometer (see Table 2).

Figure 5 depicts a comparison of the range of nitration attained by making use of the FTIR spectroscopy technique and the output obtained using the IR sensor setup transmittance. Regression analysis done on the data shows a linear trend with $R^2=0.88$ and absolute average relative deviation (AARD) % for linear curve fitting is 2.34 which is shown in Fig. 5. For oil that was unused, the output from the IR sensor setup is 4972 mv with a gradual decrease to 318 mv since the nitration rises in used oil. It can be seen that at the beginning, due to a rise in the nitration value, there is no change in the results of the IR sensor setup. A total of thirteen samples can be seen to have a nitration value that is higher than 25 (abs/cm) above the acceptable limit. 20% of the samples have a nitration value that is less than 10(abs/cm). 19% of the samples have a nitration value in the range of 10–20 (abs/cm). However, 45% of the samples are on the verge of the replaceable limit of deterioration with values in the range of 20–25 (abs/cm). Figure 6 illustrates the values for oxidation of the used engine oils attained with the FTIR spectrum and the results of transmittance as measured by the IR sensor setup. Figure 6 also depicts a correlation that is reasonable between the results attained from the samples collected randomly from the range of samples collected from the first servicing. A regression analysis done shows a correlation of $R^2=0.80$ and absolute average relative deviation (AARD) % for linear curve fitting is 2.94 between the transmittance and the oxidation. Moreover, the measuring and evaluation done by the IR transmitter sensor is on a particular band rather than a single wavelength the sensitivity range is from 800 to 1100 nm and the peak response is at 920 nm. Figure 7 below shows the results of the variation of nitration for the used oil samples from the second servicing using the IR sensor setup. In Fig. 7 the regression analysis shows a polynomial trend with $R^2=0.88$ and absolute average relative deviation (AARD) % for curve fitting is 2.12. For the unused oil samples, the IR sensor setup output is 4972 mv with a gradual decrease to 318 mv since there is a rise in the nitration of the used oil. The samples of the degraded engine oil have a value of 9 {Nitration (abs/cm)} till the maximum value of the deteriorated oil sample is 49. A comparison of the samples of oil taken from the first servicing and the second servicing shows a change in the nitration trend which is uniform with respect to the IR sensor setup. A total of 8 samples have a nitration value that is higher than 25 (abs/cm) above the acceptable limits. This is out of the 28 samples collected from the second servicing.

Figure 8 reflects the values of the oxidation of the used engine oils that were obtained with the FTIR spectrum

Table 1 First servicing oil samples testing data

Sample ID	Engine (km)	Previous (km)	Oil (km)	Nitration, (abs/cm)	Oxidation, (abs/cm)	Transmittance (IR sensor)
New Oil	0	0	0	0	0	4972
01B	12,432	0	12,432	23	12	3282
02A	4620	0	4620	8	7	4265
02B	5250	0	5250	42	23	318
02E	10,142	0	10,142	11	9	4894
03B	9131	0	9131	32	20	1834
03C	11,955	0	11,955	29	18	1228
08C	9800	0	9800	21	13	3588
08D	10,000	0	10,000	38	22	754
10A	4609	0	4609	15	13	4283
10B	7000	0	7000	21	14	3412
10E	10,000	0	10,000	9	11	4894
10F	10,000	0	10,000	23	19	1709
11E	9012	0	9012	24	19	962
11H	1040	0	1040	6	7	4953
11I	11,004	0	11,004	15	10	3445
12C	8655	0	8655	27	15	1839
12E	9433	0	9433	38	31	227
12I	10,200	0	10,200	23	15	2970
12 J	10,285	0	10,285	36	21	1228
12 K	10,337	0	10,337	41	25	559
12L	10,500	0	10,500	17	11	2489
12 M	10,900	0	10,900	24	15	3100
12 N	11,700	0	11,700	33	20	897
12O	11,800	0	11,800	8	9	4907
14D	7678	0	7678	17	11	3848
14G	9485	0	9485	8	5	4296
14I	11,000	0	11,000	34	19	1092
14 J	12,000	0	12,000	18	12	2346
17A	10,424	0	10,424	25	21	2782
17B	3328	0	3328	6	6	4953
17C	6801	0	6801	21	16	2600
17I	9577	0	9577	21	15	3100
17 K	2323	0	2323	5	8	4953
18G	7673	0	7673	21	19	2632
19A	12,046	0	12,046	35	22	604
19C	7053	0	7053	22	14	1508
19 J	11,123	0	11,123	8	6	4953
19L	4724	0	4724	19	15	2970
20D	5193	0	5193	11	7	4907
20G	9182	0	9182	31	19	1534
20I	8968	0	8968	30	22	1995
20R	2949	0	2949	6	3	4914

compared to the transmittance values measured by the IR sensor setup output. The figure also depicts a reasonable correlation to the output from the samples selected randomly from the range of the second servicing. A correlation of $R^2 = 0.85$ and absolute average relative deviation

(AARD) % for quadratic curve fitting is 3.46 was noted between the transmittance and oxidation when regression analysis was conducted. Moreover, out of a total of 28 samples of degraded oil, 2 of the samples have an oxidation value that is more than 25 (abs/cm) over and above the

Fig. 4 OMNIC software spectra analysis of **a** 10E, **b** 14G, **c** 18D, **d** 18O sample ID used engine oil sample compared w.r.to fresh engine oil sample

Table 2 Second servicing oil samples

Sample ID	Engine km	Previous km	Oil km	Nitration (abs/cm)	Oxidation (abs/cm)	Transmittance (IR sensor)
17E	19,727	8032	11,695	27	15	3003
17G	19,522	12,966	6556	24	13	4030
17 J	14,751	8927	5824	47	38	468
17L	17,366	10,347	7019	18	11	3802
17O	14,387	7735	6652	14	9	4452
17T	20,433	9183	11,250	25	14	2649
17U	7031	3151	3880	23	14	3055
18A	21,896	18,339	3557	12	7	4953
18C	8648	2039	6609	25	15	2132
18D	18,992	9567	9425	29	15	2142
18 K	6771	6593	178	34	17	1874
18L	3453	1673	1780	15	10	3912
18 M	2594	596	1998	9	8	4953
18 N	18,465	4559	13,906	32	20	1849
18O	2248	682	1566	49	28	370
19B	15,000	10,022	4978	17	10	3619
19D	10,113	6164	3949	16	10	4426
19 M	17,381	9259	8122	14	9	4658
19 N	19,530	8560	10,970	9	10	4953
20C	13,941	6542	7399	14	14	3126
20L	17,327	8327	9000	15	13	4030
20 M	18,563	9563	9000	9	3	4953
20Q	21,248	11,223	10,025	21	13	1930
20S	17,210	9850	7360	30	18	1794
20T	17,296	9851	7445	9	6	4842
20 V	19,896	11,982	7914	26	14	2873
21 N	16,581	9850	6731	25	17	2340
22Q	16,788	9175	7613	25	18	2444

Fig. 5 Nitration (abs/cm) versus change in Transmittance measured by IR sensor setup for first servicing deteriorated oil samples **Fig. 6** Oxidation (abs/cm) versus change in Transmittance measured by IR sensor for first servicing deteriorated oil samples

acceptable limit. To define a good fit between the transmittance and nitration or oxidation both RMSE calculations and regression analysis was taken into consideration.

Curve fittings shown in Figs. 5, 6, 7 and 8 are with 95% confidence interval and *P* value for all these models

Fig. 7 Nitration (abs/cm) versus change in Transmittance measured by IR sensor setup for second servicing deteriorated oil samples

Fig. 8 Oxidation (abs/cm) versus change in Transmittance measured by IR sensor for second servicing deteriorated oil samples

are < 0.05 . It can also be noted that the root mean square error (RMSE) calculations of the oil samples from the first servicing are higher compared to similar values for the second servicing samples. Since the RMSE calculations were used with the second servicing oil samples was a selection parameter for curve fitting, a quadratic equation was chosen over a linear equation for curve fitting. In addition, the second servicing oil samples curve is more appropriate with respect to the oxidation and nitration parameters of the engine oil degradation. Because the number of parts that experience friction in case of the second serving oil condition will be much lower as compared to the first servicing oil samples. Therefore, change in transmittance measurably effected by oxidation or nitration and not by wear particle contamination as compared to first servicing oil samples. Data that has been published by prior researchers, [2, 13, 18] shows that there is an

increase in the values of oxidation and nitration. According to literature published earlier, the maximum value of oxidation for gasoline (petrol) vehicles is about 36 (abs/cm) and the value for the nitration is about 33 (abs/cm) after the vehicle has been driven for 15,500 km for a 5W30 grade engine oil [13]. A different study [18] that studied oil deterioration measurement noted that as the number of kilometres driven goes up, the nitration and oxidation values go up uniformly. Both of these measurements are performed for the same vehicle/vehicles from which samples of oil are collected at a fixed interval. Then again, as per literature that has been published in the past, it can be observed that once the additives such as antioxidants, base reserve and ZDDP are depleted, after the vehicle has been driven for 7000 kms, a drastic change takes place in both, the oxidation as well as the nitration parameters of the degraded engine oil sample.

As Fig. 9 shows, good correlation $R^2 = 0.91$ (absolute average relative deviation (AARD) % for curve fitting is little poor because transmittance values less then 900 mv by setup are poorly correlated to transmittance % measured by UV spectrophotometer) is noted between the IR sensor measured transmittance and the transmittance measured by the UV spectrophotometer which happens to be a standard lab equipment. Hence the transmittance measured by the IR sensor setup is very comparable in terms of the transmittance. One more notable fact is that for a larger number of samples, the deterioration in the nitration was more compared to the oxidation. Therefore, it can be seen from the experiments that are performed that the work done provides an inexpensive and straightforward alternative to measure the degradation in the engine oil outside in the field.

Fig. 9 IR sensor measured transmittance versus Transmittance measured by UV spectrophotometer for first servicing deteriorated oil samples

Research done into the cost factors of the equipment shows that the cost of FTIR is about Rs. 27,00,000/- (depending on the make and the model) and the cost of a UV spectrophotometer is about Rs. 2,80,000/-. Again, prices may vary based on the make and model [28]. The manufacturing cost of the proposed IR sensor set up is about Rs. 4400/-. Therefore, it can be seen that the cost of this setup is drastically lower than the standard methods that are used to measure the degradation in the engine oil.

Conclusions

As per the objectives laid out in this research work, analysis is carried out for samples of Shell 5W30 oil. A discussion of the results of the analysis is done and presented with a primary focus on the values for nitration, oxidation and transmittance. Moreover, the results of this research provide data about the degradation levels of randomly collected oil samples in the field. This research has been successful in implementing a setup for taking such measurements which are extremely practical and can be done outdoors on the field. The following conclusions have been drawn based on the research:

- The experimentation clearly demonstrates the capability of the IR sensor setup as a low-cost detector and transmitter. It captures significant information that can be used for analysis with requisite sensitivity.
- The proposed setup provides an inexpensive solution and shows great potential for offline monitoring of engine lubricants.
- Compared to oxidation correlation provided by this handy set up namely, ($R^2 = 0.84$), the nitration correlation that it provides is better, namely ($R^2 = 0.87$). Therefore, it can be concluded that it is more appropriate for nitration measurement and will be able to measure degradation in engine oil in the field.
- It has the capability to measure transmittance with reasonable accuracy ($R^2 = 0.91$) because the range of this proposed set up is closer to the measuring range of the UV spectrometer near the IR range.
- Further research can be based on the work done in this paper to develop an inexpensive technique for analysis and quantification of the quality of engine oil.
- Other spectroscopic parameters such as water, glycol content and some conditions such as soot which are relevant to the monitoring of engine oil may also be measured by this set up with a selection of appropriate wavelength transmitter and receiver pair.
- Different driving conditions of specific vehicles may be the cause for slightly scattered points.

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Compliance with ethical standards

Conflict of interest The authors declare that there is no conflict of interests regarding the publication of this paper.

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