Fluorescence spectroscopy characterization of turbine oil (Caltex Regal R&O 68) used in Samanala Dam hydropower plant in Sri Lanka

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ABSTRACT

The energy crisis is a major issue not only in Sri Lanka but also globally. One of the major issues pertaining to this crisis is the extant use of nonrenewable sources such as oil, coal and natural gas. Hydro power is a major renewable energy source that can be used to generate the electricity requirements of Sri Lanka. It is necessary for a hydropower turbine to function efficiently without any failures to generate electricity. The lubricants used in gearboxes of turbines play a major role in the proper functioning of hydropower turbines. Here, researchers have studied spectroscopic differences of new and discarded Caltex Regal R & O 68 using Raman spectroscopy, Fourier Transform Infra-Red (FTIR) spectroscopy and fluorescence spectroscopy. Among spectra obtained from above spectroscopic techniques, the spectra obtained from fluorescence spectroscopy had a significant difference between two lubricant samples. The highest fluorescence intensity was recorded in the fresh/ new oil sample while the lowest intensity was in the oil which was discarded by the hydro turbines. Additionally, in this study, it was revealed how fluorescence intensity of turbine oil (Caltex Regal R&O 68) used in Samanala hydropower plant station varies with different temperatures 100 °C, 120 °C, 140 °C, and 200 °C. Moreover, 1-Naphthalenamine, N – phenyl was identified as the fluorophore used in Caltex Regal R&O 68 lubricant. Therefore, the fluorescence technique can be used as a tool for monitoring the quality of hydropower turbine oils.

KEYWORDS: *Oil degradation, Antioxidants, Fluorescence intensity, Renewable energy,*

Fluorophore

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1 INTRODUCTION

Lubricants are organic substances that reduce friction between surfaces in mutual contact and ultimately reduce the heat generated when the surfaces move (Rowe, 1966). Also, lubricants have the ability to transmit forces, transporting foreign particles and heating or cooling of surfaces (Mang and Dresel, 2007). A good lubricant has a high boiling point and low freezing point in order to stay liquid within a wide range of temperature, high viscosity index, thermal stability, hydraulic stability, demulsibility, corrosion prevention, and high resistance to oxidation (Perez, 2000). Typically, lubricants contain 90% base oil (mineral oils) and 0% additives. Synthetic liquids such as hydrogenated polyolefins, esters, silicons, and fluorocarbons or vegetable oils are used as base oils (Aguilar et al., 2010). Additives in lubricants play a major role and they reduce friction and wear, increase viscosity, improve viscosity index and deliver resistance to corrosion and oxidation, aging or contamination, etc (Rizvi, 1992).

Table 1.Typically -accompanying additives for lubricants

Additive	Function
Pour point depressants	Adhere to wax and prevent crystallization of wax. Eg.Long chain alkylbenzenes
Anti-foaming agents	Lower surface tension and reduce foam formation. Eg.typically silicone compounds
Viscosity index improvers	Assist lubricants to remain viscous at higher temperatures. Eg.Polyacrylates and butadiene.
Antioxidants	Suppress the rate of oxidative degradation of the hydrocarbon molecules within the lubricant. Eg. butylated hydroxytoluene
Detergents	Prevent formation of deposites on contact surfaces at high temperatures.
Corrosion inhibitors	Absorb acids and prevent corrosion of metal parts. Eg. alkylsulfonate salts
Anti – wear additives	Form protective "tribofilm" on metal parts and suppress wear. Eg. phosphate esters, zinc dithiophosphates
Extreme pressure(anti scuffing) additives	Form protective films on sliding metal parts Eg.dithiophosphates
Friction modifiers	Reduce wear and friction

1.1 Lubricant degradation

The main factors affecting lubricant degradation are shear, heat and oxygen. The high-speed repetitive shearing between two moving parts in close contact can be affected by the molecule breakdown in the lubricant (Ahmed et al., 2011). Oxygen is a reactive substance that can corrode metals even at room temperatures. The motor oil temperature can reach about 538º C. Exposure to oxygen at great heat can reduce a lubricant's life unexpectedly.

The hydrocarbons can be found in lubricants, and contain C=C bonds. At high temperatures these molecules react with oxygen molecules, cleaving them into carboxylic acids (Minami, 2017). When a molecule split into smaller molecules the viscosity of the lubricant is decreased. Also, the formed molecules are acids, therefore they increase metal corrosion in the engine, and finally, the metal forms salts with carboxylic acids, liberating hydrogen gas.

$$2\ RCOOH + 2M\ ---- \ 2RCOO^-M^+ + H_2$$
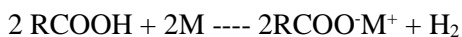
The carboxylic acids raise acidity to damaging levels and the lubrication is seriously reduced, resulting in excessive engine wear and plug fouling. Therefore, if lubricant is not changed regularly it can reduce the engine life of the vehicle. The increasing acidity of the lubricants can lead to additive depletion and it also limits the service life of the lubricant. Contamination by foreign matter (eg. fine metal particles) is another reason for lubricant degradation (Minami, 2017).

The oil must be changed periodically to avoid this deterioration and, to ensure smooth performance of the vehicle. If lubricants are changed too early, it causes inefficient use of already-depleting resources, which also has an unwanted impact on the environment. The engine failures can be avoided if oil is changed before it loses its protective properties. Furthermore, an unnecessary oil change should be avoided for environmental and economical reasons (Bhosale et al., 2014).

In this research, Caltex Regal R&O 68 lubricant samples obtained from the laboratory of Ceylon Electricity Board, Mahaweli hydropower complex in Kandy were analyzed using Raman spectroscopy which is an analytical tool widely used by researchers (Pelletier, 1999). Also, FT-IR spectroscopy (Van de Voort et al., 2004) and fluorescence spectroscopy spectroscopic techniques were used to analyze lubricant samples.

1.2 Samanala hydropower plant

There are three main categories of Sri Lankan hydroelectric plants, namely Laxapana complex, Mahaweli complex and Samanala complex (Fernando et al., 2017). Hydropower plays a vital role in electricity production in Sri Lanka, producing more than 40% of the energy requirements(Khaniya et al., 2020).

The Samanala hydropower plant was inaugurated in 1992 and is situated in "Belihul Oya" area in the Rathnapura district in the Sabaragamuwa province (Khaniya et al., 2020).

Figure 1: Francic turbine model used in "Samanala" hydro power plant.

The "Francic" turbines are commonly used turbines in hydropower plants (Trivedi et al., 2017). At turbines in the "Samanala" hydropower plant, mainly two types of lubricants are used as Caltex Regal R&O 68andCaltex Rando HD that is used for all parts of the turbine except the governor. The quality of lubricant used in hydropower turbines highly affects the performance of the turbines. Oxidation of lubricant can be caused by high temperature during operation. Moreover, when water is mixed with lubricant it gets rapidly oxidized and ultimately it tends to induce corrosions and failures in machinery parts in turbines. Therefore, monitoring the quality of lubricant used in hydropower turbines is an important process to avoid failures in hydropower stations (Iliev, 1999).

1.3 Fluorescence spectroscopy as a tool to detect lubricant degradation

Certain chemical substances absorb and store energy when they come to the ground state by emitting excessive energy in the form of electromagnetic radiation. This phenomenon is known as "fluorescence". This fluorescence generation consists of three processes, molecular absorption, simulation, and inactivation.

Although almost all kinds of substances absorb visible or UV light, while a few compounds are fluorescent. Most the organic compounds with aromatic ring structures exhibit fluorescence. The oil or lubricants are made of crude oil, which mainly consists of alkanes, aromatic compounds, and cycloalkanes. Among all the hydrocarbons in oil, about 25% to 70% contain aromatic rings with conjugated double bonds, which are good fluorescence- giving substances. These aromatic compounds include benzene, anthracene, naphthalene, phenanthrene, benzopyrene, fluoranthene, porphyrin, heavy metals, and other polycyclic aromatic hydrocarbons and their derivatives. They all have unsaturated and π- electron conjugated structures and are the material bases of fluorescence detection for oil and its derivatives.

Fluorescence-based methods have attracted more attention from researchers due to high speed, low cost, non-contact, and non-destructive testing options. Also, fluorescence spectroscopy is a near-perfect tool for lubricant analysis because

it contains much fluorescence providing molecules.

Generally the quality of lubricants is tested by measuring parameters such as viscosity and Total Acid Number (TAN) (Park and Nassar, 2003). However, in this study, a sophisticated method is presented to measure the quality of lubricants by fluorescence intensity. According to the literature, the fluorescence of antioxidant additives in lubricant oil was used as an indicator of oxidative stability of the oil (Omrani et al., 2014). It is revealed in this studyhow the fluorescence intensity correlates with lubricant degradation (Ranawaka et al., 2019b) at "Samanala" damp hydropower plant which is a valuable renewable energy source in Sri Lanka.

Previous research in our laboratory has already performed the feasibility studies of using non-dispersive Fluorescence spectroscopy for lubricant condition monitoring. Our results reveal that this technique can be used to predict the usability of different oils. According to the results we obtained, fresh oil samples showed a very-high intensity of a fluorescence emission signal, but when oil degrades, intensity appears to slowly decrease. When oil degrades completely the curvature of the graph become almost negligible (Ranawaka et al., 2019a)

Moreover, fluorescence spectroscopy is rapid, non-destructive, non-invasive, and can be used for online monitoring as well. Additionally, it does not need any additional sample preparation or wet chemistry.

Fluorescence quenching is a phenomenon that should be considered when analyzing lubricant samples using fluorescence spectroscopy. There are some researches that have done to investigate, the fluorescence quenching of anthracene, pyrene, and phenanthrene has studied in the presence of humic acid in water. The humic acid was obtained as sodium salts and de-ionized water was used as a solvent in the experiment. The fluorescence experiment was performed at room temperature. Here,the author defined two terms as dynamic quenching and static quenching. Dynamic quenching is defined as the reduction of a fluorescence lifetime with increasing humic acid concentration which is obtained as time-resolved measurements. The reduction of fluorescence intensity with increasing humic acid concentration is defined as "static quenching". In this study, it has found that the static quenching of fluorescence in phenanthrene is less efficient than the fluorescence quenching of anthracene and pyrene. The high solubility of phenanthrene than other selected polyaromatic hydrocarbons was suggested as the reason for the low static fluorescence efficiency. According to this study there is a significant effect from pH for the static quenching and there were no pH effect for dynamic quenching. According to past literature, the structure of the humic acid changes from coil type to extended chain type when the pH of the solution is increased. In coil structure, there is more cage- like structures and it results in more binding sites for the PACs, hence in high pH conditions, the static

fluorescence quenching becomes more effective. Although both static and dynamic quenching have effects on fluorescence quenching, static quenching process is the strongly dominating factor for quenching.

2 RESEARCH METHODOLOGY

A new and a discarded Caltex Regal R&O 68 lubricant samples which are used in the hydropower plant in Samanala dam in Sri Lanka were obtained from the laboratory of Ceylon Electricity Board, Mahaweli hydropower complex in Kandy.

Samples were characterized using Thermo Scientific Lumina Fluorescence Spectrometer (150 W Ozone Free Xenon Lamp, Scan speed 300 (nm/min), Emission slit 10 nm, Excitation wavelength 373 nm), Thermo Scientific Nicolet S10 FT-IR spectrometer (Liquid cell was used), Thermo Scientific Raman spectrometer (785 nm laser) and Gas chromatography-mass spectroscopy (GC-MS) (HP 5 ms ultra inert column).

1. FT-IR spectroscopy

First, 1.0 ml of both Caltex Regal R&O 68 oils was dissolved in 3.0 ml of hexane (Sigma Aldrich analytical grade 99.7%). Then, anhydrous sodium sulphate was added to each prepared sample. After, samples were loaded into a liquid cell of the FT-IR spectrometer.

2. GC-MS analysis of lubricant samples.

First, oil samples were prepared by dissolving in 3.0 ml of hexane (Sigma Aldrich analytical GC grade > 99.7%). In here only a small amount of oil was added using a glass pipette. Before, the testprepared lubricant samples were filtered using syringe filters (PTFE, 0.2 μm).

3. Fluorescence and Raman analysis of lubricants.

No sample preparations were needed and original lubricant samples were used without any dilutions.

2.1 Experimental setup used for artificial heating of new Caltex Regal R&O 68 in laboratory

First, 3.0 ml of oil was used for each sample and the fresh oil sample was artificially heated at 100 °C, 140 °C, and 200 °C for 15 minutes in the lab. Clean and dried glassware were used at all time. Temperature was monitored using a thermometer while a hot plate was used to heat the sample to the required temperature. In this experiment, all samples were inserted into a paraffin bath to achieve the required temperature.

Figure 2: Experimental setup used for artificial degradation of new Caltex Regal R&O 68

3 RESULTS & DISCUSSION
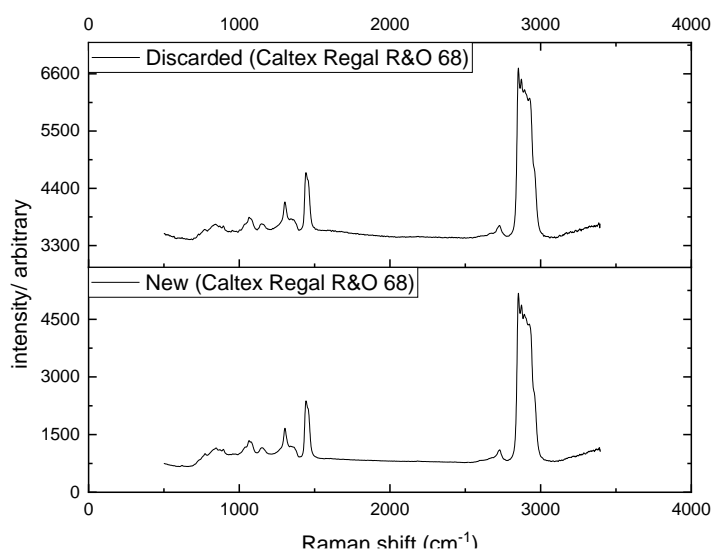
Figure 3 : Raman spectra of new and discarded Caltex Regal R&O lubricant from "Samanala" hydropower plant in Sri Lanka

Raman spectroscopy is used to detect chemical structures based on the vibrational modes of molecules. With FT-IR technique, the new bond formations and breakages can be identified using Raman spectroscopy. Unfortunately, there were no significant differences in spectra of lubricant samples (Caltex Regal R&O 68) that were detected.

Although aromatic rings were displayed around 1500 cm^{-1} in both Raman spectra, there was no significant difference in spectra obtained for the new and discarded Caltex Regal R&O 68 lubricant samples.
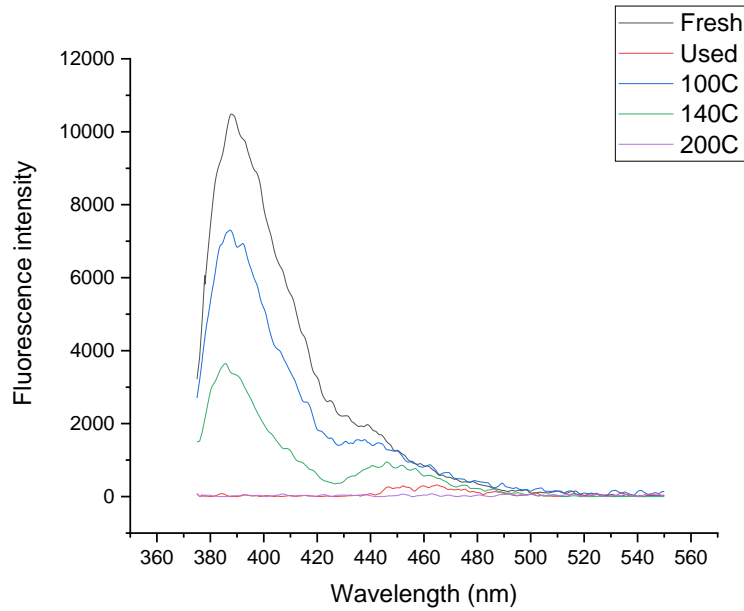
Figure 4 : Fluorescence spectra (Fluorescence excitation wavelength 373 nm) of Caltex Regal R&O 68 oil used in "Samanala" damp hydropower plant at 100 °C, 140 °C and 200 °C temperatures.

According to fig 3, the highest fluorescence intensity was recorded for the new Caltex Regal R&O 68 lubricant sample while the lowest fluorescence intensity was for the naturally degraded sample (discarded). When oil was artificially degraded at 100 °C, 140 °C, and 200 °C the fluorescence intensities were decreased: respectively.
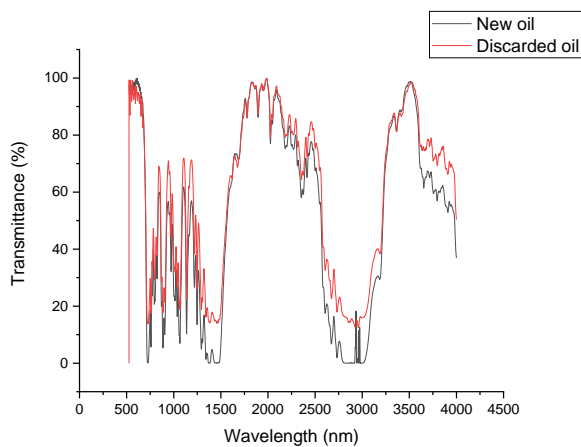

Figure 5 : Obtained same FTIR spectra of new and discarded Caltex Regal R&O 68 used in "Samanala" hydro power plant.

The Fourier Transfer Infra-Red (FT-IR) spectroscopy is used to study additive depletion or oxidative changes in lubricants. As an example, there may be a production of polyaromatic hydrocarbon in lubricants other than depletion of antioxidants in lubricant samples. However, there were no significant differences between FTIR spectra of fresh and discarded samples obtained from turbines of hydropower plant.
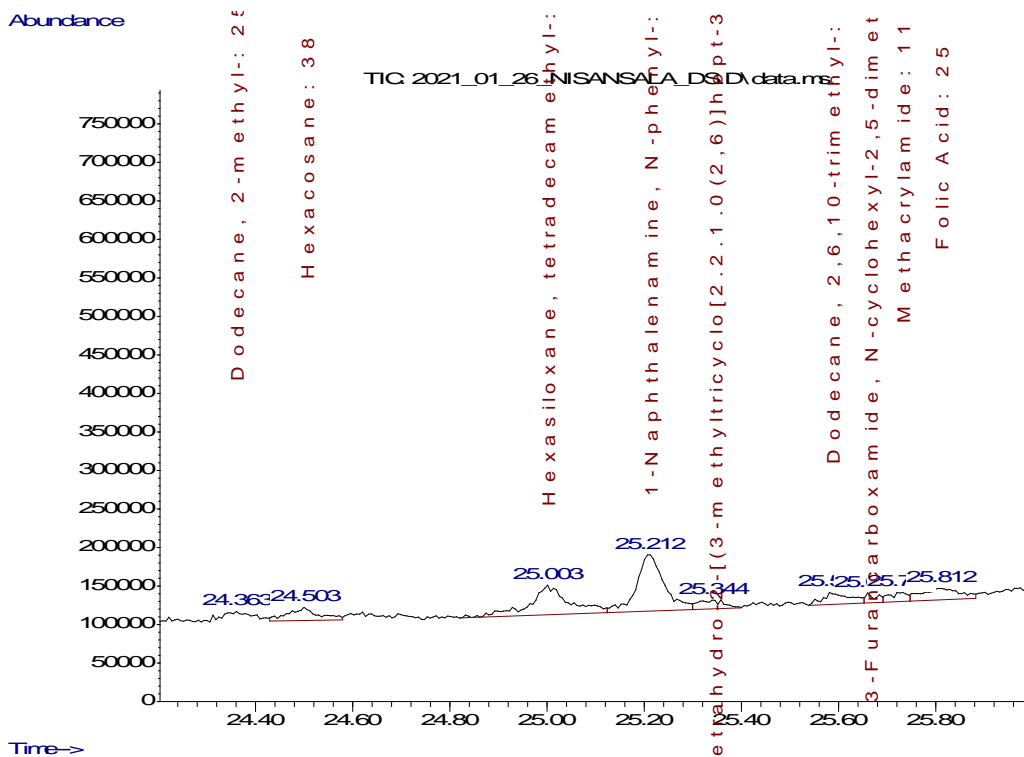
Figure 6: GC-MS result of new Caltex Regal R&O lubricant obtained from "Samanala" hydropower plant in Sri Lanka

A high matching percentage (95%) was obtained for 1- Naphthalenamine, N-phenyl compound after SIM mode in GC-MS. Here researcher could not identify the amount of 1- Naphthalenamine, N-phenyl quantitatively in each lubricant sample of Caltex Regal R&O 68 because of, unavailability of standard 1-Naphthalenamine, N-phenyl. 1-Naphthalenamine, N-phenyl has a rigid structure that consists of two fused benzene rings that enables it to act as a fluorescent indicator (Brito and Vaz, 1986). However, further research will be done by the researcher for the quantitative identification of N-Phenyl-1-naphthylamine in Caltex Regal R&O 68 lubricant.

Also, as the depletion of antioxidants, there might be poly aromatic hydrocarbons formed in the lubricant samples. Therefore, careful attention must be given to both antioxidant depletion and polyaromatic hydrocarbon formation.

However, as the highest fluorescence intensity was in the new Caltex Regal R&O 68 lubricant. It can be assumed that the highest fluorophore concentration might be in a new sample, without a quantitative analysis of N-Phenyl-1-naphthylamine in Caltex Regal R&O 68 lubricant. Consequently, antioxidants or N-Phenyl-1-naphthylamine might be degraded with the use of Caltex Regal R&O 68 in hydropower turbines.

Sample preparations for the GC-MS analysis were done carefully without any fiber particles or moisture in prepared samples, in order to avoid column damage in the instrument. Furthermore, a small quantity of lubricant was added to the solvent using a dry and clean glass pipette. To avoid addition of fibres into prepared GC-MS samples, it is recommended not to use tissue papers to wipe glassware used in the sample preparation.

Moreover, samples for both FT-IR and GC-MS were dried using anhydrous sodium sulphate to remove moisture in lubricants. Furthermore, this procedure was thoroughly performed in FT- IR analysis because the liquid cell contains a sodium chloride aperture. Also, the lubricant was loaded to a liquid cell of FT-IR using syringes to avoid air bubble trapping in the cell.

Figure 7: Liquid cell used in FT-IR analysis that contains a sodium chloride aperture.

The new lubricant of Caltex Regal R&O 68 was artificially degraded up to 200 °C, which is the flashpoint of the lubricant, in order to study the behavior of the fluorophore with temperature.

4 CONCLUSION

The fluorescence technique is sensitive than other spectroscopic techniques to identify the quality of Caltex Regal R&O68 oil. Furthermore, it is a non-destructive test and sample preparation is not needed for this fluorescence technique. The added antioxidant quantity decreased with the lubricant degradation and aromatic antioxidants can be considered as fluorescence indicators in lubricants. Fluorescence spectroscopy is a promising analytical technique that can be used to monitor the condition of hydropower lubricants.

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